PROBLEM-SOLVING DIFFICULTIES EXPERIENCED BY NIGERIAN STUDENTS OF SCHOOLS OF BASIC STUDIES IN MECHANISTIC ORGANIC CHEMISTRY

BY

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DEDICATION

To my:

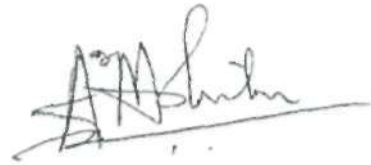
Parents Shaibu and Nanashe, who never had an opportunity but gave me one,

wife Folake, who gave me support and loving companionship,

children Mąinąji and Mąną, in the hope that they will attain greater heights.

FOREWORD

The research presented in this thesis is, to the best of my knowledge original, except where due references have been made.



A.A.M Shaibu.

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ABSTRACT

This study concerns an investigation into the difficulties that the students of Schools of Basic Studies in Nigeria experience when they solve problems in mechanisms of organic reactions. It is basically an analysis of their conceptual and strategic or procedural difficulties in the area specified.

The Schools offer pre-degree (A-level standard) courses, preparatory to university entry. The sample comprised 190 students drawn from 5 out of the 13 colleges in the country. Their average age was 18.5 years. They were well motivated.

The study had two major components:

(a) Diagnosis, which focused on probing the nature and causes of the difficulties.

It comprised three parts:

(i) The preliminary part, which is dealt with in chapters 1 and 2. It involved a preliminary survey to establish and define the research problem, and the review of relevant literature that paved the way for the development and design of research instruments,

(ii) Part 1A, covered in chapters 3-6, describing the paper-and-pencil method used to investigate the difficulties,

(iii) Part IB, covered in chapters 7-9, in which protocol analysis (referred to as TAPS) is used for probing the thought-processes that underlie the

students' problem solving behaviour observed in part 1A.

(b) Remediation: This is dealt with in chapters 10-11, describing a remedial programme aimed at reducing the students' difficulties identified in part I of the study.

Chapter 12 is an overall conclusion of the study.

The results from the study showed that:

(a) The students possessed the requisite chemical knowledge required for solving the problems posed.

(b) They were, however, unsuccessful in solving the problems. Some of the reasons are:

(i) They lack functional understanding of the chemical concepts which they have acquired,

(ii) They lack the requisite strategies for solving the problems.

(c) There is a positive, but low correlation ($r = 0.45$) between the students' reservoir of chemical knowledge and their ability to utilise the knowledge in solving problems requiring them as pre-requisites.

(d) The students' reservoir of chemical knowledge is not a reliable guide for predicting their ability to solve problems requiring such knowledge as pre-requisites.

(e) The focus of the students' ideas about organic reactions revolve around the concepts of charge and the electrostatic attractions between oppositely-charged species.

(f) The students have a number of chemical misconceptions which contributed to their failure in solving the problems. These include:

(i) the electronic nature of covalent bonding.

(ii) the processes of bond-breaking and bond-making and the accompanying structural changes as reactants are converted to products.

(iii) formal and partial charge symbolisms.

(iv) curved arrow formalisms.

(v) common technical terms frequently used (by teachers and in texts) to convey chemical ideas.

(g) The male students performed significantly better than the female students, even though, there seemed to be no significant difference in their possession of chemical knowledge.

(h) The students problem solving approach did not show any clear and/or consistent pattern that could be used to classify their strategies into any formal categories. They were characterised by a random, trial-and-error search for solutions.

(i) The "structured text" remedial programme represents an effective method of improving the problem solving capability of the students.

The limitations of the study are outlined, its implications for curriculum design and instruction in Nigeria highlighted, and suggestions for direction of further research are made.

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"The teaching of science should involve much more than the mere transmission of factual information. Indeed, most people would agree that a more important goal is teaching students to use basic facts and concepts flexibly so that they can deal with new situations, predict various consequences and solve problems".

Reif etal (1976)

CHAPTER ONE

BACKGROUND AND STATEMENT OF RESEARCH PROBLEM

1.1 Overview

In this chapter, the preliminary ideas regarding the rationale for and basis of the research problem are discussed. The summary is that the problem is real, its investigation worthwhile, and its results have potentials for positive impact on curriculum design and implementation in respect of science teaching in Nigeria.

1.2 The Problem

1.2.1 Introduction

Chemical reactions lead to transformation of compounds. In reactions of organic compounds molecules are involved. Their chemical transformation involves the breaking and making of covalent bonds. These are sequential in some cases and concerted in others. A detailed description of this transformation constitutes an organic reaction mechanism. (Tewari et al, 1980; Caserio, 1965).

One of the major aims of chemistry teaching is to give the student such a knowledge of the framework of the subject as to enable him understand the structure and chemical transformation of matter (Thompson, 1971). In recent years, the teaching of organic chemistry has been done from a mechanistic approach (Norman and Waddington, 1979). This is presumably with a view to promoting in the student the establishment of a functional conceptual framework that enhances the understanding referred to by Thompson.

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The ability of the student to display such an understanding when called upon to do so (ie problem solving) constitutes an index of learning that has occurred; for problem solving is the hall-mark of learning (Gagne, 1977).

However, Stewart (1982) has observed that science educators know very little about what students learn from science instruction. Thus he suggested that "one way to fill this void would be for researchers to do detailed analyses of the conceptual and procedural knowledge that students are expected to learn in science courses". He further contended that "with these descriptions, it would be possible to detail the knowledge (especially misconceptions) that students take away from instruction, thus providing a rational basis for changing science instruction". This, in effect, summarises the central consideration upon which the whole essence of this study is based.

1.2.2 Background to the problem

There are various levels within the educational structure of the Nigerian schooling system. These are interspaced between primary school at the lower end and the university at the upper end.

The educational structure can be broadly categorised into three: primary, secondary and tertiary levels. The primary section is represented by the primary schools. The secondary level of education is the concern of secondary schools, teacher grade II training colleges, technical colleges and their equivalents. The tertiary level of education is

undertaken in the polytechnics, Advanced Teachers' Colleges, Colleges of Education and ultimately, the universities. It is a hierarchical structure with the universities at the apex. University education has been and continues to be a symbol of academic achievement. It has thus become a prime aspiration and ultimate goal of a majority of the students at the lower levels. However, a large proportion of the aspirants do not usually realise this ambition due to a combination of factors ranging from limited placement vacancies to difficulties arising from financial constraints. In fact university admission figures for science and science-based courses (Table 1.1) shows that only about 13% of the prospective candidates end up finding places in the universities. The table gives the figures for five consecutive years, 1980-85.

TABLE 1.1 APPLICATIONS AND CORRESPONDING ADMISSIONS FOR SCIENCE AND SCIENCE-BASED COURSES IN NIGERIAN UNIVERSITIES, 1980-85

YEAR	TOTAL NUMBER OF APPLICATIONS	TOTAL NUMBER OF ADMISSIONS	% ADMISSIONS
1980/81	57,207	8,359	14.6
1981/82	56,877	8,748	15.4
1982/83	64,322	4,128	6.4
1983/84	62,105	7,910	12.7
1984/85	60,612	10,573	17.4
TOTALS	301,123	39,718	13.3

This rather high attrition figure raises an educationally pragmatic question, which is: what skill(s) should science instruction in Nigeria seek to develop in the student that would remain of long-term effect irrespective of what point along the "ladder" the students' formal education terminates? Quite a number could be suggested. However, it can be argued that the development of problem solving skills constitutes an important educational outcome, and thus cannot be ignored.

As Selvaratnam (1983) pointed out, a systematic approach to problem solving stands the student in good stead when he is confronted with problems of his daily life.

Although the primary concern of this study is not with the philosophical basis for development of a science curriculum, the question of the utility of what the student takes away with him from science education finds place in its wider context.

The schools of Basic Studies are transitional stages within the educational profile - a transition from the secondary to tertiary level. The schools draw their intake mainly from graduates of secondary schools who possess the required admission qualifications. The programme offered is of A-level standard, preliminary to university entry. The qualifying examination is conducted by a central examination body known as the Interim Joint and Matriculation Board (IJMB). Students who satisfy

the requirements laid down by a separate central university admission body known as the Joint Admissions and Matriculation Board (JAMB) are given placements in the universities.

There are now thirteen schools of Basic Studies scattered all over the country. The geographical distribution of the schools is shown in appendix 1.1 while the chemistry syllabus operated by the schools is included as appendix 1.2.

The schools have through their programmes become vital links between the secondary and tertiary levels of education in Nigeria.

It is in this setting that the author works as a classroom teacher of organic chemistry. Participation at the grading and moderation exercises by the author coupled with personal professional experience and observation suggested to him that the students suffer severe difficulties in the learning of organic chemistry, especially in the use of supposedly acquired concepts to solve problems in organic reaction mechanisms. These observed difficulties suggest to the author the likelihood of a fundamental conceptual deficiency in the rallying principles that underlie organic reactions generally.

Earlier studies have shown, for example that the students have difficulties with the study of molecular structure, especially stereochemistry (Eniayeju, 1982). If that is the case, then in what other form(s) do the students' difficulties manifest

themselves? It was these background details that prompted the subsequent processes that culminated in the identification of the research problem.

1.2.3 Identification of the problem

Given the background already discussed in the last section (1.2.2), the author set out to survey ways in which the problem manifests itself with a view to gaining some insight into the relevant facets. Consequently an investigation was conducted into;

(a) the documented views and comments of IJMB examiners for a period of five consecutive years, 1980-84

(b) the IJMB answer scripts of randomly selected students from 1980-84

(c) findings from the literature of related studies.

The author considered that this method yields a more objective assessment of the ramifications of the problem than other methods involving, for example, use of questionnaires (Ahmed, 1982, Patwary, 1983) for gathering similar information. The details of the survey are now presented.

Comments of IJMB Chief Examiners and Moderators: 1976-84

(A) Introduction

Samples of comments and observations of the IJMB chief examiners that are relevant to this study are reproduced below. They cover the

period 1976-84 and serve to give some guidance in seeking to identify the problem.

(B) Moderator's Report for IJMB Examination Results: 1976

"From reading the individual scripts this moderator comes away with the feeling that the high scores are more a reflection of good teaching than a revelation of absolute brilliance or creativity on the part of the student. The examination itself should show less emphasis on questions that necessitate direct recall of facts, or direct response to explicitly stated situations, and more of the type of questions which call for interpretive skills based on principles, and requiring a broader scope of greater depth of understanding of subject matter ..."

(C) Chief Examiner's Report for IJMB Examination Results: 1983

"The questions set in both papers I and II were considered to be comparable to the GCE (A-Level) standard.

Question 4: In part (a) the mechanism of the reactions were not discussed well. Eighteen candidates out of two thousand, eight hundred and seventy eight attempted the question.

Question 6: Though fifty seven candiates attempted this question, the overall performance was poor. S_N1 and S_N2 reactions were rarely named. In describing

the reactions of alcohols, no systematic approach was followed ..."

(D) Chief Examiner's Report for IJMB Examination Results: 1984

"The overall results are much better than usual and probably project too rosy a picture of the candiates' actual knowledge and competence. In broad terms, it would appear that compared to the results from the previous years, marks in paper II (organic chemistry) have fallen while those in paper I (physical and inorganic chemistry) have improved ..."

The common strand which runs through these reports is that of a generally poor student perforamance in organic chemistry. These support the author's preliminary observation which is that students of the schools of Basic Studies in Nigeria have problem solving difficulties in organic chemistry.

1.2.3.2 Survey of IJMB Answer Scripts of the Students for 1980-84

(A) Introduction

Samples of IJMB answer scripts of the students, randomly selected were reviewed. These consist of the examination scripts for a period of five consecutive years; 1980-84. The strategies adopted by the students in solving problems of organic reaction mechanisms along with their relative

performances were surveyed. The results showed that the students hold inaccurate and sometimes inconsistent chemical concepts in respect of mechanisms in organic reactions. This was reflected by the frequently incorrect manner in which these concepts were used to tackle problems; culminating in abysmal failure in the task of solving the problems.

(B) Result of the Survey:

The results which emerged from the review are summarised below. They showed some of the students' difficulties which appear to include:

(a) lack of chemical knowledge required for problem solving in organic reaction mechanisms.

(b) lack of basic understanding of chemical concepts frequently used for problem solving, prominent amongst these are:

(i) electronic concept of covalent bonds

(ii) bond-breaking and bond-making processes in organic reactions.

(iii) electronic nature of reacting species, e.g nucleophiles and electrophiles.

(iv) molecular formulae and structure.

(v) structural changes involved in organic reactions.

(c) lack of conceptual understanding and ability to use conventional chemical symbols. These include:

(i) curly arrows

(ii) partial charges, usually designated by $\delta+$ and $\delta-$

(d) lack of capability in problem solving skills. These include:

(i) structuring the problem situation with a view to conceptualizing it in a global sense.

(ii) understanding the basic elements of the problem.

(iii) understanding the structural relationship of the elements.

(iv) selecting relevant information required for finding a solution.

(v) organising information selected to produce a solution.

The survey showed a general pattern of lack of capability on the part of the students to solve problems. For example, some of the solutions were out of tune with the demands of the problem, while some others were simply inept, portraying the solver as having no clear direction in the search for solutions. The results of the survey seem to indicate difficulties that can be summed up into two broad areas as follows:

The students lack:

(a) pre-requisite conceptual knowledge required for problem solving.

(b) skills in:

(i) the use of conventional chemical symbols as tools for describing their conceptualization of the processes of organic reactions, curly arrows, formal and partial charge formalisms feature prominently in this respect.

(ii) devising viable and logical strategies for reaching a solution state.

1.2.3.3 Findings from Related Literature

There appears to be a paucity of literature regarding the problems that students encounter as they attempt to solve problems in organic reaction mechanisms. A few authors have however reported their findings in related fields.

Khan (1980) investigated students' problem solving difficulties in electrophilic aromatic substitution and synthesis of polysubstituted benzenes. He found that students actually have difficulties in solving problems in electrophilic substitution and synthesis of polysubstituted benzenes. He reported that the factors responsible are:

(a) students' failure to use the relevant information of a problem.

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(b) students' failure to approach problems in a systematic, step-by-step manner but only by jumping to conclusions.

(c) students lack confidence in their ability to solve problems.

Bojezuk (1982) conducted a survey into students' difficulties in a number of topics in chemistry. He found that the subjects rated organic reaction mechnisms as second most difficult, the first being problems in organic synthetic pathways. This finding is not totally unexpected since problem solving in organic synthetic pathways require some basic understanding of organic reaction mechanisms.

Johnstone (1974) carried out an evaluation of chemistry syllabus in Scotland. He reported that organic reaction mechanisms, especially S_N1 and S_N2 types were rated by the students as being difficult.

These research findings highlight the fact that there is some empirical evidence showing that students have difficulties with organic reaction mechanisms as an approach for representing the process of organic reactions. They serve to give additional support to the results of the survey conducted into the Nigerian situation, reports of which have been presented in the two preceding sub-sections. The question is: What factor(s) is/are responsible for the difficulties? This is probed into in the course of the research.

1.2.4 Statement of the Research Problem

In the previous sections, attempts have been made to show that the problem being investigated in this study does exist, and that it has manifested symptoms that necessitated an investigation of the underlying difficulty. It is in this light that the research problem is now stated as:

An investigation aimed at analysing the problem solving behaviour of Nigerian students at the schools of Basic Studies in mechanisms of organic reactions. This is with a view to:

(a) identifying difficulties of the students in solving mechanistic organic problems.

(b) identifying possible reasons that underlie the existence of the difficulties; and to

(c) propose a remedial package.

To focus the search light of the study, the research problem is broken down into the following underlying questions:

(a) Do the students possess relevant chemical knowledge required for solving problems?

(b) Do they succeed in solving such problems?

(c) Do their performances differ for different formats of the same test?

(d) What effect does possession of relevent chemical knowledge have on ability of the students to solve problems requiring the knowledge?

(e) Does sex constitute a significant factor in the ability of the students to solve problems?

(f) What are the students' difficulties in solving *mechanistic organic problems*?

(g) What implications do the answers to above questions (a-f) hold for chemical education in Nigeria?

Answers will be sought for these questions and other related ones that may unfold in the course of the study.

1.3 Working Assumptions

The following constitute the working assumptions for this study. They derive from the reviews discussed earlier in this chapter. The working assumptions represent the author's guess about a possible direction of the study. In other words, they are tentative postulations about the nature and possible causes of the difficulties based on insight gained from the initial preliminary survey of the research problem. Whether or not the assumptions are tenable remains to be seen from the findings of the investigation.

The assumptions are that the problem solving difficulties of students of Nigerian schools of Basic Studies in organic reaction mechanisms are due to:-

(a) lack of basic chemical knowledge of the subject matter.

(b) lack of basic understanding of the rules, principles and conventional symbols frequently used for problem solving in organic reaction mechanisms.

(c) lack of capability in using chemical symbols to express chemical concepts relating to the process of organic reactions.

(d) lack of problem solving skills, the essential elements of which are:

  (a) lack of understanding of problem-situations.

  (b) lack of capability to recall and reason with relevant information.

1.4 Scope of the Study

The scope of the study refers to the areas of knowledge domain that are investigated in the process of probing the students' difficulties. These are as follows:

(a) substitution reactions: nucleophilic and electrophilic.

(b) addition reactions: nucleophilic and electrophilic.

(c) elimination reactions.

(d) some areas of the interrelationship of these reaction types.

Considering the structure of the study, it covers two broad dimensions. These are:

(a) diagnostic dimension: an indepth investigation of the factors causing problem solving difficulties in the areas delineated.

(b) remediation dimension: some remedial treatment aimed at reducing the difficulties revealed in (a).

1.5 Significance of the Study

The development in students of the ability to solve problems is a major goal of science education. Thus a geat deal of attention has been directed to studies on the processes of problem solving. These studies continue to flourish unabated, suggesting that our understanding of the requirements and processes of problem solving, and thus our capability to design instruction based on that understanding, is still limited.

Pérez and Torregrosa (1983), for example, have reported that students encounter a lot of difficulties in solving chemical problems. They argued that inability in problem solving constitutes one of the major causes of failure in chemistry, which they suggested was because students did not learn how to solve problems. Jones etal.(1982) went a step further by indicating that students actually shy away from chemical problems. They pointed out that:

> "chemistry teachers often assert that one of the benefits students gain from studying chemistry is the ability to solve problems, yet most teachers are well aware that in examinations, it is the problem questions that students tend to avoid if they have the choice, and to answer badly if they do not".

These observations are further supported by Norman and Waddington (1979) who indicated that students experience learning difficulties in organic reaction mechanisms. They suggested that the prevalence of the difficulty is because the subject matter is taught separately from the principles of chemical kinetics and thermodynamics which serve to clarify the underlying principles.

The significance of this study can be viewed against the background of the above discussion. Firstly, it consitutes an attempt to make some contribution to the on-going research into problem solving in science, and its implications for improving instruction in schools. Secondly, it focuses on an important area of organic chemistry, ie reaction mechanisms. This importance has been highlighted by a number of authors, for example, Tedder and Nechvatal (1983), Jones (1984) and West (1986). In addition, research into problem solving generally, and analyses of students' problem solving difficulties in particular, are relatively novel educational undertakings in the Nigerian

setting where the study is considered significant for improving curriculum design and implementation, especially in chemical education.

1.6 Summary

In this chapter, the background to the research problem has been presented. The nature and manifestations of the problem has been outlined. The need for the study and its potentials for making positive impact on the teaching/learning of chemistry in Nigeria has been highlighted.

In the next chapter, a review of literature relevant to the study is made. Its implications for developing a theoretical framework for the study, and the consequent choice and design of research instrument are considered.

CHAPTER TWO

REVIEW OF LITERATURE

2.1 Overview

The review of literature relevant to this study is presented in this chapter. The main thrust of the review gave guidance in proposing a framework for the study.

2.2 Problem

2.2.1 Definition

Problem, like many psychological constructs (eg attitude, intelligence, creativity), seems to defy precise, universally acceptable definition. Berlyne (1965) compiled the ideas of various authors about the definition of a problem. A summary of these is presented (in a-d) below. Problem:

(a) refers to a situation of high drive which lacks a readily available drive-relieving response.

(b) is a state of disequilibrium in the human thought structure.

(c) represents a gap between pieces of information.

(d) is a conflict within the individual; a conflict between the conditions at hand and a desired result, between an end and the means to reach it.

Merrifield etal. (1962) view a problem as: "a situation in which certain initial information is given, and some goal is more or less specified, but the relationships between

the given and the goal are not apparent".

The focal point of these definitions is that they portray a problem as a situation in which an individual wishes to reach a desired state from the present position, but does not immediately come to terms with the means for doing so.

2.2.2 Types of Problems

Problems can be classified into two broad categories. These, according to Frazer (1982) are artificial and real problems. Artificial problems have definite solutions known to somebody, which in the school setting is usually the teacher. Artificial problems are used to assist students in learning, through an application of their knowledge as a requisite preparation for solving day-to-day life's problems.

Artificial problems are considered to comprise two sub-classes. These are open and closed problems. In open problems, there is no single correct solution, but rather a multiplicity of possible alternatives. On the other hand, closed problems usually have single, unique solution, for example, numerical problems.

Real problems, unlike artificial problems do not have known solutions. Thus, solutions to real problems would have to be weighed against the balance of the "best approach in the circumstance". There are two kinds of real problems. Those that are mission-directed and others that are non-mission directed. The former category are those in which

the solution has an immediate application to society while the latter are those in which the solution does not have an immediate application. A graphic representation is shown in fig 2.1 below.

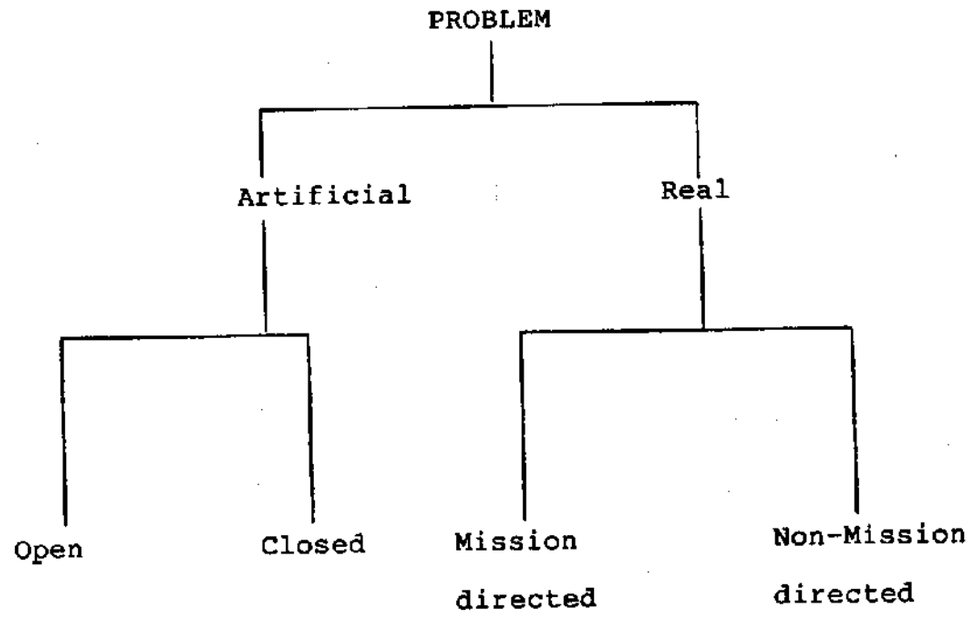


Fig 2.1

The problems involved in this study are thus artificial and closed problems.

2.3 Problem Solving

2.3.1 Toward a definition

There has been, and still is some confusion about what constitutes problem solving. For example, concept formation, recall of complex rules, creativity, deductive and inductive reasoning and many aspects of thinking processes have at one time or another considered to constitute problem solving (Bapat, 1975). The views of some authors regarding the meaning of problem solving are now presented.

The definition of problem solving compiled by Berlyne, and corresponding to his definitions of a problem, already outlined, are as follows.

Problem solving:

(a) is a situation that relieves a drive.

(b) refers to restoration of equilibrium in the human thought structure.

(c) is a process of closing the gap between pieces of information.

(d) refers to a process of devising a means to resolve the conflict within the individual, such that the desired goal is attained.

Gagné (1977) considered problem solving to involve assembling and using rules already known (by the solver) to create a new superior rule that allows a solution to be obtained. He said:

> "Problem solving may be viewed as a process by which the learner discovers a combination of previously learnt rules which can be applied to achieve a solution for a novel situation".

Ausubel (1968) defined problem solving in terms of bridging the gap between the learner's existing knowledge and the solution to the problem.

According to Ashmore etal. (1979) problem solving represents the end-product of a process of application of knowledge and procedures to a problem situation.

Mayer (1977) viewed problem solving in terms of a cognitive process - thinking. He said "...thinking is what happens when a person solves a problem". Polya (1968) considered problem solving as based on a cognitive process that results in "finding a way out of a difficulty, a way around an obstacle, attaining an aim that was not immediately attainable".

The common strand that appears to run through these definitions is that problem solving involves two integral dimensions. These are the possession of relevant knowledge and the appropriate deployment of the knowledge toward attainment of a solution.

Consequently, problem solving is viewed in this study to involve:

(i) possession of relevant knowledge in some form.

(ii) skill or strategic capability to use the knowledge to reach a desired state.

2.3.2 Problem Solving and Learning

Problem solving is an integral and fundamental aspect of learning (sec 1.2.1). Child (1986) has described this integral relationship in terms of Gagnés proposition of eight types of learning, which are considered to have a hierarchical structure, with problem solving at the apex. This is illustrated in fig 2.2, the highlights of which are briefly discussed below.

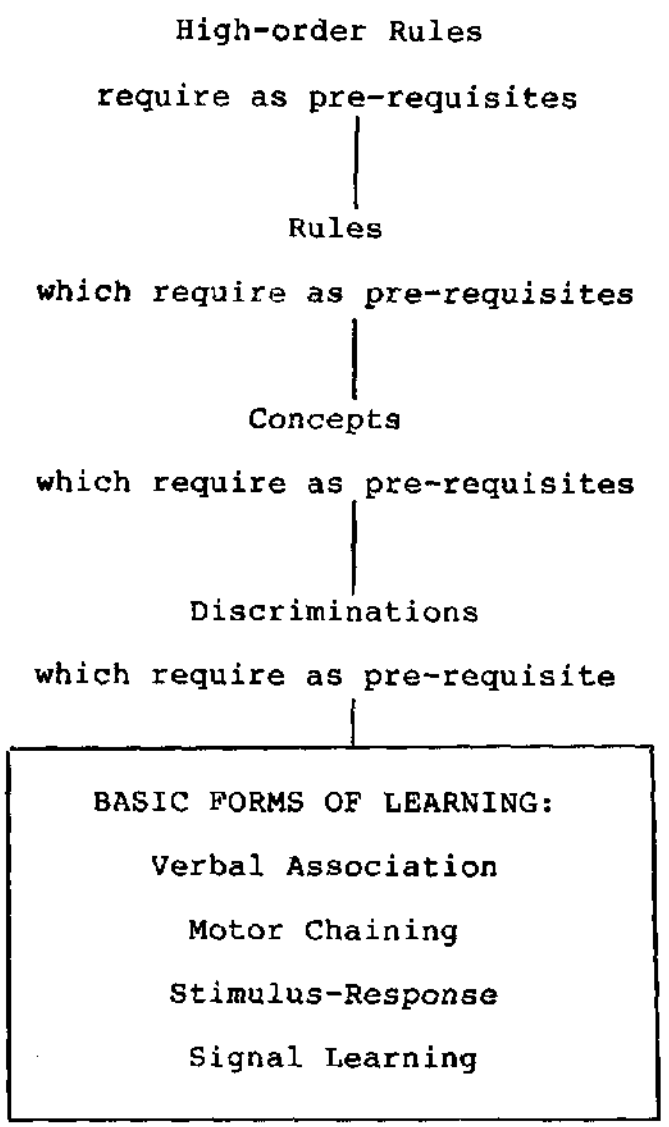


Fig 2.2 Adapted from Child (1986)

(a) Signal learning: This is typified by Pavlov's classical conditioning involving production of a general involuntary response to an impinging signal.

(b) Stimulus-response learning: This is exemplified by the studies of Thorndike and Skinner in which a given signal becomes associated with a particular voluntary response.

(c) Motor Chaining: This refers to sensory motor behaviour which develops as a result of some response patterns.

(d) Verbal Association; This refers to developing a combination of human sounds to make a meaningful pattern.

(e) Discrimination: Is the process of making different responses to different members of a given class.

(f) Concept Learning: This refers to the process of making a single response to a collection of objects (or events) as constituting a class. It is thus a form of generalization of discrimination learning.

(g) Rule Learning: This is the association of two or more concepts to form a pattern.

(h) Higher-order Rules: This is the process of combining rules to form new ones; which according to Gagnē (1977) leads to a solution. He regarded it as the pinnacle of learning. Problem solving, according to Gagné, thus involves a process of setting up and testing hypothesis using various rules known to the solver, which is both a process and hallmark of learning.

This study, which focuses on problem solving difficulties can thus be seen as that of learning difficulties in a sense. This draws support from Novak (1977) who said "... I see problem solving as essentially a special case of meaningful learning"

and from Gagné (1977) when he said "... problem solving, then,must definitely be considered a form of learning".

2.4 Some Psychological Theories of Problem Solving

2.4.1 The Associationist Theory

The main assumption of this theory about problem solving is that for any given problem situation (S), there are associations to many possible responses (R). The theory views problem solving as requiring three conditions:

(a) the stimulus (given problem situation)

(b) the response (a given problem solving behaviour)

(c) the association between a particular stimulus and particular response.

The latter is assumed to be in the problem solver's head; forming what is termed a family of possible responses associated with a particular stimulus. This is illustrated in fig 2.3

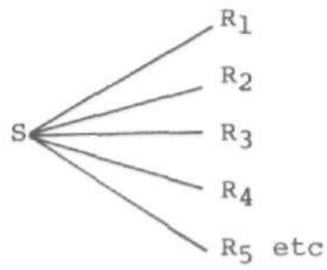


Fig 2.3

The basic ingredient of the theory is that problem solving involves a trial-and-error application of knowledge to a problem situation.

2.4.2 Theory of rule-learning and rule-using

The theory views problem solving in terms of acquiring and using concepts (Mayer, 1977). It presents two platforms, represented by two supporting theories to explain problem solving. These are continuity theory which views problem solving as attempts (by the solver) to tally past experiences into hierarchies of responses, and non-continuity theory which conceives of the problem solver as actively formulating and testing hypothesis. Results of studies (eg Bower and Trabasso, 1963) showed non-continuity theory to represent a better description of college students' problem solving behaviour.

Gagné (1977) stated that "... a defined concept is a particular kind of rule". He considered a rule to be an internal state (to the individual) which governs his behaviour and enables the individual to demonstrate a relationship. It is in this context that he considered problem solving as "a process by which the learner discovers a combination of previously learnt rules which can be applied to achieve a solution for a novel solution" (sec 2.3.1).

2.4.3 Gestalt Theory of problem solving

Gestalt psychologists conceive of a problem as a unit consisting of a number of structural units. In order to solve the problem, the solver needs to have an insight into the contextual configuration of the component parts. The insight is gained mostly

through re-organising and structuring the problem elements. They contended that broad, non-specific general experience and certain basic past learning represent an essential repertoire of behaviour which must be available for re-structuring when the new situation demands. They referred to this kind of problem solving as productive application, as opposed to reproductive application, in which the problem solver routinely follows some laid down procedure or algorithm (Mayer, 1983).

2.4.4 The Theory of Intellectual Development

This was proposed by Piaget. It represented an attempt to formally describe the human organism's knowledge or competence at different points in time (Case, 1974). As Elkind (1967) pointed out, Piaget is a genetic epistemologist, concerned with the nature of knowledge, and the structures and processes by which it is acquired.

The immediate implication of Piaget's theory to the practice of problem solving is that, for optimum positive response, the conceptual demands of a problem situation should, in some way, match the level of cognitive skills of the problem solver (Rowell, 1984). Problems demanding higher cognitive skill than is available to the solver may lead to frustration while those demanding cognitive skill below that available to the solver may lead to boredom. This represents a rough guide, notwithstanding the difficult question of how conceptual demand of a task is matched with the level

of cognitive development. A diagramatic representation is shown in fig 2.4.

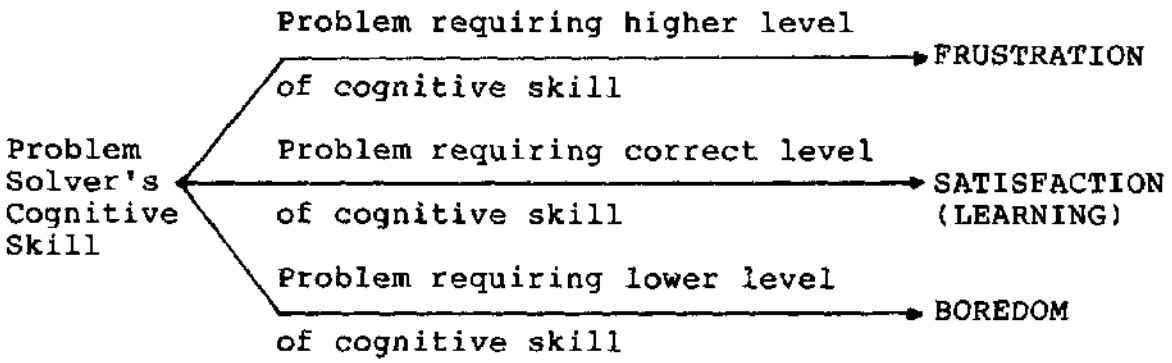


Fig 2.4

2.4.5 The Theory of Meaningful Learning

This was proposed by Ausubel (1968). The theory conceives of learning as a continuum with two extremes, represented by meaningful and rote learning. According to Novak (1978), meaningful learning involves a conscious effort on the part of the learner to relate new knowledge in a substantive, non-arbitrary way to relevant existing concepts or propositions in the learner's cognitive structure. In contrast, rote learning is an arbitrary, verbatim incorporation of new knowledge into the cognitive structure. Novak considered meaningful learning to be equivalent to the use of knowledge in problem solving.

The immediate implication of this theory to problem solving is this: problem solving requires knowledge ie prior knowledge as pre-requisite. Further more, it is not enough to have just prior knowledge, it must, in addition, be adequate, relevant and organised.

2.4.6 Information-processing Approach to Problem Solving

This theory views problem solving in terms of an activity which involves some processing or transformation of raw information in a manner and into a product that yields a solution. It attempts to detail the cognitive processes that intervene between a problem situation and a solution state. It assumes that during the process of problem solving, a solver applies operators to problem states. An operator is any move that the solver deems legitimate in solving the problem. A problem state is the description of the elements in the problem.

According to Mayer (1983) when an operator is applied, the problem is changed from one state to another. Thus, problem solving can be represented in one of two ways:

(a) a sequence of mental operations performed on information in a subjects memory

(b) a sequence of internal states or changes in information that progresses toward a solution.

The major highlight of these theories reviewed is that they link problem solving on one hand to acquisition and application of knowledge on the other. This is further developed in section 2.9.

2.5 Models of Problem Solving

Problem solving models are proposals that attempt to describe some form of theoretical framework within which problem solving behaviour is thought to occur. The structure of some frameworks

consist of stages while others consist of statements of procedure based on heuristics. Different authors have proposed different problem solving models based on their individual epistemological persuasions. Some of these are outlined below.

2.5.1 Models based on Information-Processing Approach

Simon (1978) has suggested that any discussion of problem solving must deal with three major components:

(a) the problem solver - which he called the information processing system.

(b) the problem - which he called the task environment.

(c) the problem representation - which he called the problem space.

According to him, problem solving occurs when:

(i) a problem solver translates a problem into an internal problem repesentation, and then

(ii) searches for a path through the problem space from the given to the goal state.

Thus Simon's model of problem solving revolves around two central ideas, which are:

(i) representation of problem as problem space

(ii) solution of problem as search strategies through the problem space.

Lindsay and Norman (1972) have focused on what the problem solver brings to the problem solving situation. They identified three types of knowledge

which they considered that the problem solver brings to bear on problem solving. These are:

(a) facts: basic propositions that are immediately available to the solver.

(b) algorithms: sets of rules that automatically generate answers.

(c) heuristics: rules of thumb or general plans of action or strategies.

Earnst and Newell (1969) proposed a four stage model consisting of the following:

(a) the input - representing the problem which is acted upon by

(b) a translator - which converts it into

(c) an internal representation - which generates

(d) a solution.

This is illustrated in fig 2.5.

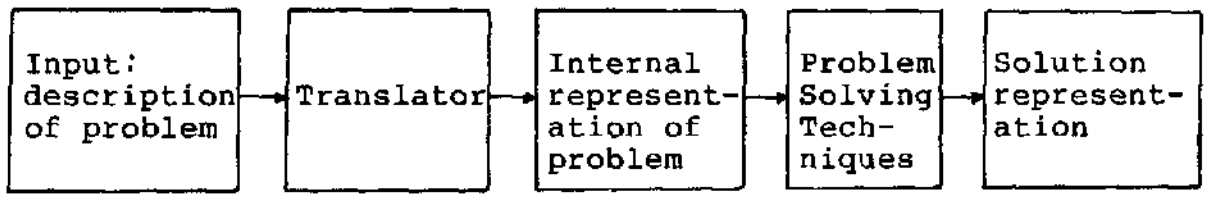


Fig 2.5 Earnst and Newell problem solving model

Greeno (1973) proposed a memory model of problem solving in which the three main components of describing problem solving behaviour are:

(a) short-term memory (STM) - through which the external description of the problem is input.

(b) long-term memory (LTM) - which stores past experiences with solving problems.

(c) working memory (WM) - in which the information from STM and LTM interact, and a solution route is generated and tested. The model is illustrated in fig 2.6

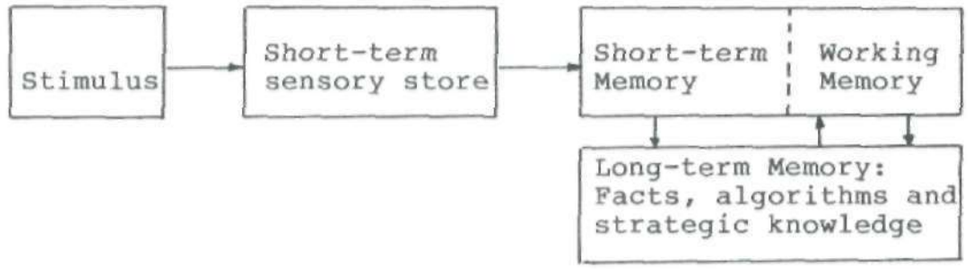


Fig 2.6 Greeno's problem solving model

According to Greeno, a description of the problem, including the initial state, the goal state and the legitimate operators come into the working memory by way of the short-term memory. Past experiences enter working memory from the long-term memory. More information may be needed from outside world as the problem solving progresses. The generation of new problem-states in working memory may require more information from past experience.

According to Mayer (1983), the concept of working memory has a central role in the structure of Greeno's model, in the sense that:

(i) the internal representation of the problem occurs there

(ii) the construction of links between givens and unknowns occurs there

(iii) the relevant past experience is used to modify the structures held in the working memory.

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2.5.2 Models based on Gestalt Psychology

Some examples of problem solving models based on gestalt theory are those proposed by Wallas (1931), Polya (1957) and Duncker (1945).

Wallas proposed a four stage model composed of the following units:

(a) Preparation: the gathering of information and the initial attempts at a solution.

(b) Incubation: putting the problem aside to work on other activities.

(c) Illumination: the key to the solution appears - a flash of insight occurs.

(d) Verification: checking out the solution to ensure that it works.

Polya also suggested a four-stage model of problem solving, which are:

(a) Understanding the problem: the solver gathers information about the problem.

(b) Devising a plan: the solver attempts to bring past experience to bear on the demands of the problem, so as to find a solution path. The solver re-structures the problem and atempts to find a relationship between the unknown and the known, working backwards. The flash of insight occurs at this stage.

(c) Carrying out the plan: the solver tries out the plan of solution, checking each step.

(d) Looking back: the solver evaluates the solution to see how it fits the requirements of the problem.

The models of Wallas and Polya are essentially the same. For example, Polya's second stage of "devising a plan" is similar to and includes elements of Wallas' second and third stages. Wallas' fourth stage ie "verification" is similar to, and incorporates elements of Polya's third and fourth stages.

Duncker proposed a "solution tree" model in which he specified three phenomena involved in the process of problem solving. They are:

(a) Functional solution: the elements of the problem must be seen in terms of their general or functional usefulness in the problem. He argued that functional (general) solutions come before the specific ones.

(b) Reformulating or Centering: problem solving involves successive stages of reformulating or structuring of the problem, with each partial solution obtained, creating a new, more specific problem.

(c) Suggestions from above and from below: reformulating the goal to make it closer to the givens, and reformulating the givens to make them closer to the goal. This stage is similar to Polya's second stage - devising a plan.

2.5.3 Model based on gap-bridging

Frazer (1982) advocates the use of a model based on the theory which views problem solving as bridging the gap between a problem situation and a

solution state, using information and reasoning. He argued that a problem is manifest as a question to answer, a task to execute or a goal to reach. This is illustrated in fig 2.7 below.

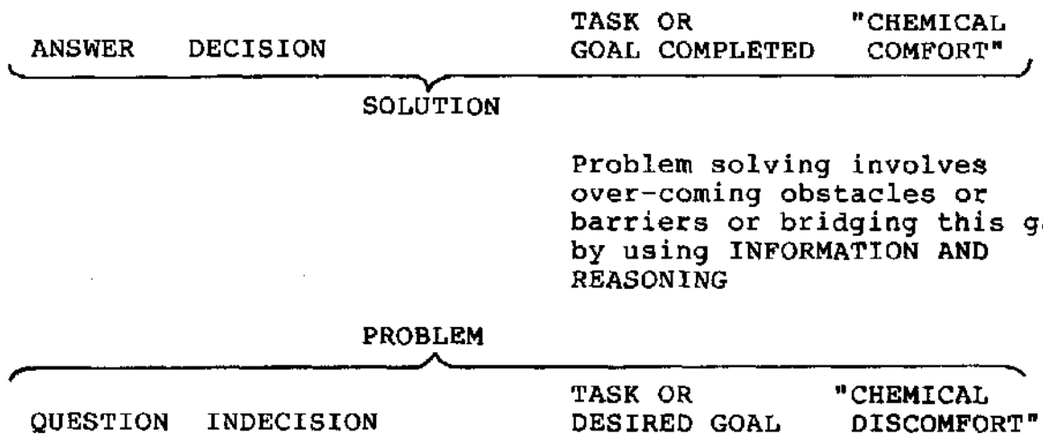


Fig 2.7 Adapted from Frazer (1982)

Thus, he proposed the following four-stage problem solving model:

(a) Defining the problem.

(b) Collecting information relevant to the problem.

(c) Reasoning, using the information collected.

(d) Checking or evaluating solution obtained.

2.5.4 Model based on Scientific Investigation Approach

Pérez and Torregrosa (1983) considered problem solving as one of the principal causes of scholastic failure in chemistry. They argued that the failures are attributable to lack of theoretical knowledge on the part of the pupils. Their problem solving strategy consisted in an approach they termed "scientific investigation" which constituted a

central idea in their problem solving model outlined below:

(a) a qualitative analysis of the situation and putting forward a hypothesis.

(b) devising strategies for solving the problem.

(c) solving the problem.

(d) analysis of the results.

2.6 A Critique of the Models

Inspite of the articulation built into the models they are, nonetheless, subject to some limitations. One of such limitations relates to the fact that the scope of the problems the models represent is relatively narrow. The models seem to focus predominantly on artificial, closed problems (see sec 2.2.2). Frazer (1982), while reviewing problem solving models, also made this point when he said "... emphasis is on the classroom-type of problem in which a well defined problem with a unique answer is presented to the student".

Another area of limitation lies in the nature of the models; which Pérez etal (1983) observed to have portrayed problem solving only as a task of "simply finding a link between data and unknown quantities". They argued that problem solving models should be viewed and developed in terms of "scientific methodology" involving formulation and testing of hypotheses. It is with this background that they proposed the model discussed in sec 2.5.4.

A further area of limitation relates to the question of whether or not the models could be relied upon for use as a theoretical basis for devising instructional strategies of teaching problem solving. In reference to the stages specified by the models, Lester (1982) raised the question of their applicability in teaching a person to become a successful problem solver and the conditions that most enhance success. In apparent appreciation of these limitations, Merwin (1977) cautioned teachers "to exercise a good deal of flexibility" in the use of problem solving models. He asserted that "research evidence indicates that the sequence of the steps is not fixed, but varies considerably with the problem and the investigator. They are at best an approximation of what actually occurs during the problem solving process".

These limitations are not unexpected however, if consideration is given to the fact that there is no single, universally accepted definition of problem solving (see sec 2.3.1). Thus the fluidity along with the limitations that characterise problem solving models appear to be a direct result of this fact.

2.7 Requirements for Problem Solving

Problem solving does not occur in a vacuum (Gagné, 1977). A number of factors are held to constitute requirements for solving problems. These are classified by Gagné (1977) into internal and external (to the solver) factors. Some of the

internal factors include: possession of relevant knowledge, process skills, problem recognition, reading and language fluency and confidence. Some of the external factors include: instructions and cues embedded in the problem situation, conceptual demands of the problem situation, the physical conditions in which problem solving occurs. Some of the factors considered to be closely related to this study are now discussed in some greater detail.

(a) *Problem recognition*

This refers to the solver's awareness that a problem actually exists. It serves as a spring board for prompting the solver to initiate a problem solving process, which include the identification, isolation and structural representation of the problem. Merrifield etal. (1962) consider problem recognition to occur during the preparation stage, and involves "an appreciation of a need or that things are not as they should be".

(b) Knowledge of the subject matter

Possession of a relevant knowledge base is a pre-requisite in the process of problem solving. Even in situations where problems are thought to be solved through a flash of insight; it is usually preceded by a period of incubation during which some form of relevant kowledge item is brought to bear on the problem.

Selvaratnam (1983) observed that successful problem solving requires the individual to be able to "understand and recall the necessary items of knowledge of the subject matter". This view is supported by Case (1974) Larkin etal. (1980) Lindsay etal. (1972) and of course, by common sense. Larkin etal, for example, opined: "... regardless of the sophistication of the solver's procedural and strategic knowledge, deficiencies in knowledge of facts, concepts and principles constrain the scope of that individual's problem solving ability".

(c) Process Skill

This refers to the ability of the problem solver to process and transform possessed knowledge and available information in order to solve a problem. High facility with this skill leads to high probability of successful problem solving, other factors being held constant.

Selvaratnam (1983) observed that it represents a fundamental requirement for problem solving. He considered that it constitutes the "required skill to logically reason out the solution". Larkin etal (1980) referred to it as strategic knowledge, which, according to them, "consists of procedures for planning and for setting and representing goals during work on the problem". They

argued that it "determines the way in which problem solving performance is organised". Gagné (1977) labelled it cognitive strategy which he defined as "skills with which learners regulate and modulate their internal processes of attending and selective perceiving, coding for long-term storage; retrieval and problem solving".

(d) Confidence

This simply refers to a condition of mind in which the problem solver nurses sustained hope in his ability, and faith in his efforts to yield a solution. It serves to arouse and sustain motivation and endurance which are required as necessary psychological props to the problem solver. Without confidence, there is little room for making effort, and consequently, M-space Case (1974) is not utilised, leading to failure in a problem solving that could have otherwise succeeded. This point was also highlighted by Selvaratnam (1983) when he said "... in order to solve a problem, we must have confidence in our ability to solve the problem".

The immediate implication of these requirements to this study is that individuals succeed or fail in problem solving depending on whether or not they possess these requirements. Consequently, they may represent a basis for individual differences

in problem solving. It follows, therefore, that the question of why people fail to solve problems may be answered (at least patially) by taking these requirements into contextual focus.

2.8 Some Studies on Problem Solving in UEA

A number of studies on problem solving have been carried out in the University of East Anglia. The central aim of the studies seem to be the identification of students' learning difficulties. Some of the studies that are considered to have implications for the present work are now briefly discussed.

(a) McCabe (1977) investigated amongst sixth form students in England how mis-use or non-use of information affected problem solving proficiency of the students. She found that students:

(i) had difficulties solving problems. Only 21.8% correctly solved the problems posed.

(ii) possessed relevant chemical knowledge required to solve the problems, yet failed to do so.

(iii) failed to use information both *from memory* and *from problem* statement.

(b) Khan (1980) investigated students' problem solving difficulties with electrophilic aromatic substitution and the synthesis of

polysubstituted benzenes amongst undergraduate chemistry students in UEA. He found that:

(i) the students possessed the requisite background knowledge required for solving the problems, yet they were unsuccessful in solving the problems.

(ii) the failure is attributable to students' inability to apply pre-requisite knowledge in attempting to solve the problems.

(iii) the students lacked confidence (presumably in their ability to solve the problems).

(c) Ahmed (1982) conducted research into learning difficulties in some chemistry topics amongst secondary school students in Nigeria. His findings showed that students had difficulties in:

(i) recall, recognition or identification of items of correct knowledge, information or rule.

(ii) realising and retrieving information relevant to problem situation.

(iii) applying information or rules in given problem situation.

(d) Patwary (1983) studied learning difficulties in organic stereochemistry amongst university undergraduates in Bangladesh. His study focused on both diagnostic and remediation aspects of the problem. His findings regarding students' learning difficulties include:

(i) weak imaginative power in visualizing molecules in three dimension.

(ii) lack of understanding of molecular conformation.

(iii) lack of concentration (on the part of the students) on the problems.

(iv) inability to pick up, recall and sequence necessary information.

(v) misunderstanding about relationship between semmetry and molecular structure.

(e) Dupigny (1985) investigated learning difficulties that sixth form students in England had with molecular structures, having regard to the multiplicity of methods in which the structures are usually presented in chemistry text books. His findings showed that:

(i) the students had difficulties in recognising, interpreting and representing molecular structures.

(ii) the level of the difficulty is related in some way to the kind of method used in representing the structure.

2.9 Implication of Literature for the Present Study: Toward a Working Model

The literature reviewed in this chapter represented a wide range of views about the nature and process of problem solving. What now follows is an attempt to collate the main themes into a framework that will serve to guide the conduct of this study.

The summary of literature survey having direct implication for this study is as follows:

(a) The process of problem solving begins from an individual's awareness of an existence of a problem.

(b) To solve a problem requires that the individual possess pre-requisite knowledge for solving the problem. Usually, this refers to knowledge of facts, rules, principles and pattern recognition. This is referred to by various names, such as, conceptual knowledge, verbal knowledge, information, proposition etc.

(c) The knowledge has to be accessed, selected and recalled by the solver in line with the nature of the problem at hand. It is then acted upon by a set of operators which transform it

to yield a solution. This has also been referred to by different names, for example: strategic knowledge, procedural knowledge, process skill, understanding, etc.

(d) Thinking or reasoning is held to mediate between problem-situation and a desired solution state and also in integrating conceptual and strategic knowledge for problem execution.

The insight derived from literature reviewed guided the proposal of a working model for this study which is shown in fig 2.8.

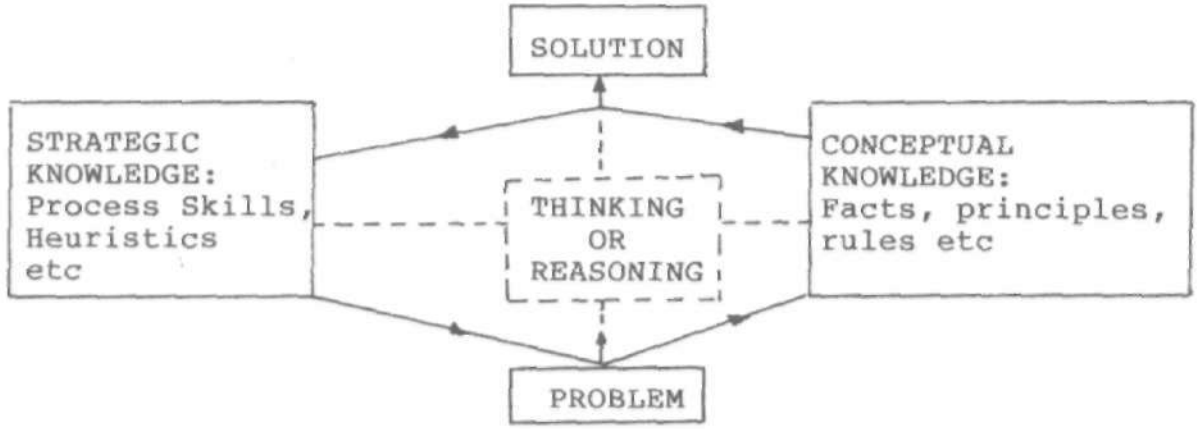


Fig 2.8 Structure of a problem solving model

It comprised four main components:

(a) a problem situation.

(b) a desired solution state.

(c) conceptual knowledge (of the solver).

(d) strategic knowledge (of the solver).

The problem represents the existing state, while the solution represents the desired state. The solver needs to recognise and structure the problem. This effectively means constructing an

understanding of the problem. "Understanding" is defined as the ability to construct a representation of the various elements in a situation and the conceptualisation of the relationships between the elements (Larkin etal, 1980). Relevant information is selected and recalled from LTM. This represents conceptual knowledge, which in problem solving can be likened to weapons in war. Their possession is one thing, their usefulness to the situation at hand, or indeed, the capability to use them to meet the desired goal is yet another. This is where strategic knowledge features. It is the capability to piece together, organise and process conceptual knowledge into a form that leads to a solution. The process involves thinking or reasoning. Thus, there is a cyclic interaction between the problem situation, conceptual knowledge and strategic knowledge through the medium of thinking or reasoning, within which the solver crystallises a plan of action, having selected, retrieved and organised relevant information. Failure in this phase leads to failure to start the problem and if a start is made, it is haphazard and often dies out prematurely.

Having integrated conceptual and strategic knowledge, the solver fits the product into the demands of the problem. This represents execution process.

The model, thus represents a two-stage problem solving phenomena which are: planning and execution. Such events as definition or statement of problem and formulation of hypothesis are deemed to fall under planning. Evaluation is considered to be carried out at each stage of the problem solving process, including after the problem is thought to have been solved. It is thus not construed to represent a distinct phase. In fact, a distinct phase does not exist in practice, as the solver is viewed to move forth and back within the phases in the act of problem solving. The thinking or reasoning processes which serve as the life-wire, linking and integrating conceptual and strategic knowledge is held to occur in the working memory (see fig 2.6).

The development of research instruments for this study (chapter 3) is influenced by the working model. They are designed to probe students':

(i) conceptual knowledge (Test A)

(ii) strategic knowledge (Test B)

(iii) thought processes that guide and integrate (i) and (ii) in the process of problem solving - (protocol analysis).

The structural relationship between the working model, literature reviewed and development of research instruments is depicted in fig 2.9.

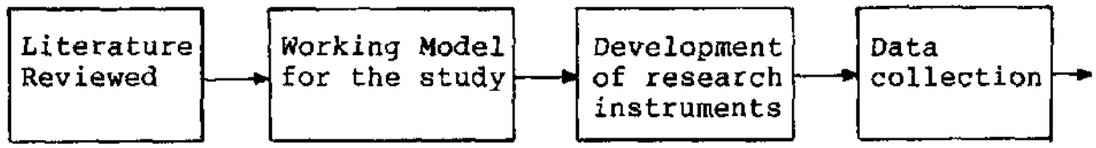


Fig 2.9 Relationships of literature reviewed with development of research instruments

The persistence of students' problem solving difficulties in our school system could mean that either:

(a) findings from relevant studies have not been carried to the classrooms for practical implementation or

(b) their implementation have been ineffective; and thus has yielded little or no positive results.

This presents an urge for continued search for an improvement in students' problem solving abilities in science education in Nigeria.

2.10 Summary and Conclusion

In this chapter, literature that is relevant to this study is presented. It represents an attempt to bring to focus, the views of various authors regarding problem solving. The main thrust of the views are collated to evolve a theoretical framework for the study.

The next chapter deals with development of instruments for data collection.

PART 1A

PROBING STUDENTS' DIFFICULTIES IN PROBLEM SOLVING

CHAPTER THREE

DEVELOPMENT AND DESIGN OF INSTRUMENTS FOR DATA COLLECTION

3.1 Overview

In chapter one, the problem being investigated in this study is stated (sec 1.2.4). The highlight is that Nigerian students in Schools of Basic Studies have difficulties in solving organic chemistry problems. A preliminary survey (sec 1.2.3.2) gave an impressionistic view of the nature of the difficulties.

It is required that a systematic investigation be conducted into the nature and causes of the difficulties. The implementation of this calls for development and utilisation of measuring instruments. This chapter deals with the description of the development and construction of such instruments.

3.2 A theoretical basis for using tests in data collection

A major aim of education is development of cognitive ability in students. Ebel and Frisbie (1986) defined cognitive ability as referring to particular kinds of tasks that can be done using the mind. They observed that cognitive abilities are taught specifically and are learnt specifically.

Acquisition of cognitive abilities, thus, requires learning, the latter producing knowledge. They view knowledge as consisting of two integral components. These are information and

understanding. They argued that individuals, equipped with both components are said to command knowledge. These individuals are usually successful in problem solving tasks. Those who acquire information without the related understanding are said to possess knowledge. These individuals are usually unable to see the relation of the information they possess to other related information they have acquired, and thus, are unable to solve problems.

These views have three implications for the development of instruments for this study:

(a) That problem solving (an example of cognitive activity) involves pre-requisite knowledge which is taught and learnt specifically.

(b) That students' problem solving ability can be measured through the measurement of underlying knowledge.

(c) That a comprehensive measurement of such knowledge involves both an information acquisition and an understanding components.

These views correspond to, and reinforce the validity of the working model proposed (sec 2.9). The assumptions for the construction, and the structure of the instruments, are, thus, based on these stand-points.

3.3 Statement of knowledge domain and related abilities being measured

It is essential to specify the knowledge domain and the associated abilities which the instruments are designed to measure, even though a

general overview of these have been given in chapter one (sec 1.4). This specification is essential because it is only when we know unambiguously, what is to be measured that we can select (or construct) the kind of instrument that measures it. This consideration is closely related to the question of test validity discussed in section 3.7.

The mapping out of the knowledge domain related to this study is done on the basis of insight derived from the preliminary survey referred to already in this chapter. The summary is shown in table 3.1.

TABLE 3.1 STATEMENT OF KNOWLEDGE AND RELATED SKILLS MEASURED BY RESEARCH INSTRUMENTS

TOPIC AREAS	KNOWLEDGE DOMAIN: TRANSLATED INTO TEST A	OPERATIONAL DEFINITIONS OR SKILLS: TRANSLATED INTO TEST B
Reagents	Electrophiles and nucleophiles	(i) To be able to identify electrophilic or nucleophilic species in a given reaction. (ii) To be able to describe the process of their reactive interactions with other given reacting structures.
Chemical structures	(i) Primary, secondary and tertiary structures (ii) Functional groups (iii) Electronegativity and polarity of bonds	To be able to use these concepts to: (i) identify reactive sites in given organic molecules involved in reactions (ii) explain formation of different products from compounds of similar structure
Covalent bonds in organic reactions	Electronic concept of bond-formation and bond-breaking in organic reactions	(i) To be able to represent the process of bond-breaking in organic reactions (ii) To be able to represent the process of bond-formation in organic reactions
Reactive Intermediates	Carbocations	(i) To be able to represent the structure of intermediate carbocations in organic reactions (ii) To be able to represent the subsequent conversion of the intermediates to products
Symbolisms	Chemical conventions generally used to show reaction processes: (i) Curved arrows: ↷ (ii) Charge separation signs: $\delta+$; $\delta-$ (iii) Electron-pair transfer signs: + ; —	(i) To be able to use curved arrows to describe progression of organic reactions (ii) To be able to use charge separation signs to show relative electron distribution in the molecule (iii) To be able to represent structural changes resulting from electron-pair transfer
Chemical Reactions: (Reaction-types)	(i) Nucleophilic and electrophilic substitution reactions (ii) Nucleophilic and electrophilic addition reactions (iii) Elimination reactions	(a) To be able to describe, using appropriate symbols, mechanisms of: (i) nucleophilic substitution reactions (ii) electrophilic substitution reactions (iii) nucleophilic addition reactions (iv) nucleophilic addition reactions (v) elimination reactions (b) To be able to relate some of the principles underlying these reaction-types to each other in the process of solving problems

3.4 Choice of instruments for this study

A number of research instruments have been used by various authors, at one time or another, to investigate learning difficulties in science education. In the University of East Anglia for example, some authors (sec 2.8) have used relevant combinations of multiple-choice items, structured tests, free-response problems and the "think aloud" method.

The main purpose of employing test instruments to investigate learning difficulties is to locate concepts that students fail to grasp in a given area of the subject, and sometimes to determine the source(s) of the difficulties. Tests which require students to select correct responses from a number of given options represent suitable tools for revealing what the students fail to know and where they fail to solve problems within a defined knowledge domain. Protocol analysis is useful for describing students' thought processes, thus complementing written tests which only show the products of thought.

Having regard to the stated aim of this study, and the theoretical assumptions that underlie the proposed framework (sec 2.9) structured tests, comprising multiple-choice items and free-response problems are chosen as suitable diagnostic tools.

Protocol analysis, later described as the "think aloud" problem solving (TAPS) method is also chosen for an indepth study of the sources of the difficulties. This two-pronged approach, illustrated in fig 3.1 appears appropriate and

adequate for probing the difficulties.

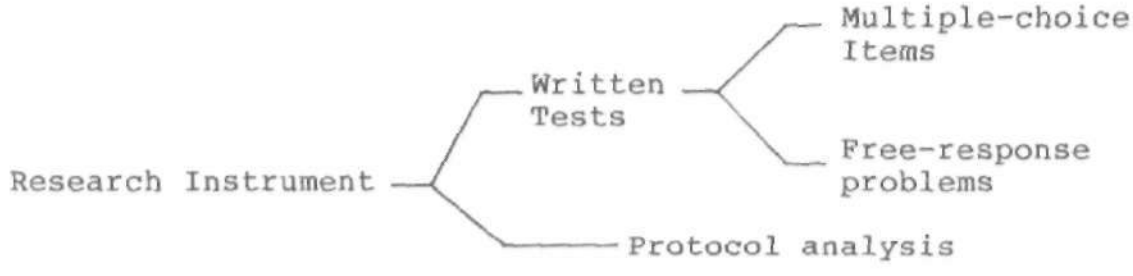


Fig 3.1 Research Instrument for this study

3.5 Structure of the Instruments

The instruments consist of three parts. They are:

(a) Test A which consists of multiple-choice items, designed to probe the level of students' posession of pre-requisite conceptual knowledge.

(b) Test B which consists of free-response problems, designed to investigate students' overt problem solving behaviour with a view to locating the nature and causes of their difficulties.

(c) "Think Aloud" Problem Solving (TAPS): this involves the students verbalising their thoughts as they solve free-response problems contained in test B.

The structural relationship of the tests derive from the fact that the substance of one test is based on that of the other. Test B is closely related to Test A, such that solving the problems in the former requires the knowledge items contained in the latter. The cognitive demands of the tests are also structured. Test A requires lower cognitive

skills, such as recognition and recall, while test B calls for higher skills which include selection, organisation and application of information. The construction of test A derived from statement of knowledge domain and associated skills, while that of test B is based on test A. Thus, we have structural relationships amongst the tests, both from the point of view of construction and cognitive demands. This is illustrated in fig 3.2 below.

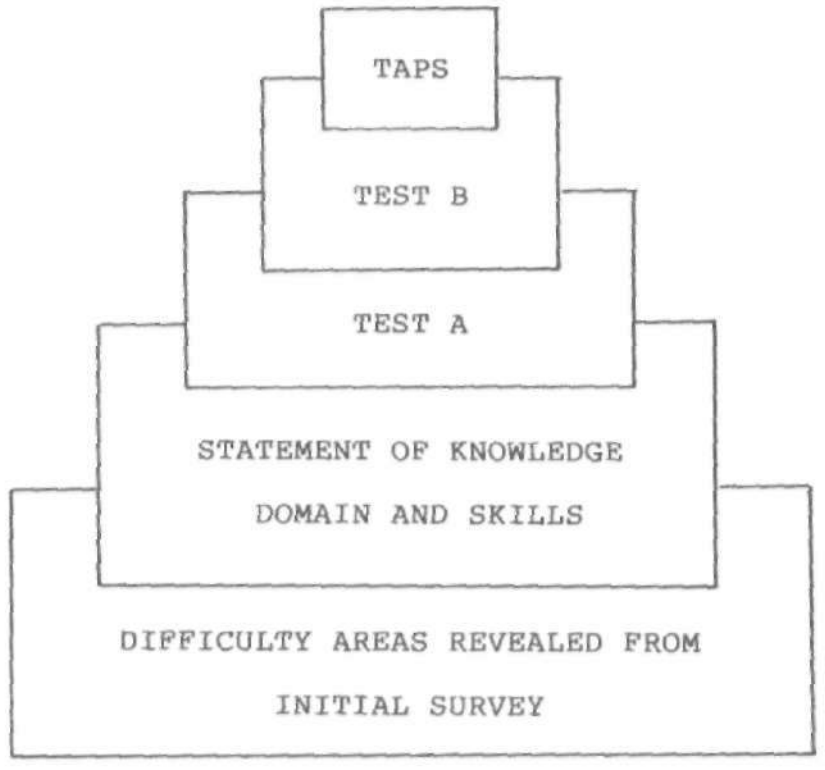


Fig 3.2 Structural Relationship and Derivation of the Tests.

Detailed discussion of TAPS is taken up in chapters seven to nine. The remaining of this chapter concentrates on Tests A and B.

3.6 Construction of the Tests

The stated knowledge domain and the related abilities specified (Table 3.1) guided the choice of items that were assembled to form the tests. A content analysis of the syllabus operated by the students (appendix 1.2) helped to guide the level of item/problem difficulty incorporated.

3.6.1 Test A

This consists of objective items, rendered in two formats - structural communication grids (Johnstone et al, 1983) and multiple-choice. It is designed to probe the relevant knowledge-base of the students. The test initially consisted of 50 items which were later reduced to 40 after they were pilot-tested.

The structural communication grids format comprised the first twelve items, with corresponding twelve response options. Each item has only one correct response option. The multiple-choice format comprised items, each made up of a stem and four response options, the latter consisting of a key and three distractors. The distractors were chosen to be as closely related as possible to the students' mistakes and misconceptions revealed during the initial survey of their past examination answer scripts (sec 1.2.3.2). This contributes to making the test rational and functional. Each response option was made as plausible as any other in the

group. It was an attempt to provide as much a distraction from the key as possible. This helps to ensure that students select correct options because they possess the required knowledge, and wrong ones where they do not.

The test items were made up from three main sources. These were:

(a) advanced level past examination questions in organic chemistry. For example, West African Examinations Council question papers, 1980.

(b) relevant information obtained from text books in organic chemistry. For example, Tedder etal, part I, 1983; Sykes, 1981.

(c) experience and initiative of the author.

A summary of the basic concepts probed by the items is shown in table 3.2. Test A and the answer sheet are included as appendices 3.1 and 3.2 respectively.

TABLE 3.2 CATEGORIZATION OF CONCEPTS PROBED BY TEST A

TOPIC AREA	CHEMICAL CONCEPTS	ITEM NUMBERS
Chemical Structure	Charge distribution in molecules, polarity of bonds, reactive sites, functional groups	1, 2, 3, 5, 6, 7, 8, 11, 20, 21, 23, 26, 30, 31
Reagents	Nucleophiles and electrophiles	13, 14, 24, 25, 34
Chemical Reactions: (Reaction-types)	Substitution reactions	7, 12, 15, 17, 19, 27, 29, 37
	Addition reactions	22, 28, 33, 36
	Elimination reactions	4, 16, 35, 38
	Reaction intermediates	9, 10, 18, 39, 40

3.6.2 Test B

This consists of free-response problems. They were designed, such that they required the knowledge of the items in test A as pre-requisite basis for solving them. That is, items of test A formed sub-tasks of the problems consisted in test B, designed to probe students' problem solving behaviour with a view to locating their learning difficulties.

The test consisted of 7 problems, reduced to 5 after they were pilot-tested. They were formulated on the basis of the operational definitions of abilities mapped out for investigation (table 3.1). Problems having two or more parts to them generally require similar or closely related chemical principles for solving each part. Such a design constituted part of an attempt to probe how students use or fail to use knowledge both within and across problems. Such tasks would reveal students' ability to visualise and demonstrate the interrelationships of chemical principles and pattern recognition in chemical problems. For example, problem 2 involved two parts: electrophilic substitution in an aromatic hydrocarbon, and electrophilic addition in an olefinic hydrocarbon. The general principles involved are:

(i) electrophilic addition, followed by elimination, in the case of the aromatic hydrocarbon

(ii) electrophilic addition, followed by nucleophilic addition, in the case of the olefinic hydrocarbon.

Thus, in addition to solving the problem contained in each part, the design further probes students' ability to, and the consistency with which they apply knowledge to problems that require interrelationships of chemical principles.

Each problem was followed by a questionnaire consisting of four items. They sought to elicit from the students whether or not they:

(i) were familiar with the problems

(ii) found the problems difficult

(iii) were confident about the correctness of their answers.

The fourth item listed a number of possible reasons that could account for the students' difficulties with the problems. They were required to select one reason that corresponded to their opinion or to state their own reason in a space provided, where none of the reasons given fitted their opinion. This was done to gather information about the students' perception of the problems. Such information were useful, as they supplemented those obtained from their written responses to the main problems.

There was also a six-item questionnaire at the end of the test. They sought a combination of information from the students, ranging from their interest to the relevance of chemistry to their proposed careers. This was an attempt to gather information about the students' perception of chemistry generally, and organic chemistry in [illegible] Test B is included as appendix 3.3.

3.7 Validity of the Tests

In the design of the tests, what the author sought to achieve was intrinsic, rational content validity, which, according to Ebel and Frisbie (1986), should be developed concurrently with the development of the test. Such a validity is intrinsic because it is built into the test, rational, because it is derived from rational inferences about the kind of tasks that will measure the intended ability/abilities.

They argued that "the answer to the validity question is inherent in the test-development process". They pointed out three criteria which tests must meet for validity. They stated these criteria as follows: "Those who develop tests of cognitive ability produce validity evidence in the process if they:

(a) define explicitly the ability to be measured

(b) describe in detail the tasks to be included in the test

(c) explain the reasons for using such tasks to measure the ability in question".

In developing these tests, this procedure was followed fairly closely.

(a) The abilities to be measured are defined operationally (table 3.1).

(b) The knowledge domain relating to these abilities was defined conceptually (table 3.1).

(c) (a) and (b) above were used to determine suitable tasks to be included in the tests.

(d) The reasons for using each test are given in sec 3.5. Following from these, therefore, the tests are considered to have the necessary content validity.

The tests were, further more, submitted to three colleagues in the sector for comments. All, except one who observed that problem No 4 was slightly difficult, returned a verdict of "good tests".

3.8 Limitations of the Tests

The test design suffered from some limitations that the author could do little to eliminate. These included:

(a) Structuring of the tests:
Ideally, each item in test A should conform to a particular sub-task in the problems of test B. It was not possible to achieve this exactly. For example, nucleophiles and electrophiles, which formed part of items in test A, feature across all the problems in test B. This tends to weaken the structural relationship between the two versions of the tests.

(b) The fact that the tests were paper-pencil types, in which the performance of the students was taken to represent their cognitive ability, posed a limitation. This was because there were a number of relevant

factors that the tests could not take into account. These included reading ability, language fluency and general learning facilities available to the students.

3.9 Summary and Conclusions

The development of the research instruments have been discussed in this chapter. They involved the students in paper-pencil tests, A and B, designed to probe the students' possession of relevant chemical knowledge-base, and the use of the knowledge in solving problems respectively. Test validity was ensured through a process of careful definition of the abilities to be measured, related knowledge domain identified from content analysis of the students' syllabus, and subsequent formulation of the tasks that measure the specified abilities. This was referred to as intrinsic, rational content validity.

The next chapter deals with the use of these instruments for data collection, beginning with an account of how the instruments were initially refined through pilot-testing.

CHAPTER FOUR

DATA COLLECTION

4.1 Overview

This chapter describes the processes and conduct of data collection. It is in two sections. The first section deals with the pilot study which preceded the main study discussed in the second section.

4.2 The pilot study

4.2.1 Purpose of pilot study

Satterly (1983) presented an outline of the basic aims of a pilot study. These were considered relevant and adequate for this study. The pilot study was thus carried out in an attempt to achieve those aims, which are:

(a) To identify items that have weak construction, and thus should be modified or discarded on grounds of their ambiguity, misleading instruction or undue complexity.

(b) To determine the degree of difficulty of each item.

(c) To examine the plausibility of distractors.

(d) To gain information on the number of items to make up the test for the main study and to determine a suitable time-limit for it.

(e) To examine the relationship among the items chosen in order to eliminate redundancy of information; that is, to streamline items that do not basically differ with respect to the attribute they are measuring.

4.2.2 The sample

The sample for the pilot study was drawn from the students of the School of Basic Studies, Ahmadu Bello University Zaria (Nigeria) that were registered for chemistry during the 1984/85 academic session. The total number of chemistry students was 992 out of which 144 were females. The target population represented what has come to be known as "federal character" in the mode of admission. This connotes fair amount of representation across the country. This formed the basis for an assumption that the relevant characteristics of the sample for the pilot study was equivalent to those of the samples later used for the main study across the country.

The sample consisted of 50 students obtained by random selection. The male and female composition was 38 and 12 respectively. The basic assumption of randomization in the practice of sample selection is outlined in section two of this chapter. The age range of the sample was between 15 and 22, representing an average of 18 years.

4.2.3 Instruments for data collection

The development, design and structure of the tests used for data collection have been discussed in chapter three. They consisted of tests A and B rendered in multiple-choice items and free-response problems.

4.2.4 Trip to Nigeria for the pilot study

After the printing of the tests was completed, the next stage was to administer them. The author was at this stage faced with the decision of how to conduct the administration. Two obvious options were:

(a) to send the tests to Nigeria by post with necessary instructions and trust a friend or colleague to administer the tests on his behalf and to mail them back to him in Norwich.

(b) to travel to Nigeria and administer the tests by himself.

Some of the variables that are closely associated with the first option include the long distance involved, the efficiency with which postal services are operated and the level to which someone else can be relied upon to conduct the tests. Having regard to the fact that the author had no means of controlling any of these variables, he decided for the second option and travelled to Nigeria at the end of May 1985 for the conduct of the pilot study.

4.2.5 Administration of the Tests

Having selected the sample, the author agreed with the group upon day, time and venue for the test to be administered. The sample selection was done on a Friday and it was arranged to have the test

taken the next morning. On the appointed day, 4 members of the sample did not turn up, leaving a group of 46 that took the test. This comprised 35 males and 11 females. The pilot study was carried out in June 1985.

Before the test administration, the purpose of it was explained to the students. It was further made clear to them that the results from the study were expected to have positive effects for the improvement of the chemistry curriculum generally and the learning of organic chemistry in particular. The enthusiasm which marked the general attitude of the students suggested that they were motivated to take the tests. A brief discussion on the role of motivation in test administration is made in section 4.3.6

Test A was administered first. It took an average time of 37 minutes to complete. There was a break of about 10 minutes before the administration of test B which, on the whole, took a total of 2 hours 50 minutes to complete, representing an average of 25 minutes taken to solve each problem.

4.2.6 Scoring of the Tests

(a) The multiple-choice items: Test A

These were scored on a dichotomous basis. In this scoring format, each correct response was awarded a grade of one and an incorrect response was awarded a grade of zero. The maximum score obtainable was thus 50.

(b) The free-response problems: Test B

Scoring of test B required a grading scheme. This was prepared using the conceptual and procedural requirements upon which the design of the problems constituting the test was based. The process involved breaking each problem into the constituent operational steps, sub-goal(s) and final goal or solution.

The author discussed the suitability of the grading scheme (vis-a-vis the demands of the problems) with his supervisor and colleagues in the sector. Their observations were useful in producing the final shape of the scheme. Three colleagues of the author judged the scheme to be valid for grading the test, thus giving it a face-validity.

Scoring of the test involved the awarding of one grade to each operational step correctly demonstrated as the student moved from the problem situation to a solution state. An incorrect operation or failure to generate any answer attracted a grade of zero. Table 4.1 shows the distribution of the maximum scores for each problem.

TABLE 4.1 MAXIMUM SCORES FOR THE PROBLEM IN TEST B

PROBLEM	MAXIMUM SCORE OBTAINABLE
1	5.0
2	10.0
3	10.0
4	5.0
5	5.0
6	8.0
7	8.0
TOTAL	51.0

The scoring was done twice with an interval of two weeks. This was with a view to enhancing the accuracy of the scoring exercise, which was gauged from the measure of self-consistency obtained from calculation of the spearman rank-order correlation coefficient. A reliability coefficient of 0.90 was obtained.

4.2.7 Presentation and discussion of the Results

The pilot study was conducted to achieve the aims spelt out earlier (sec 4.2.1). The results together with the discussions are now presented in the light of these aims, starting with test A.

TABLE 4.2 FACILITY INDICES OF MC ITEMS

ITEM NO	FACILITY INDEX	ITEM NO	FACILITY INDEX
1	0.83	26	0.37
2	0.46	27	0.65
3	0.80	28	0.83
4	0.24	29	0.54
5	0.72	30	0.78
6	0.63	31	0.44
7	0.52	32	0.85
8	0.74	33	0.24
9	0.80	34	0.54
10	0.61	35	0.44
11	0.72	36	0.80
12	0.41	37	0.94
13	0.87	38	0.87
14	0.94	39	0.63
15	0.89	40	0.89
16	0.70	41	0.80
17	0.70	42	0.17
18	0.74	43	0.54
19	0.61	44	0.48
20	0.80	45	0.52
21	0.87	46	0.35
22	0.87	47	0.63
23	0.24	48	0.48
24	0.76	49	0.61
25	0.20	50	0.70

TABLE 4.3 THE FACILITY INDICES IN RANKS

ITEM NO	FACILITY INDEX	ITEM NO	FACILITY INDEX
14	0.94	27	0.65
37	0.94	6	0.63
15	0.89	39	0.63
40	0.89	47	0.63
13	0.87	10	0.61
21	0.87	19	0.61
22	0.87	49	0.61
38	0.87	29	0.54
32	0.85	34	0.54
1	0.83	43	0.54
28	0.83	7	0.52
3	0.80	45	0.52
9	0.80	44	0.48
20	0.80	48	0.48
36	0.80	2	0.46
41	0.80	31	0.44
30	0.78	35	0.44
11	0.77	12	0.41
24	0.76	26	0.37
8	0.74	46	0.35
18	0.74	4	0.24
5	0.72	23	0.24
16	0.70	33	0.24
17	0.70	25	0.20
50	0.70	42	0.17

TABLE 4.4 DISTRIBUTION OF STUDENTS AMONG THE VARIOUS ITEM OPTIONS

Options/ Items	NO OF STUDENTS SELECTING EACH OPTION												OMIT	% of students selecting correct responses
	1	2	3	4	5	6	7	8	9	10	11	12		
1	4	38*	0	3	0	1	0	0	0	0	0	0	0	82.6
2	21*	3	0	15	4	1	0	0	0	1	1	0	0	45.7
3	0	0	1	0	0	3	1	1	37*	0	1	2	0	80.4
4	0	0	0	1	0	10	10	5	4	5	0	11*	0	23.9
5	5	1	2	1	33*	1	0	0	1	1	0	1	0	71.7
6	0	2	0	30*	1	2	1	4	0	3	1	2	0	62.5
7	0	0	0	2	0	3	2	24*	0	9	1	5	0	52.2
8	1	0	34*	0	0	0	0	1	0	0	10	0	0	73.9
9	0	0	1	0	1	37*	2	0	2	3	0	0	0	80.4
10	1	0	0	1	1	3	28*	2	7	3	0	0	0	60.9
11	0	1	8	0	1	0	0	2	0	0	33*	1	0	71.7
12	0	0	0	0	0	4	2	8	0	19*	0	13	0	41.3

	NO OF STUDENTS SELECTING EACH OPTION				OMIT	% Students selecting Correct Responses
	A	B	C	D		
13	4	40*	1	1	0	87.0
14	0	3	0	43*	0	93.5
15	41*	1	0	4	0	89.1
16	2	32*	11	1	0	69.6
17	10	4	0	32*	0	69.6
18	5	5	2	34*	0	73.9
19	10	26*	7	1	0	60.9
20	0	2	37*	7	0	80.4
21	6	40*	0	0	0	87.0
22	3	2	1	40*	0	87.0
23	15	11*	14	5	1	23.9
24	8	35*	3	0	0	76.1

	NO OF STUDENTS SELECTING EACH OPTION				OMIT	% Students selecting Correct Responses
	A	B	C	D		
26	17*	6	9	13	1	37.0
27	30*	14	1	1	0	65.2
28	1	2	38*	5	0	82.6
29	1	25*	2	18	0	54.3
30	36*	1	1	8	0	78.3
31	0	10	16	20*	0	43.5
32	5	39*	2	0	0	84.8
33	30	3	11*	2	0	23.9
34	11	25*	5	5	0	54.3
35	21	3	2	20*	0	43.5
36	6	1	2	37*	0	80.4
37	2	43*	1	0	0	93.5
38	40*	5	1	0	0	87.0
39	2	15	29*	0	0	63.0
40	41*	2	1	1	1	89.1
41	0	4	37*	5	0	80.4
42	16	14	7	8*	1	17.4
43	0	2	19	25*	0	54.3
44	22*	9	3	12	0	47.8
45	6	12	4	24*	0	52.2
46	7	15	16*	8	0	34.8
47	29*	7	7	3	0	63.0
48	1	12	11	22*	0	47.8
49	28*	10	5	3	0	60.9
50	32*	10	1	3	0	69.6

N = 46

4.2.1.1 Test A

(a) Item difficulty

The facility indices of the items are shown in table 4.2, while table 4.3 showed these arranged in ranks. Both tables indicate the relative difficulty of the items.

The results showed that the students found 16 of the items (F.I $\geqslant$ 0.80) quite easy, 27 (F.I $\geqslant$ 0.40 $\leqslant$ 0.80) moderately difficult and 7 items (F.I < 0.40) quite difficult.

(b) Plausibility of the options

Table 4.4 showed the distribution of the responses amongst the options. It showed that some distractors failed to sway the students from the key. This meant that the distractors were either defective or the students were so sure of the correct option that they could not be distracted. These distractors were scrutinised and the following modifications made:

Item 17: "Br_2/ccl4" was replaced with "cl2/ccl4".

Item 19: "solution of Na/EtoH" was changed to "alcoholic NH_3".

Item 24: "nucleophilic substitution" was changed to "rearrangement reaction".

Item 39: "an aldehyde" was replaced with "anhydride".

Item 43: "electrophilic substitution" was

replaced with "elimination reaction".

(c) Number of items to make the mainstudy and time-limit

About 90% of the testees informally interviewed orally by the author opined that they found the items too many. Moreover the results of the pilot study showed that they found some of the items very simple. These indications were used as the basis for reducing the number of the items to 40. In the process, the easy items (F.I > 0.80) were dropped as they were considered to be of little use in the attempt to diagnose students' conceptual difficulties. The time-limit for the main study was fixed at 30 minutes.

(d) Spelling errors and clarity of the stems

The results showed that the instructions and stems of the items were clearly spelt out. There was only one spelling error, "addion" which was corrected to "addition"

4.2.7.2 Test B

(a) Item difficulty

The facility indices of the problems that constituted test B are shown in table 4.5.

TABLE 4.5 FACILITY INDICES OF PROBLEMS IN TEST B

Problem No	F.I
1	0.49
2	0.47
3	0.17
4	0.30
5	0.17
6	0.22
7	0.30

(b) Statistical Parameters

Some of the statistical properties of the scores are shown in table 4.6 below.

TABLE 4.6 STATISTICAL PROPERTIES OF THE SCORES

Sample size (N)	46
Sum of scores (ΣX)	746.00
Mean score ($\bar{X}$)	16.22
Std.Dev (S)	5.21

The results showed that the students had difficulty in solving the problems. The mean score was 16.22, the maximum obtainable score being 51.0, and the facility indices ranged between 0.17 and 0.49.

The students found problems 1 and 2 difficult, 4 and 7 more difficult, while 3, 5 and 6 were found most difficult. On the whole, the results support the initial claim that the students had difficulties in solving organic mechanistic problems.

(c) Number of problems to make up the main study and time-limit

Some of the factors that were considered in arriving at the number of problems to constitute the main study and those that were finally selected were as follows:

(i) A reasonable number of problems that could be solved by the students without undue tiredness or boredom.

(ii) The relative difficulty of the problems.

(iii) The need to scrutinise the problems that were conceptually structured on the items removed from test A, with a view to dropping the former as well.

These factors were borne in mind in the process of reviewing and examining the problems. In the end, problems 2 and 5 were removed, leaving a total of 5 problems for the main study.

The time-limit for solving the problems was fixed at $2^1/2$ hours, using as a guide the results of the pilot study in which the 7 problems were solved in 2 hours 50 minutes.

(d) Spelling Errors and clarity of Instructions

There were no spelling errors. The instructions were clear, but were considered

inadequate, in the light of the difficulty experienced by the students in solving the problems. Thus additional instructional information that served only as prompts for starting off the problems was provided for the more difficult problems.

4.2.7.3 Results of the Questionnaire

The results from the questionnaire are shown in table 4.7. They showed that the students considered the problems to be familiar, except problem 4 where opinion was divided. They judged the problems to be difficult or moderately so, having only moderate confidence in the correctness of the solutions that they produced.

The three questions immediately following each problem were revised and made dichotomous. Hills (1982) points out the basis for using such a questionnaire format. The last six items of the questionnaire were re-structured in order to focus the pattern of responses in the same direction.

TABLE 4.7 RESPONSES TO THE QUESTIONNAIRE GIVEN IN PERCENTAGE DISTRIBUTION

RESPONSES / PROBLEMS	FAMILIARITY WITH THE PROBLEM			DIFFICULTY OF THE PROBLEM			CONFIDENCE IN SOLUTION TO THE PROBLEM		
	FAMILIAR	MODERATELY FAMILIAR	NOT FAMILIAR	DIFFICULT	MODERATELY DIFFICULT	EASY	CONFIDENT	MODERATELY CONFIDENT	NOT CONFIDENT
1	78.2	19.6	2.2	4.3	76.1	19.6	23.9	63.0	13.1
2	80.4	10.9	8.7	30.4	52.2	17.4	21.7	52.2	26.1
3	71.7	19.6	8.7	17.4	56.5	26.1	23.9	52.2	23.9
4	37.0	26.0	37.0	54.3	43.5	2.2	10.9	34.8	54.3
5	63.0	19.6	17.3	43.5	54.3	2.2	6.5	39.4	54.4
6	52.2	23.9	23.9	45.6	52.2	2.2	4.4	39.1	56.5
7	54.4	30.4	15.2	37.0	54.3	8.7	8.7	43.5	47.8

4.3 The Main Study

4.3.1 Introduction

The main study was undertaken between February and April, 1986. Permission was sought and obtained from the authorities of the participating institutions to enable the author to administer the chemical tests to the students. This was achieved through postal communication between the author and his supervisor on one hand and the authorities of the institutions concerned on the other. The relevant postal correspondences are included as appendices 4.1-5.

4.3.2 Purpose of the Study

The purpose of the main study was to administer the tests to the target students that constituted the focus of the study. This was with a view to collecting relevant data that would provide some basis for answering the research questions which have been stated earlier (sec 1.2.4).

4.3.3 The Field-Trip

In December, 1985, the author travelled to Nigeria to conduct the main study. On arrival in Nigeria, he wrote letters to the participating institutions, suggesting to them possible dates he would visit the respective schools. The suggested dates were accepted by the schools, following which the author drew up an itinerary guiding his visits from one school to the next. This commenced on the 10th February 1986 with visits to Sokato, Port-Harcourt, Makurdi and Zaria in that sequence.

The trips were considered successful given that they were safe and the high level of co-operation received from the school authorities and the enthusiasm that the students demonstrated as participants in the main study.

4.3.4 The Sample

(a) Composition and characteristics

The students that constituted the sample for this study were the second year students of the schools of Basic Studies in Nigeria. The relevant characteristics of these schools and their intakes have been discussed in chapter one (sec 1.2.2).

The students were drawn from 5 out of the 13 institutions in the country. The second year students were involved because they were at the point of completing the course programme, and thus their abilities were judged to be more suited to the conceptual demands of the tests than the first year students. The geographical distributions of the participating institutions within the country is shown in the map included as appendix 1.1.

The average age of the students was 19.5 years. They were above average in ability. The sample consisted of 169 male and 21 female students. In the selection of the schools, attention was paid to the geographical spread of the institutions. Thus the distribution

of the five schools chosen were: three from the northern part of the country, one from the middle section, and one from the southern end. Table 4.8 shows the schools and the corresponding number of students from each that participated in taking the tests.

TABLE 4.8 THE SCHOOLS COMPRISING THE SAMPLE FOR MAIN STUDY

Name of State in which school is located	Name of School	Number of students
Kaduna	College of Advance Studies, Zaria	50
Kaduna	School of Basic Studies, AhmaduBello University, Zaria	50
Sokoto	College of Arts and Science, Sokoto	43
Benue	School of Basic Studies, Makurdi	36
Rivers	School of Basic Studies, Port-Harcourt	11
TOTAL	5	190

(b) Method of Selecting the Samples

The samples from the five institutions were obtained by random sampling. The principle of random sampling which is generally used to obtain an unbiased collection of subjects is built on the assumption that membership or exclusion of

individuals belonging to the target population from the sample is determined entirely by chance and nothing else. This implies that all members of the population have equal probability of becoming a member of the sample. As Robson (1983) defined it "... a sample which is unbiased, in the sense that each member of the population has got an equal chance of appearing in the sample, is known as a random sample". The randomised sample is central to the basic assumptions that underlie inferential statistical analysis, especially that of normality of population distribution.

In this study, an attempt was made to obtain unbiased samples by employing tables of digits (Snodgrass, 1977). In schools where the number of second year students was less than 50, eg Port-Harcourt, the entire population formed the sample.

4.3.5 The Tests for the Main Study

The modifications that were made to the tests for the pilot study resulted in the final version used for the main study. They comprised 40 multiple-choice items designated as Test A and 5 free-response problems, as Test B.

The tests were printed into booklets by the University (UEA) printers, and were air freighted to Nigeria. Tests A and B are included as appendices 3.2 and 3.3 respectively.

4.3.6 Administration of the Tests

(a) Some Psychological Factors Associated with Testing

There are a number of psychological factors that have direct bearing on performance, thus having implications for test administration. According to Satterly (1983) some of these are: motivation, anxiety and effort. The author took these into account in the conduct of the test administration. Thus a brief discussion about these factors with respect to the test administration is briefly outlined as a relevant prelude to discussing the actual test administration.

(i) Motivation

Child (1986) presented what can be described a working definition of motivation as "... internal processes that spur us on to satisfy some need" The role of motivation in the administration of this test is to promote uninhibited demonstraion of individual potentials, thereby minimising the chances of arbitrary deviation of observed performance from true ability. One of the ways of arousing and sustaining motivation is by making the subjects see the point in what they are being asked to do and the

advantages into which the results can be put (Satterly, 1983).

(ii) Anxiety

Anxiety is an innate psychological factor that is closely related to motivation in its role and effect on performance. Psychologists appear to take the view that whilst some anxiety tends to increase alertness, generally, it depresses performance. Karmel (1978) observed that some students are "intellectually frozen" by it. Thus, factors that promote a familiar and relaxed atmosphere are likely to minimise anxiety, thereby allowing an unrestricted manifestation of the capability of individual students.

(iii) Effort

In order to perform, the testee needs to make an effort. Case (1974) related this to maximum mental effort which he called M-power. He considered that success in problem solving is related in some way to the subject's tendency to utilise the M-power that is available. He asserted that subjects that respond to problems with a set of operations involving the least possible mental

effort are unlikely to do well.

Lack of effort is attributable amongst other factors to lack of motivation, interest and confidence.

(b) Taking the Test

The factors discussed above were borne in mind in the course of test administration. On arrival at the schools, the author took time to explain the purpose of the tests to the authorities and chemistry staff. It was explained to them that the tests were not meant to judge the academic standing of the students, either individually or collectively. It was also explained that they were not meant to compare the schools nor were they intended to be a forum for making an incursion into the academic life of the schools.

In summary, the aim of the test administration was not to test the schools, but to monitor the understanding of the students in the chosen topic areas.

The purpose of the tests was also explained to the students before the booklets were handed out to them. The need for their participation in the exercise, and the use to which the results of the study could be put were made explicit to the students. During this time, the author made allowance for the students to ask questions, either pertaining

to the tests or to related matters of general interest. This increased familiarity between the students and the "intruding" test administrator; thereby establishing mutual confidence, which had the effect of arousing and sustaining motivation and interest, while at the same time reducing anxiety and suspicion.

The chemistry lecturers of the schools assisted the author in giving out the test booklets and in supervision. About 90% of the subjects completed Test A within the time alloted to it. The remaining few were allowed an extra ten minutes within which they all finished. All the subjects completed Test B within the $2\frac{1}{2}$ hours alloted to it.

In all the schools, the author had co-operation from the staff concerned, and the students that participated in the tests. In all cases (except the school of Basic Studies, Zaria where a free practical period was used) normal lectures were cancelled to give time for the administration of the tests.

4.3.7 The "Think Aloud" Technique Used for Data Collection

So far, the pencil-and-paper method that was employed for data collection has been discussed. The "think aloud" technique - a method used for probing the thought processes of the students as they solved problems was also an integral part of the design of the instruments for collecting data. It

was aimed at obtaining information about the thought processes in the context of which the observed pencil-and-paper problem solving behaviour occurred. As Aaron (1971) said, "thinking is a process and knowledge is a product, but the two are intimately related". The full account of the conduct of data collection using this method is taken up in chapters seven to nine.

4.3.8 Summary and Conclusion

This chapter, which described the conduct of data collection, was presented in two sections, the first dealing with the pilot study, and the second, the main study. The results of the pilot study showed that the students had difficulty solving the problems in test B. They performed better in test A. They considered the problems to be familiar and moderately difficult. They expressed a lower level of confidence in the correctness of their solutions. The results of the pilot study were useful as guide for arriving at the final version of the tests for the main study.

The next chapter deals with analysis and presentation of results from the data.

CHAPTER FIVE

ANALYSIS OF DATA AND PRESENTATION OF RESULTS

5.1 Overview

This chapter deals with the analysis of data and the presentation of the results. The data were analysed by the "MINITAB" statistical package established in the University of East Anglia.

The results are presented along two main streams. The first section of the presentation involves the scores and some statistical treatments applied to them. These are shown in sections 5.4-5. The second involves an analytical examination of the students' scripts. This covers a comparative analysis of the operational tasks underlying the problems and the related knowledge items, the strategy adopted by the students in solving the problems and their responses to the questionnaire. These are presented in sections 5.6-8. The sample comprised 190 students.

5.2 Scoring the Tests

The scoring of tests A and B was done in the same manner as in the pilot study (sec 4.2.5). The number of operational tasks embedded in each problem is summarised in table 5.1 below while the grading scheme is included as appendix 5.1.

TABLE 5.1 NUMBER OF OPERATIONAL TASKS ASSOCIATED WITH EACH PROBLEM

Problem No	1	2			3	4	5			TOTAL
Sections		I	II	III			I	II	III	
No of Operations	5	5	5	2	5	9	5	5	2	43
Total	5	12			5	9	12			43

5.3 Statement of the Research Questions

It is considered necessary to re-state the research questions at this point. This is with a view to guiding the presentation of the results. They are:

(a) Do the students possess relevant chemical knowledge required for solving the problems posed?

(b) Were the students successful in solving the problems?

(c) Does the performance of the students in test A significantly differ from that in test B?

(d) What effect does possession of relevant chemical knowledge have on ability to solve problems requiring the knowledge domain?

(e) Is sex a significant factor in the students' ability to solve the problems?

(f) What are the students' difficulties in solving mechanistic organic problems?

5.4 The results

5.4.1 Statistical parameters

Some of the statistical properties of the scores are shown in table 5.2.

TABLE 5.2 SOME STATISTICAL PROPERTIES OF TESTS A AND B

Statistical Properties \ Tests	A	B
Sample Size (N)	190	190
Sum of Scores (ΣX)	3695	1643
Mean Score ($\bar{X}$)	19.45	8.65
Std. Dev (S)	5.05	3.95

These results show the group mean scores and standard deviations for the tests. The mean for test A is 19.45 with standard deviation of 5.05. The corresponding values for test B are 8.65 and 3.95.

5.4.2 Facility Indices and choice of Options in Test A

Table 5.3 shows the facility indices (F.I) of the items. Table 5.4 shows the distribution of the students amongst the item options, and the percentage of students selecting the correct option for each item.

TABLE 5.3 FACILITY INDICES OF THE ITEMS

ITEM No	F.I	ITEM No	F.I
1	0.63	21	0.24
2	0.42	22	0.54
3	0.63	23	0.75
4	0.18	24	0.48
5	0.64	25	0.46
6	0.42	26	0.62
7	0.50	27	0.50
8	0.57	28	0.38
9	0.73	29	0.56
10	0.36	30	0.52
11	0.56	31	0.68
12	0.32	32	0.29
13	0.83	33	0.48
14	0.34	34	0.40
15	0.77	35	0.28
16	0.53	36	0.34
17	0.63	37	0.44
18	0.29	38	0.36
19	0.71	39	0.34
20	0.49	40	0.34

TABLE 5.4 DISTRIBUTION OF STUDENTS AMONG ITEM OPTIONS IN TEST A FOR TOTAL SAMPLE: N = 190

Options / Items	NO OF STUDENTS SELECTING EACH OPTION												OMIT	% SELECTING CORRECT OPTIONS
	1	2	3	4	5	6	7	8	9	10	11	12		
1	3	120*	9	18	3	3	11	1	4		7	6	5	63.2
2	80*	8	2	68	18	2				6	2	2	2	42.1
3	1	3	3	3	2	13	25	7	119*	2	1	5	6	62.6
4	5	5	1	4	2	39	33	30	8	24	1	34*	4	17.9
5	18	10	12	9	122*	5	5		7			3	4	64.2
6	10	26	3	79*	1	9	8	11	3	15	7	10	8	41.6
7	3	1	2	2	1	7	8	94*	6	40	4	14	8	49.5
8			109*			3	1	6		3	60	2	6	57.4
9	10	2	2	6	4	138*	5	2	5	10		2	4	72.6
10	4	8	2	6	6	20	69*	6	27	22	1	11	8	36.3
11	2		68	2		1		3		1	106*	3	4	55.8
12	2	2		1	3	34	17	25	11	61*	2	29	3	32.1

	A	B	C	D	OMIT	% SELECTING CORRECT RESPONSE
13	4	157*	29			82.6
14	67	30	24	64*	5	33.7
15	9	20	12	147*	2	77.4
16	50	100*	12	26	2	52.6
17	14	43	119*	13	1	62.6
18	90	55*	32	4	9	29.0
19	4	34	17	135*		71.1
20	20	7	93*	63	7	49.0
21	46*	21	63	59	1	24.2
22	58	26	3	102*	1	53.7
23	14	14	143*	14	5	75.3
24	28	38	33	91*		47.9
					1	45.8

	A	B	C	D	OMIT	% SELECTING CORRECT RESPONSE
26	118*	18	16	37	1	62.1
27	19	40	37	94*		49.5
28	15	73*	25	75	2	38.4
29	46	14	18	107*	5	56.3
30	27	55	99*	9		52.1
31	13	19	130*	28		68.4
32	44	60	27	55*	4	29.0
33	91*	70	13	14	2	47.9
34	76*	21	45	44	4	40.0
35	54	54*	50	29	3	28.4
36	36	48	65*	37	4	34.2
37	19	42	42	83*	3	43.7
38	34	45	40	69*	2	36.3
39	65*	59	29	19	18	34.2
40	28	37	65*	44	16	34.2

NOTE:

* = CORRECT OPTION (THE KEY)

"OMIT" = NUMBER OF STUDENTS OMITTING AN ITEM

N = 190

The results show the relative difficulty of the items with respect to the students' ability to respond to the correct options of the items. The range lies between 0.18 and 0.83, with 35 out of the 40 items having facility indices above 0.30. The facility indices, taken alongside the group mean score indicate that the students found most of the items moderately easy.

The distribution of the students amongst the item options reflects the degree of attraction posed by the keys and distractors. The pattern of distribution is a useful source from which some insight can be gained into the nature of students' conceptual difficulties.

5.4.3 Facility Indices of the Free-Response Problems

The facility indices of the free-response problems are shown in table 5.5 below.

TABLE 5.5 FACILITY INDICES OF THE FREE-RESPONSE PROBLEMS

Problem No	Mean Score ($\bar{X}$)	Maximum Scores	F.I
1	2.18	5.00	0.44
2	2.51	12.00	0.21
3	1.39	5.00	0.28
4	1.43	9.00	0.16
5	2.16	12.00	0.18

The range of the facility indices lies between 0.16 and 0.44. All the problems, except number 1 had facility indices below 0.30. The group mean score (table 5.2) is 8.65. These results indicate that the students had difficulty solving the problems.

5.5 Treatment of the Scores

The scores were further analysed in the light of the underlying research questions. The results are shown in tables 5.6~5.9.

5.5.1 Comparison between Tests A and B

The results that have been presented showed that performances of the students in tests A and B are different. The question is: how different are they? An attempt to answer the question calls for closer comparison of the mean scores. This is done by computation of a one-tailed t-ratio using a directional hypothesis that the two mean scores are not equal.

$$H_0 : \mu_A - \mu_B \neq 0$$

where μ_A = the mean score of test A

μ_B = the mean score of test B

The results are shown in table 5.6

TABLE 5.6 COMPARISON BETWEEN STUDENTS' PERFORMANCES IN TESTS A AND B

STATISTICAL PROPERTIES / TESTS	N	$\bar{X}$	S	Standard error of difference	t-ratio	Confidence level	df	Remark
A	190	19.45	5.05	0.47	22.98	0.05	378	SIGNIFI-CANT
B	190	8.65	3.95					

The result of the treatment shows a t-ratio of 22.98 which is significant at the 0.05 confidence level, showing that $\mu_A > \mu_B$. This is an indication that there exists a real difference in students' peformance between tests A and B. The implication of this is discussed in chapter six.

5.5.2 Further comparison of Tests A and B

The results that have been so far presented indicate that the performance of the students in test A is superior to that in test B. This justifies a closer comparison of the tests with a view to determining the level to which the chemical knowledge-base of the students, as revealed by their performance in test A influenced their problem solving capability in test B. This called for the determination of:

(a) the degree and direction of association between tests A and B, obtained from computation of their correlation coefficient (r).

(b) the regression of test B scores on those of test A, measured by their regression coefficient.

(c) the fitted regression equation from which the number, and hence the percentage of students reaching the predicted scores was obtained.

These were done in order to obtain a relevant empirical basis for making some deductions in an attempt to answer the question:

"What effect does the possession of relevant chemical knowledge have on the ability to solve problems requiring the knowledge?"

The Pearson's product-moment correlation coefficient was obtained. This is shown in table 5.7.

TABLE 5.7 ASSOCIATION BETWEEN TESTS A AND B

STATISTICAL PROPERTIES / TESTS	N	$\bar{X}$	S	r	r^2
A	190	19.45	5.05	0.45	0.20
B	190	8.65	3.95		

The result shows that there is a positive and linear relationship between tests A and B. The strength of the relationship as indicated by the magnitude of r is only a moderate one.

The results of simple regression analysis carried out on the test scores are shown in table 5.8 below.

TABLE 5.8 REGRESSION INTERRELATIONSHIPS OF TESTS A AND B

STATISTICAL PROPERTIES / TESTS	N	X	S	No reaching predicted Scores	% reaching predicted Scores	Coefficient of Regression
A	190	19.45	5.05	80.00	42.00	0.35
B	190	8.65	3.95			

It showed that only 80 out of the 190 students, representing a total of 42% reached the predicted score.

This was arrived at after entering the scores of each student in test A into the fitted regression equation. The results further showed that the coefficient of regression is 0.35. The discussion of these results are undertaken in the next chapter.

5.5.3 Comparison between male and female students

The question of the relative abilities of male and female students to perform in problem solving situations requiring knowledge of science is a variable that has attracted the attention of a number of scholars. An answer is sought to the question of whether sex constitutes a significant factor in the ability to solve problems, and in this case, mechanistic organic problems. The statistical question is: does the performance of the male students differ significantly from that of female students?

In an attempt to answer the question, a two-tailed t-test was carried out on the relevant statistical variables of the male and female groups. It was to test the null hypothesis formally stated thus:

$$H_0 : \mu_M - \mu_F = 0$$

where μ_M = mean score of male students

μ_F = mean score of female students.

The results are shown in table 5.9.

TABLE 5.9 COMPARISON BETWEEN MALE AND FEMALE STUDENTS

STATISTICAL PROPERTIES / VARIABLES	TEST A				TEST B			
	Sample size (N)	Mean score ($\bar{X}$)	Std. Dev (S)	Std. Error of diff (SEd)	Sample size (N)	Mean score ($\bar{X}$)	Std. Dev (S)	Std. Error of diff (SEd)
Male	169	19.65	5.17	1.16	169	8.87	4.02	0.90
Female	21	17.86	3.72		21	6.76	2.51	
t-ratio	1.54				2.35			
degree of freedom (df)	188				188			
Confidence level (α)	0.05				0.05			
Remark	NOT SIGNIFICANT				SIGNIFICANT			

The result showed that the t-ratio for the difference (in means) between the performances of male and female students in test A is not significant at the 0.05 confidence level. The null hypothesis is thus not rejected. The t-ratio for the difference in their respective performances in test B is, however, found to be significant at the same confidence level, implying that there exists a real difference between performances of the male and female students in test B. The null hypothesis is thus rejected.

It can be recalled that test A is composed of multiple-choice items and test B of free-response problems structured on the items of test A. The indication from these results (table 5.9) of no significant difference in performance between male and female students in test A, and a significant difference in their respective performances in test B appears revealing. One of the questions that seems to arise directly from this is: do the formats in which problems are presented, and the sex of the individuals to whom the problems are presented, constitute significant or incidental factors that affect their ability to solve the problems? If so, what are the reasons, and how can these be harnessed to improve curriculum design and implementation?

The first question arises as a consequence of the results (table 5.9) obtained, and the second is a pragmatic one that arises as a follow-up of the

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first. Both are difficult questions to which the author cannot claim to have answers. To do so will require another direction of research to dissentangle the associations, elucidate the nature of the relationships and offer explanations for the actual role played by the variables (i.e sex and format of problem presentation) in problem solving. These seem to be outside the immediate concern of this study. A closer examination and discussion of these results are however undertaken in the next chapter.

5.6 Closer comparative analysis of tests A and B

Results of the treatment of students' scores in tests A and B have shown that their level of performances in each of the tests differs significantly. This called for a closer, comparative examination of the component parts of both tests in terms of the tasks involved.

The problems in test B are analysed alongside the related items in test A. The problems analysed and the topic areas they represent are summarised in table 5.10 below.

TABLE 5.10 TEST B AND THE ASSOCIATED CHEMICAL KNOWLEDGE

PROBLEM No	TOPIC AREAS
1	Nucleophilic substitution
2 (i)	Electrophilic substitution
2 (ii)	Electrophilic addition
2 (iii)	Some aspects of interrelationships
4	Elimination
5 (ii)	Nucleophilic substitution

The analysis was carried out with a view to obtaining more information about how the students used or failed to use relevant knowledge items as they attempted to solve the problems. One of the main aims for this was to establish some basis upon which deductions can be made regarding possible factors that were responsible for the students' difficulties in solving the problems.

5.6.1 Problem No 1

"Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$"

To solve the problem requires that the student:

(i) recognise the structural units of the reacting molecule

(ii) identify the nucleophile

(iii) locate the centre of nucleophilic attack

(iv) use appropriate symbols to represent or describe the interaction of the reacting species

(v) detail the bond-breaking and bond-making processes (in appropriate sequence) to arrive at a solution.

The information required for these operations comes from both the problem statement and from memory. Table 5.11 is a summary of the students' capabilities of these underlying problem tasks compared to the operationally related knowledge items in test A.

TABLE 5.11 OPERATIONAL TASKS UNDERLYING PROBLEM 1 AND RELATED KNOWLEDGE ITEMS IN TEST A

TEST B		TEST A	
OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS	F.I
Recognition of the structural units of the reacting molecule	0.48	Item No 5	0.64
Identification of the nucleophile	0.45	Item No 25	0.46
Identification of centre of nucleophilic attack	0.60	Item No 26	0.62
Correct use of symbols to represent the interaction of the reacting species	0.28	Item No 7	0.50
Details of bond-breaking and bond-making processes to arrive at a solution	0.30	Item No 29	0.56

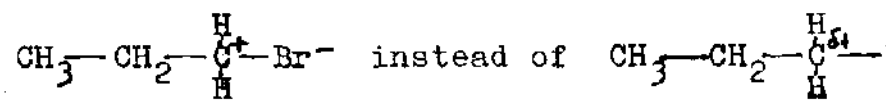
Table 5.11 shows the facility that the students had in handling the knowledge items in test A compared to that for using them to solve the free-response problem. As can be seen, the students had greater difficulties in using the knowledge item in solving problems compared to recognition of the knowledge items per se. Substantial discrepancies revealed from this problem include:

(i) recognition of the structural units of the reacting molecule.

(ii) correct use of symbols to show the mode of interaction between the reacting species.

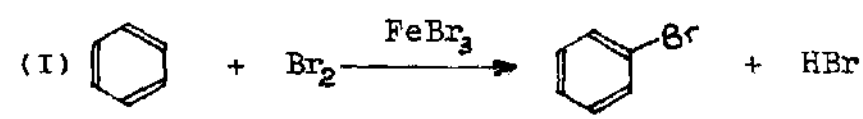
(iii) the bond-breaking and bond-making sequence, which apparently accounted for the students' failure to see the reaction process as being concerted in this case.

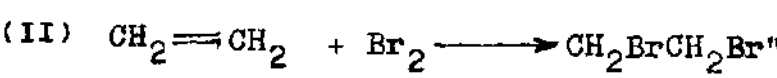
There is little difference between the students' capability in identification and using the knowledge item related to "nucleophiles". They seemed capable of locating the centre of nucleophilic attack, even though they frequently used the wrong symbols to show the relative electron densities in the molecule. For example:



5.6.2 Problem No 2

"Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction, but not the second. The reactions are:





This problem consisted of three related sections. The first is an example of electrophilic substitution, the second, electrophilic addition and the third, a drawing out of some relationships between the first and second sections.

Both sections I and II rquire basically the same conceptual frames to solve the problems. There are mainly five of these, leading to five operational steps. These are:

(i) identification of the reactive sites within the respective reacting molecules

(ii) identification of the electrophile

(iii) representation of reaction processes between the hydrocarbon and the electrophile

(iv) representation of an intermediate carbocation

(v) elimination of H^+ from which the intermediate in case of electrophilic substitution and addition of a nucleophile in the addition.

Thus the major operational difference in solving problems 2 (i) and 2 (ii) lies in step (v). To solve the problem in the third section required that the student recognise that:

(i) benzene is resonance stabilised, ethene is not.

(ii) the activitation energy for the formation of the respective carbocation is thus higher for benzene than for ethene.

(iii) a catalyst assists in providing a reaction route requiring a lower activation energy, thus making bromination of benzene more favourable than would have been the case.

A breakdown of some relevant statistical properties of each of the sections is shown in table 5.12.

TABLE 5.12 FACILITY INDICES OF THE SECTIONS TO PROBLEM No 2

SUB-SECTIONS / STATISTICAL PROPERTIES	I	II	III
ΣX	304.0	228.0	38.0
$\bar{X}$	1.60	1.20	0.20
F.I	0.32	0.24	0.10

Table 5.12 shows the students' facility with each of the three sections of problem 2.

Table 5.13 (1-3) show the facility that the students had with each operational task underlying each section as they attempted to solve the problem, compared to that of the related knowledge items in test A.

5.6.2.1 Section I

"Outline the mechanism of the reaction of bromine with benzene. The reaction is:

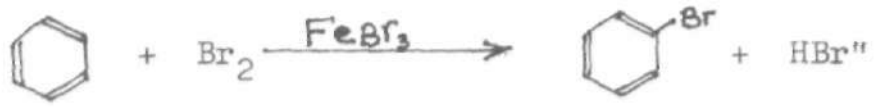


Table 5.13.1 shows a summary of students' facility with the underlying operational tasks along with the related items in test A.

TABLE 5.13.1 OPERATIONAL TASKS UNDERLYING PROBLEM 2 (I) AND RELATED KNOWLEDGE ITEMS IN TEST A

OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS IN TEST A	F.I
Recognition of benzene structure in relation to site of reaction	0.50	Item No 8	0.57
Identification of the electrophile	0.26	Item No 24	0.48
Symbolic representation of electrophilic interaction between the reacting species	0.24	Item No 34	0.40
Correct representation of the intermediate carbocation	0.36	Item No 19	0.71
Conversion of the intermediate to product	0.28	Item No 27	0.50

Table 5.13.1 shows that the students had greater difficulties with the use of correct symbols to show the electrophilic interaction between benzene and the electrophile, (F.I = 0.24) and also applying

the required operations to convert the intermediate to the product (F.I = 0.28).

5.6.2.2 **Section II**

The problem is as follows:

"Outline the mechanism of the reaction of bromine with ethene. The reaction is:

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br"$$

Table 5.13.2 shows the students' facility with the underlying operational tasks and also with the related knowledge items in test A.

TABLE 5.13.2 OPERATIONAL TASKS UNDERLYING PROBLEM 2 (II) AND RELATED KNOWLEDGE ITEMS IN TEST A

OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS	F.I
Recognition of the reacting molecule in relation to the reaction site	0.40	Item No 1	0.63
Identification of the electrophile	0.28	Item No 24	0.48
Representation of reactive interaction between the electrophile and the molecule	0.15	Item No 28	0.38
Representation of an intermediate carbocation	0.20	Item No 9	0.73
Representation of conversion of the intermediate to product	0.21	Item No 33	0.48

Table 5.13.2 shows the students' facility with identification of required knowledge items and that with which they used them in solving the problem. The pattern which emerged seems to be that the students had greater difficulty in using the knowledge items to solve the problem in comparison to identification or recognition of the items.

Comparing 2(I) and 2 (II) one finds that the students' problem solving behaviour fluctuated across the problems, not withstanding that the conceptual principles underlying both problems are basically the same.

5.6.2.3 Section III

The objective of section III of the problem was to probe the students' understanding of some relationships between chemical structure and chemical reactivity. The facility indices of the main chemical concepts involved are shown in table 5.13.3.

TABLE 5.13.3 OPERATIONAL TASKS UNDERLYING PROBLEM 2 (III) AND RELATED KNOWLEDGE ITEMS IN TEST A

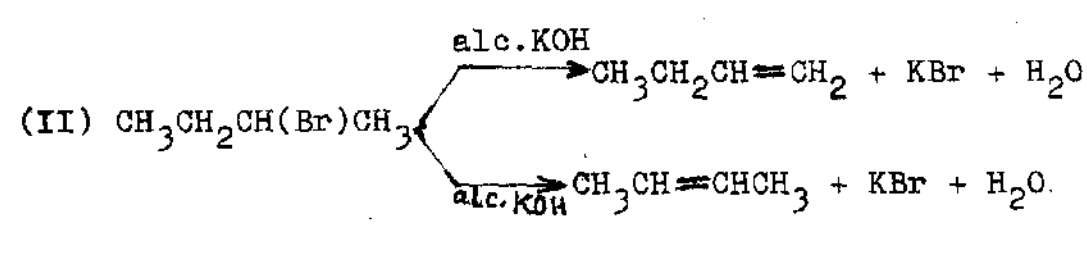
OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS	F.I
Resonance stabilization of benzene molecule compared to ethene	0.18	Item No 20	0.49
Activation energies of the rate determining step of the respective reactions	0.04	Item No 39	0.34

5.6.3 Problem No 4

"Using the relevant mechanisms of the respective reactions;

(a) Explain why 1-bromobutane forms only one isomer, while 2-bromobutane forms three isomers respectively when treated with an alcoholic solution of potassium hydroxide. The reactions are as follows:





(b) What name is usually given to the mechanism that you have described?"

The chemical principles underlying both sections are the same. The major difference the student was expected to spot was that whereas there are two positions from which H-atom can be removed (as H^+) in section II, leading to the formation of more than one isomeric products, there is only one of such positions in section I.

A summary of the facility indices of the underlying tasks is shown in table 5.14.

TABLE 5.14 OPERATIONAL TASKS AND RELATED KNOWLEDGE ITEMS IN TEST A

OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS	F.I
Recognition of structural units of the reacting molecule	0.30	Item No 2	0.42
Identification of the nucleophile	0.25	Item No 16	0.53
Using symbols to show reactive interaction between the nucleophile and the molecule	0.12	Item No 4	0.18
Representation of the bond-breaking processes	0.08	Item No 12	0.34
Representation of the bond-making processes	0.06	Item No 38	0.36

The students had least facility with this problem in comparison with the other problems. It does appear that the students were unable to come to terms with the structure of the secondary halogenoalkane (F.I = 0.30). This apparently seemed to push the students to a corner where they failed to visualise how rationally to attack the problem.

The students also had greater difficulty identifying the requisite knowledge items for this problem compared to other problems.

5.6.4 Problem No 5

"Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:

(I) $CH_2{=}CH{-}CH_3 + HBr \longrightarrow CH_3{-}CHBr{-}CH_3$
electrophilic addition.

(II) $CH_2{=}CH{-}CHO + HBr \longrightarrow CH_2Br{-}CH_2{-}CHO$
nucleophilic addition.

Outline the mechanisms of the reactions, and use it to explain why reaction II behaves differently from reaction I.

Note: - CHO is an electron withdrawing group".

The problem consists of three sections. They are:

(i) electrophilic addition mechanism

(ii) nucleophilic addition mechanism

(iii) a drawing out of relationships between (i) and (ii).

The facility indices of the three sections to the problem are shown in table 5.15.1, while the facility indices of the tasks embedded in sections (ii) and (iii) are shown in tables 5.15.2-3.

TABLE 5.15.1 FACILITY INDICES OF THE SECTIONS TO PROBLEM No 5

SUB-SECTIONS / STATISTICAL PROPERTIES	I	II	III
$\leqslant X$	247.0	181.0	34.0
$\bar{X}$	1.30	0.95	0.18
F.I	0.26	0.19	0.09

TABLE 5.15.2 OPERATIONAL TASKS UNDERLYING PROBLEM 5 (II) AND RELATED KNOWLEDGE ITEMS IN TEST A

OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS	F.I
Recognition of the structural features of the molecule in relation to reaction site	0.28	Item No 32	0.29
Identification of the nucleophile	0.30	Item NO 25	0.46
Representation of reactive processes between the nucleophile and the molecule	0.12	Item No 36	0.34
Representation of an intermediate	0.15	Item No 22	0.54
Representation of conversion of the intermediate to product	0.12	Item No 33	0.48

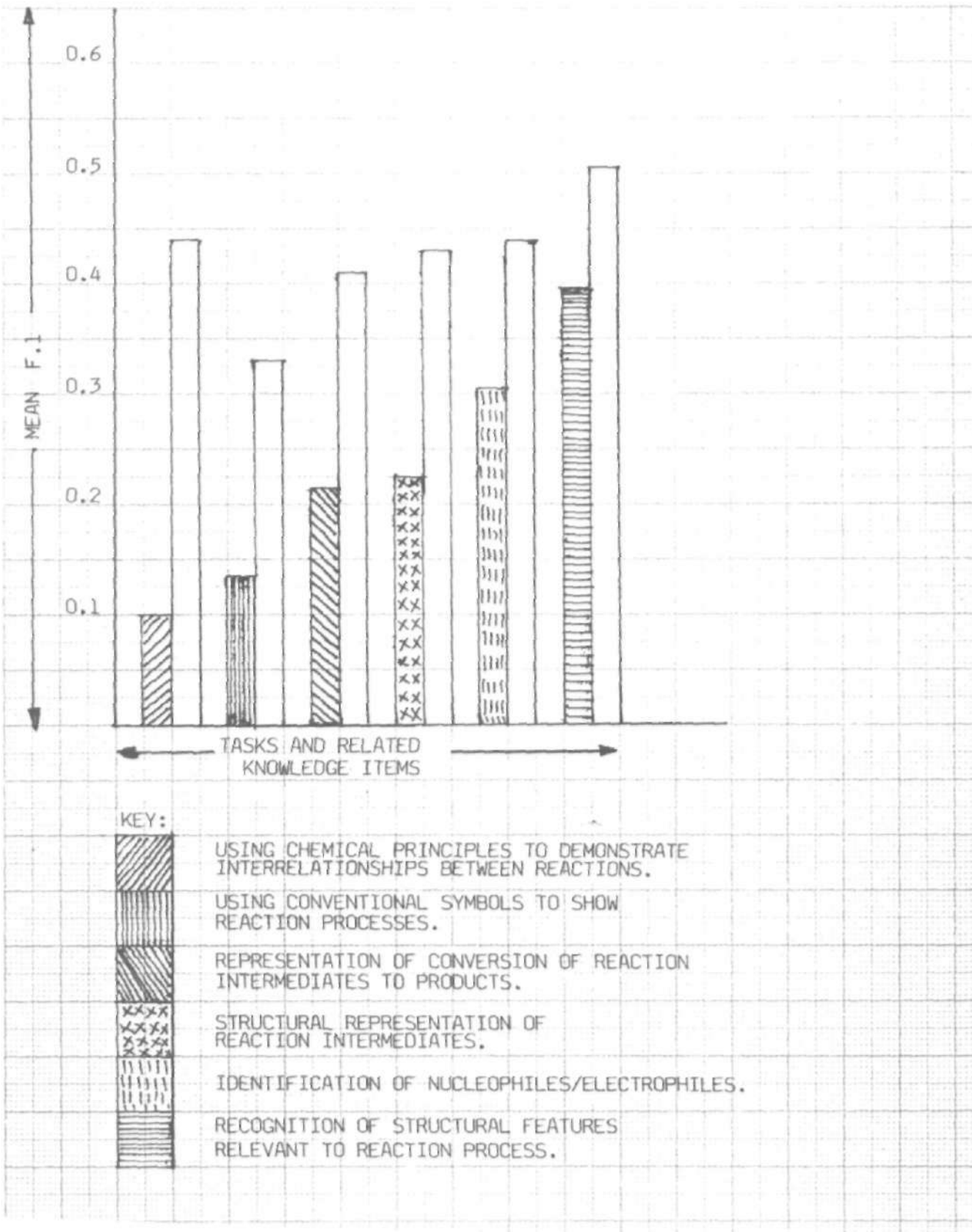
TABLE 5.15.3 OPERATIONAL TASKS UNDERLYING PROBLEM 5 (III) AND RELATED KNOWLEDGE ITEMS IN TEST A

OPERATIONAL TASKS	F.I	RELATED KNOWLEDGE ITEMS	
Inductive effect of -CHO group	0.17	Item No 26	0.62
Mesomeric effects of the C=C and C=O groups	0.02	Item No 20	0.49

A graphic representation of the results presented in this section (5.6) is given as fig 5.1. It shows the relative strengths of the students' responses to the tasks embedded in the free-response problems compared with the responses to the knowledge items related to the tasks.

The mean facility indices of the tasks were used to arrive at the figure which gives a general overview of the students' difficulties in solving the problems.

FIG 5.1


0.6
0.5
0.4
0.3
0.2
0.1
MEAN F.1
TASKS AND RELATED KNOWLEDGE ITEMS
KEY:
USING CHEMICAL PRINCIPLES TO DEMONSTRATE INTERRELATIONSHIPS BETWEEN REACTIONS.
USING CONVENTIONAL SYMBOLS TO SHOW REACTION PROCESSES.
REPRESENTATION OF CONVERSION OF REACTION INTERMEDIATES TO PRODUCTS.
STRUCTURAL REPRESENTATION OF REACTION INTERMEDIATES.
IDENTIFICATION OF NUCLEOPHILES/ELECTROPHILES.
RECOGNITION OF STRUCTURAL FEATURES RELEVANT TO REACTION PROCESS.

5.7 Students' problem solving strategies

Strategy is used here to denote students' observed behaviour in planning and directing kowledge and skills (use of rules) in an attempt to move from a problem situation to a solution state. The students' problem solving strategy is given attention as a further step in probing their difficulties in solving mechanistic organic problems.

This involved a qualitative analysis of the students' scripts. The major limitation in this approach is the inherent subjectivity involved. Nonetheless, it gives an impressionistic overview of the strategies that the students adopted as they attempted to solve the problems. The results are useful in seeking answers to the question of what constituted the students' difficulties.

To solve the problems requires that the students:

(a) understand the problem

(b) recall relevant knowledge items

(c) organise the knowledge items in line with the demands of the problem

(d) use relevant symbols to demonstrate such knowledge organization

(e) use such symbols in a systematic and logical manner along the problem-solution route.

These broad requirements were used to guide the procedure of the analysis.

The results obtained showed that the students:

(a) lacked functional understanding of basic chemical concepts and principles routinely required for solving the problems in test B. Those that were mostly affected include:

  (i) electronic concept of covalent bonding

  (ii) bond-breaking and bond-making in organic reactions

  (iii) structural changes that accompany organic reactions together with use of symbols to represent them.

(b) lacked capability to organise relevant pieces of information (given or recalled from Long Term Memory) appropriately, presumably resulting from lack of clarity of thought on the part of the students.

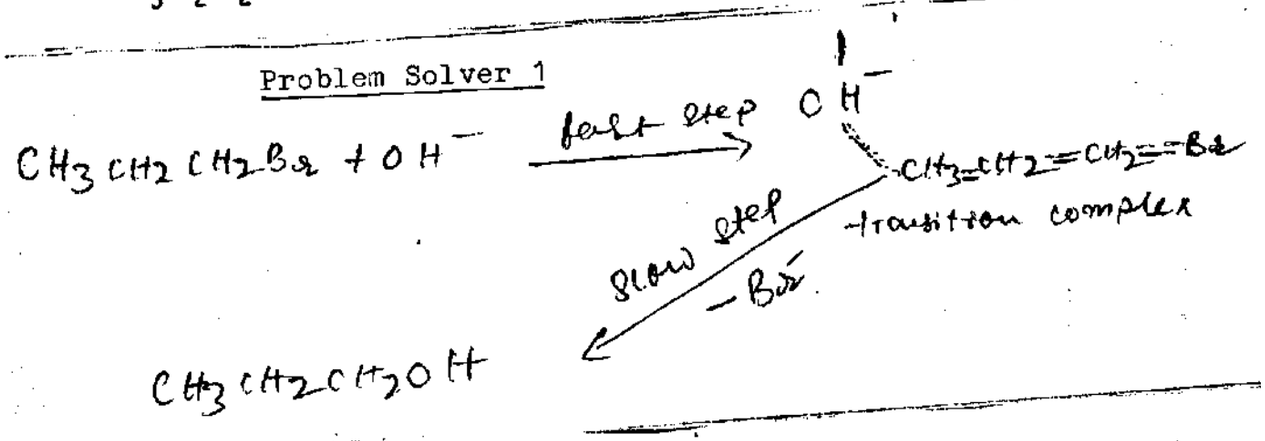
(c) seemed to rely on rote memory as basis for problem solving rather than reliance on an understanding of the underlying chemical principles that guide and promote successful problem solving behaviour.

Resulting from a, b, and c above, the problem solving behaviour of the students appears to be ill-defined, haphazard and lacking in logical direction. Some excerpts from the students' scripts are shown below to illustrate these conclusions. At best, the students' strategy for solving the problems can be described as consisting of trial-and-error approach.

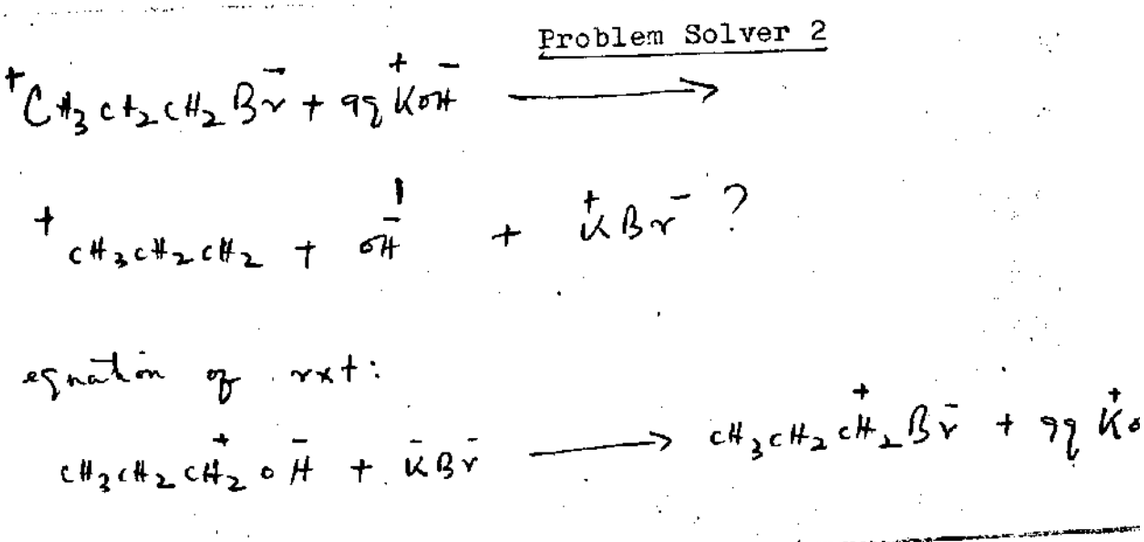
1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$

Problem Solver 1

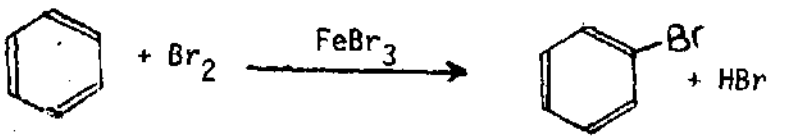


Problem Solver 2

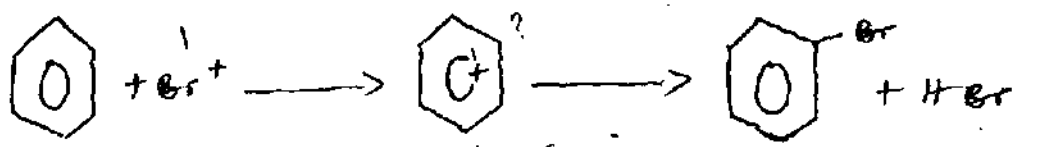


Problem Solver 3

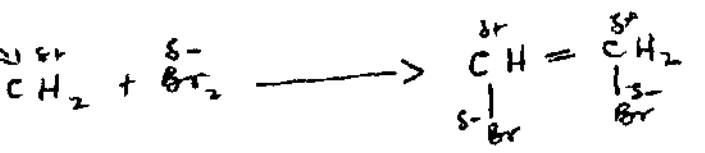
2. Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction but not with the second. The reactions are:

(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

(I) 

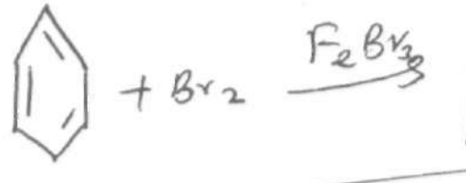
$FeBr_2^- + Br^+ \longrightarrow FeBr_3$

(II) 

The reason why a catalyst is used in the first reaction is that, since carbonium ion going to be formed the catalyst is needed in order to break into ions which will later on combine and form the catalyst again.

While in case (II) since it is undergoing substitution reaction catalyst is not needed.

Problem Solver 4

I)  + Br_2 $\xrightarrow{FeBr_3}$  + HBr, goes thus,

II)  + Br_2 $\xrightarrow{FeBr_3}$  + $2Br^-$ $\xrightarrow{-H^+}$  + HBr

III) $CH_2=CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$ goes thus,

$CH_2 \overset{\curvearrowright}{=} CH_2 \longrightarrow CH_2^+ - CH_2^-$

$Br_2 \longrightarrow Br^{\delta+} - Br^{\delta-}$

$\therefore$ ~~$CH_2=CH_2 + Br_2$~~ $CH_2^+ \leftarrow CH_2^- + Br^+ - Br^-$

$\downarrow$

CH_2BrCH_2Br

The first reaction is an electrophilic substitution reaction and equired energy for its effectiveness, hence a catalyst is equired. while the second is a simple addition reaction and does not require any energy, hence requires no ca

Problem Solver 5

4. Using the relevant mechanisms of the respective reactions

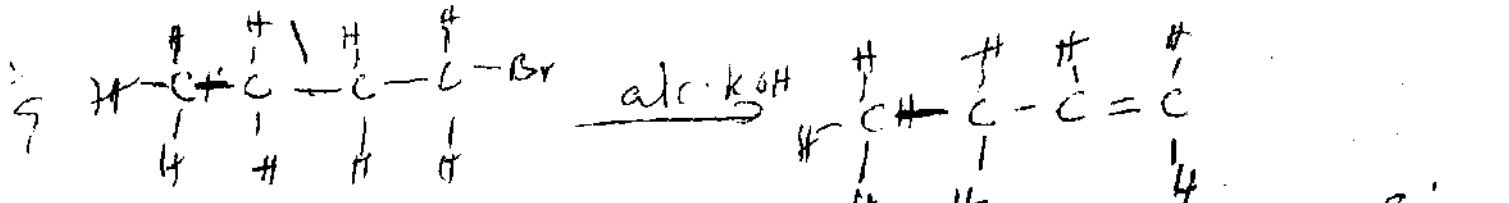
(a) Explain why 1-bromobutane forms only one isomer, while 2-bromobutane forms three isomers respectively, when treated with an alcoholic solution of potassium hydroxide. The reactions are as follows:

(I) $CH_3CH_2CH_2CH_2Br \xrightarrow{\text{alc. KoH}} CH_3CH_2CH=CH_2 + H_2O + Br$
1-bromobutane — but-1-ene

(II) $CH_3CH_2CH(Br)CH_3$ (2-bromobutane)
$\xrightarrow{\text{alc. KoH}} CH_3CH_2CH=CH_2 + H_2O + KBr$ — but-1-ene — (1)
$\xrightarrow{\text{alc. KoH}} CH_3CH=CHCH_3 + H_2O + KBr$ — but-2-ene — (2)

Note: Work out the third isomeric butene from reaction II.

(b) What name is usually given to the mechanism that you have described?



Since it is obeying Markovnikoff's rule, i.e the Br is attached to last carbon atom then the hydrogen atom will be attached to the next carbon atom to which the Br was attached, like adding HBr to $CH_3CH_2CH=CH_2$. Hence when adding eliminating HBr from $CH_3CH_2CH_2CH_2Br$ the only isomers it can form is the one above.

ii) the hydrogen can either be removed from the 1°c hence it will leave the product assigned (1), by Also the hydrogen can be removed from the 2° carbon atom, labelled 3, then the product formed will be product (2)

iii) Markovnikoff's rule; ~~accepted~~ mechanism

5. Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:

(I) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3} + HBr \longrightarrow \overset{1}{CH_3}-\overset{2}{CHBr}-\overset{3}{CH_3}$

electrophilic addition

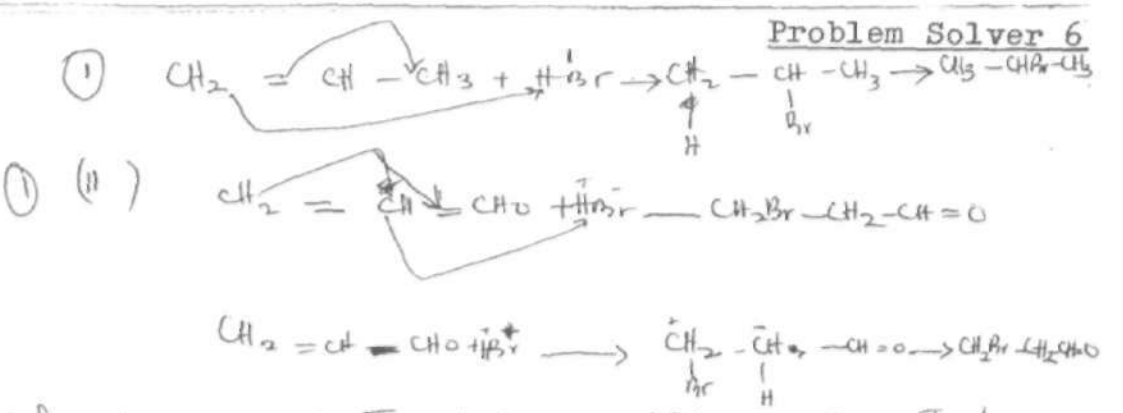
(II) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CHO} + HBr \longrightarrow \overset{1}{CH_2Br}-\overset{2}{CH_2}-\overset{3}{CH}=O$

nucleophilic addition

Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.

Problem Solver 6

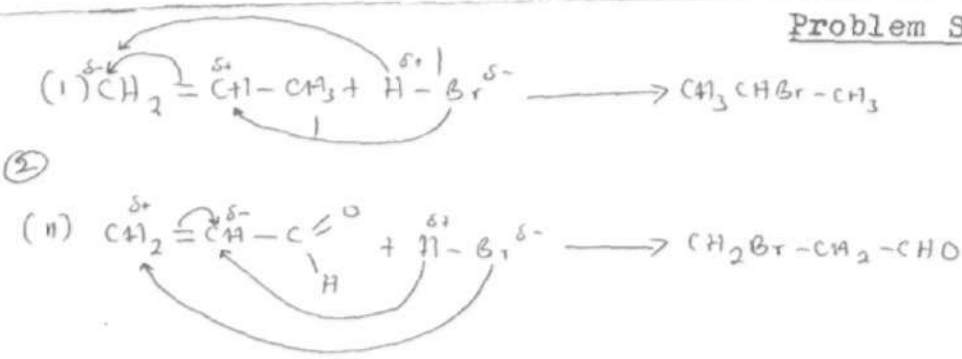


why the reaction I behaves differently from II, is in one it follows the rule of markownikoff, which the unsymetrical reagent goes to the higher carbon substituted while in II it is the reverse of the rule i.e anti Markownikoffs rule

I — it is the markownikoff

II — it is anti markownikoff.

Problem Solver 7



reaction (II) has a carbonyl group (CHO) which attracts the delocalised pi electrons from the double bond (~~I effect~~) Hence the reaction behaves differently

5.8 Response to the Questionnaires

The results of the students' response to the questionnaires are presented in tables 5.16.1 and 5.16.2. The first consists of the results from items one through five. These concern the students' assessment or judgement of the free response problems contained in test B. The second set consists of results from items six to ten of the questionnaire.

The results are presented showing the distributions in percentages. The thrust of the results showed that the students:

(a) were familiar with the problems

(b) found the problems only moderately difficult

(c) were moderately confident in the correctness of their solutions.

The only exception to this trend is problem 3 which the students opined that they found unfamiliar, difficult and had little confidence in the correctness of their solutions.

(d) found the major reason for difficulty in solving the problems was inability to apply known facts

(e) liked organic chemistry, liked studying it from a mechanistic approach and found chemistry moderately boring

(f) ranked difficulty of the problems in the order 3>4>5>2>1.

TABLE 5.16.1 % DISTRIBUTION OF STUDENTS' RESPONSE TO ITEMS 1-5 OF THE QUESTIONNAIRE

VARIABLES / PROBLEMS	FAMILIARITY		DIFFICULTY		CONFIDENCE		REASONS FOR DIFFICULTY					RANKING OF DIFFICULTY		OMIT
	FA	NF	DF	ES	CN	NC	I	II	III	IV	V	DIFFICULTY	EASE	
1	88.4	6.9	21.6	73.7	69.5	25.8	5.3	62.5	5.4	0.0	26.8	11.2	28.9	4.7
2	89.5	7.9	33.2	64.2	67.9	29.5	15.7	65.2	6.8	1.1	11.2	12.8	27.2	2.6
3	43.7	46.3	66.3	23.7	24.2	65.8	23.6	43.6	12.8	12.1	7.9	30.0	8.5	10.0
4	60.5	30.0	51.0	39.5	41.6	48.9	18.1	46.8	13.5	9.9	11.7	25.2	16.8	9.5
5	73.7	20.5	48.4	45.8	42.1	52.1	11.9	59.4	4.0	6.9	17.8	20.8	18.6	5.8
AVERAGE	71.2	22.3	44.1	49.4	49.1	44.4	14.9	55.5	8.5	6.0	15.1	3>4>5>2>1		6.5

TABLE 5.16.2 % DISTRIBUTION OF STUDENTS' RESPONSE TO ITEMS 6-10 OF THE QUESTIONNAIRE

QUESTIONNAIRE	VERY MUCH	NOT MUCH	NOT AT ALL	OMIT
HOW MUCH DO YOU LIKE ORGANIC CHEMISTRY?	71.1	18.4	2.6	7.9
HOW MUCH DO YOU LIKE LEARNING ORGANIC CHEMISTRY FROM A MECHANISTIC APPROACH?	63.1	27.4	4.2	5.3
HOW MUCH IS CHEMISTRY A NECESSARY REQUIREMENT FOR YOUR PROPOSED CAREER?	73.7	15.8	4.2	6.3
HOW MUCH IS CHEMISTRY (AS A SUBJECT) BORING TO YOU?	11.6	48.4	33.7	6.3
HOW MUCH HAS YOUR O-LEVEL EDUCATION IN CHEMISTRY HELPED TO PREPARE YOU FOR YOUR PRESENT COURSE?	62.1	31.6	1.0	5.3

The abbreviations used in table 5.16.1 are explained below:

FA = Familiar

NF = Not familiar

DF = Difficult

ES = Easy

CN = Confident

NC = Not confident

I = I do not have the grasp of the basic chemical knowledge

II = I knew the facts, but I did not know how to apply them to arrive at a solution

III = I cannot understand the question, so I was not able to proceed to solve it

IV = I was never taught this

V = I got mixed up along the way.

5.9 Summary and conclusions

The results have been presented in this chapter. Both statistical and qualitative analytic methods were used in the attempt to unravel the difficulties of the students in solving the problems.

Discussions of the results and findings from them are presented in the next chapter.

CHAPTER SIX

DISCUSSION OF THE RESULTS AND FINDINGS

6.1 Overview

The discussion of the results is presented in this chapter. The presentation is set out in the following order:

(a) the conceptual chemical knowledge of the students.

(b) the effect of students' conceptual knowledge on their problem solving capability.

(c) the differences between male and female students in solving the problems.

(d) the strategic knowledge of the students.

(e) students' difficulties in solving mechanistic organic problems.

(f) summary of discussions, findings and conclusion.

6.2 The conceptual chemical knowledge of the students

The relevance of conceptual knowledge as a requirement for solving problems has been highlighted (sec 2.8). Test A was designed to probe this. An answer is now sought to the question: do the students possess relevant conceptual chemical knowledge?

Table 5.4 shows the number of students selecting the correct response for each test item. The facility indices are shown in table 5.3. Except for a few items (4, 18, 21, 32 & 35) with facility indices below 0.30, the result shows that the students had high facility with the test items.

This is evidenced by the fact that 20 out of the 40 items have facility indices of 0.50 and above; 15 items have facility indices between 0.30-0.49, and 5 items, 0.18-0.29.

For the purpose of the discussion, facility indices of 0.50 and above are taken to indicate possession of good conceptual knowledge, 0.30-0.49, to indicate possession of average conceptual knowledge, and 0.0-0.29, possession of weak or poor conceptual knowledge of the test items. The results thus indicate that the students possessed the conceptual chemical knowledge sought by the test items.

The two measures of central tendency shown in table 5.2, namely the group mean score and standard deviation, indicate an average students' performance of 50%. These, taken together also indicate that the students possessed the required conceptual knowledge of the test items.

6.3 The effect of students' conceptual knowledge on their problem solving capability

This section deals with the relationship between the students' reservoir of conceptual chemical knowledge and their capability to solve problems based on that knowledge. The conceptual chemical knowledge of test A constituted the required pre-requisites for solving the problems in test B. Ideally, a large percentage of the variance in test B should be accounted for by test A. Also, scores on test A should be good predictors of test B scores.

The relevant results are shown in tables 5.7 and 5.8. There is a positive, but low correlation ($r = 0.45$) between tests A and B. The coefficient of determination (r^2) between the tests is 0.20. This shows that the variance in test B accounted for by test A is only 20%. The result of simple regression analysis of the scores is shown in table 5.8. The result obtained after entering the score of each student in test A into the fitted regression equation showed that only 42% of the students obtained scores in test B that were $\geq$ those predicted by their scores in test A.

These results indicate that less than half of the students were able to apply the pre-requisite chemical knowledge that they possessed in solving the problems. This suggests that there is a weak link between the students' possession of relevant conceptual knowledge and their capability to effectively solve problems based on that knowledge. Some of the factors that underlie the disparity are discussed later in sections 6.5 and 6.6.

Similar findings as above have been reported in a number of studies involving other areas of chemistry e.g Ahmed (1982), Adeyegbe (1985).

6.4 Sex differences in solving the problems

The role of sex differences in science achievement at college level has received attention in a number of studies. The reports indicate that male students perform better than their female counterparts (e.g Zerega etal, 1986, Adeyegbe, 1985,

Macoby etal, 1974, Walberg (1967). Adeyegbe's findings for example, show that the situation is not different for secondary school students in Nigeria. The discussion that follows is undertaken in the light of three questions:

(a) Is there a significant difference between male and female students' capabilities in solving the problems in this study?

(b) If so, are sex differences, a significant factor in dealing with students' difficulties regarding mechanistic organic problems?

(c) What are some of the educational implications?

6.4.1 Differences between the male and female students' performances in the tests

The relevant results are shown in table 5.9. A two-tailed t-test showed that there is no significant difference between the male and female students' performances in test A. There is, however, a significant difference in test B, in which the performance of the male students is found to be significantly superior to that of the female students. These results show two things:

(i) there is no significant difference between the male and female students regarding the reservoir of conceptual chemical knowledge they possessed.

(ii) there is a significant difference between the two sexes in their abilities to solve problems requiring the use of the knowledge.

6.4.2 Sex differences as a factor in problem solving

The discussion in this sub-section draws upon inferences arising from results discussed in the preceding sub-section and literature cited earlier in the section. Following the results outlined in section 6.4.1, it is reasonable to infer that sex differences constitute an important factor in some aspects of students' learning difficulties.

This inference, in itself, provokes many more questions than it attempts to answer. One such relevant question is this: Is there a cognitive difference between the sexes in so far as learning of science is concerned?

Some documented reports provide answers in the affirmative with some attempts by the authors to elucidate the variables involved.

For example, Stafford (1972) proposed the psychobiological hypothesis to explain the difference. The social-psychological theory which attributes the differences to "cultural function and pressure" was proposed by Strauss (1972). Zerega etal.(1986) made reference to what they termed the potential determinants of sex differences. These, according to them are: student age, ability and motivation, the quality and quantity of instruction (including self instruction) the social and psychological environment, peer-group and exposure to mass media.

Some studies have shown different results from those discussed above. For example, Haertel etal. (1981) investigated sex differences in science learning and performance amongst students whose average age was 13 years. They found no significant difference in performance between the two sexes. Thus, in view of the conflicting nature of reported findings, and given the difference in the sizes of the male and female samples in this study, the present results regarding sex differences in the capability to solve the problems posed, can only be interpreted with some caution.

The following conclusions can, however be drawn from the discussions presented in this section:

(a) sex difference seems to be an important factor in the consideration of students' problem solving difficulties in mechanisms of organic reactions.

(b) there is need for greater research efforts into the nature, manner of interactions and functioning of "potential determinants" of sex differences amongst Nigerian students in relation to their problem solving capabilities in mechanistic organic chemistry.

6.4.3 Some educational implications

A significant difference between students' capabilities, presumably caused by sex differences, is not a desirable educational outcome. It is necessary that a concerted effort be made by all bodies concerned with educational matters to close

the gap. This is desirable in Nigeria where culture and tradition have some influence on students' attitutde to, and perception of formal education. It is also to be given urgent attention if Nigeria is to witness an era of science for all, required for a scientifically literate and technologically progressive society.

6.5 The strategic knowledge of the students

Strategic knowledge has been defined, and its relevance to problem solving has been highlighted (sec 2.8). It formed an aspect of the assumptions that underlie the working model of this study (fig 2.9). Test B was designed to probe this.

The results are shown in table 5.5. All the problems, except No 1 (F.I = 0.44) have facility indices below 0.30. The relevant statistical properties of the students' performances are shown in table 5.2. These results show that the students found the problems very difficult to solve, suggesting that they were incapable of solving the problems, notwithstanding that they possessed the relevant conceptual knowledge (sec 6.2). The inference seems to be that the students lacked strategies required for solving the problems.

Strategic knowledge has little significance as a problem solving heuristic outside of the relevant conceptual knowledge (Larkin etal., 1980, Stewart, 1982).

Therefore, the interpretation of students' strategic knowledge or lack of it can only be done

within the context of the knowledge structures on which the strategies of problem solving must necessarily operate.

Kean (1982) identified such knowledge structures relevant to this discussion. They are:

(a) concept acquisition.

(b) recognition of relationship of one concept to other related concepts.

(c) the use of concepts to solve problems.

6.5.1 Concept acquisition

Although there are different levels of concept acquisition (Kempa etal.,1976), what is being referred to here is the basic acquisition of chemical, factual knowledge. This was discussed earlier (sec 6.2). The inference from the results is that this level of concept acquisition does not constitute a bar to students' possession of strategic knowledge.

6.5.2 Recognition of relationships amongst related concepts

Some theories regarding the structure of concepts have been reported in the literature. In the spreading activation theory for example, (Child, 1986), knowledge is viewed as consisting of a net-work of concepts, in which the related ones are inter-linked to form an organised body of knowledge in the cognitive structure of the learner.

Activation of one concept simultaneously activates other related ones. To visualize relationships amongst related concepts requires that they are inter-linked in the cognitive structure.

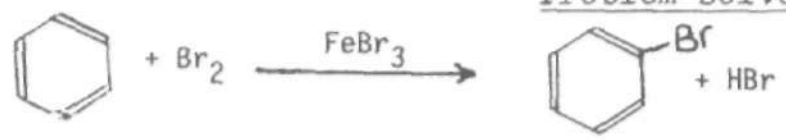
Elements of problems are coded into concepts. Thus for students to understand and represent problems, the recognition of the relationships of the underlying concepts is a necessary pre-requisite. The view is taken in this discussion that students' failure in this requirement contributed highly to their lack of the required strategic knowledge.

The excerpts shown below exemplify some aspects of students' failure to see relationships amongst chemical concepts while solving problems.

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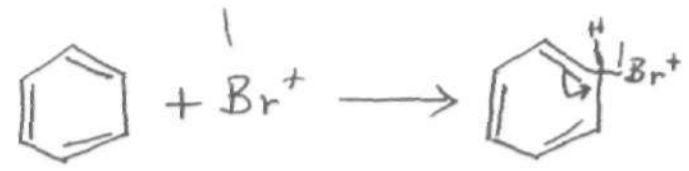
2. Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction but not with the second. The reactions are:

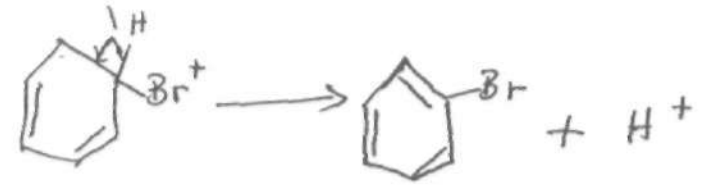
Problem Solver 8

(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

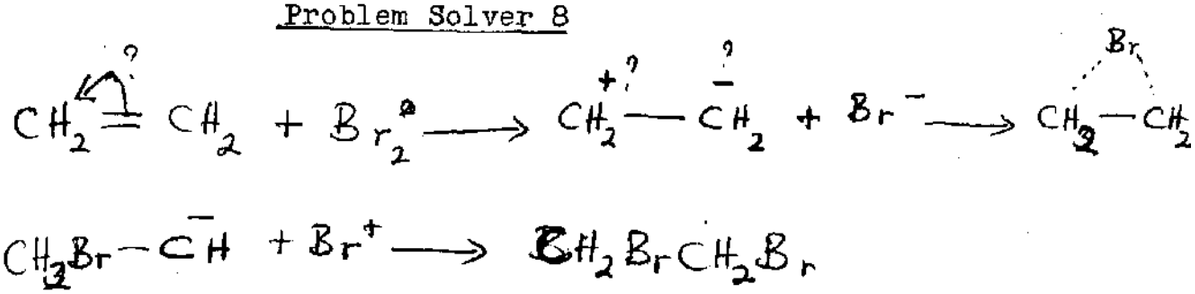
1. $Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$

2. 

3 

4 $FeBr_4^- + H^+ \longrightarrow FeBr_3 + HBr$

Problem Solver 8



This student, for example, failed to recognise the following relationships:

(a) the relationship between valence electrons of reacting species and the species involved in reaction.

(b) the relationship between electron pair movement and the processes of bond-breaking and bond-making.

(c) the relationship between curved arrows (↷) and electron-pair movement.

(d) the relationship between an electron pair represented by a dash (-) and the valence electrons of the bonded atoms in a classical Lewis structure.

(e) the structural relationship between atoms constituting a molecule on one hand, and the bonding and non-bonding electrons on the other.

It is reasonable to suggest that this problem solver relied on rote memory, reproducing what he was taught rather than using them as rules for solving the problem. Certainly, the blame (if some should be alloted) cannot rest with the students alone. All the facets of the curriculum - aim, content,

instructional methods, assessment, feed back and adjustment procedures employed in the schools need scrutiny.

The conclusion is this: the students involved in this study spend much time acquiring chemical concepts. However, the concepts remain unlinked and unrelated. This results in failure to form conceptual patterns required for decoding problem elements. Thus, students' problem solving difficulties lie, not so much in concept acquisition, but in lack of necessary linkages of the concepts to form comprehensive patterns.

6.5.3 Using concepts to solve problems

The distinction between acquisition and use of concepts in relation to problem solving has been made. These were referred to as conceptual and strategic knowledge respectively (sec 2.8). The use of concepts in problem solving involve the following aspects:

(a) understanding the problem.

(b) selecting information (from LTM and problem statement).

(c) organising the information to generate a solution.

These aspects of concept usage in problem solving are equivalent to the two-stage problem solving model (planning and execution) proposed in section 2.8; and illustrated in fig 2.9. Planning comprises (a) and (b) above, while (c) constitutes execution.

6.5.3.1 Understanding the problem situation

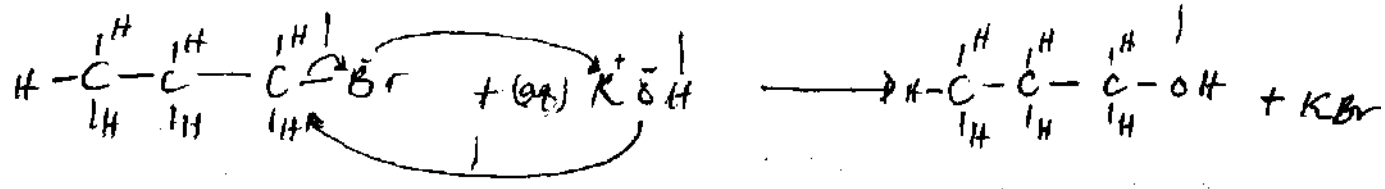
The results of qualitative analysis of the students' scripts showed that they lacked meaningful understanding of the concepts required for solving the problems (sec 5.7). It has been stated that problem elements are generally coded into these concepts (sec 6.5.2). The sum of these amount to students' lack of understanding of the problem situation. The examples shown below typify students' failure to conceptualize the problem situation.

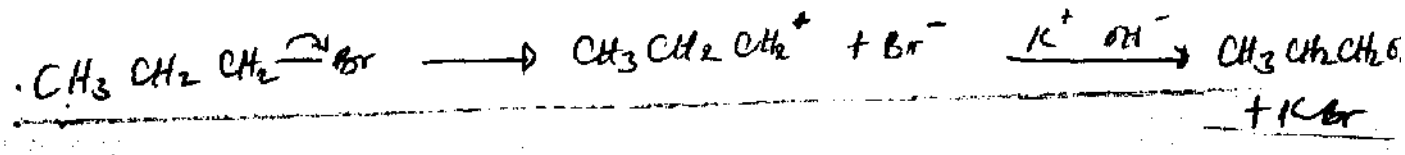
1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$

~~$CH_3CH_2CH_2Br$~~

Problem Solver 9





Problem Solver 10

$KOH_{(aq)} \longrightarrow K^+ + OH^-$

~~$CH_3CH_2CH_2Br \longrightarrow CH_3CH_2CH_2^{\oplus} + Br^-$~~

$CH_3CH_2CH^{\oplus}Br^{\ominus} + OH^- \longrightarrow CH_3CH_2CH_2OH + Br^-$

$Br^- + K^+ \longrightarrow KBr$

Problem solver 9, in an attempt to solve the problem, presented two incongruent mechanisms, S_N2 and S_N1 operating at the same time. This suggests a trial-and-error strategy in which the solver hopes to get at least one of the mechanisms correct. Alternatively he does not recognise the differences. Both cases indicate lack of understanding of the problem situation.

Problem solver 10 sees and treats the bromoalkane as an ionic compound. In solving the problem, he merely correlated the charged species to arrive at the given product. He lacks an understanding of the problem situation which requires a general conceptual overview of:

(i) the C-Br covalent bond, based on an understanding of the molecular structure of the bromoalkane.

(ii) the distortion of C-Br bond electrons, based on differential electronegativities.

(iii) decreased electron density at α-carbon centre which prompts,

(iv) a nucleophilic attack of OH^- on that carbon.

It is reasonable to deduce that the solver lacks a global perception (hence understanding) of

the problem i.e a bimolecular nucleophilic substitution. It is a matter for concern that about 74% of the students involved in the study showed similar difficulties. These point to more deeply-seated conceptual difficulties. Some of these are discussed in section 6.6.

6.5.3.2 Selecting relevant information

This refers to distinguishing concepts that are relevant from those that are not relevant to the process of solving the problem at hand. The importance of information selection to successful problem solving is highlighted in the literature (e.g Selvaratnam, 1983). Since the students failed to understand the problem situation (sec 6.5.3.1), a logical implication is that they would, as a result, fail to select relevant information required for solving the problem. Evidence from qualitative analysis of the students' scripts (sec 5.7) together with two examples shown below support this conclusion.

Problem Solver 11

5. *Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:*

(I) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH_3} + HBr \longrightarrow \underset{\text{electrophilic addition}}{\overset{1}{CH_3} - \overset{2}{CHBr} - \overset{3}{CH_3}}$

(II) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CHO} + HBr \longrightarrow \underset{\text{nucleophilic addition}}{\overset{1}{CH_2Br} - \overset{2}{CH_2} - \overset{3}{CH} = O}$

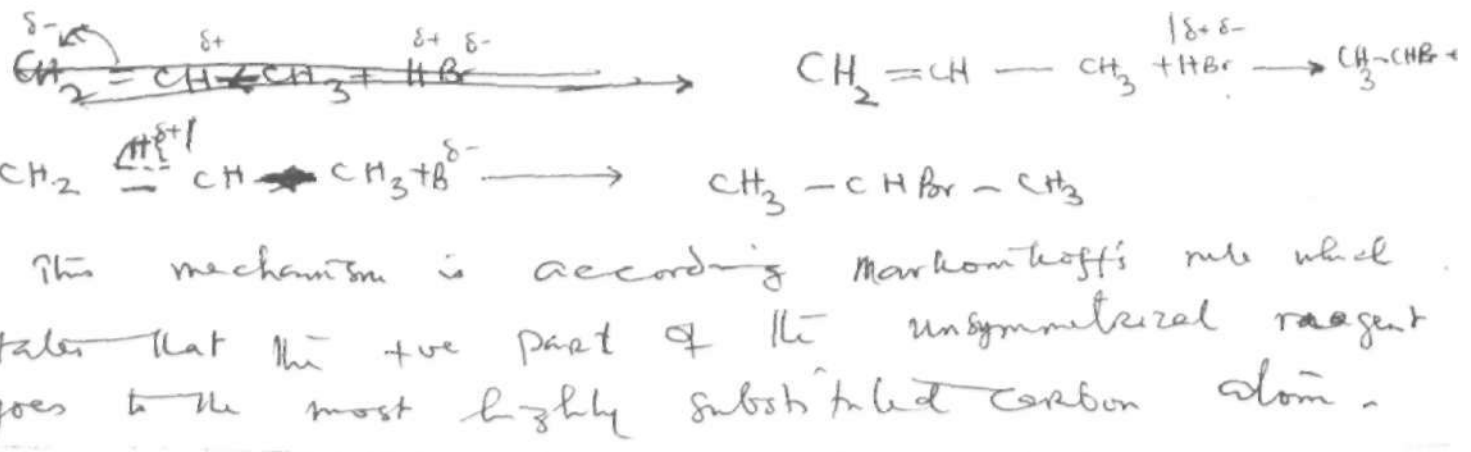
Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.

Problem Solver 11



Problem Solver 12



The excerpts show that the solvers 11 and 12 selected and used an algorithm which, though related to the problem, is irrelevant to the process of solving it. There is some evidence to suggest that selection of information is guided by rote memory, in which the students attempt to reduce the difference between the reactants and the products, both of which are given. However, this behaviour is characterised by application of wrong strategies.

6.5.3.3 Organising the information to generate a solution

This phase of problem solving has been referred to in this section as execution. It is dependent on the planning phase for success. Where planning is faulty, execution is hampered, and even if it is "bull-dozed" as it was by most students involved in this study, the resultant solution is generally wrong.

The excerpts included in this section show that the students made what could be described as reasonable attempts to organise the information-bits to generate a solution. But most of them are based on a wrong conceptual premise. For example, problem solver 11 merely assigned H and Br (atoms) to C_1 and C_2 respectively to arrive at the given product. This might look a reasonable attempt to organise information,but it is wrong chemistry, portraying a whole range of fundamental misconceptions.

While it cannot be said that the students lack the ability to organise information to generate a solution, the evidence is that they do so wrongly. So, there is the issue of what is superficially reasonable (at least to the solver) and what is fundamentally correct. Where the two are in question, as they appear to be here, the latter should, of course, prevail. The conclusion, therefore is that the students were unsuccessful in organising information-bits to reach a solution.

Similar findings have been reported by some researchers, for example, Patwary, 1982; Ahmed, 1982.

From the discussions in this section, the following conclusions can be drawn:

(a) the students lack strategies for solving the problems notwithstanding that they possess the conceptual knowledge underlying the former.

(b) students' lack of strategic knowledge is attributable to:

  (i) lack of concept-linkages, resulting in failure to form conceptual patterns of chemical principles.

  (ii) failure to understand the elements of the problem situation.

  (iii) failure to select relevant information required for solving the problem at hand.

  (iv) combined effects of i-iii above which rendered their attempts to organise information-bits to generate a solution unfruitful.

6.6 Students' difficulties in solving mechanistic problems: a conceptual interpretation

The strategies adopted by the students in solving the problems are reported in section 5.7. Results from tests A and B have led to the conclusion that the students possessed pre-requisite conceptual knowledge, but were incapable of extending them for

use in solving problems (sec 6.3). The gap between students' possession of conceptual knowledge and ability to use them is accounted for (within the framework and conduct of this study) by misconceptions or conceptual difficulties, these being held to underlie students' difficulties in solving the problems. Misconception is taken to mean a departure of the privately-held knowledge of an individual from a publicly-accepted view of a given knowledge domain.

The grades from the paper-and-pencil tests do not give much information about these conceptual difficulties. The discussions that follow in this section highlight some of them. The discussions draw upon analysis of the strategies adopted by the students to solve the problems (sec 5.7), excerpts shown in section 6.5 and further qualitative analysis of the students' scripts from which excerpts included subsequently in this chapter are derived.

The difficulties fall into three main categories:

(a) chemical structure of reacting species.

(b) formalisms of chemical symbols.

(c) chemical interactions of reacting species and the resultant structural changes.

These are briefly discussed below:

6.6.1 Chemical structure

Two major difficulties were identified. They are:

(i) the electronic concept of covalent bonds and

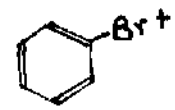
the related concept of unshared electron-pairs in the valance shell of constituent atoms of the molecule. These are referred to here as electronic concepts in molecules.

(ii) the visualization of the positions of atoms (using the planar Lewis structure model) in the molecule relative to each other. This is being referred to as atomic linkages.

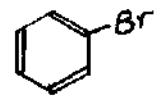
6.6.1.1 Electronic concepts in molecules

The students have difficulties with the electronic arrangements (Lewis structure) within the molecule that give rise to covalent bonds. The idea of a covalent bond being represented by a pair of electrons appears familiar, but the implication of this for the structure of molecules presents difficulty. A closely related difficulty is that of an unshared electron pair in the valence shell of bonded atoms. Most of the students appear to be unaware of these, resulting in difficulties in coping with co-ordination number and formal charges. Examples of such difficulties showed up in students writing:

$CH_3CH_2\overset{+}{C}H_2—Br^-$ instead of $CH_3CH_2\overset{\delta+}{C}H_2—Br^{\delta-}$



instead of

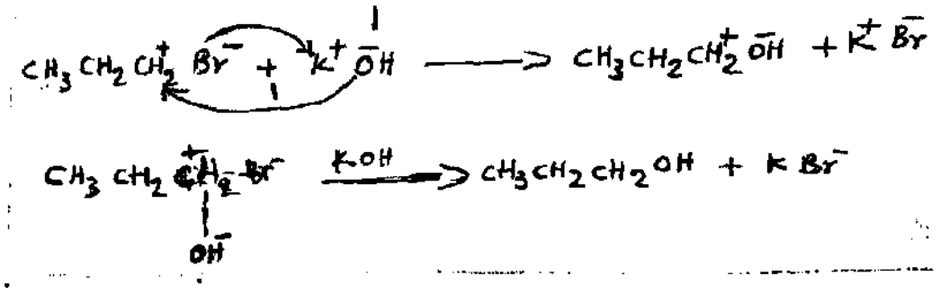


Two excerpts which further exemplify the difficulties are shown below:

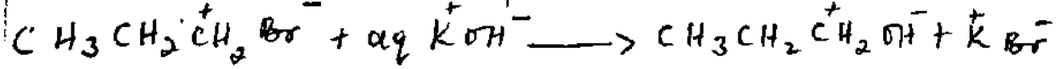
1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$

Problem Solver 13



Problem Solver 14

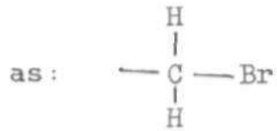


The teaching of organic chemistry, using Lewis structures, with all valence electrons indicated at every stage, is likely to help in reducing the difficulties. The use of different styles of representing molecules, often adopted by different teachers in these schools is partly to blame for the difficulties. The proliferation of these different styles in different organic chemistry texts only compound the situation.

6.6.1.2 Atomic linkages

It is apparent to the author that the students had difficulties in conceptualising the arrangements of the atoms relative to each other in a given molecule. This was not tested directly, but

indirectly monitored especially through problem 1, in which the condensed formula of the reacting molecule (bromopropane) was given. To solve the problem successfully requires that the molecule is "opened up" into its structural formula, or at least that the $-CH_2Br$ part of the molecule is opened up.

as: 

The results showed that only a quarter of the students attempted to do this. The view is taken that the students could not conceptualise the relative linkages of the constituent atoms. Students' structural representations of the bromopropane molecule, e.g $CH_3CH_2\overset{+}{C}H_2Br^-$; $^+CH_3CH_2CH_2Br^-$; $CH_3CH_2\overset{+}{C}H_2\text{---}Br^-$ lend credence to the validity of the conclusion. The findings of Dupigny (1985) also support it.

It is probable that the students were unable to mentally manipulate the structures. Representation of molecules showing the relative attachment of the constituent atoms by both teachers and authors of organic texts might reduce this difficulty. The emphasis of some recent texts in this regard gives some encouragement.

6.6.2 Symbolic formalisms

These refer to some of the symbols that are frequently used in describing chemical processes involved in organic reactions together with the chemical concepts that they represent. Those that

are relevant to the study are briefly discussed below:

(i) curly arrows (↷).

(ii) partial and full charges.

6.6.2.1 Curly arrows

The understanding of curly arrow formalism is an important pre-requisite for the understanding of mechanisms of organic reactions (William, 1971). Loudon (1984) considers the formalism as "a device for keeping track of electrons in reactions". The curly arrow represents movement of electron-pair from the tail to the head of the arrow.

This constitutes an area of fundamental conceptual difficulty for the students, who used curly arrows both inconsistently and inaccurately. The following are some of the conceptual difficulties that feature most prominently:

(a) the students do not seem to visualize a relationship between the use of curly arrows and an underlying electron-pair movement.

(b) the students used curly arrows as indicating:

  (i) movement of protons.

  (ii) movement of atoms or groups of atoms, radicals and molecules.

(c) many of the students constructed the curly arrows so that they originate and terminate in "empty space" giving no particular chemical information.

(d) some curly arrows have double heads, one at each end, while others are merely curved

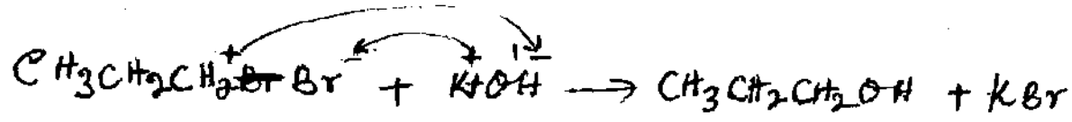
lines.

The excerpts shown below exemplify each category of the conceptual difficulties presented, with comments describing the most significant conceptual difficulties in each category.

Problem Solver 15

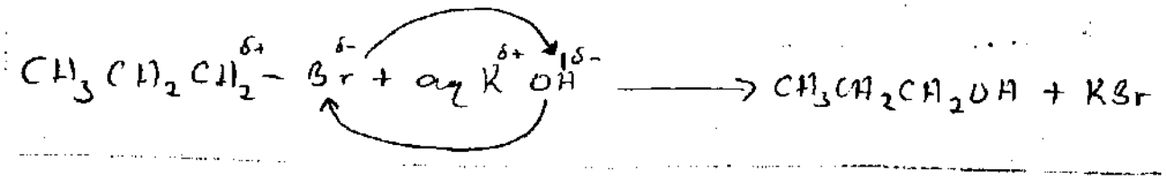
1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$



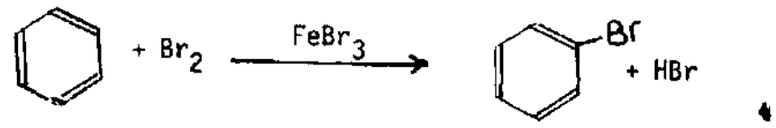
Problem Solver 16

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$

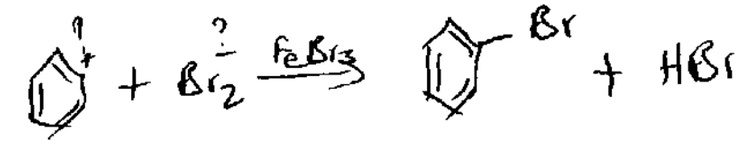


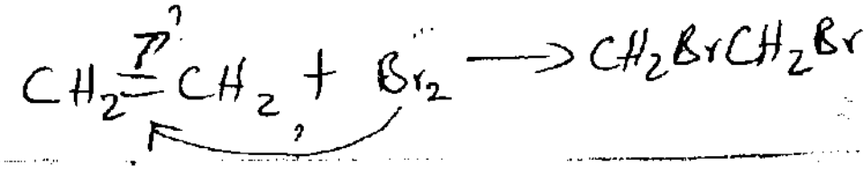
2. Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction but not with the second. The reactions are:

Problem Solver 17

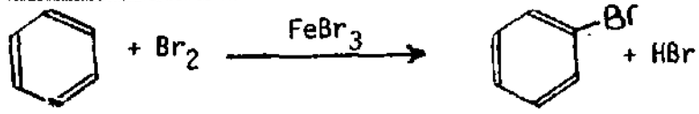
(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

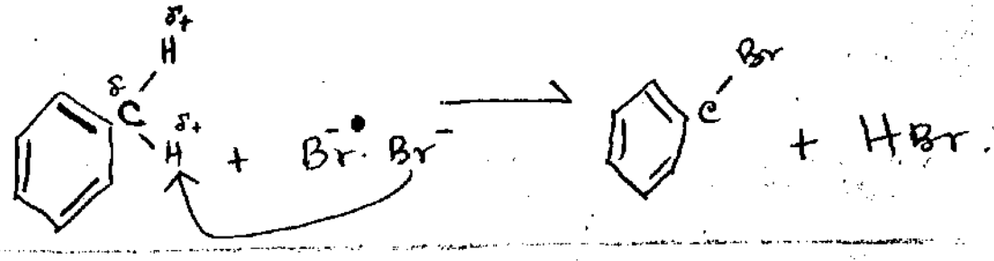
(I) 

(II) 

Problem Solver 18

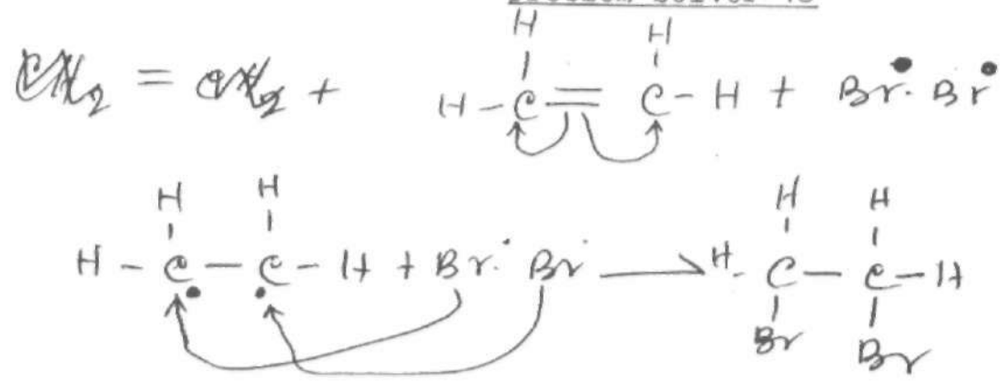
(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$



Problem Solver 18

ii



5. Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:

Problem Solver 19

(I) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3} + HBr \longrightarrow \overset{1}{CH_3}-\overset{2}{CHBr}-\overset{3}{CH_3}$

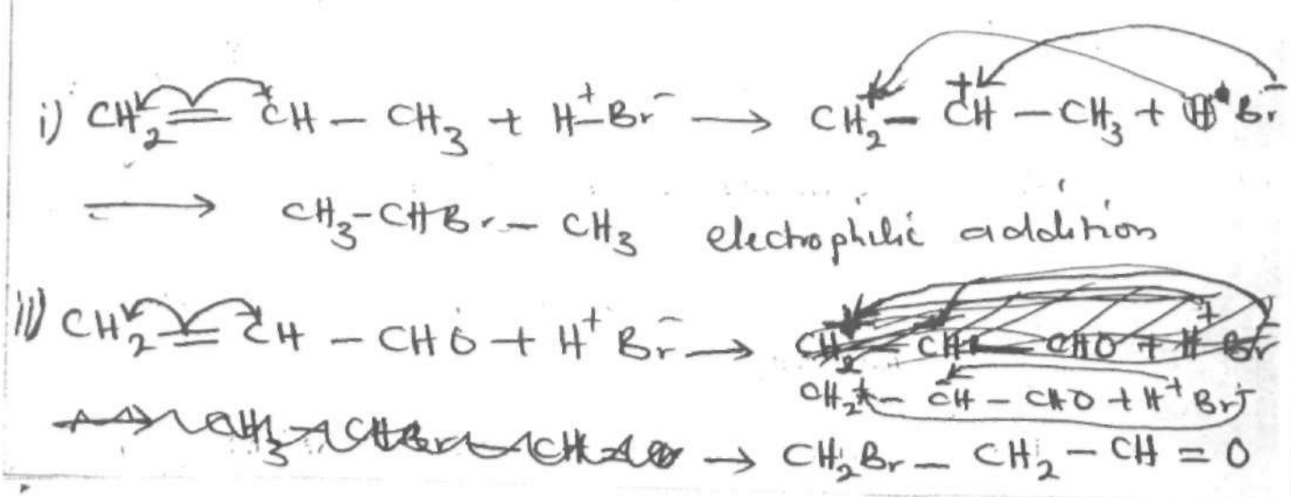
electrophilic addition

(II) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CHO} + HBr \longrightarrow \overset{1}{CH_2Br}-\overset{2}{CH_2}-\overset{3}{CH}=O$

nucleophilic addition

Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.



Problem Solver 20

$CH_2=CH\,CHO + HBr \longrightarrow CH_2Br-CH_2-CH=O$

$CH_2=CH-CH=O \longrightarrow$ ~~CH_2-CH~~

$\overset{\delta-}{C}H_2 = \overset{\delta+}{C}H - \overset{\delta-}{C}H=O$

$HBr \longrightarrow \overset{\delta+}{H}-\overset{\delta-}{Br}$

$\overset{\delta-}{C}H_2 = \overset{\delta+}{C}H-\overset{\delta-}{C}H=O + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow CH_2Br-CH_2-CH=O$

One of the conclusions that emerges from these findings is that the students do not have the conceptual understanding of electron movements involved in organic reactions. The second conclusion is consequent upon the first. It is this: the students are incapable of using curly arrows to describe the processes involved in organic reactions because they do not possess an understanding of the chemical concepts that they represent. Simpson (1983) has reported that A-level English students studying organic chemistry experienced difficulties with the use of curly arrows similar to those discussed above.

The teaching of organic chemistry from a mechanistic approach, in which curved arrows are used to detail electron movements, should receive emphasis in the schools of Basic Studies. This will develop in the students an understanding of the chemical processes involved in organic reactions. It would require, of course, that the students are led, in the first instance, to understand the concepts that curly arrows represent, and how to use them, based on a firm understanding of the chemical structure of molecules.

It appears the teachers have taken these basic skills for granted, in the students involved in this study. These results reveal that the assumptions are unrealistic. It could also be that the content and structure of the organic chemistry syllabus is partly unsuitable.

6.6.2.2 Partial and full charges

The symbols $\delta+$ and $\delta-$ are referred to here as partial charges, and + and - as full charges. The students used these symbols inaccurately and in wrong contexts. They used $\delta+$ and + interchangeably; so also $\delta-$ and -. Futhermore, these symbols are often assigned to the wrong atoms within the molecule. Examples include structures represented by the students as:

$CH_3CH_2CH^+_2\text{-}Br^-$ instead of $CH_3CH_2\overset{\delta+}{C}H_2\text{-}Br^{\delta-}$

$H^+\text{—}Br^-$ instead of $H\overset{\delta+}{\text{—}}Br^{\delta-}$

$CH_2Br\text{-}\bar{C}H_2$ instead of $CH_2Br\text{-}\overset{+}{C}H_2$

Problem solvers 10, 13, 14, 19 and 20 are typical examples. These are not isolated instances. A closer examination of the students' scripts showed that 84% of them used these symbols wrongly at one stage or another in solving the problems.

These suggest that there is an enormous amount of confusion in the mind of the students regarding:

(i) electronic concepts of covalent bonding.

(ii) the electron distribution about atoms constituting a molecule (see 6.6.1.1 also).

(iii) the conceptual meaning and structural implications of the symbols they chose to use.

The conclusion can be drawn from these findings that the students' understanding regarding

the basic concepts that underlie molecular structure is fundamentally defective. Secondly, teachers' (often tacit) assumptions that students would pick up the capability to use symbols alongside the learning of the concepts that the former represent is apparently not valid. It does appear that the skills of using symbols should be taught specifically. Whether they are taught at the same time as the concepts they represent or separately from them is a separate pedagogic matter.

6.6.3 Chemical interactions

One of the requirements for solving mechanistic organic problems is that the student possess a conceptual understanding of the chemical interactions of the reacting species involved. Chemical interaction is explained in terms of the bond-breaking and bond-making processes, involving movements of electrons and resultant structural changes. The analysis of the underlying sub-tasks of the problems (test B) draws heavily on the conceptual understanding of such chemical interactions. The results are shown in tables 5.11-5.15.

The results show that the students had low facility with each of the sub-tasks embedded in all the problems. When these results are taken alongside those shown by the analysis of the students' strategies for solving the problems, they lead to the conclusion that they lack a conceptual understanding of the interactive processes in which

the reacting species are involved. Problem solvers 1, 2, 3, 4, 6 and 7 (sec 5.7) amply exemplify this conclusion. It is most probable that students' difficulties with chemical structures (sec 6.6.1) contribute fundamentally to their difficulties in conceptualising the chemical interactions of the reacting species.

These results further reinforce the case made earlier (sec 6.6.2.1) for a mechanistic approach to teaching organic chemistry at these institutions (SBS). This should, of course, be based on a firm understanding of the chemical structures of molecules in relation to their chemical reactivity.

6.7 Response to questionnaires

The result of students' responses to the questionnaires in the free-response problems are shown in tables 5.16 (1 and 2). They show that the problems were familiar to the students, except problem 3 on which opinion was split. The problems were considered moderately difficult, except 1 and 2, which were judged to be easy. The students indicated moderate confidence in the correctness of their solutions to the problems. The most fundamental factor causing difficulty seems to be students' inability to apply the chemical, factual knowledge that they possess to solving the problems.

The following inferences can be drawn from the results:

(a) the knowledge tested by the problems is within the cognitive competence of the students.

(b) there is a weak correlation between students' familiarity with the problems and the level of difficulty experienced.

(c) the students tended to have underestimated their level of difficulties with the problems compared with their actual performances.

(d) the students' estimation of their confidence in the correctness of their solutions to the problems is consistent with their difficulties with the problems. However, there is some over estimation of the former.

(e) the students seemed to like organic chemistry as a subject, and also were favourably disposed toward the learning of the subject from a mechanistic approach.

The conclusions drawn from this section are as follows:

(a) the problems are familiar to the students. This justifies some aspects of the assumptions underlying the construction of the test consisting the problems.

(b) the students, on the average, have a fair impression about their problem solving capabilities.

(c) the students' obstacles in solving the problems lie mostly in lack of ability to apply conceptual or factual knowledge to solving the problems.

(d) the students' estimation of the order of

decreasing difficulty of the problems is: 3>4>5>2>1. Their performances show that the order is: 4>5>2>3>1. Apart from the odd position of problem 3, the assessments agree very well with their performances, further supporting conclusion (b) above. In spite of this general agreement, a closer examination of each problem shows that a large proportion of the students underestimated the level of the difficulties and overestimated their confidence in the correctness of their solutions. This tends to suggest that either the students do not know what they know or that they did not take the questionnaire seriously. The former is more probable.

(e) the students indicated positive disposition toward organic chemistry as a subject, and the learning of it from a mechanistic approach.

6.8 Summary of discussions, findings and conclusions

6.8.1 Summary of discussions and findings

The discussions presented in this chapter highlight the nature of students' difficulties in solving mechanistic organic problems. They are both conceptual and strategic. They are conceptual because the students lack an understanding of, and connections amongst related chemical concepts that they have learnt. This contributes fundamentally to failure in generating conceptual patterns or principles that guide the cognitive processes of solving the problems. They are strategic because

the students are incapable of structuring and representing the problems in any logical and systematic manner. During the process of solving the problems, wrong heuristics were used in which incorrect operators were selected for use in reducing the difference between the problem and the solution. A strategy of trial-and-error, haphazardly adopted, was used to achieve this.

There are really no clear boundaries between conceptual and strategic knowledge in the cognitive processes of solving these (academic) problems. This fluidity is amply highlighted (sec 6.5). Students' conceptual difficulties (sec 6.6) directly affected their strategic knowledge.

The following constitute the major findings from the discussions:

(a) The students were incapable of solving the problems, notwithstanding that they possessed the pre-requisite conceptual knowledge. This gap (between the students' conceptual knowledge and capability to solve the problems) is attributable to the students' conceptual difficulties which are due to lack of:

(i) understanding of the electronic structure of molecules, involving the structural relationships of covalent bonds, atoms and valence electrons within the molecule in a classical Lewis model.

(ii) understanding of the formalism of chemical symbols. Curly arrows and representation of charges feature most prominently.

(iii) understanding of interative processes of bond-breaking and bond-making which reactants undergo to reach products.

(iv) visualization of connective links between related chemical concepts to form broad-based chemical principles.

(b) The students lack strategic knowledge. This is evidenced by their:

(i) failure to understand the problem situation.

(ii) failure to select relevant information given the demands of the problem.

(iii) haphazard organisation of information-bits in an attempt to generate a solution.

(c) (i) There is a positive, but low correlation between the students' possession of chemical knowledge and their capability to use the knowledge in solving problems that are based on it.

(ii) The students' reservoir of chemical knowledge is not a good predictor of their capability to solve problems that require such knowledge as pre-requisites.

(d) (i) The male students perform significantly better than the female students in solving mechanistic organic problems.

(ii) Sex differences seems to be a significant factor in educational matters concerning students' difficulties in learning of organic chemistry in Nigerian Schools of Basic Studies.

(e) The students' problem solving approach is guided, mostly by rote-memory, rather than by a logical application of conceptual or chemical principles. This is evidenced by the students' problem solving strategies which indicate a trial-and-error approach rooted in chemical misconceptions of the nature discussed in this chapter.

(f) The students' difficulties in solving mechanistic organic problems, can be summarised as due to their failure to marry conceptual knowledge (which they possessed) with the demands of the problems. This failure can be explained in terms of their lack of concept-understanding, concept-linkage and concept-utilization. These tended to constitute "stumbling-blocks" in the students' moves to solve the problems.

6.8.2 Conclusions

The difficulties of students in solving structured organic reaction problems which require them to describe the mechanisms have been discussed in this chapter. Some conclusions were drawn in the course of the discussions, and a summary of these have been presented as the findings.

The conclusions were drawn, based on results obtained from paper-and-pencil performances of the students. But these provide us with no information about, and thus with no insight into, the thought processes that led the students to the right or wrong solutions. In the next three chapters, an attempt is made to probe these.

PART IB

PROBING STUDENTS' THOUGHT PROCESSES AS THEY SOLVE MECHANISTIC ORGANIC PROBLEMS

"Thinking is a process and knowledge is a product, but the two are intimately related"

Aaron, 1971

"The psychologist studying individual differences through the use of tests and questionnaires of various kinds must, if he is to interprete the results with any degree of accuracy, investigate the nature of mental processes underlying the responses to the instruments"

Bloom and Broder, 1950

CHAPTER SEVEN

INTRODUCTION, REVIEW OF LITERATURE AND PROCEDURE FOR DATA COLLECTION

7.1 Overview

The transcript of a person's tape-recorded statements as he/she talks aloud about his/her thought processes while he/she is solving problems, together with his/her written work constitutes a protocol (Reif, 1983). This method of gathering evidence about an individual's problem solving behaviour has come to be known as the "thinking aloud" technique, referred to in section 3.4 as TAPS - "Thinking Aloud Problem Solving".

The role of this technique in gathering evidence about, and analysing problem solving behaviour of individuals has been considered very significant in studies of problem solving. Bloom and Broder (1950), for example, view the evidence upon which judgements about problem solving behaviour must necessarily be based from two complementary stand-points:

(a) the thought products

(b) the thought processes.

They argue that what paper-and-pencil tests usually show are the thought-products from which the investigator makes inferences about the problem solving behaviour of the subject(s). They contend that such methods, though indispensible, must necessarily be complemented by tests that give information about the thought-processes that

culminate in the products that are observed. In other words, the overt behaviour exhibited during a problem solving situation should be studied alongside the underlying cognitive strategies as complementary phenomena. This part of the study is geared towards achieving this.

In this chapter, the purpose of the study, review of relevant literature and procedure of data collection are presented.

7.2 Purpose of the study

Students' difficulties in solving the problems presented to them in part IA of this study are apparent. Inferences were made and conclusions drawn about the nature of, and reasons for these difficulties (see 6.5 and 6.6). Such inferences and conclusions were based on the author's interpretation of the students' solutions to the problems. In all cases, the processes of thought that led to these solutions (right or wrong) were unknown. The purpose of this part of the study was to employ the "thinking aloud" technique to:

(a) investigate the processes of thinking that underlie the overt problem solving behaviour of the students.

(b) describe ways in which students' thought processes are related to their success or failure in solving problems.

(c) determine if observed variations in students' problem solving behaviour is ascribable to certain thought patterns or cognitive

strategies.

(d) gain deeper insight into the problem solving difficulties of the students, with a view to confirming or modifying conclusions reached about the conceptual and strategic difficulties in part IA of the study.

(e) expose the nature of students' problem solving difficulties from their own view-points.

7.3 Methods of investigation

There are basically two approaches generally employed in collecting data using the "think aloud" technique. These are:

(i) one in which the student verbalizes his/her thoughts as he/she solves the problem, without any intervention from the experimenter.

(ii) one in which the experimenter interviews the student in the course of the TAPS.

In the first method, the student is placed in a quiet room where he/she is given the problem(s) to solve, speaking out his/her thoughts as he/she progresses through every stage of the problem. An audio-cassette recorder records his/her verbalizations. The experimenter sometimes disappears from sight or else remains as a passive spectator throughout the problem solving session. One of the major advantages of this method is that it allows for an unbroken, natural flow of the student's thought during the problem solving period. The possibilities of unwittingly guiding the students' responses through clues, often embedded in the

interviews, are eliminated. Some of the disadvantages, however, are that such unlimited lattitude gives the student too much room to say anything, anyhow. The result may be an incomprehensible data. Secondly, the experimenter loses the advantage of probing deeper at points where it becomes necessary. Thirdly, the student may become frustrated and consequently give up, if provided with no prompts that may serve to break a conceptual impasse.

In the second method, both the student and the experimenter work together as a team in a quiet room. The experimenter interjects once in a while by asking particular questions, or making certain expressions as the TAPS progresses. These serve the purposes of probing for more details, clarifying ambiguities and prompting the student in the process.

This method suffers the following disadvantages:

(a) The student's line of thought is subjected to external interference. He/she may, consequently, become confused and/or incoherent, depending on the frequency of interjection and the tact employed.

(b) The phraseology of the questions or expressions, could, unknown to the experimenter, lead the student towards or away from a response originally contemplated by him/her.

(c) The student may become nervous and frustrated

by the constant requirement to answer questions and thus lose confidence.

The advantages of the method include the following:

(a) It minimises possibilities of the student editing his/her thoughts which could, otherwise have occurred.

(b) It gives the experimenter opportunity to clarify vague statements, probe deeper and prompt the student, if he/she is heading for a deadlock.

(c) In situations where prompting fails to avert or resolve conceptual stagnation, the interviews are valuable in determining the underlying causes(s).

An approach which represents a compromise of the two methods outlined above involves:

(i) allowing the student to carry out the TAPS process without any form of intervention from the experimenter, combined with

(ii) the experimenter interviewing the student on his/her verbalized thoughts in conjunction with his/her written responses after a solution is produced or when the student is deadlocked and is clearly unable to proceed.

This method, which is a variant of methods (i) and (ii) put together, combines most of their advantages while eliminating many of the disadvantages. The main limitation, however, is that it lacks what has been described as "advantage

of immediacy" (Adeyegbe, 1985); occasioned by the time lag between the problem solving session and the interview session.

7.4 Review of literature

A survey of literature relevant to this part of the study is now presented.

7.4.1 Recording students' "thoughts" without interviews

A number of researchers have, at various times, adopted this method in the conduct of their studies. Paige and Simon (1966) used this technique to investigate the methods that problem solvers employ in attacking problems. Based on their findings, they classified problem solvers into two categories: physical and verbal solvers. The physical solvers tend to set up some internal representation of the situation involved in the problem. The verbal solvers are those who concentrate on the direct, literal translation of the words of the problem.

Thorsland and Novak (1974) carried out an investigation involving 25 students. They reported that the results obtained from analysis of the protocols led them to classify the subjects into two categories: intuitive and analytic problem solvers. They explained that intuitive solvers depend on some implicit feeling rather than a conscious awareness of the explicit steps leading to a solution. Analytic solvers are characterised by a tendency to carry out careful analysis of the steps leading to a solution.

Bapat (1975) used this method to record the verbalized thoughts of 41 subjects, comprising university teachers, post-graduate and under-graduate students while solving problems of organic chemistry. He reported that over 90% of the subjects appeared to have used the analytical approach in solving the problems. He further indicated that protocol analysis was a useful method for investigating problem solving strategies and the cognitive factors that may underlie such strategies. His studies culminated in the development and evaluation of what he called a methodology for studying problem solving strategies.

Bree (1975) carried out an investigation in which he attempted to study the understanding of students in structured problems. He used 12 subjects, and employed a computer program for the analysis of the protocol. He reported that students' understanding has some consistent relationship with the kind of the task involved.

Simon and Simon (1978) investigated the problem solving behaviour of individuals they had classifed as experts and novices, using computer program. They reported that many of the differences in skills between the two groups can be ascribed to a generalised practice effect. They explained that the skilled subjects have, over a period of time, acquired a vastly greater level of experience in solving arithmetical and algebraic problems, hence their superior performance relative to the novices.

Onwu (1980) investigated some aspects of the concept of amount of substance, using a total of 27 subjects selected from fourth and sixth forms. His analysis was based on Pascual-Leone's theory. He showed that a direct comparison between performances of younger and older students conveys little meaning without reference to the intellectual levels of the two groups.

Ahmed (1982) carried out a study involving 10 students in Kano state of Nigeria, in which he attempted to probe the underlying causes of students' difficulties in some aspects of electrochemsitry. He analysed his protocols using a method he described as a "pragmatic" approach. It does not rely on any formal theory, but involves piecing together the information gathered in order to make sense of it. His findings showed that a distinction exists between the private knowledge held by the subjects about some scientific concepts, and the publicly-accepted version of the same concepts. This seems to point to the individualistic nature of learning.

7.4.2 Interviewing students

Menis and Novick (1976) used this method to investigate the understanding of 29 high school students about aspects of the concept of amount of substance. They showed that the subjects held certain misconceptions, in particular that the mole represents a mass.

Lazonby etal.(1982) employed this method to investigate students' difficulties in some

calculations involving the concept of amount. They reported that the method was useful in obtaining information about the thought patterns of the students and the mistakes that they most frequently make. They showed, for example, that the students often adopted haphazard strategies for solving the problems.

Gabel etal. (1984) employed the technique to determine the general problem solving skills of high school chemistry students. They used Polya's heuristics as basis for coding and analysis of the protocols. It involved the determination of whether the solver understood the problem, devised a plan to solve it, carried out the plan and in the end, evaluated the solution in relation to the demands of the problem. They found that students who were successful in solving the problems tended to use strategies involving algorithms more often than those that were unsuccessful.

Adeyegbe (1985) used the method to investigate the strategies that Nigerian secondary school students used in solving arithmetical problems involving the concept of the amount of substance. He found, amongst other things that their problem solving approach could not be categorized into any generalizable pattern.

7.4.3 Effects of "thinking aloud" on performance

The question of how the requirement to verbalize affects performance in problem solving, if it does at all, has received some attention. Gagné

and Smith (1962), for example, reported that the very act of verbalizing encouraged their subjects to think of new reasons for their moves, facilitating the discovery of general principles and their use in problem solving.

Cohen (1977) concluded that the instruction requiring the solver to "think aloud" may have the effect of distorting normal thought processes which tends to induce the subject to make his thinking more intelligible and orderly than would have otherwise been the case.

Flaherty (1975), using 100 students showed that the requirement to "think aloud" has no significant effect on performance in a given task.

Satterly (1983), however, observed that the requirement to "think aloud" amounts to asking the individual to perform two operational tasks at the same time. He suggested that humans are incapable of doing that. The argument may continue, but the utility of TAPS as a useful diagnostic tool is not in question. It does mean, however, that research using this method, should employ a technique that attempts to minimise whatever interference there may be between "thinking aloud" and actually performing the task.

7.4.4 Main highlights from the literature

The literature reviewed showed that:

(a) protocol analyses have been widely used as a method for describing cognitive structure and functioning.

(b) protocol analyses provide useful information about the nature and underlying causes of learning difficulties.

(c) both methods (sec 7.3) have been widely used by researchers at various times across wide-ranging subject matters.

(d) there is no clear answer to the question of whether the requirement to "think aloud" significantly affects actual performance; and if so, in what direction. The inference that can be drawn from the pool of arguments is that performance is not significantly inhibited.

7.5 Limitations of "thinking aloud" as a diagnostic instrument

Inspite of the advantages of "thinking aloud" (sections 7.1 and 7.4) as a tool for an indepth diagnosis of learning difficulties, it suffers certain short-comings. Some of these are outlined below:

(a) It is highly time-consuming considering the processes involved in data collection, transcription and subsequent analysis of protocols.

(b) Consequently:

  (i) only samples of relatively small sizes can be effectively used.

  (ii) the scope of subject-matter that can be dealt with at any given time is necessarily narrow.

(c) Protocols represent only verbal behaviour from which inferences are made about cognitive strategies. The reliability of results are, thus dependent on the match between the strategies and the statements purported to have expressed them. The certainty that this match exists, and indeed, its quantification are uncertain.

(d) Not all cognitive functioning can be verbalized, especially in problems that rely mostly on recall of information for generating a solution.

7.6 Choice of method for data collection

The two major approaches generally adopted for data collection have been discussed in section 7.3. The strengths and weaknesses of each method were highlighted.

A major consideration that underlies the choice of method for the conduct of data collection has to do with an attempt to avoid interjections from the experimenter during the TAPS session, but also to provide an opportunity to clarify ambiguities and probe for more details where necessary. A method that seems to satisfy this requirement is the integrationist approach described in section 7.3 as intermediate between methods (i) and (ii). This approach was adopted for data collection in this part of the study. A number of researchers, for example Gabel etal.(1983), Adeyegbe (1985) have used the method in the conduct of the investigations cited in section 7.4.2.

7.7 Procedure of data collection

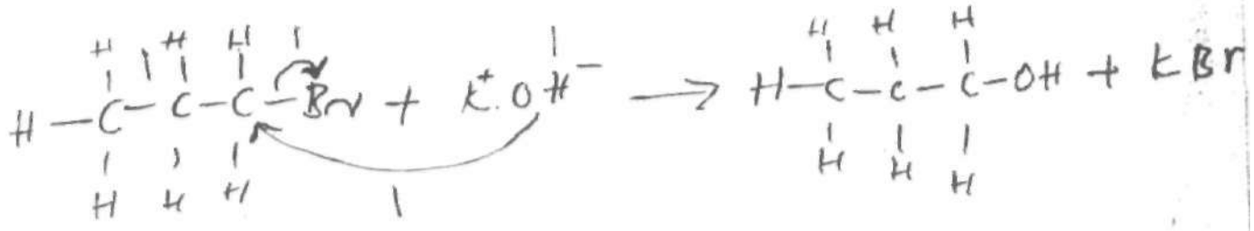
The remainder of this chapter describes the procedure employed in the conduct of data collection - from the underlying theoretical considerations to the actual recording of the students' verbalizations.

7.7.1 Establishing a basis for sample and problem selection

The collection of data was undertaken the day after the written tests in each school visited. Immediately after completion of the written tests, the author examined all the written responses in detail. From this exercise, a fair idea was obtained about the performances of the students. The overall picture that emerged in all the schools visited was that the students performed poorly in test B and fairly well in test A. Attention was thus focused on test B, which was further scrutinised in an attempt to separate the scripts into two categories, based on what was judged as good and poor performances. There were few students in the first category, generally ranging between 2 and 6 students from each school. The scripts were also scrutinised problem by problem. It was fairly obvious to the author that while the students generally found the problems difficult to solve, problem 1 was the least difficult. Two excerpts included below serve to exemplify what was considered relatively good and poor performances respectively.

1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$



~~$CH_3CH_2Br + OH^-$~~

$CH_3CH_2\overset{+}{C}H_2 + Br^- + H^+ + OH^- \longrightarrow \underset{\text{carbonium}}{CH_3CH_2CH_2^{\oplus}} + OH^-$

(1)

$CH_3CH_2CH_2OH + KBr$

Note Heat of Alcohol KOH it will form double bond. that alkene.

The outcome of the evaluations and categorization of the students and the problems formed the basis for selecting the students and problems included in the TAPS study. One limitation of this impressionistic approach of judging the written responses concerned the inherent subjectivity involved. However, it was the best option under the circumstances, as the other more reliable approach using the actual scores, would have required a number of weeks to complete. If such a long period of time was allowed to elapse between the written tests and the conduct of TAPS, it would have been likely to result in reconstruction, edition, and in some cases, maturation of the thought processes that guided the students' responses. That would have largely defeated the purpose of the study.

7.7.2 Selection of samples

The sample selected from each school comprised 4 students, giving a total of 20 students (16 males and 4 females) for the study. The samples were obtained by randomly selecting 2 students from each category. It was considered that a relevant comparison of protocols from the two groups would yield some useful information about the nature of link (if any) between students' thought patterns and academic success and failure; in addition to the overall objective of exposing the students' difficulties from their own view-points.

The students were not informed beforehand that they would be required to participate in the study.

The Heads of the chemistry departments were informed as their assistance were sought in providing a suitable place for conducting the TAPS, and to help in keeping track of the participating students. They were, however, requested not to inform the students in advance. A summary of the composition of the samples is shown in table 7.1.

TABLE 7.1 COMPOSITION OF THE SAMPLES FOR THE STUDY

Name of School	Male	Female	Total
College of Advanced Studies, Zaria	3	1	4
School of Basic Studies, Zaria	3	1	4
College of Arts and Science, Sokoto	3	1	4
School of Basic Studies, Makurdi	3	1	4
School of Basic Studies, Port-Harcourt	4	0	4
TOTAL	16	4	20

7.7.3 Selection of problems

The problems (test B) were grouped into two categories, based on the information obtained from a detailed examination of the answer scripts (section 7.7.1). These comprised the difficult and moderately easy problems. Problem 1 belonged to the latter category and the remaining 4, to the former.

The decision about the number of problems, and

which ones to include in the study was influenced by the following considerations:

(a) Motivation:

TAPS is highly time-consuming, thus the students would get easily bored and consequently lose interest if the number of the problems were not kept manageably few.

(b) Indepth study:

The level of detail desired from the study limited the scope of content that could be covered.

(c) Spread of tasks:

The choice of the problems was made to include at least one problem from each category. This is relevant, for example, to "purpose b" (sec 7.2).

Based on these considerations, amongst others, three problems, 1, 2, 5 were selected for the study. Problems 2 and 5 were chosen in preference to 3 and 4 because the former set involved not only reasoning within a topic domain, but also using related chemical principles to reason across different topic areas. The topic areas represented by the selected problems are summarised in table 7.2.

TABLE 7.2 TOPIC AREAS COVERED BY PROBLEMS INCLUDED FOR TAPS

Problem No	Section	Topic Areas
1		Nucleophilic substitution
2	i	Aromatic electrophilic substitution
	ii	Electrophilic addition to symmetrical olefinic bonds
	iii	Some relationships of chemical structure and chemical reactivity
5	i	Electrophilic addition to unsymmetrical olefinic bonds
	ii	Nucleophilic addition
	iii	Some influences of inductive and mesomeric effects on the course of chemical reactions

7.8 Conduct of TAPS

The "think aloud" problem solving sessions took place in quiet venues, usually the chemistry laboratories, arranged for the purpose by the Heads of chemistry departments of the schools. It involved the author working with one student at a time, each session lasting about one and a half hours. The design of the precedure involved two successive stages: a general introduction and the actual recording.

7.8.1 The introductory stage

This involved two phases - familiarization and general explanation. The familiarization phase involved a conscious attempt by the author to acquaint himself with the student as prelude to the "thinking aloud". For this purpose, the author developed a general format used in all the schools. The wordings are as follows:

> "My name is Amos Shaibu. I am a chemistry lecturer at the School of Basic Studies, AhmaduBello University, Zaria. I am currently a post-graduate student at the University of East Anglia, Norwich, United Kingdom".

After this brief self-introduction, the author paused for a moment, expecting the student to also introduce himself. In about 60% of the cases, the students responded spontaneously and introduced themselves in a manner similar to the author's. In few cases where the student responded by only a nod of appreciation, the author asked:

> "What about you? What is your name?"

After this simple prompt, the student introduced himself, sometimes with apology for having waited for a request to do so.

This introduction phase was immediately followed by a general explanation phase. This involved the author explaining to the student, the purpose of the study, and what he (the student) was

expected to do. The phraseology was as follows:

> "You remember that you, along with other students, participated in solving some problems for me yesterday. I have gone through your scripts. I could see your responses, but I have no way of knowing the thoughts that led you to respond like you did. Now, here is the problem text again (putting test B before the student). I want you to solve problems 1, 2 and 5 for me, but this time, I want you to speak out the thoughts in your mind that lead you as you solve the problems. Do not do anything in silence. Speak out everything you are doing from the time you start the problem until you finish. Do you understand what I mean?"

The author paused again for response. In nearly all the cases, the students understood. In other few cases further clarification was given by the author; after which he continued:

> "I am interested in both what you write down and what you say. You know that I cannot possibly remember everything that you say. Therefore I have this audio-cassette recorder (showing the recorder to the student) which I wish to use to record your statements, if you don't mind. I assure you that your recorded statements will be kept absolutely confidential. The purpose of the recording is to help me find out why you solved some

problems in certain ways when I look at your script later. Do you mind the recording?"

About 80% of the students willingly obliged. A few who had reservations ask such questions like: Will I get to know the results when you finish? The author took "results" to mean the findings from the research; and he responded:

"Your school will have access to them, so you can get to know from your school".

After such replies, the students appeared satisfied and gave consent. In no case did the student decline the request to have his statement recorded.

The introduction stage was considered very important to the conduct of the "thinking aloud". It allowed for establishment of familiarity, mutual trust and confidence between the student and the author. It also served as a period during which the anxious and nervous student became relaxed. All these put together, had a motivating effect, aimed at stimulating the student to make maximum effort (sec 4.3.6)

7.8.2 The actual recording

After completion of the introductory formalities, the problem text (test B) was then handed to the student, who was asked to proceed to solve the problems, speaking aloud what he was thinking as he solved the problems. These were recorded for each student in all the schools. After completing each problem, the student was interviewed.

The interview consisted of a number of questions, most of which followed from the students' procedure in solving the problems, and the related verbalizations. These were also tape-recorded. A total of ten 90-minutes audio-cassette tapes were collected.

7.9 Summary and conclusion

In this chapter, a description of the procedure adopted in colleting data about students' problem solving behaviour, and underlying cognitive strategies, using the "think aloud" technique is presented. A review of relevant literature is also undertaken. The next chapter deals with transcription of the tapes, analysis of the protocols and presentation of results.

CHAPTER EIGHT

ANALYSIS AND PRESENTATION OF RESULTS

8.1 Introduction

The procedure employed to analyse the protocols and the results obtained are reported in this chapter. There are two methods generally used for analysing protocols - formal and informal methods. The formal approach involves adoption of a model, which usually consists of an organised statement categories that are held to predict the problem solving behaviour of the subjects and, in some instances, the conditions under which the behaviour is expected to occur. This approach has been used by a number of researchers (e.g Onwu, 1980; Gabel etal., 1984, Larkin etal., 1984). The informal method involves a systematic, impressionistic survey of the data (protocols) with a view to bringing out the main features that relate to the aim(s) of collecting the data. Generally it involves a guided exhibition of protocol excerpts from which the features are revealed. This method, referred to as a "pragmatic approach" by Ahmed (sec 7.4.1) has been used by a number of researchers; for example, Bloom and Broder, 1950, Khan, 1980. Both methods are used in this part of the study, as one complements the other.

8.2 Transcription of the protocols

Transcription constitutes the first step in the process of protocol analysis. The recorded verbalizations of the subjects were transcribed

verbatim, including where pauses, indicated by dotted lines, occurred.

There were a total of 20 subjects, and 5 problems. All the problems were attempted, thus giving a total of 100 protocols transcribed. It was found, however, that the verbalizations from problem solver No 6 were both incoherent and unintelligible. The resulting protocols were accordingly omitted from subsequent analysis, leaving 95 protocols that were subjected to the analysis described in the remaining part of this chapter. The breakdown is shown in table 8.1 below.

TABLE 8.1 BREAKDOWN OF PROTOCOLS TREATED

Problem Number	No of Protocols Treated
1	19
2I	19
2II	19
5I	19
5II	19
TOTAL	95

8.3 Treatment of the protocols

8.3.1 Procedure for coding the protocols

Coding requires a framework that can be used, or adapted for use in describing and categorizing students' cognitive strategies and the related overt

problem solving behaviour. The formulation of the framework, spelt out below, is based on the problem solving model described in chapter two (sec 2.8). The main elements of the model (sec 6.5.3) are used as the major statement categories for coding the protocols. The procedures adopted by Gabel etal,, (1984) also provided a useful guide in deriving the categories which are:

1. Understanding the problem
2. Devising a strategy
3. Executing the strategy.

The sub-categories, which are predictive statements of behavioural profile expected of an expert solving the problems, were derived by the author. They are as follows:

1.0 Understanding the problem

- 1.1 Getting acquainted with the problem.
- 1.2 Disembedding the key information from the problem statement.
- 1.3 Forming a global overview of the problem.

2.0 Devising a solution strategy

- 2.1 Breaking the problem statement into smaller, relevant sub-units.
- 2.2 Retrieval of relevant information from memory.
- 2.3 Selection and refinement of key information.

3.0 Executing the strategy

3.1 Functional awareness of information recalled and obtained from problem statement.

3.2 Organizing/applying information.

8.3.2 Coding the protocols

The coding of the protocols involves translation of the protocol categories into predictive statements that characterize each category. Ideally, the reliability of the coding should have been judged by an independent party. The author, unable to obtain such volunteer(s), undertook the coding exercise twice within an interval of three weeks. There was high level of agreement between the two codings. Inspite of the limitations of self-consistency as guide for reliability, it was nonetheless taken in the circumstance as indicative of it.

The protocol categories and the characteristics indicative of their occurrence in the protocols are illustrated in table 8.2 below.

TABLE 8.2 CHARACTERISTICS OF THE PROTOCOL CATEGORIES

Category	Evidence for occurrence of category in protocol
1.1	Reading the direction of the problem
1.2	Stating aspects of the direction that clarify the nature of the problem to be solved
1.3	Stating some feature(s) that relate(s) the main elements of the problem to the goal
2.1	Interpreting/expanding the problem statement, generally using words familiar to the solver
2.2	Stating pre-requisite knowledge not provided in the problem statement
2.3	Stating some feature(s) or rule(s) that provide(s) a basis for attack on the problem
3.1	Stating some functional relevance/relationship of 2.3 to the procedure adopted for attacking the problem
3.2	Fitting the information-bits together to generate a solution

8.3.3 Scoring the protocols

The scoring of the protocols was done by assigning a grade of one to statement(s) expressing a unit of thought that underlie successive problem solving moves made. A grade of zero was awarded for wrong or incomplete statements. Each correct written representation of the stated unit thought was also awarded a grade of one, and zero for a wrong or incomplete representation. This approach represents a rule-action scheme.

Rule refers to chemical principles conveyed by the unit thought employed to make each move along a solution route, while action is the translation of the principles to a written response. The scheme, which is based on some aspects of the propositions of Larkin etal.(1984), has the advantage of revealing both the thought processes of the subjects and how they are translated into written products.

In scoring the protocols, the author sought to achieve two things:

(a) To categorize the protocols into two groups - successful and unsuccessful, as a basis for further analysis.

(b) To use the results from the analysis as a quantitative basis for describing students' general problem solving strategies, and the thought processes underlying them.

The criteria for devising the scoring scheme (appendix 8.1) are derived from the sub-tasks embedded in each problem (see chapter five). They are as follows:

4.1 Representing the reacting molecule (substrate)

4.2 Identifying the reactive site

4.3 Identifying the electrophile/nucleophile (reagent)

4.4 Demonstrating how the electrophile/nucleophile may be generated

4.5 Representing substrate/reagent interaction

4.6 Representing an intermediate

4.7 Demonstrating how a product is generated (from 4.5 or 4.6).

The distribution of the maximum scores, for each problem, according to the scheme is illustrated in table 8.3.

TABLE 8.3 DISTRIBUTION OF MAXIMUM SCORES OBTAINABLE

Problem No	SCORE		TOTAL
	RULE	ACTION	
1	5	5	10
2I	6	6	12
2II	6	6	12
5I	6	6	12
5II	6	6	12
TOTAL	29	29	58

8.3.4 Criterion for grouping the protocols

The result obtained from the scoring process was used as basis for grouping the protocols into successful and unsuccessful protocols. The maximum score obtainable in each problem is shown in table 8.3. Protocols with scores $\geqslant$ 50% of these scores were taken as successful, while those scoring less than 50% were taken as unsuccessful. Based on this categorization, 20 protocols were grouped successful and 75, unsuccessful. Also, the maximum score that can be obtained by any subject for all the problems

was 58. For purposes of this study, those whose scores were 30 or above were classified successful problem solvers, and those scoring less than 30 were classified as unsuccessful. On this basis, 4 subjects were successful and 15, unsuccessful problem solvers. Table 8.4 illustrates the results.

8.3.5 Display of the category variables in the protocols

The frequency of display of the category variables (see table 8.2) in the two groups of protocols was detemined. For this purpose, a frequency count of the variables was made. The result is shown in table 8.5.

8.3.6 Statistical analysis

Is there any real difference in the display frequency of category variables between the two groups - successful and unsuccessful protocols? This is the basic question that this sub-section attempts to answer. To this end, a chi-square test of association was used to test the hypothesis that:

> "There is no real difference in the display frequency of the category variables in the two groups of the protocols".

The result is shown in table 8.6.

TABLE 8.4 DISTRIBUTION OF SCORES

PROBLEM / SOLVER No	1		2I		2II		5I		5II		TOTAL	REMARK
	R	A	R	A	R	A	R	A	R	A		
1	3	1	1	1	1	1	0	2	0	1	11	-
2	1	1	0	0	0	0	0	1	0	1	04	-
3	2	0	1	0	2	3	3	1	0	0	12	-
4	2	2	1	2	1	2	3	3*	0	0	16	-
5	2	2	1	2	1	2	4	4*	1	1	20	-
7	2	1	6	3*	6	6*	6	5*	0	1	36	+
8	1	1	1	0	1	1	1	0	0	1	07	-
9	3	1	3	1	1	0	0	0	1	0	11	-
10	4	4*	1	1	4	3*	4	2*	4	3*	30	+
11	1	2	0	0	2	2	1	1	1	1	11	-
12	1	1	0	0	2	0	1	1	0	0	06	-
13	1	1	2	4*	5	5*	2	2	0	0	22	-
14	3	3*	5	3*	5	3*	3	2	2	2	31	+
15	2	1	1	1	1	2	2	1	0	0	11	-
16	2	1	4	2*	3	1	3	3*	1	0	20	-
17	2	1	2	2	1	1	2	1	1	0	13	-
18	5	4*	2	1	6	6*	6	6*	1	1	38	+
19	2	1	0	0	1	2	3	3*	1	1	14	-
20	2	2	0	0	1	1	1	1	1	1	10	-

KEY

R = Rule

A = Action

* = Successful Protocol

+ = Successful Problem Solver

- = Unsuccessful Problem Solver

TABLE 8.5 FREQUENCY DISTRIBUTION OF THE DISPLAY OF CATEGORY VARIABLES

FREQUENCY OF DISPLAY PER PROBLEM / PROTOCOL CATEGORIES	SUCCESSFUL PROTOCOLS						UNSUCCESSFUL PROTOCOLS					
	1	2I	2II	5I	5II	TOTAL	1	2I	2II	5I	5II	TOTAL
1.1	3	4	3	3	3	16	12	13	13	14	13	65
1.2	3	3	4	4	2	16	6	7	6	7	4	30
1.3	3	2	3	3	2	13	6	8	6	5	3	28
2.1	3	2	3	2	2	12	6	7	7	10	5	35
2.2	2	3	3	3	1	12	11	12	11	12	3	51
2.3	3	3	3	4	1	14	2	7	5	4	3	26
3.1	3	4	4	3	2	16	3	4	7	6	2	22
3.2	3	2	3	3	2	13	2	3	7	6	1	19

TABLE 8.6 VALUES OF X^2 FOR THE DISPLAY OF CATEGORY VARIABLES IN THE TWO GROUPS OF PROTOCOL

PROTOCOL CATEGORY	EVIDENCE OF OCCURRENCE IN PROTOCOLS	X^2	REMARK
1.1	Reading the direction of the problem	0.46	X
1.2	Stating aspects of the direction that clarifies the nature of the problem to be solved	7.76	✓
1.3	Stating some feature(s) that relate(s) the main elements of the problem to the goal	5.32	✓
2.1	Interpreting/expanding the problem statement, generally using familiar (to the solver) words	1.09	X
2.2	Stating pre-requisite knowledge not provided in the problem statement	0.46	X
2.3	Stating some feature(s) or rule(s) that provide(s) a basis for attack on the problem	6.59	✓
3.1	Stating some functional relevance/ relationship of 2.3 to adopted procedure of attacking the problem	17.12	✓
3.2	Fitting the information-bits together to generate a solution	11.27	✓

KEY

✓ = Values of X^2 significant at $\alpha \leqslant 0.05$

X = Values of X^2 below significance at $\alpha \ll 0.05$

8.4 Analysis for conceptual difficulties and general approach to problem solving

8.4.1 Introduction

In this section, the informal approach to protocol analysis (sec 8.1) is adopted. A selection of protocols considered to typify both the successful and unsuccessful groups are included. They are presented unedited along with the post-problem solving interviews which also contributed in the summing up of the protocol features. The symbols, "I" and "S" are used to designate the interviewer and the student respectively.

Pauses are shown by dotted lines. Words or expressions in brackets, mostly following the dotted lines originate from the author to indicate where dotted lines do not mean passive silence. A summary of the protocol features is given in table 8.14 under the following main headings:

(a) general problem solving approach

(b) major conceptual framework used to solve the problems

(c) major problem solving pitfalls.

A summary of the main chemical misconceptions and comparative tendencies of the successful/unsuccessful groups are also given in tables 8.15 and 8.16 respectively.

The author introduced punctuations to aid the clarity of the protocols which are shown in tables 8.8-8.13. Table 8.7 shown below gives an overview of the presentation.

TABLE 8.7 PRESENTATION OF THE PROTOCOLS

Problem No	Tables	
	Unsuccessful Protocols	Successful Protocols
1	8.8	8.9
2I	8.10 (a)	8.11 (a)
2II	8.10 (b)	8.11 (b)
5I	8.12	8.13
5II	8.12	8.13

TABLE 8.8 PROBLEM No 1: NUCLEOPHILIC SUBSTITUTION SOLVER No 3

Protocol	Features	Post-Problem Solving Interview
Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is bromopropane plus aqueous potassium hydroxide and the products are ... propyl alcohol plus potassium bromide. These are the products. We can see that aqueous potassium hydroxide is ionic and this equation we have bromopropane. In the bromopropane, we have two radicals, in this case, alkyl radical and bromine ion. The bromine ion is more electronegative than the alkyl radical, as such it attracts the electron toward itself or the electron density is moved toward the bromine ion, so it acquires a negative charge while the alkyl radical acquires a positive charge, as such there will be exchange of radicals in this case. This gives rise to the product propyl alcohol plus potassium bromide. These are the products ... OK .. this reaction can be described as Sw1 reaction .. I mean Sw2 reaction because there is covalency change between the reactants ... and two moles are taking part in the reaction, that is, in the rate determining step. It is a one step process. It is called nucleophilic substitution reaction bimolecular. It is bimolecular because exchange of radicals takes place between the two compounds in the rate determining step. It is substitution because one ion in this case is replaced by another. For example, potassium ... I mean bromine is replaced by OH group that's all.	1. Read direction of the problem 2. Indicated that KOH is ionic but immediately dropped the idea without indicating the relevance of that piece of information. 3. Did not show how the radicals are produced, neither did the solver indicate how the idea was arrived at. There seems to be a tremendous confusion (in the solver's mind) about radicals on one hand and ionic reagents on the other. 4(a) The idea of radical exchange appears central to solver's strategy. This idea, expanded upon by the solver in the interview appears to involve an attraction between reacting species of opposite charges. (b) Solver was unable to identify the major product of the reaction (i.e alcohol) and thus failed to concentrate his ideas on the process of its formation. 5. Stated some relevant knowledge which were not brought to bear on solving the problem. Perhaps, their contextual relevance was not perceived. 6. Apparently, the solver's problem solving strategy revolve around assignment of charges to reacting species and balancing of those charges on a postive/negative basis. 7. On the whole, the attempt to solve the problem was typified by a haphazard, random approach.	I: OK thank you very much. You talked about radicals. Where are they? S: .....(silence) I: You remember that you talked about radicals? S: Yes I: Where are they in your solution? S: The alkyl radical here (pointing to $CH_3CH_2\dot{C}H_2$ I: Why do you call it a radical? S: Well, because it carries charge I: What type of charge? S: Positive charge I: Suppose it carried negative charge, would it still have been a radical? S: Yes I: You talked about radical exchange. What do you mean? S: .....(silence) I: Can you show me the exchange from your solution? S: Yes. It is seen in the product. Exchange between bromopropane and potassium bromide. I: Which radicals have been exchanged in this case? S: Here bromine ion goes to potassium and OH group goes to alkyl radical. I: Why do these exchanges occur? S: It is because of the differences in the charges. I: Mechanism deals with description of how reactions occur. Can you tell me how these radical exchanges occur? S: The radical, I mean the bromine radical carries a negative charge, and it is more electronegative, so it gets extracted here to form the product. I: I can see positive charge here (pointing to the carbonium ion), it was not there in the question. How did you come about it in the process of solving the problem? S: It means that dissociation takes place. The bromopropane is dissociated into bromine ion and alkyl radical. /Continued ...

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TABLE 8.8 PROBLEM No 1: NUCLEOPHILIC SUBSTITUTION SOLVER No 3 (CONTINUED ...)

Protocol	Features	Post-Problem Solving Interview
		I: Why does that happen? S: Because of the presence of the potassium hydroxide. I: What does the potassium hydroxide do? S: Dissociation takes place. The compound splits, the alkyl radical with positive charge and bromine with negative charge. I: So what next? S: The alkyl radical with positive charge attracts the OH with negative charge. On the other hand, the potassium with positive charge attracts bromine which is bearing negative charge in this case. This leads to the formation of the product. I: Thank you very much S: Thank you.

TABLE 8.9 PROBLEM No 1: NUCLEOPHILIC SUBSTITUTION SOLVER No 18

Protocol	Features	Post-Problem Solving Interview
Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide ... OK This is propyl bromide. I can write the structure like this ... (writing) the bromine here then the aqueous potassium hydroxide. Since it will ionise and the species taking reaction here is the hydroxide, so we can write the hydroxide ion and omit the other species. Now the hydroxide will ..... since this is a primary bromide the hydroxide will attack the carbon atom that is carrying the bromine from the side that is remote from the bromine ion .... eh ... bromine atom. So ... (writing) and the attack of hydroxide will weaken the bond between carbon and eh ..... carbon and bromine ..... then a ..... a transition product is formed in which the hydroxide is partially attached to the ..... eh ..... to the carbon atom, and then ..... the bond between carbon and bromine will cut off with the electrons being moved to the bromine atom, and the bond between carbon and hydroxide will be formed and there will be inversion of the strucutre ..... plus bromide ..... that's all.	1. Read direction of the problem and established the chemical nature of reacting species. 2. Identified and isolated the main relevant information from the problem statement. 3. Showed an understanding of a structural feature on the basis of which the problem was attacked. 4(a) The substrate/reagent interaction was vividly described. (b) Solver's strategy revolved around bond-breaking and bond-making based on a functional understanding of the electron-pair movements involved. 5. **Problem was solved with success.**	I: You have finished? S: Yes I: You said that hydroxyl attacked the carbon bearing bromine. Why does that happen? S: Because the hydroxide is a nucleophile ... eh ... Yes, is a nucleophile. Now this hydroxide ..... because bromine is more electronegative than carbon, the distribution of electron between the bromine and the carbon will shift more toward the bromine atom than to the carbon atom giving the carbon atom a partial positive charge and bromine a partial negative charge. Now because this carbon is partial positive and this hydroxide is a nucleophile, it will attack the carbon. I: You talked about transition product ... S: Transition stage. I: Oh ..... transition stage. S: Yes. I: Which is the transition stage from your solution? S: This is it. It is the stage where the hydroxide is partially attached to the carbon and also bromine is partially attached to the carbon. I: I can see these broken lines between carbon and the hydroxyl group and also between the carbon and bromine. What does it mean? S: To show that it is not the real bond ..... it is not formed yet, it is just a partial bond. I: I can see you put a full negative charge on the hydroxyl group, but here (transition state) it is not there. Where has it gone? S: Well, the negative charge is dispersed between the bromine and the hydroxide. No new charge is developed. I: OK. Thank you very much.

FIG.8.1 Written response for the protocol shown in Table 8.8

1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$

$CH_3CH_2CH_2Br + aq\ KOH \longrightarrow CH_3CH_2CH_2OH + KBr$

$CH_3CH_2\overset{+}{C}H_2\ \bar{B}r + aq\ K^+\ O\bar{H} \longrightarrow CH_3CH_2CH_2OH + KBr$

FIG.8.2 Written response for the protocol shown in Table 8.9

$$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$$

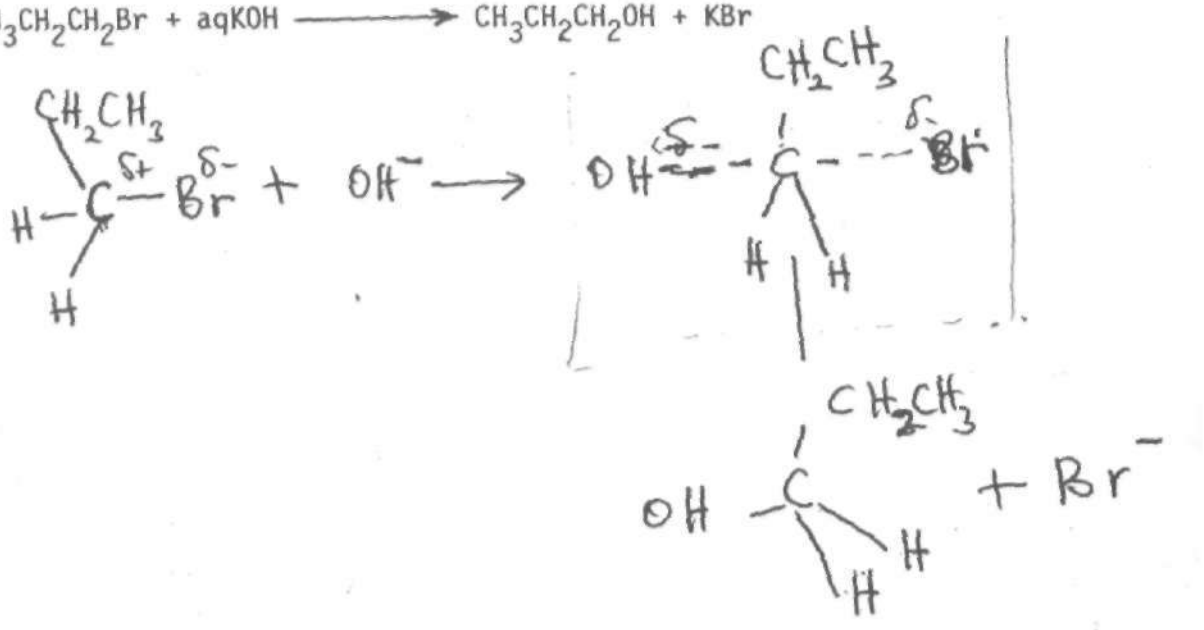


TABLE 8.10(a) PROBLEM No 2I: ELECTROPHILIC SUBSTITUTION SOLVER No 5

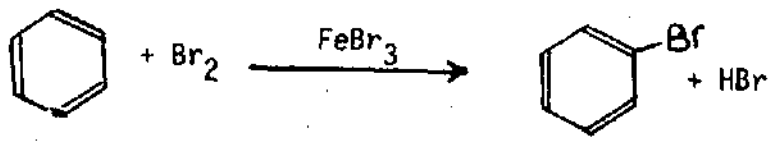
Protocol	Features	Post-Problem Solving Interview
This is problem No 2. It says outline the mechanism of the reaction of bromine with benzene and with ethene and briefly explain why a catalyst is required for the first reaction but not the second ..OK .. the first reaction goes like this ..OK .. the reaction is .. I mean the mechanism .. first the bromine will react .. eh .. you know this is a catalyst .. OK this is the catalyst .. bromine will react with iron .. (writing) to form this .. and you know that this is a radical (referring to Br^*) and is highly reactive and since we know that the benzene ring is electron density region ..... bromine will tend to attach itself to the benzene ring to form bromobenzene. The reaction will proceed this way ..... (writing). As I said this bromine can be termed to ionise into two bromine or we can call it homolytic fission OK ..... it will break into two ... the bromine will attach itself to the benzene ring and hydrogen bromide will be formed ..... and this is it. It can be in the presence of dilute acid to activate the reaction or to speed it up ..... I: Go on please. S: That's all.	1. Read the direction of the problem, but not completely. The last bit describing the reaction equation was apparently omitted. 2(a) Referred to Br^* as a radical. There seems to be misconception about radicals and ions. (b) The process by which the so-called radical was obtained was not described neither the process of its attack on benzene. (c) There appears to be a conceptual and strategic gap here. 3. Reference to irrelevant knowledge. 4. Failure to keep direction of problem in mind during problem solving. 5(a) The overall conceptual framework seems to be: substitution reactions occur in line with the electro-positive character {ability to donate electron(s)} of the groups concerned e.g Br and H in this case. (b) A random strategy based on inaccurate reasoning.	I: You pointed to this Br with positive charge. What did you say it is ..... a radical? S: Yes, a radical because it possesses all the unpaired number of electrons and it is very reactive. I: You said that benzene is a region of high electron density .....? S: Yes. I: What do you mean by that? S: What I mean by that is that it is an electron donating specie. I: Can you explain please? S: Yes, it is because of delocalised electrons, that is, the pi electrons. You know the ..... the molecular orbital feature of the benzene shows that there is pi electron up and below the plane of benzene ring and that these electrons are delocalised. So benzene acts as a source of electron-releasing specie in a chemical reaction, and since this bromine is electron-deficient, it will tend to attach itself to the benzene ring. I: Comparing the reactants with the products, one can say that bromine has replaced hydrogen from the benzene. Do you agree with this suggestion? S: Yes, it is a displacement reaction. I: Can you describe to me the chemical processes involved in this displacement? S: OK ..... in this cse we can term hydrogen to be positive ..... assuming we term hydrogen to be positively charged ... mh ... mh ... OK ... from the electrochemical series you find out that elements displace each other from this compound and you know it can displace another element from this compound provided it is higher in the electrochemical series. OK in this bromide group the reverse is the case. OK ... elements which are lower in their group will displace the other which is higher, so bromine will tend to displace hydrogen from its position in the benzene ring ..... I: Is that all? S: Yes that's all. That's the mechanism of the reaction.

TABLE 8.10(b) PROBLEM No 2II ELECTROPHILIC ADDITION TO **SYMMETRICAL** C=C BONDS

Protocol	Features	Post-Problem Solving Interview
This is the second part of question two. It says we should outline the mechanism of the reaction of *bromine with ethene* ..... The equation is as follows CH two *double bond* CH two ... OK here bromine atom is reacting with ethene ..... and this ethene is having double bond ..... OK I am now writing the structure of ethene reacting with bromine atom. What happens is this: the *bromine* atom will first ionise to form ..... to form *bromine* ..... it will ionise into positive and negative charges although in real sense this bromine atom ..... it has not got ..... eh ... eh ... this thing ..... although in real sense though bromine atom is not polar but to some extent it will ionise into positive and negative charges. So what happens is this: in the first place the bromine ..... the bromine that is carrying the positive charge ... OK ... I will call it the cation now ... it will react with one of the carbon atoms here to form ..... (writing) ... what happens is this: in the first place the bromine that is carrying a positive charge will react with one of the carbon atoms so that this *double bond here* will be broken. When the bond is broken now then this bromine atom, this other one ..... the bromine ion, since it is atom first it will first ionise into positive and negative bromine ions respectively ... the bromine that is carrying a positive charge reacts with one carbon atom to form this structure given here and then the other bromine which is carrying a negative charge would then go on into the second phase. It will react with this so that now the product will be 1, 2- dibromoethane and the reaction here ..... the whole reaction here is what we call an addition reaction this is an addition reaction of ethene to form a saturated compound ..... that's the answer.	1. *Read the direction of the problem and* attempted to expand and draw out the key information. 2. Bromine molecule is confused with bromine atom. 3. *The fact of ethene consisting a* C=C was stressed, but solver seemed not aware of the contextual relevance of this, thus did not pursue the idea logically. 4(a) Solver appears conceptually blurred about the process of interaction between ethene and bromine. *The bond-breaking and* bond-forming processes do not seem to *have been grasped.* (b) There appears to be a conceptual bottle-neck about the involvement of electrons in the reaction. 5. Problem solving strategy seemed to revolve around positive/negative charge interaction - a faulty strategy based on inaccurate reasoning.	I: Is that all? S: Yes. I: You used the expression "react with" very much. What does it mean? S: What I mean by reaction here is that this bromine *ion here will combine* with the carbon atom here. This is what I mean. I: Can you explain further, especially that you have introduced a new term "combine"? S: Combine and react mean the same thing. I: Do they? S: Yes. I: You said the "double bond here" will be broken. Can you explain to me what you mean exactly? S: What I mean is this: since the bond in ethene, the bond joining the two atoms is a double bond and hence we say that it is unsaturated, so that what I mean by breakage of bond is that this double bond that is joining the two carbon atoms one of *them will be broken* so that what we have at last is a single bond joining the two carbon atoms and not two bonds again, so that it will from a saturated compound. That is what I mean by breakage of the bond. I: OK Thank you very much. S: Thank you.

FIG.8.3 Written response for the protocol shown in Table 8.10(a)

2. Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction but not with the second. The reactions are:

(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

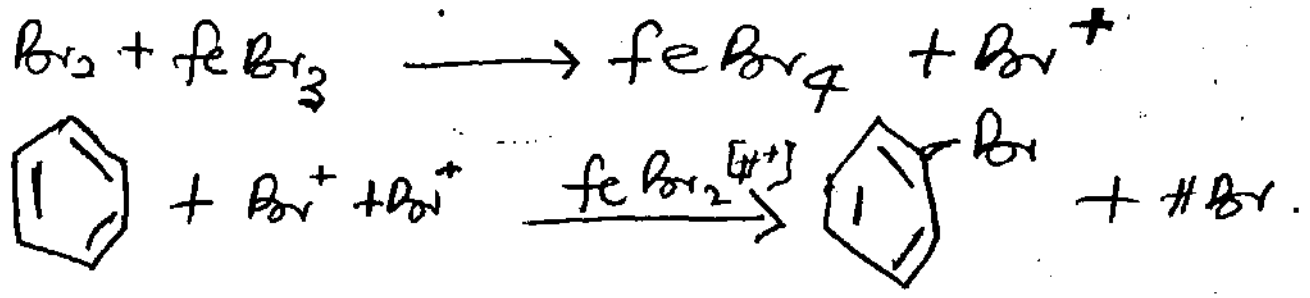


FIG.8.4 Written response for the protocol shown in Table 8.10(b)

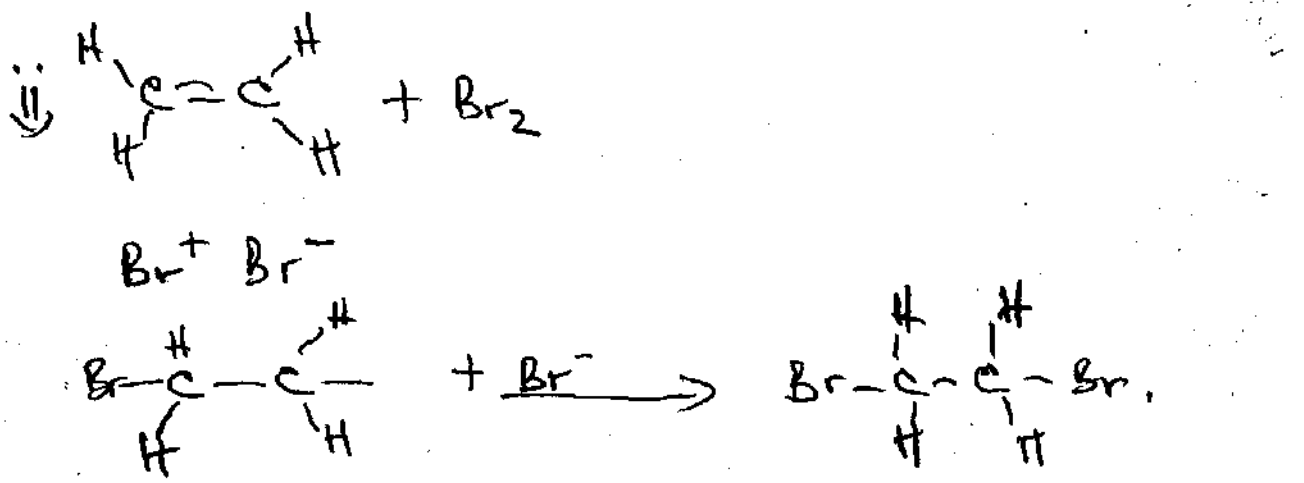


TABLE 8.11(a) PROBLEM No 2I: ELECTROPHILIC SUBSTITUTION SOLVER No 7

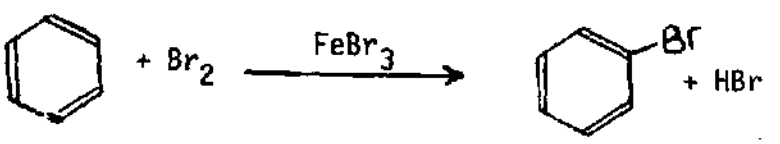
Protocol	Features	Post-Problem Solving Interview
Question No 2. It says outline the mechanisms of the reaction of bromine with benzene and with ethene and briefly explain why a catalyst is needed for the first reaction but not the second. The first reaction is as follows: benzene reacting with bromine molecule in the presence of FeBr three catalyst to give an aryl halide and hydrogen bromide ..... before bromine molecule can react with benzene ... with an aromatic ring, for example the benzene ring ... it must be an electrophile because the benzene ring is rich in electrons there is an electron cloud above and below the plane of the benzene ring, hence a catalyst is needed ... a catalyst in this reaction is iron tribromide and it effects its catalytic action by polarizing the bromine molecule. This is possible because the catalyst is a Lewis acid and as a Lewis acid it tends to accept electron from bromine molecule thereby liberating a positively charged bromine ion or an electrophile ..... Now the electrophile is electron deficient and it finds these electrons in the benzene ring because of the presence of the pi electron cloud, hence it attacks the benzene ring to produce a benzonium ion which is similar to a carbonium ion ..... the benzonium ion carries a positive charge. If this compound is to remain so as can be seen from the structure the aromaticity of benzene ring will be affected hence hydrogen ion has to be pulled out in order to give benzene its ... eh ... its stable structure ..... the proton now reacts with the $FeBr_4^-$ anion to give hydrogen bromide and the catalyst, so the catalyst is regenerated from this reaction as can be seen here ..... that's all.	1. Read direction of the problem and sought to identify the chemical entities involved in the reaction by expanding and interpreting (to himself) the problem statement. 2(a) Identified some chemical features that formed a conceptual basis for initiating a fruitful search for solution. (b) Demonstrated a functional understanding of the relationships amongst such chemical features e.g identification of the electrophilic reagent and its relationship with the cloud of pi electrons of the benzene ring. 3. Showed a functional understanding of the process by which the substrate and the reagent interact. 4. Knowledge recalled and information gathered from problem statement were logically and systematically organised in the search for a solution. 5. Problem solving strategy was characterised by a logical and economical use of information fruitfully organised on the basis of a clear understanding of the relationships of the reacting structures at an electronic level.	I: You said benzene is aromatic? S: Yes. I: What does that mean? S: That means ..... that means that it obeys the 4 + 2n Huckel rule. I: What is it? S: The 4 + 2n Huckel rule? I: Yes. S: That is all compounds which exhibit this rule are considered aromatic compounds. I: You said that Br^+ is an electrophile ...? S: Yes. I: Can you tell me what you mean? S: An electrophile is an electron-deficient specie which in the course of reacting with another compound tends to withdraw electron from that compound. That is it is capable of accepting electrons. I: You said if the structure that you called benzonium ion were to remain like that the aromaticity of benzene ring would be affected. So how is the aromaticity restored then? S: Yes. Considering the intermediate, there is a loss of proton here. I: Can you explain? S: In the presence of a nucleophile ..... the nucleophile removes the hydrogen without its electrons. In the process, two electrons are left behind which restore the aromaticity. I: OK Thank you

TABLE 8.11(b) PROBLEM No 2II: ELECTROPHILIC ADDITION TO SYMMETRICAL C=C BONDS

Protocol	Features	Post-Problem Solving Interview
The second part of the problem which is the mechanism of the reaction of ethene with bromine molecule ... as can be seen ethene is having a multiple bond that is it is having a sigma and a pi bond ... now on the approach of bromine molecule towards the bond ..... because now this ethene is acting as a nucleophile because of the presence of the pi electrons, so when this bromine atom now approaches the cloud of pi electrons the electrons tend to ..... because this bromine atom ..... this bromine molecule is formed between two bromine atoms so the pi electrons tend to repel the pair of electrons which form the bond between the two bromine atoms to one of the bromine atoms thereby creating a positive charge in one of the bromine atoms and negative in the other. So with this the positively charged bromine atom ... ion now gets attached to one of the carbon atoms ..... it gets attached to any of the two carbon atoms because this is a symmetrical alkene ..... so in this process a carbonium ion is formed, that is, carbon now exhibits trivalency here. Now since it is positively charged ... now since the carbonium ion is positive it tends to react with the bromine ion here. It is important to know that when this one is attached to this carbon, this one is liberated as a full ... eh ... nucleophile, there is no partial negative charge. It now attacks the carbonium ion that is formed to give this product ..... (writing) ..... I've finished.	1. Read the problem direction and then highlighted some key structural features. 2. Held on to the features highlighted and used them subsequently in the attempt to solve the problem. 3. Recalled knowledge that is relevant to the process of solving the problem at hand. 4. Articulated the knowledge recalled and information from problem statement in a logical and sequential manner, based on visualization of relationships amongst the various elements which the solver had assembled for purposes of finding a solution. 5. An understanding of the concepts of bonds, positively and negatively charged species, molecules and reagents in terms of their electronic nature appeared fundamental to solvers conceptual frame of reference. 6. Problem solving behaviour was characterized by guided planning coupled with logical and systematic execution.	I: You have finished? S: Yes. I: From what you have said, you seem to give me the impression that the reaction is initiated at the instance of the double bonds. Am I right? S: Exactly. I: Are you then saying that if there were no double bond, that is, if the double bond were single bond, for example, the reaction would not have occurred? S: No it will not. I: What kind of reaction would you call this? S: Electrophilic addition reaction. I: OK Thank you very much. S: Thank you

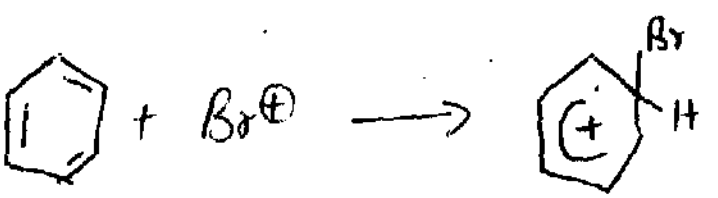
FIG.8.5 Written response for the protocol shown in Table 8.11(a)

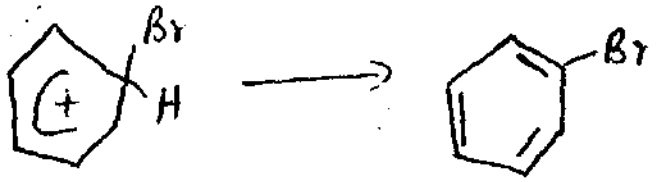
2. Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction but not with the second. The reactions are:

(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

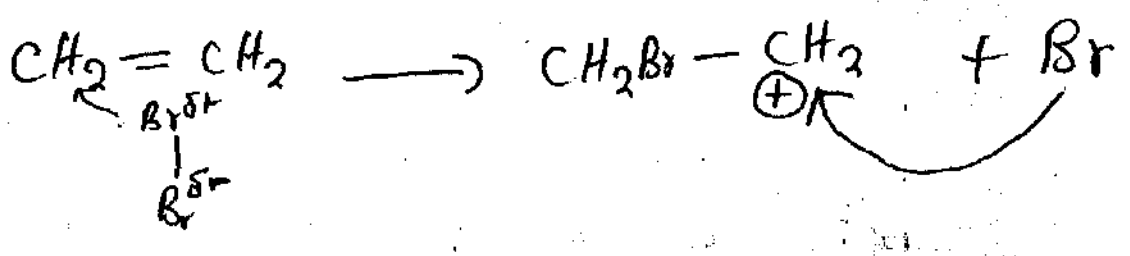
(I) $FeBr_3 + Br_2 \longrightarrow FeBr_4^- + Br^{\oplus}$





$FeBr_4^- + H^+ \longrightarrow FeBr_3 + HBr$

FIG.8.6 Written response for the protocol shown in Table 8.11(b)

(II) 

$CH_2Br - CH_2 + Br^- \longrightarrow CH_2BrCH_2Br$

TABLE 8.12 PROBLEM No 5(I & II) ELECTROPHILIC AND NUCLEOPHILIC ADDITION TO C=C BOND SOLVER No 13

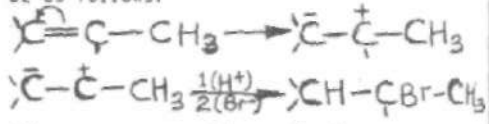
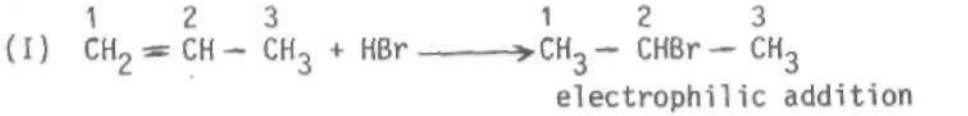
Protocol	Features	Post-Problem Solving Interview
This is question five ..... consider reaction I and II below in which HBr adds across carbon - carbon olefinic bonds ..... Outline the mechanisms and use it to explain why reaction II behaves differently ..... OK ... as stated this is an electrophilic addition reaction ..... there is a transfer of one of the pi bonds to the hydrogen then this one will be formed ..... no ... this one is electron withdrawing ..... electron releasing (referring to $-CH_3$) ... it releases electrons to this group ..... this makes this carbon here positive and this one negatively charged ..... OK ..... what happens here is that the alkyl group ..... the CH_3 is electron releasing so it releases electron to the double bond then making carbon ..... then making the carbon adjacent to it negatively charged and this positively charged ..... then forms an intermediate here .. then hydrogen ion which is positively charged attack the negative carbon ion which forms the final product ..... Then in the second case ..... (referring back to direction) it is the mechanism of HBr with this compound ... eh . m... eh . a CH two double bond CH single bond then CHO ... OK the CHO is an aldehyde ... is electron withdrawing. It withdraws electrons here then this bromine becomes positive ion ... no ... this becomes negative and this becomes positive ..... so this forms ... plus the hydrogen ion here ... and this can also follow Markownikov's rule ... which says that in the addition of a reaction of an unsymmetrical reagent to unsymmetrical alkene, the negative part will try to attach itself to the carbon with the	1. Read the direction of the problem and attempted to interprete it. 2. Solver introduced an idea which appears central to her thought processes - transfer of pi bond. This might have been based on the observation that there was double C-C bonds in the reactant, but a single C-C bond in the product. There is no evidence, however to suggest that solver conceptualised the so-called transfer in terms of electron-pair movement. 3. The conceptual framework that guided problem solving behaviour seemed to be based on some kind of mechanical attraction between positively and negatively charged species. Thus the summary of the solvers strategy seemed to be as follows:  Solver was apparently unable to conceptualise and handle reactions without having first contemplated development and formation of formal charges in the reacting entities. Even then, the underlying phenomenon of electron re-distribution seemed not to have been grasped. 4. A blind, non-functional use of a rule. Solver did not seem to know the relevance nor the implication of stated rule for the processes of reaching a solution; thus it was not logically followed nor was it actually used.	I: Is that all? S: Yes. I: Are you saying that the explanation lies in Markownikov's rule? S: Well it is by ..... it is because this is electron releasing ..... that is the basic explanation. I: I can see hydrogen with positive charge in the second line of your work. How did you come about it? S: From HBr. I: How does it become positive, seeing that it is not there in HBr? S: Yes, there is heterolytic fission. I: Heterolytic fission? What is it? S: Bromine goes away with the two electrons shared, then leaving it with a negative charge and hydrogen with a positive charge because two electrons are shared there so bromine goes away with both of them. I: Shared where? S: Between hydrogen and bromine. I: You haven't said this before now. Can you explain it to me further? S: Electrons are shared to complete the octet of both atoms. I: Oh ... you are saying new things ... octet (laughter by both I & S). What is it? S: That is to make them have noble gas configuration. I: OK Let's address the original question. Can you explain to me this idea of electron sharing between hydrogen and bromine that you have earlier talked about? S: Yes, just to form a bond. I: OK ... considering your explanation of the bond, can you now explain to me this idea of heterolytic fission? S: They want to satisfy these two carbon atoms. I: What wants to satisfy the two carbon atoms? S: Bromine. That is something that is causing the heterolytic fission. /Continued ...

TABLE 8.12 PROBLEM No 5(I & II) ELECTROPHILIC AND NUCLEOPHILIC ADDITION TO C=C BOND SOLVER No 13 (CONTINUED ...)

Protocol	Features	Post-Problem Solving Interview
highest number of substituents around the double bond. So this bromine will attach to this ... then the hydrogen will attach itself to this ..... that's the explanation.	5. The problem was solved without success. This was largely due to solver's inability to conceptualise a solution process in terms of breaking of existing bonds and making of new ones, based on an understanding of the underlying movements and rearrangements of the bond electrons. Rather, the concern was on developing formal charges on the reactants, and used as basis for assigning species of opposite charges to each other.	I: Now, this curved arrow in the first line, what is it telling us? S: Yes. It is the thing that is causing the fission here. I: What do you mean? S: It means that the pi bond is transferred there or the pi bond is broken by the fission there which then reacts this with the carbon there. I: Is that all? S: Yes. I: Thank you.

FIG.8.7 *Written response for the protocol shown in Table 8.12.*

5. Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:





Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.

i) $\bar{C}H_2=\overset{+}{C}H-CH_3 + H-Br \rightarrow CH_3-CHBr-CH_3$ Markownikoff's

ii) $\overset{+}{C}H_2=\overset{\delta-}{C}H-CHO + H-Br$

$\downarrow$

$CH_2Br-CH^{-}-CHO + H^{+}$

$\downarrow$

CH_2Br-CH_2CHO.

TABLE 8.13 PROBLEM No 5 (I & II) ELECTROPHILIC AND NUCLEOPHILIC ADDITION TO >C=C< BOND SOLVER No 14

Protocol	Features	Post-Problem Solving Interview
This is a reaction between propene and hydrogen bromide ... OK propene is an unsymmetrical hydrocarbon, HBr is a polar compound because bromine atom is more electronegative than hydrogen, so hydrogen is delta positive and bromine is delta negative. The pi bond of ... the pi bond between carbon 1 and carbon 2 will ... or as the hydrogen bromide approach the pi bond between the carbon atoms, the electrons between the hydrogen and the bromine will be distorted, producing a delta positive on hydrogen and delta negative on bromine. The delta positive hydrogen will attach to carbon 1 and ... producing a transition state. Now the delta negative bromine will attack the positive carbon 2 to produce this compound ..... that's the first one. The second question goes like this ... the -CHO group withdraws electrons from carbon 2 which withdraws electrons from carbon 1 thereby making carbon 1 positive. The delta negative bromine will attach itself to carbon 1 which produces an ...eh .. e .. a transition state. The hydrogen attacks the carbon 2 and attach itself to it to produce this result ... (writing). Reaction II behaves differently because of the -CHO group which withdraws the electrons toward itself, thereby making carbon 1 to be positive ..... that's it.	1. Identified the reactants and their features that are relevant for the process of initiating the search for a solution. 2. Additional information recalled from memory to transform the state of existing information. 3. Persisted with assembled information and progressively refined them through a transformation process toward a solution goal. 4. Solver misconceived reaction intermediate for transition state. 5. The underlying electronic re-distributions and accompanying structural changes seem to be within the cognitive functioning of the solver, though the specifics of the bond-breaking and bond-forming processes are vaguely spelt out. Problem was solved with a measure of success. 6(a) The solver relied wholly on inductive effect of -CHO as conceptual basis for solving second part of the problem. The dominant roles of mesomeric and tautomeric effects were entirely missed out. The problem was thus solved without success. 7(b) A major factor that seemed to thwart solvers efforts was the failure to conceptualise the structure of propenal in which C=C is conjugated to C=O; consequently, wrong strategy was set up and inaccurate reasoning applied.	I: Is that all? S: Yes. I: You said that HBr is a polar compound. What does that mean? S: It means that the bromine is more electronegative than hydrogen, so the electron density shifts more towards bromine making hydrogen to be delta positive and bromine to be delta negative. I: How is this feature important to the reaction process? You understand what I mean? S: Yes ... eh . e ... it is important because it helps the reaction to take place. I: How? S: Because the delta positive hydrogen attach or attack one carbon to produce a transition state and bromine attach to the second carbon atom. I: OK You said that hydrogen attach to carbon number 1, why not carbon number 2? S: It is because of Markownikov's rule. It says that the negative part of a polar reagent adds to the carbon that is more substituted. I: But this does not happen in reaction II, does it? S: No. I: Why not? S: This is anti-Markownikov's reaction. I: What features bring about the anti-Markownikov's reaction? S: Eh ... e .. e .. I ... I think it is the electron withdrawing effect of -CHO group ..... but I am not sure ... but I think so. I: OK Just one last question. Would you say that learning organic chemistry from a mechanistic approach is a useful one? You know what I mean by mechanistic approach? S: Yes. It is the steps that reactions go through. I: Would you say that it is a useful method for learning organic chemistry? S: Yes, I believe that it is the most useful way one can learn organic chemistry, because if you know all the mechanisms, you don't even need to cram them ... you don't even need to know what sort of compound, because if you say you cram it, it has to be the compound you are familiar with, but if you know the reaction mechanism, you can apply it to any sort of compound. That's why I think learning organic chemistry from mechanistic direction is more effective. I: Thank you vey much.

FIG.8.8 Written response for the protocol in Table 8.13.

5. Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:

(I) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3} + HBr \longrightarrow \overset{1}{CH_3}-\overset{2}{CHBr}-\overset{3}{CH_3}$

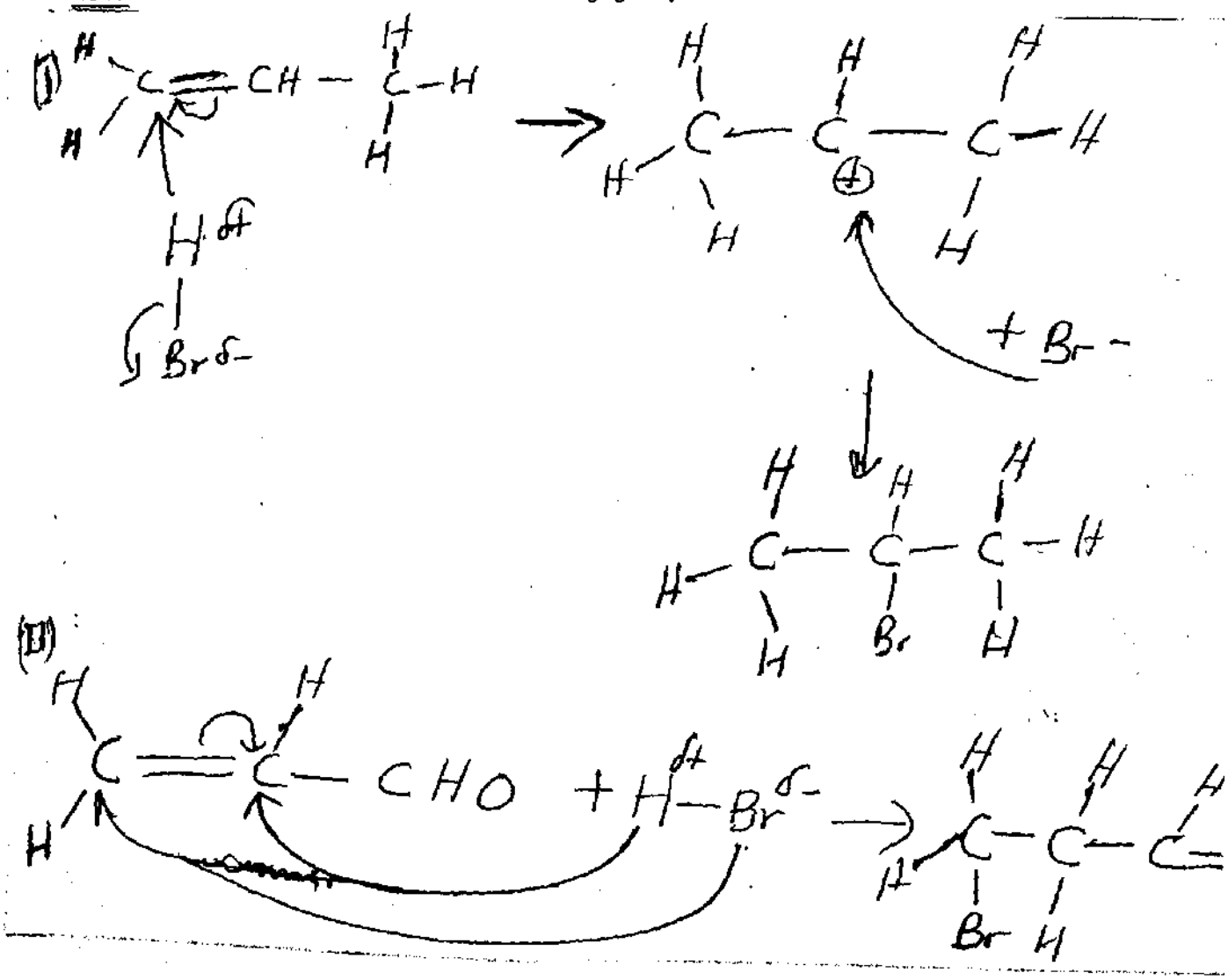
electrophilic addition

(II) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CHO} + HBr \longrightarrow \overset{1}{CH_2Br}-\overset{2}{CH_2}-\overset{3}{CH}=O$

nucleophilic addition

Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.



8.4.2 Summary of Features

A summary of the main features of the protocols (tables 8.8-8.13) that constituted impediments to successful problem solving is given in table 8.14.

TABLE 8.14 SUMMARY OF FEATURES

Description	Features
General problem solving approach	A zig-zag non-directed approach characterised by failure to: (a) understand the nature of the problem to be solved, even though problem directions were generally read. (b) visualize the relationship between given and retrieved information on one hand, and a process of generating a correct solution on the other.
Major conceptual framework used for solving the problems	(a) Attraction between negative and positive species to form compounds, apparently based on the idea that opposite charges attract, similar charges repel. One implication of using this framework is that ionic bonds are formed; even though this was not indicated at any stage by the students. (b) Complete electron-pair transfer rather than electron-pair sharing. Thus, substitution reactions, for example were treated from the stand-point of the more electropositive specie donating electrons to and displacing the specie that accept them. (c) Transference of bonds from one reacting specie to another. This framework was used, apparently to acount for multiple bonds that were "missing" from the products in comparison to the reactants. It does appear that the underlying electron-pair movement did not form a functional unit of this framework. (d) A mechanical process of assigning atoms or groups from the reagent to the substrate simply based on visual correlation with the given product.
Major problem solving pitfalls	(a) Problem directions were read with little effort to conceptualise the problem situation. Thus in problem 1 for example, right solutions were produced for a wrong problem. (b) Failure to keep the demands of the problem in perspective leading to: (i) recalling correct, but irrelevant information from memory (ii) blurred vision of the goal (iii) unnecessary meandering as a result of (b). (c) Acquisition of chemical concepts without simultaneously acquiring the meaning (understanding) of such concepts. The post-problem solving interviews bore testimony to this.

8.4.3 Summary of the chemical misconceptions

The protocols showed a catalogue of chemical misconceptions characterising the thought pattern and processes of the students. A summary of the prominent ones is given in table 8.15 below.

TABLE 8.15 SUMMARY OF CHEMICAL MISCONCEPTIONS

Serial No	Misconceptions	Pattern of Occurrence in the Protocols	
		Persistent	Sporadic
1	Radicals taken to mean the same as ions	✓	
2	Molecules as similar to atoms		✓
3	Reactive intermediates synonymous with transition states	✓	
4	Electrophiles confused with nucleophiles	✓	
5	Inductive and mesomeric effects mean the same	✓	
6	Being electronegative means the same as being electrophilic	✓	
7	Organic reactions occur primarily between ions rather than between molecules	✓	
8	Organic reactions occur by the attraction for each other of reactants with opposite charges rather than by a process of breaking existing bonds and making of new ones	✓	
9	The process of reaction involves loss and gain of electrons by the reacting species		✓
10	During reactions bonds are transferred		✓
11	Some expressions commonly used to describe chemical processes, but found to constitute sources of chemical misconception include the following: (i) electron-rich (ii) electron-deficient (iii) donate (iv) attack (v) attach to (viii) ring (e.g benzene ring) ✓ (all) (vi) react with (ix) bond-breaking (vii) combine with (x) bond-formation		

8.4.4 Summary of problem solving behaviour

Based on the results of the statistical analysis and the overall trend revealed in the protocols, a summary of the general tendencies indicated by successful and unsuccessful problem solvers is shown in table 8.16.

TABLE 8.16 GENERAL PROBLEM SOLVING BEHAVIOUR

Serial No	Successful Solvers tend to:	Unsuccessful Solvers tend to:
1	produce shorter, precise and directed protocols	produce longer, vague and non-directed protocols
2	isolate key information from problem statement and use it subsequently in the process of solving the problem	be oblivious to vital information in problem statement
3	visualize feature(s) in the problem situation which can be used as starting point(s) to initiate a process of reaching a solution i.e visualize a structural basis for the reaction process	attack problems without apparent operational base
4	visualize some relationships between available information and a process by which to reach a solution	be incapable of forming a link between the available information and a legitimate operational step that yields a correct solution
5	be competent in fitting the information-bits together in a logical manner along a solution route	be incompetent in fitting the information-bits together in a logical manner in the process of solving problems
6	be systematic and sequential, involving the breaking of problems into parts and then to solve them in some logical steps	be haphazard and random, involving a global attack on the problems followed by adoption of inaccurate and inconsistent procedures to solve them

8.5 Conclusion

In this chapter, the analysis of data collected from TAPS has been discussed and the results presented. These results are discussed in the next chapter.

CHAPTER NINE

DISCUSSION OF THE RESULTS

9.1 Overview

The results showed, on the whole, that the students were unsuccessful in the "think aloud" problem solving (table 8.4). This observation is consistent with the finding in part 1A of the study. Furthermore, some of the thought processes underlying the performances are revealed in the protocol. The discussion is set out under the following headings:

(a) strategies adopted to solve the problems

(b) major conceptual framework underlying the strategies

(c) chemical misconceptions

(d) general problem solving tendencies of the successful/unsuccessful groups

(e) conclusion.

9.2 Strategy adopted to solve the problems.

Strategies generally adopted by students to solve closed problems have been outlined in chapter seven. In this section, the general problem solving behaviour of the students (involved in TAPS) that depicts their strategy is discussed. The results showed that the students seemed to know the individual chemical facts required for solving the problems. Thus, there is no significant difference between the successful and the unsuccessful solvers in this variable ($\chi^2 = 0.47$). Beyond this, however, the students seemed to have only acquired the facts without an understanding of the ideas that

link them into functional conceptual patterns. Thus, they were unable to visualize how the individual facts relate to each other on one hand, and the relevance of the relationships to the process of finding a solution to the problems on the other. Thus, we find (table 8.6) that the chi-square values for these categories (3.1 and 3.2) in the protocol are quite significant.

The observation by Novak (1965) that the ability to solve problems is directly related to the breadth of the concepts formed seems to offer part of the explanation of these results. It does appear that the students have only acquired a narrow conceptualization of the chemical propositions they attempted to use. Thus they failed. It was indicated in the literature reviewed in chapter two that students needed to bring to a problem situation other things beside the required facts (sec 2.5.1). The suggestion can be made that the students' problem solving behaviour is partly characterised by failure to bring to the problem situation other skills beside the bare chemical facts.

A general behaviour that characterised the students' problem solving approach consisted of a surface scanning through the problem direction, motivated by some implicit feel for what the solution path should be. They then impulsively dashed at it, taking some zigzag steps which consequently led them to wrong solutions. This procedural behaviour appears similar to what Thorsland and Novak (1974)

described as an intuitive approach, which in this case is typified by random, trial-and-error search for a solution. This result is consistent with the one earlier reported in part 1A (sec 5.7).

The protocols show that the students had great difficulty with the chemical structure of the reacting species. The chemical misconceptions that underline this difficulty are taken up elsewhere in this chapter. However, the point can be made that the students' difficulty with such chemical structures and an understanding of how they relate to chemical reactions seemed to make the largest contributions to their inability to solve the problems. Thus, we find this aspect in the protocols (category 3.1) showing the highest χ^2 value = 17.12.

The students did not do everything wrong. The results showed that they did a few things that could be said to be in accordance with theoretical expectations. For example, they read the problem directions, and attempted to explain/interpret the problem apparently to construct a representation of the task environment (Frederiksen, 1984). This is reflected by the lack of significant difference, in these categories of the protocol, 1.1 and 2.1, between the successful and the unsuccessful groups (table 8.6). These apparently correct responses notwithstanding, they failed to make any headway in solving the problems due to strategic or procedural lapses in isolating and selecting key aspects of the

problem directions for emphasis and clarification. This is shown by the protocol category, 1.2 in table 8.6.

The conclusion from this section is as follows:

The students:

(a) possessed individual chemical facts or propositions without the chemical ideas that link them into functional conceptual patterns.

(b) did not seem to understand the demands of the problems that they set out to solve because they failed to isolate and select key information from the problem statements.

(c) had a very poor vision of the goal state partly because of (b) above and partly because of conceptual difficulties, some of which have been highlighted above.

(d) following from (b) and (c) above, took steps that were illogical and often irrelevant in what appeared to be a desperate bid to set up some strategy for arriving at a solution.

(e) had a problem solving strategy characterised by some intuitive feel for a solution rather than by an analytic process of arriving at it.

One of the implications of these results is that the students were not gaining effectively from instructions, notwithstanding that they scored high grades at examinations, according to the observation of the chief examiner (sec 1.2.3). It appears that some remediation measures are called for to redress

the deficiencies. This may involve taking a second look at the volume and structure of the course contents and the approach to instructional delivery.

9.3 Major conceptual framework used by the students

Conceptual framework refers to the main chemical thought that the students tended to rely on as the core or rallying point of the thought processes that guided their search for a solution. A summary of these is shown in table 8.14. The focus of the students' thought pattern seems to be that organic reactions simply involve charged species in which the resulting chemical combinations occur as a result of the electrostatic attraction between opposite charges. Thus, such vague expressions, "attract" "attach to" "combine with" etc were frequently used by the students to describe their thought processes.

Undoubtedly, the reactions in some cases, have polar characteristics involving formal charges, such as the students sought to depict. But to focus entirely on that conceptual premise, and use it exclusively to describe the reactions as if that was all that there is to the reaction processes is to miss the point. That is what the protocols, sadly seem to show. A fuller discussion about students' misconceptions of charged species and formal charges is undertaken in section 9.4.3. For now, it can be said that the students' almost complete dependence on these related concepts as the focal point of their chemical thoughts paints an ugly picture of their

conceptualization of the basic idea of organic reactions as involving a process of breaking existing bonds and forming of new ones.

The findings reported in this section are similar to Simpson's (1983). He indicated that "most (referring to students) clearly believe that a positively charged carbon must be attacked by a negatively charged nucleophile and that the charges are the reasons for the reactions occurring". The reason behind this thought pattern is not clear, however what is clear is that it is a product of their idiosyncratic knowledge which might need to be probed further.

9.4 Chemical misconceptions

The protocols show a number of chemical misconceptions constituting part of students' chemical thought processes. A summary of these is given in table 8.15 and they are discussed below under the following headings:

(a) nature of organic reactions

(b) chemical structure of the reacting species

(c) symbolisms: formal charges and "curved arrows"

(d) use of words/expressions as concept labels.

9.4.1 Nature of organic reactions

Nature of organic reactions is used to connote the main chemical events that characterise the reaction processes. Some descriptions of these have been given in section 1.2.1. The protocols show that the students have fundamental misconceptions in

this respect. The main strand of this has been dealt with in section 9.3, indicating that students' conception of the nature of organic reactions centred around charges and the resultant attractions between them. All that will be done in this section is to illustrate the point with problem No 1, for example, in which the idea used by 90% of the students to solve the problem is as follows:

(i) $CH_3CH_2CH_2Br \xrightarrow{\text{ionises}} CH_3CH_2CH_2^+ + Br^-$

(ii) $CH_3CH_2CH_2^+ + OH^- \xrightarrow{\text{attraction}} CH_3CH_2CH_2OH$

(iii) $K^+ + Br^- \xrightarrow{\text{attraction}} KBr$

The approach indicates that there is some degree of confusion in the students' minds regarding the nature and the processes leading to formation of new bonds, hence the nature of the reactions.

9.4.2 Chemical structure of the reacting species

A number of students' misconceptions relating to the chemical structure of the reacting species are revealed in the protocols, shown by table 9.1 (see table 8.15 also). In these examples, the students were unable to conceptually distinguish between the corresponding pairs from groups A and B shown in the table.

TABLE 9.1 EXAMPLES OF CHEMICAL MISCONCEPTIONS ABOUT REACTING SPECIES

A	B
Radicals	Ions
Molecules	Atoms
Reaction intermediates	Transition states
Electrophiles	Nucleophiles
Electronegative species	Electrophilic species
Resonance structures	Charged reaction intermediates

One of the post-problem solving interviews reproduced below serves as a typical example:

I: You talked about radicals. Where are they?
S: ..... (silence).
I: You remember that you talked about radicals?
S: Yes.
I: Where are they in your solution?
S: The alkyl radical here (pointing to $CH_3CH_2\dot{C}H_2$).
I: Why do you call it a radical?
S: Well, because it carries charge.
I: What type of charge?
S: Positive charge.
I: Suppose it carried a negative charge, would it still have been a radical?
S: Yes.

These results may not have told all the story about the misconceptions, nor in fact, unravelled the sources from which they emanate. However, one point which seems clear is this: the defining attributes of these chemical concepts were not understood by the students, hence the incorrect generalizations.

9.4.3 Symbolisms: formal charges and "curved arrows"

9.4.3.1 Formal charges

Both the protocols and the written responses showed the students' use of "+" and "-" symbolisms to designate formal charges. An understanding of the electronic basis of this formalism, referred to by Loudon (1984) as "electronic book keeping", seems to be lacking in the students' conceptual framework. In table 8.12, for example, the solver showed a "carbanion" as $\bar{C}H_2\text{-}\overset{+}{C}H\text{-}CH_3$. An understanding of formal charges as described by Loudon would have shown to the student that the structure was only a resonance form of propene as indicated below:



Other manifestations of this kind of misconception include students' inability to identify which carbon atom of the carbonium ion for example, should be formally assigned the positive charge. This is shown by the written responses accompanying the protocols.

The origin of this misconception is not quite clear. It does appear, however, that the students' used them (the formal charges) to concretize their conception of the so-called electron-rich and electron-deficient species that they often referred to in the protocols. Thus, the variations amongst the students in the use of the symbols are products of their individualised concepts of what qualifies as electron-rich or electron-deficient species.

9.4.3.2 Curved arrows

The protocols show that the students were relatively "silent" about "curved arrows" in their verbalizations, even though their written responses showed that they were used. Some of the misconceptions held by students surfaced mostly from the post-problem solving interviews. They include: a means of showing attraction between two reacting species, transference of atoms, radicals and bonds from one species to another during the process of chemical reactions; and also have causative effects on the reactions.

The post-problem solving interview reproduced below illustrates the point:

I: Now this curved arrow in the first line, what is it telling us?
S: Yes. It is the thing causing the fission here.
I: What do you mean?
S: It means that the pi bond is transferred there or the pi bond is broken by the fission there which then reacts this with the carbon there.

This excerpt exemplifies some of the misconceptions already indicated, especially those about bond transfer, bond-breaking and "curved arrow" as causal to organic reactions instead of a short-hand for describing the processes involved in the reactions.

Two reasons appear relevant in an attempt to offer some explanation for the source(s) of the misconception. The first is an extension of the one discussed in section 9.4.1. Because the

conceptualization of organic reaction in electronic terms was not part of the students' working repertoire, a descriptive process that details electron movements (curved arrows) would not be a functional part of it either. It does appear that their misconceptions of "curved arrows" is a product of their faulty conceptual framework (sec 9.3). The second reason seems to be the paucity of emphasis of the curved arrow formalism in the school curriculum. The syllabus operated by the students (appendix 1.2) for example is built very much on the traditional approach with little emphasis on the formalism. Also, Loudon (1984) observed that curved arrow formalism which he described as a standard mechanistic tool "has received surprisingly little emphasis in fundamental texts". It does seem that the teaching/learning of organic reactions through a carefully-planned mechanistic approach would enhance understanding and reduce misconceptions. These results confirm and further expand on those reported in part IA of the study (see sec 6.6.2.1).

9.4.4 Usage of words/expressions as concept labels

Knowledge is stored in the memory as propositions (Gagné, 1978). Thus its construction and retrieval involve the use of words, and expressions, that give it meaning to the individual. The danger, which if often subtle, is that these words or expressions may be held by the student as the knowledge itself, rather than a means of its construction and retrieval. This situation is further compounded in cases where such words or

expressions function in both scientific and non-scientific usages. If this occurs, the ultimate result is misconception of the substantive knowledge, often evidenced by its misrepresentation in relevant contexts. The protocols showed this situation to occur in this study.

All through the protocols, the students relied on the use of certain words and expressions to describe their chemical thoughts about the reaction processes. These are summarised in table 8.15. Two examples of interviews, involving the expressions "react with" used to describe chemical combination between reacting species, and "break" used in reference to bond-cleavage are given below. They serve to illustrate the main issues discussed in this sub-section.

A

I: You used the expression "react with" very much. What does it mean?
S: What I mean by reaction here is that this bromine ion here will combine with the carbon atom here. This is what I mean.
I: Can you explain further, especially that you have introduced a new term "combine"?
S: Combine and react mean the same thing.
I: Do they?
S: Yes.

B

I: You said that the double bond here will be broken. Can you explain to me what you mean exactly?
S: What I mean is this. Since the bond in ethene, the bond joining the two atoms is a double bond and hence we say that it is unsaturated, so that what I mean by breakage of bond is that this double bond one of them will be broken so that what we have at last is a single bond joining the two carbon atoms and not two bonds again. That is what I mean by the breakage of the bond.

These examples may well be the "tip of an iceberg". The conceptual pitfall presented by these words/expressions is elaborated by their centrality of usage for instruction in classroom situations and in printed texts of organic chemistry. It is not uncommon for example, to hear a teacher say, or read from texts that "species A is electron-rich or is electron-deficient or that species A attacks species B". Sometimes, the meanings of such technical terms are not made explicit in chemical terms. The students, consequently adopt a literal meaning to them. When this happens over a period of time, the result is obvious - a profound mass of misconception, as the protocols seem to have shown.

These results provide a basis for making a clarion call to teachers of chemistry to adopt a good measure of sensitivity and self-appraisal in the choice of words/expressions used to convey chemical concepts. And at another level, he/she should not rest under the comfort of the assumption that what is meaningful to him/her is equally meaningful to the student, but strive to make it explicit to the student.

9.5 A comparative spotlight on successful and unsuccessful solvers

An overview of the protocols from the successful and unsuccessful solvers is given in table 8.7. In this section, only a summary of the major strategic differences between the two groups is

outlined, having discussed the broad details in sections 9.2 and 9.3.

The differences are shown in tables 8.6 and 8.16. They show that the successful solvers tended to visualize the key features in a problem, isolate and progressively refine them in the search for a solution. Their problem solving strategy can be described as a systematic one. The unsuccessful solvers were unable to demonstrate such features (sec 9.2). Their problem solving strategy is characterised by implicit and intuitive behaviour.

While these results show the existence of the differences, they do not account for it. A further investigation to unravel this is potentially useful for improving instruction in organic reactions.

9.6 Summary and conclusion

A discussion of the chemical thoughts which underlie the problem solving behaviour of the students (as reported in part IA of the study) has been presented in this chapter. A summary of the conclusions are as follows:

(a) The results corroborate those obtained in part IA, and give further insight into the nature and sources of the conceptual difficulties.

(b) One of the major sources of students' problem solving difficulties lies in chemical misconceptions, which is partly due to students' failure to grasp the meaning of the chemical concepts they have acquired, and the implication(s) of such for problem solving.

(c) Students who were successful in solving the problems differ from those who were unsuccessful in clarity of thoughts, and the ability to organize them in the process of devising a solution route.

(d) Successful and unsuccessful students do not differ in ability to state knowledge in propositional terms. However, they differ in structuring and progressive refinement of the knowledge in an attempt to execute a solution route. A basic skill that accounts for the difference seems to be the ability to visualize functional relationships between and amongst concepts at various levels of complexity.

(e) Students' thought patterns (conceptual framework) that guide their general problem solving behaviour in organic reaction mechanism are dominated by the idea of charges, and the attraction between opposite charges, which they conceive to cause the reactions to occur.

(f) There seems to be no apparent logical pattern in the students' approach to solving the problems. At best they can be described as being characterised by some implicit feel for a solution - a sort of an intuitive strategy typified by random, trial-and-error kind of search.

(g) It is apparent that the variations in the problem solving proficiency amongst the students can be explained, not so much in terms of the chemical propositions (or facts) available to them, but in terms of acquisition of the ideas that link them into conceptually functional patterns.

PART II

IMPROVING STUDENTS' PROBLEM SOLVING CAPABILITY: A REMEDIAL STUDY

"It seems that students may be aided by instruction to solve formal problems which they were unable to solve prior to instruction"

Rowell, 1984

"Only after one has achieved a good understanding of initial performance and of the desired final performance, can one hope to teach students how to become effective problem solvers"

Reif, 1983

CHAPTER TEN

BACKGROUND LITERATURE, REMEDIAL PACKAGE AND EXPERIMENTAL PROCEDURE

10.1 Introduction

Part I of this study is diagnostic, in which some of the nature and sources of students' problem solving difficulties have been revealed. Generally, diagnoses presuppose remediation. The value of diagnostic studies becomes limited if it is not followed by some remedial treatment (Ozsogomonyan, 1979).

This part of the study (chapters ten and eleven) comprises a remedial programme undertaken in the light of the results obtained in part I. In this chapter, the remedial package and method of its implementation is discussed.

10.2 Background literature

Remediation of problem solving difficulties is shown from literature, to have been undertaken by a number of approaches. One approach consists in specific teaching of problem solving skills. A number of researchers who used this approach include Reif et al, 1976 and Bloom and Broder, 1950. Reif et al, for example, taught students specific problem solving heuristics consisting of four procedural steps referred to as description, planning, implementation and checking. The design of Bloom and Broder consisted in what they called "training in the methods of problem solving" which involved instruction about specific problem solving procedures

aimed at improving students' skills in problem solving. While these studies recognise the requirement for underlying knowledge base in problem solving, the overall implementation was targeted on teaching general skills of problem solving.

Another method takes the form of guidance and counselling. This method which is essentially individualised consists mostly in verbal exchange between the teacher or researcher and the student, sometimes accompanied by quizzes which are done by the student as homework. Feedback is usually provided. The method entails for example, advising the student to adopt certain study habits and/or to drop others, having initially diagnosed the nature of the difficulties concerned. Herron (1984) used the method to remediate his students' difficulties in chemistry. The method requires a measure of rapport and mutual confidence between the teacher or researcher and the student. These requirements, and others (e.g time, follow up etc) do not make the method a promising one for conventional research, but an excellent one for classroom teaching.

Another approach consists in a "lecture" method. This method, like others requires that the nature of the difficulties are identified, followed by instruction delivered to the affected students in normal classroom teaching. Usually, the content of instruction is structured to promote understanding of the difficult concepts. Adeyegbe (1985) used this method to remediate the difficulties of Nigerian

secondary school students in some aspects of calculations involving the concept of amount. The method requires effective verbal communication style, efficient classroom management and expertise in general classroom instructional procedures. These do not commend themselves to every one that desired them.

The "printed instruction" approach shares the same assumption as the "lecture" method, but uses a different method for achieving the objective. In this method, printed texts are given to the students concerned. The texts generally contain a well organised format of instruction in the relevant area. They are geared toward the promotion of students' understanding of the underlying chemical concepts. The assumption is that understanding enhances the ability to command knowledge (sec 3.2); thus promoting problem solving skills.

The structure and format of texts vary according to related factors such as the nature and scope of the difficulties, and the theoretical assumptions that guide remedial processes. Examples include programmed learning such as was used by Patwary (1983) to remediate students' difficulties in some aspects of organic structure and a structured text used by Ali (1984) to remediate students' deficiencies in some aspects of calculations involving concentrations of solutions.

The approach used in this study is that of structured texts. The choice of the method was

based on such practical considerations as simplicity, adaptability and time constraints. Some of the theoretical assumptions that additionally guided the choice, and thus implementation of the method are discussed in section 10.3.

10.3 The remedial package for the study

10.3.1 Design of the package

The remedial package called "structured text" consists of instructional booklets. Each booklet comprised one topic, dealing with a particular chemical subject. The package, shown as appendix 10.1 was presented in simple and clear language. The theoretical considerations that guided the nature and structure of the text included the following:

(a) The constructivist view of learning

The main thrust of the theory as explained by Herron (1984) is that all of us construct knowledge in our heads. It is never transmitted intact from one individual to another. This view is supported by others, for example, Pocztar (1972) and Driver and Bell (1986).

A sense in which the theory was applicable to the remedial package was that it sought to actively engage the students in interacting with the instructional material primarily, through the structural arrangements of each topic (sec 10.3.2). This was considered to have an overall effect of

stimulating, in the students a process of critical thinking that would result in constructing knowledge, and hence understanding.

(b) The hierarchy of learning sets

The theory of learning hierarchies was proposed by Gagné (1977). It describes a psychological organization of intellectual skills in which the related concepts are structurally linked to form a hierarchy for achieving instructional objectives. Generally, the simpler concepts precede the more complex ones, and the latter are considered to subsume the former. The purpose, according to Gagné is the "attainment of an organized set of intellectual skills which represents understanding of a topic".

The idea of the theory influenced the arrangement of the topics, in which the pre-requisite concepts about chemical structure (topics 1-3), and conventional symbols used for describing reactions processes (topic 4), were presented before those of chemical reactions. Attempts were also made to present the content of each topic in a progressively increasing order of conceptual complexity with a view to enhance understanding of the concepts presented.

(c) Prior knowledge

The role of prior knowledge in learning (and thus remedial studies) has been emphasized by Ausubel (1968) in his theory of meaningful learning. His thesis is as follows:

> "The most important single factor influencing learning is what the learner already knows. Ascertain this and teach him accordingly".

Since remediation is a form of instruction, the underlying principles of the theory is also applicable. The initial knowledge state of the students was determined from the first part of the study. It was in the light of the results that the remedial package was composed.

Reif (1983) had likened the situation to a chemical transformation of the sort:

$$S_i \longrightarrow S_f$$

where S = the student

S_i = an initial knowledge state of the student

S_f = a final (desired) knowledge state of the student.

Part I of the study had revealed the initial state of the student, while the remedial programme (part II) represents a process of transforming the student to a level of conceptual understanding represented by

S_f, where he is enabled to solve problems he was unable to solve prior to instruction.

10.3.2 Format of the package

The remedial package consisted of ten topics each comprising three parts arranged as follows:

(a) Presentation: This provided information about the key concepts contained in the topic. It is made up of two parts:

(i) Introduction: This comprised an overview of the topic. It highlights the theme of the topic, and an outline of how the topic is related to the preceding one.

(ii) Unit lesson: This contained detailed information about the topic. Attempts were made to keep the unit lesson as concise and precise as possible so as to focus the students' attention on the main chemical ideas to be learnt.

(b) Exercises: These consisted of questions about the presentation. They were intended to direct students' attention to the key ideas and to serve as a means by which they could assess their understanding of the topic.

(c) Responses: These were the answers to the questions contained in the exercises. They served as feedback by which the students could cross-check the correctness of their answers, thus prompting a further review of difficult

There are generally two approaches to the placement of questions in structured texts. One of pre-questioning and the other of post-questioning. In the former approach, the questions are placed immediately preceding the presentation, while in the latter, they are placed immediately after. The effect of the relative position of questions on mastery of learning has been investigated in a number of studies. Rothkopf (1965) showed that placing the question before the material to which they relate results in greater learning of the material. Studies by Fraze (1968) and Bruning (1968) have al shown similar results. These results served to strengthen the author's choice of pre-questioning adopted in the structured text.

10.4 Experimental design and procedure of implementation

10.4.1 Experimental design

A basic assumption that underlies the administration of the remedial package is that it provided an effective instruction which helped to improve the problem solving capability of the students in organic reaction mechanism, through increased understanding of the relevant, pre-requisite chemical knowledge. The validity of the assumption has to rest on some empirical evidence. To achieve this, a controlled experiment described in this section was undertaken.

The matched group design, involving pre-post testing strategy (Plutchik, 1968; Ndagi, 1984) was used. The underlying aim was to determine the

effectiveness of the remedial programme, in reducing the students' problem solving difficulties earlier discussed in part I.

The two groups involved in the experiment (sec 10.4.2) were matched at the beginning, using their respective pre-test group mean scores and standard deviations as criteria for determining equivalence. The evidence for attainment of equivalence was based on the indication that there was no significant statistical difference between the two groups in the characteristics referred to above. This is illustrated in table 10.1 below:

TABLE 10.1 STATISTICAL PROPERTIES FOR DETERMINING EQUIVALENCE BETWEEN THE TWO GROUPS

Statistical Properties / Groups	Mean Score ($\bar{X}$)	Std.dev (S)	t-ratio	Remark
Experi-mental Group	8.68	4.19	0.25	Not Significant $\alpha < 0.05$
Control Group	8.60	3.21		

The experimental group received treatment as described in section 10.4.3, the control group received none. Both groups were tested at the end of the experiment. The main features of the design is summarised in table 10.2.

TABLE 10.2 BASIC DESIGN OF REMEDIAL EXPERIMENT

Treatment / Groups	Pre-Test	Remediation	Post-Test
Experimental Group	+	+	+
Control Group	+	-	+

KEY:

+ = treatment applied
- = no treatment applied

10.4.2 The samples and selection

The experimental group (EG) comprised 25 students from the unsuccessful students in one of the schools. The control group (CG) also comprised 25 students from another school, who were shown in part I to be unsuccessful in solving the problems. Both groups were obtained by simple random selection. The groups were requested to persist through the programme to the end. They gave indication (verbal at that stage) of their willingness not only to particpate, but to do so with dedication.

The groups came from two different schools separated by an approximate distance of 30 km (≏ 19 miles). This was part of an attempt to reduce interactive effects that would have been the case if both groups were located in the same school. The composition of the groups is illusted in table 10.3 below.

TABLE 10.3 COMPOSITION OF THE REMEDIAL GROUPS

	EG	CG	TOTAL
Male	22	22	44
Female	3	3	6
Total	25	25	50

10.4.3 Experimental procedure

The administration of the remedial package consisted of meeting with the students once a week, usually on Fridays, during which the text (appendix 10.1) was handed out to them, one topic at a time. At the meeting the following week, the problems and difficulties which they were unable to tackle by themselves were usually brought forward for discussion in which everyone was encouraged to participate. After the difficulties were resolved, the text for the next topic was handed out to be read and "digested" during the week before the next scheduled meeting. This procedure was continued until all the topics were exhausted, the programme lasting 11 weeks.

During the first meeting, the author explained the purpose of the programme to the students and highlighted the possible benefits that they would derive from the programme. This was done to let the students see the need for participating, so that they would do it willingly and meaningfully.

It was encouraging to see that the interest

and confidence of the students grew steadily as the programme progressed. The sheer enthusiasm that they constantly exhibited served as an evidence of this. As the programme progressed, the spontaneity of the students' responses grew. Many times they gathered and were waiting before the appointed time. It was a wonderful experience for the author, especially that his initial fears of some students falling back half way through the programme proved unrealistic.

At the end of the programme, a post-test (test B) was administered along with questionnaires which sought information from the students about their opinions regarding the programme.

10.5 Conclusion

The design of the remedial package and the experimental procedure adopted for its administration have been presented in this chapter. In the next chapter, the results of data from the experiment are presented and discussed.

CHAPTER ELEVEN

PRESENTATION AND DISCUSSION OF THE RESULTS

11.1 The aim of the remedial programme was to provide instruction to reduce students' observed difficulties through enhanced understanding of the underlying chemical concepts. The effectiveness or success of the programme was determined from the pre- and post-tests results which are presented and discussed in this chapter.

11.2 Scoring and analysis of the post-test scores

The scoring procedure adopted for the pre-test (sec 5.2) was also used for the post-test. The data was computer-analysed, using the "Minitab" package.

11.3 Presentation of the results

The results obtained from the analysis are shown in tables 11.1-5.

11.3.1 Some statistical parameters of the scores

The results shown in table 11.1 below illustrate some of the relevant statistical properties of the pre- and post-tests.

TABLE 11.1 SOME STATISTICAL PROPERTIES OF THE SCORES

Tests / Statistical Properties	Pre-test		Post-test	
Groups	EG	CG	EG	CG
Sample Size (N)	25	25	25	25
Sum of Scores (ΣX)	219.00	231.00	409.00	261.00
Mean Score ($\bar{X}$)	8.76	9.24	16.36	10.44
Std. Dev (S)	4.10	3.28	6.78	4.74

11.3.2 Facility indices of the scores

The facility indices of the two groups in both the pre- and post-test scores are presented in table 11.2 below.

TABLE 11.2 COMPARISON OF PRE- AND POST-TESTS FACILITY INDICES

Groups / Problems	EG		CG	
	Pre-test	Post-test	Pre-test	Post-test
1	0.29	0.56	0.52	0.55
2	0.30	0.43	0.16	0.26
3	0.16	0.40	0.23	0.29
4	0.13	0.52	0.17	0.17
5	0.14	0.26	0.14	0.15
Mean F.I	0.20	0.43	0.24	0.28

11.3.3 Further comparison of the group mean scores

A further comparative analysis of the scores, both within and between the groups, was carried out using the matched groups t-test method. The results are presented in table 11.3.

TABLE 11.3 COMPARISON OF PRE- AND POST-TEST GROUP MEAN SCORES

	Pre-test		Post-test				
Group	$\bar{X}$	S	$\bar{X}$	S	SEd	t-ratio	Remark
EG	8.76	4.10	16.36	6.78	1.41	5.37 (df = 24)	✓
CG	9.24	3.28	10.44	4.74	0.77	1.56 (df = 24)	X
SEd	1.02		1.67				
t-ratio	0.47 (df = 24)		3.55 (df = 24)				
Remark	X		✓				

KEY:

✓ = t-value was statistically significant at $\alpha \leq 0.05$

X = t-value was not statistically significant at $\alpha \leq 0.05$

SEd = standard error of the difference between the mean scores being compared

df = degrees of freedom

11.3.4 Response to the post-test questionnaire

An evaluation questionnaire (appendix 10.2) was administered immediately following the post-test to obtain from the students (EG) their assessment of the effectiveness of the remedial text.

The results are presented in table 10.4. The numbers show % responses.

11.3.5 Students' perception of their difficulties before and after remediation

The responses of the students to the questionnaires immediately following the problems were compared for the pre- and post-test. The results are shown in table 11.5. The abbreviations used have the usual meanings (sec 5.9).

TABLE 11.4 RESPONSE TO EVALUATIVE QUESTIONNAIRES ON THE REMEDIAL TEST

S/No	Response scale / Questionnaire	VERY DIFFICULT	MODERATELY DIFFICULT	EASY
1	How difficult do you normally find studying organic chemistry?	8.0	76.0	16.0
2	How did you find reading through this "Text on organic reaction mechanism" that you have just completed?	-	20.0	80.0
3	Having completed this course (i.e the text) how much has it helped to improve your understanding of organic chemistry?	VERY MUCH 92.0	NOT MUCH 8.0	NOT AT ALL -
4	How much has this text helped to improve your learning or studying of organic chemistry?	96.0	4.0	-
5	Having completed this text, how much would you like to be taught organic chemistry from a mechanistic approach?	72.0	28.0	-
6	On the whole, how would you assess this text, considering the extent to which it has helped to reduce your difficulties in organic chemistry?	VERY GOOD 76.0	JUST GOOD 24.0	POOR -

TABLE 11.5 % DISTRIBUTION OF STUDENTS' RESPONSES TO QUESTIONNAIRES BEFORE AND AFTER REMEDIATION

Variables / Problem	Pre-test											Post-test										
	FAMILIARITY		DIFFICULTY		CONFIDENCE		REASONS FOR DIFFICULTY					FAMILIARITY		DIFFICULTY		CONFIDENCE		REASONS FOR DIFFICULTY				
	FA	NF	DF	ES	CN	NC	I	II	III	IV	V	FA	NF	DF	ES	CN	NC	I	II	III	IV	V
1	92.0	8.0	28.0	72.0	64.0	36.0	8.0	24.0	4.0	-	-	96.0	4.0	8.0	92.0	88.0	12.0	-	4.0	-	-	4.0
2	100.0	-	40.0	60.0	68.0	32.0	12.0	24.0	4.0	-	8.0	100.0	-	4.0	96.0	88.0	12.0	-	4.0	-	-	8.0
3	36.0	64.0	64.0	36.0	32.0	68.0	12.0	32.0	20.0	12.0	-	68.0	32.0	32.0	68.0	68.0	32.0	4.0	12.0	4.0	-	16.0
4	84.0	16.0	56.0	44.0	48.0	52.0	4.0	40.0	20.0	-	-	92.0	8.0	24.0	76.0	72.0	28.0	-	12.0	-	-	16.0
5	80.0	20.0	56.0	44.0	44.0	56.0	4.0	32.0	12.0	8.0	8.0	96.0	4.0	16.0	84.0	76.0	24.0	-	4.0	8.0	-	12.0
AVERAGE	78.4	21.6	48.8	51.2	51.2	48.8	8.0	30.4	12.0	4.0	3.2	90.4	9.6	16.8	83.2	78.4	21.6	0.8	7.2	2.4	-	11.2

11.4 Discussion of the results

The results of the remedial experiment are shown in table 11.1-5. They indicate that:

(a) the performances of both the EG and CG generally improved in the post-test relative to the pre-test, indicating some net gain in the terminal performances.

(b) both the remedial programme and the pre-test produced positive net gains in the students' performances from pre- to post-test.

(c) the net gain by the EG from the remedial treatment was statistically significant.

(d) the net gain by the CG from the pre-test effects was not statistically significant.

(e) the post-test performance of the EG was significantly superior to that of the CG. Both groups were equivalent at the beginning of the experiment.

(f) the post-test performance of the EG was significantly superior to their pre-test performance.

(g) the post-test performance of the CG, though improved, was not significantly better than their performance in the pre-test.

(h) the students (EG) expressed greater confidence in their post-test solutions, and less degree of difficulties in the process of solving the problems relative to the pre-test.

These results are now discussed in greater details.

The results shown in tables 11.1-2 indicate that the post-test performances of both the EG and CG were better than those of the pre-test. The implication is that both the remedial treatment and the initial exposure to the pre-test produced some positive learning effects in the students. However, table 11.3 indicates a distinction between these effects. It shows that the net gains from remediation are statistically significant, while those due to the pre-testing effects are not significant. Thus we find that the t-ratio of the EG/CG post-test group mean scores, and that of the EG/EG pre-post tests group mean scores are statistically significant at $\alpha \leq 0.05$, while the corresponding values for the EG/CG pre-test and CG/CG pre- post test scores are not significant at that level.

It does appear, therefore, that the significantly improved post-test performance of the EG, shown also to be significantly superior to that of the CG, can be explained mostly in terms of the positive impacts of the remedial treatment.

Furthermore, the students' opinions, expressed in the questionnaires (table 11.5) showed that they considered they had less difficulty with the problems, and more confidence in their ability to solve the problems correctly after they had been exposed to the remedial programme. Thus, we find that the average frequency distribution of students

indicating difficulty with the problems decreased from 49% to 17% after remediation. Similar values for their confidence in the solutions they had produced rose from 51% for the pre-test to 78% following remediation. This situation of increased confidence and a lower level of difficulty is seen to be reflected in the "reasons for difficulty" columns which were left mostly empty at post-test compared to the pre-test. It appears logical that the students gave no explanations for difficulties which they perceived to have been remediated, indicating their conviction of the positive impact they considered the programme to have had on them.

These results, put together, indicate that the remedial treatment produced a positive impact on the students which significantly helped to reduce their difficulties reported in part I. Based on this outcome, the remedial programme can thus be described as successful, and to have achieved the aim for which it was designed and implemented.

11.4.2 Excerpts from the students' solutions

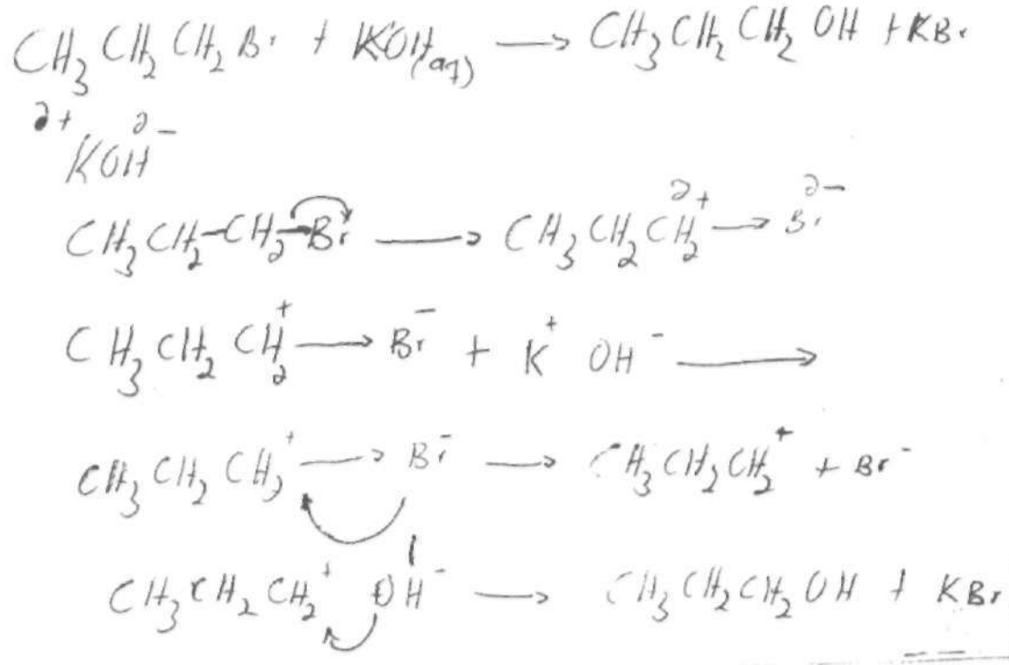
Some examples of pre- and post-test excerpts of the EG are shown below. Each pair of pre- and post-test excerpts for each problem originate from the same student to facilitate comparison. They are displayed as another piece of relevant evidence indicating the students' improved problem solving capability resulting from remediation.

It is seen, for example that the students, following remediation, used symbols (e.g curved arrows, formal charges) more accurately, and tackled the problems more in terms of processes involving breaking and making of bonds rather than in terms of charges and the associated attractions - a conceptualization that characterized their pre-remediation approach. Three of these, problems 1, 4 and 5 are included to exemplify both ends of the difficulty spectrum (table 11.2), problem 1 on the easier side, 4 and 5 representing those they found most difficult.

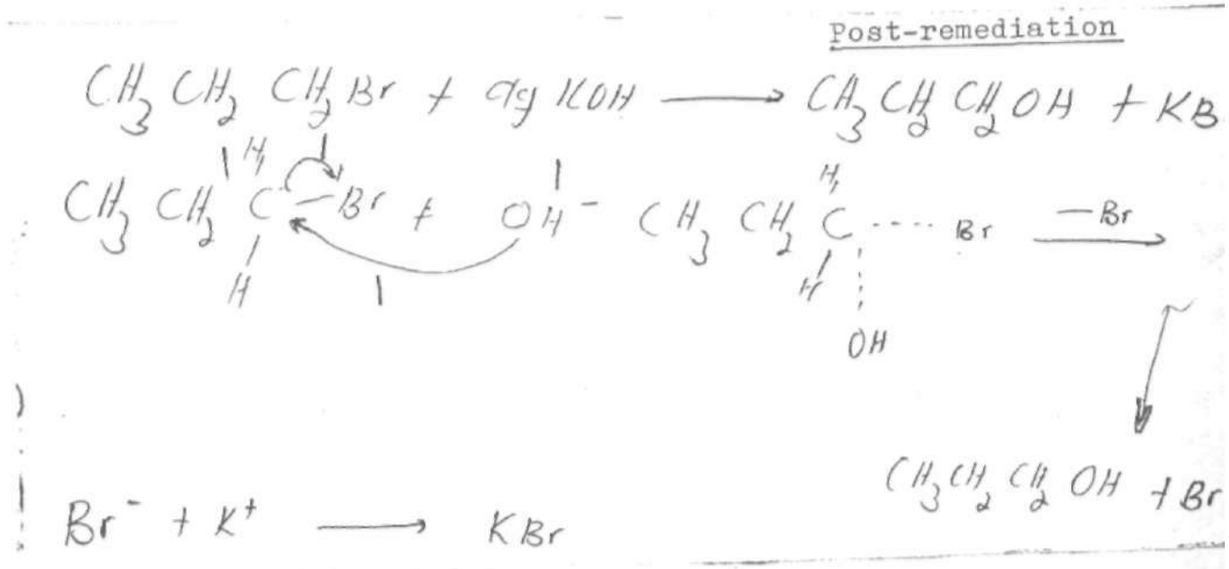
1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$CH_3CH_2CH_2Br + aqKOH \longrightarrow CH_3CH_2CH_2OH + KBr$

Pre-remediation



Post-remediation



Pre-remediation.

4. Using the relevant mechanisms of the respective reactions

(a) Explain why 1-bromobutane forms only one isomer, while 2-bromobutane forms three isomers respectively, when treated with an alcoholic solution of potassium hydroxide. The reactions are as follows:

(I) $CH_3CH_2CH_2CH_2Br \xrightarrow{\text{alc. KoH}} CH_3CH_2CH=CH_2 + H_2O + Br$
1-bromobutane — but-1-ene

(II) $CH_3CH_2CH(Br)CH_3 \xrightarrow{\text{alc. KoH}} CH_3CH_2CH=CH_2 + H_2O + KBr$
2-bromobutane — but-1-ene

$CH_3CH_2CH(Br)CH_3 \xrightarrow{\text{alc. KoH}} CH_3CH=CHCH_3 + H_2O + KBr$
but-2-ene

Note: Work out the third isomeric butene from reaction II.

(b) What name is usually given to the mechanism that you have described?

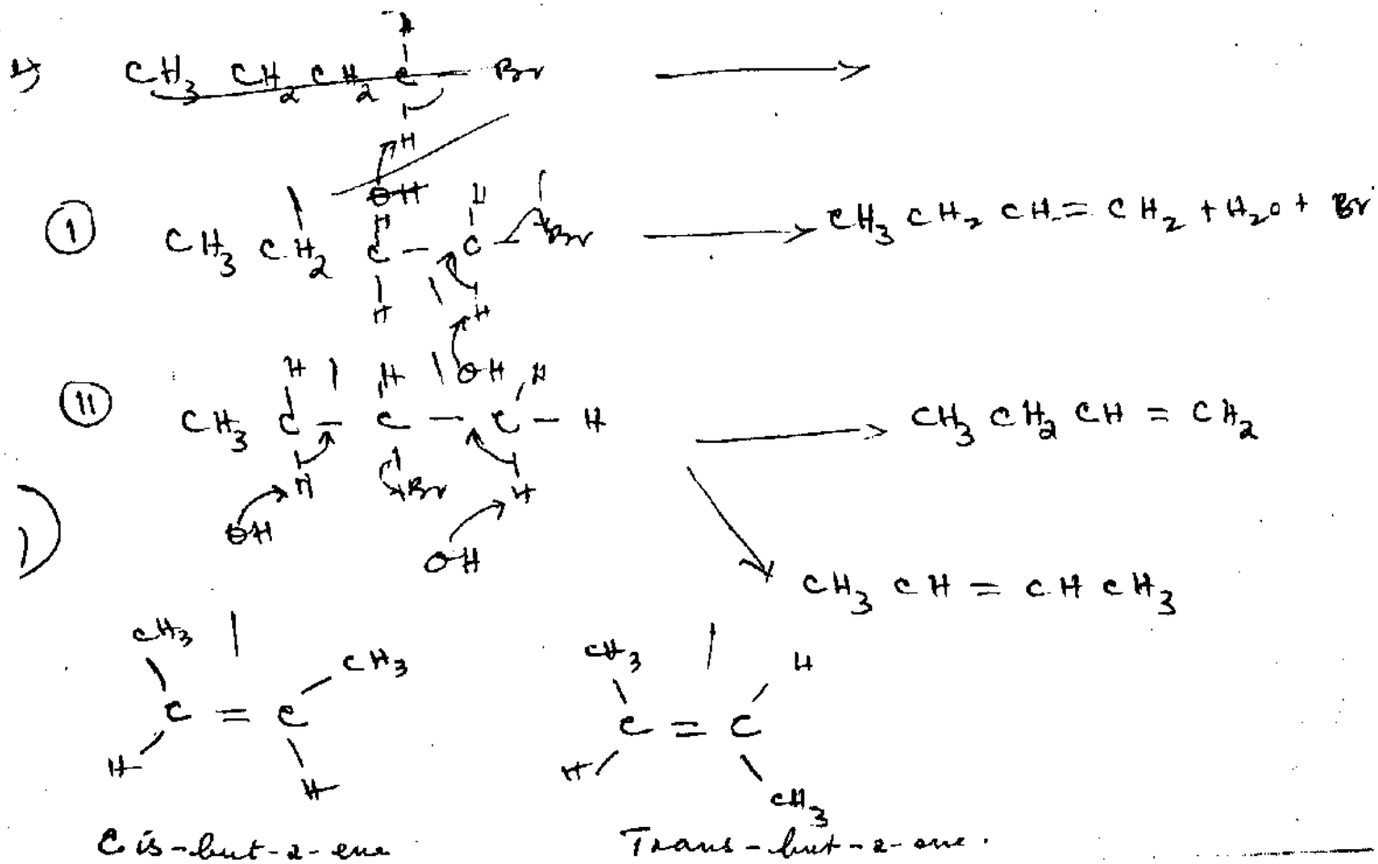
(i) (1) 1-Bromobutane forms only one isomer because the Boron atom is attached to the primary carbon atom.

(1) $CH_3CH_2CH_2-Br \xrightarrow{\text{alc. KoH}} CH_3CH_2CH=CH_2 + H_2O + Br$.

and the electromeric shift is only to one side. And also the removal of the H-atom of the 2° carbon atom follows Saytzeff's rule.

(ii) (2) 2-bromobutane forms three isomers because the Bromine atom is attached to a secondary carbon atoms.
and the electromeric shift is on both sides.

Post-remediation.



5. Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:

(I) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH_3} + HBr \longrightarrow \overset{1}{CH_3} - \overset{2}{CHBr} - \overset{3}{CH_3}$

electrophilic addition

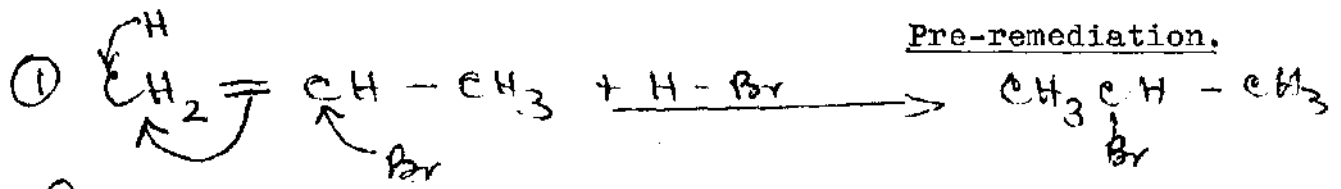
(II) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CHO} + HBr \longrightarrow \overset{1}{CH_2Br} - \overset{2}{CH_2} - \overset{3}{CH} = O$

nucleophilic addition

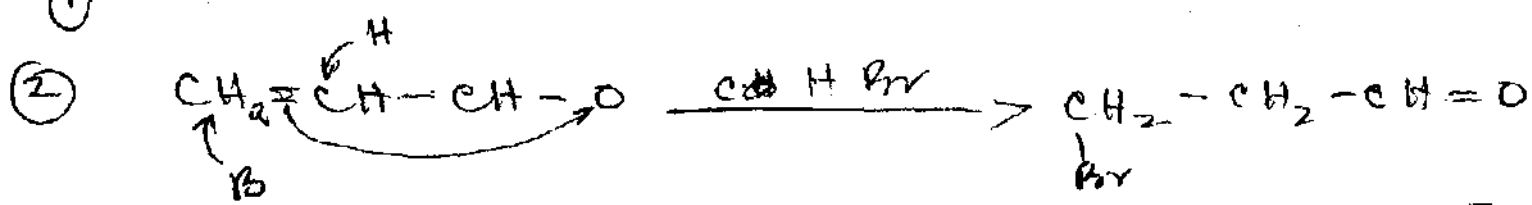
Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.

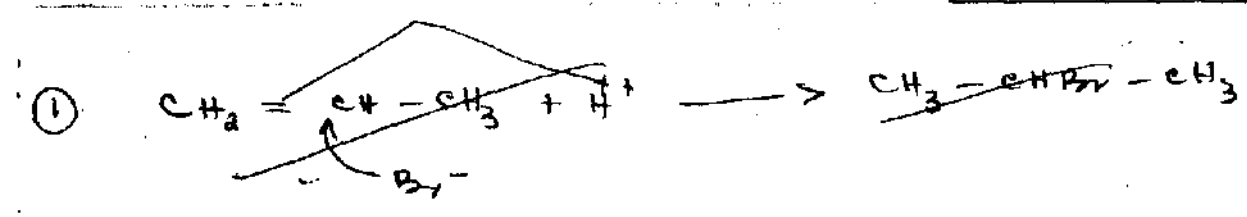
Pre-remediation.

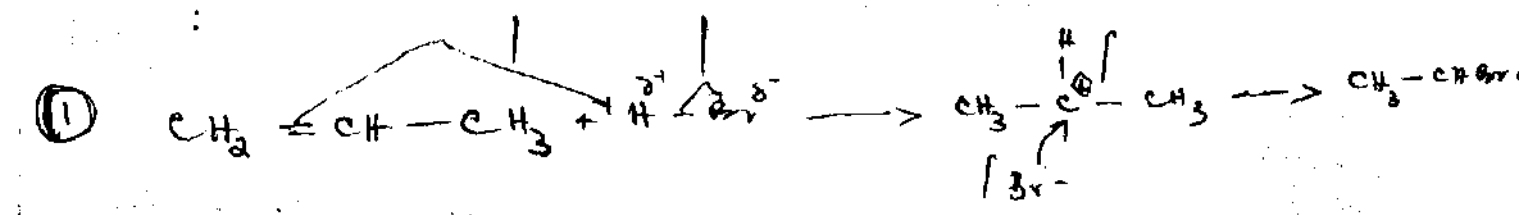
(1) 

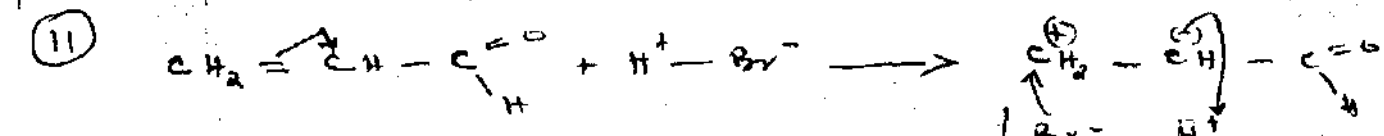
(1)

(2) 

Post-remediation.

(1) 

(1) 

(11) 

(5)



11.4.3 Evaluative questionnaire and comments

The questionnaire (appendix 10.2) sought the students' (EG) opinion about the effectiveness of the remedial programme. The results are shown in table 11.4. The students expressed satisfaction with the programme and indicated that it had helped reduce their difficulties. For example, 92% of the students indicated that the programme had helped to improve their understanding of organic chemistry, while 96% reckoned that it had generally helped to improve their learning of organic chemistry. The results also showed that 76% of the students considered the remedial text very good, 24% opined that it was good. None of them rated it poor.

These results indicate that the treatment did have real remediation effects on the students, and they acknowledged it. This deduction receives further support from the students' responses to the free, personal comments sought from them in item 8 of the quesionnaire. Eighteen of the students commented, from which fifteen excerpts are shown below. The remaining were written in pencil, and were not legible enough for inclusion.

8. Any other comments: This text had improve my

1. knowledge of mechanism of organic reactions and the effect of structures on reactivity.

8. Any other comments: I ~~find~~ found learning organic

2. Chemistry some what difficult, but this text ~~has~~ helk me much to reduce the difficulties ~~ecleciall~~ especially ~~conc~~ Concerning mechanistic approach

8. Any other comments: The text is self explanatory.

3. and it has so much reduced my difficulties in the Subject.

8. Any other comments: This text ~~help~~ improve

4. My understanding of Organic Chemistry due to shortage of time, I was unable to complet the conse (~~cont~~ topic 9).

8. Any other comments: ~~no comments~~. The text is very well

5. simplified with important facts and points on how to understand the organic chemistry in a short time.

8. Any other comments: With a little more

6. Specific examples on reaction mechanisms with high carbon content it will help a lot.

7. Any other comments: Okay & straight forward.

8. Any other comments: To me the problem with organic

8. chemistry is the teacher and how he presents what he has to teach the students. Any teacher who presents his/her material as in this text organic chemistry will be interesting

8. Any other comments: The exercise has been a very

9. good one I really enjoyed going through them. The only set back was that it was done in a squeezed up condition i.e when we were busy preparing for our final papers.

8. Any other comments: It was all good, interesting,

10. educating and worth the time taken.

8. Any other comments: Before this course, I have many difficulties

11. concerning organic reactions especially the mechanisms, but having finished with the course, almost my difficulties were clarified concerning mechanisms.

8. Any other comments: You should keep up!!

12. I believe if the other organic master should be like yourself, they think there should not be any problems on Organic Chemistry. thanks.

13. **8. Any other comments:** Reduction of Organic reaction mechanism should be taught throughly. for students to understand the principle behind the reactions of organi reaction.

14. **8. Any other comments:** It's a nice text so far and this should be continues, as we gained much from the programme because some of the things we don't know before was known during the course.

15. **8. Any other comments:** The text gives the basic processes of organic reaction. By going ~~thor~~ through it one would be able to cope with any organic reaction. In short the text is comprehensible.

11.5 Findings and conclusions

The findings from the results of the remedial studies have been outlined in section 11.4. The discussions that followed in the chapter elaborated the findings.

It is concluded from these that:

(a) the structured text was a suitable instructional medium for remediating the students' difficulties observed in part I.

(b) the remedial programme was effective and successful as it significantly reduced the students' initial difficulties.

(c) the assumption that the design and implementation of the remedial package constituted an effective approach of reducing the students' problem solving difficulties was shown to have validity.

There is no particular instruction method that can be held to satisfy all the conditions under which learning occurs at all times. However, it does appear from these results that the learning of organic reactions and the capability to use the acquired knowledge to solve problems would be enhanced if students' difficulties are continuously monitored, constantly diagnosed and remedied. In that case as much emphasis will be given to the question of "what do the students not know?" as that of "what do they know?"

CHAPTER TWELVE

SUMMARY, FINDINGS, IMPLICATIONS AND SUGGESTIONS FOR FURTHER RESEARCH

12.1 Overview

Although findings were reported, and conclusions drawn at appropriate stages along the course of this study, this chapter comprises an overall summary of the findings and conclusions. It also comprises a summary of implications arising from the findings and suggestions for the direction of future research.

12.2 Summary of research aim and procedure

The underlying aim of this study concerns the identification of the nature and causes of the problem solving difficulties of the students of Schools of Basic Studies in mechanisms of organic reactions. The literature reviewed indicated, amongst other things, that success in problem solving requires the possession, by the student of the relevant chemical knowledge and an understanding of how these can be arranged to fit the demands of the problem posed.

In part I of the study, paper-and-pencil tests and the "think aloud" method were used to probe the students' problem solving difficulties. In part II of the study, a remedial programme, aimed at reducing the difficulties, was carried out. The results showed that the programme was successful as it significantly reduced the students' difficulties.

12.3 The findings from the study

The following constitutes an overall summary of findings from the entire study:

(a) The initial observation (sec 1.2.3.2) that the students lacked chemical knowledge, and that this was responsible for their failure in solving problems was not wholly supported by the results of the study. Rather, they showed that while the students possessed much of the requisite chemical knowledge, the component concepts were acquired in an isolated fashion, such that the links and interrelationships were not understood. This tended to constrain their ability to apply the knowledge that they possessed in solving the problems.

(b) The students were unsuccessful in solving the problems posed. This failure was due to a number of underlying difficulties, which included lack of understanding of the:

  (i) nature and structural relationships of covalent bonds, atoms and valence electrons within the molecule in a classical Lewis model.

  (ii) formalism of chemical symbols. Curly arrows and the representation of charges were among the prominent difficulties.

  (iii) interactive processes of bond-breaking and bond-making that reactants undergo as they are converted to products.

(c) The students lacked requisite strategies for solving the problems. This was exemplified by their:

(i) failure to understand the demands of the problems posed.

(ii) failure to select relevant information required to meet the demands of the problems.

(iii) haphazard and illogical organization of the information-bits in an attempt to produce a solution.

(d) There was a positive, but low correlation between the students' reservoir of chemical knowledge and the ability to utilize the knolwedge in solving problems requiring them as pre-requisites.

(e) The students' reservoir of chemical knowledge cannot be relied upon as an effective means of predicting or estimating their potential success in a problem solving exercise based on the knowledge.

(f) The male students performed significantly better than the female students in solving the problems, even though there seemed to be no difference in their possession of the underlying chemical knowledge.

(g) The thought-processes that underlie the students' problem solving behaviour in mechanistic organic chemistry seemed to be

guided by the idea that organic reactions are caused by an attraction between oppositely-charged species. Thus they felt that the reactions must necessarily involve charged reactants in one form or another.

(h) The students' problem solving approach did not show any clear, consistent pattern that could be used as basis for classifying their strategies into any formal categories. They were typified by a random, trial-and-error approach.

(i) The few students shown by the TAPS to be successful in solving the problems were significantly better than those that were unsuccessful in structuring, progressive refinement and organizing the relevant information - both from the problem situation and the long term memory.

(j) The variations in the students' successes in solving the problems seem to be explainable, not so much in terms of the chemical knowledge they possessed but more in terms of the ability to transform the knowledge to meet the demands of the problems.

(k) The remedial programme produced positive impact on the students, as it significantly reduced their problem solving difficulties.

(l) Structured texts constituted an effective instructional approach that helped the students to overcome most of their difficulties.

(m) Some of the assumptions made by the curriculum planners in designing the course contents, and the teachers in devising instructional strategy and sequence do not seem to be authentic. A typical example concerns the prior chemical knowledge of the students.

12.4 Implications of the findings for curriculum planning and implementation: recommendations

The findings from this study, which have been outlined above, have relevance for appraising, and subsequent improvement of the planning and implementation of the curriculum in chemical education. This is with particular regard to the teaching and learning of organic chemistry in the Schools of Basic Studies, and by extrapolation, the pre-degree organic chemistry course in Nigeria. These are now presented as recommendations:

12.4.1 Implications for the teaching of organic chemistry

(a) The teaching of organic reactions should be pursued from an instructional approach that facilitates students' understanding of the chemical processes occurring as the reactants are converted to products, and also the intimate relationships between chemical structure and chemical reactivity. From the results of this study, one such method is the mechanistic approach.

(b) The procedure for teaching organic chemistry should be appraised with a view to diversifying, and taking on board other instructional strategies to supplement the existing lecture method. A fundamental objective of such method(s) should involve the provision of opportunity for the students to interact, at individual levels, with the materials to be learnt, as knowledge and understanding are idiosyncratic phenomena constructed by individuals. This study had indicated that the structured text, which is not the same as traditional hand-outs, constitutes a viable choice.

(c) The traditional approach of teaching organic reactions, typified by reactants and products connected by arrows or equation signs appears grossly inadequate for a functional understanding of the underlying concepts, as the procedure does not show the chemical processes involved. A more efficient approach seems to be that which describes the interactive processes at every stage of the reaction - one depicting the breaking of existing bonds and the formation of new ones, and the consequent structural changes in structure. The use of Lewis model of molecular structure representation, showing bonds and valence electrons, and their movements and rearrangements during chemical

reactions, seems a reasonable proposition.

(d) The teaching of organic chemistry should seek to establish in the students a firm understanding of the conventional symbols generally used in describing reaction processes. Typical examples include, curly arrows, the dash (-) symbolism, representation of molecules in terms of formulae, and partial and formal charges. The knowledge of these seems to have been taken for granted by teachers and curriculum planners, but this study showed that such knowledge is not always within the working repertoire of the students. The syllabus should spell them out clearly and they should be taught specifically.

(e) A basic, generalized procedure or theoretical model of solving chemical problems in organic reactions should be suitably incorporated in the syllabus. It is suggested that such may include two broad elements: problem understanding and problem execution. Thus, instructions in this area should be geared toward assisting the students to understand problem situations, select relevant information and to organize the information-bits to fit the requirements of the problem posed. It is believed that a start in this direction could be made, notwithstanding the intractable question of

whether problem solving can be taught, and the conditions that enhance success.

12.4.2 Implications for the teachers

(a) A central consideration that should influence the teachers' instructional attitude and approach involves the realization that what is structured and logical to them is not necessarily so to the students. Consequently, they should approach instruction from the students' stand-point rather than their own.

Some of the underlying assumptions that the teachers seemed to have made, and which influenced their instructional approach, have been shown to have little correlation with the practical situation of the students, e.g their prior chemical knowledge.

(b) The teachers should be aware that the technical terms they use to communicate chemical knowledge have profound influence on the students' process of encoding information, and hence on their construction of chemical knowledge and the required understanding of the subject matter. Thus, teachers should be sensitive to, and exercise reasonable care in the choice of words/expressions that they use to convey chemical ideas, especially where such have dual usages.

(c) The teachers should diversify emphasis from routinely seeking to establish what the

students know or are competent in performing to periodic diagnosis, through appropriate tests, discussions and small-scale research, of what they fail to know and the reason(s) for the failure. Both approaches complement each other, for without knowing what constitutes the students' difficulties in their learning situations, teachers may be in danger of pursuing half-baked instructional strategies.

(d) The teachers should, from time to time, plan and carry out remedial programmes, once the students in need of remediation have been identified and the nature of the difficulty diagnosed. This could take various forms, some of which were discussed in section 10.2. It is not enough for teachers to wait for students to bring forward their difficulties for remediation, as such action assumes that students know what they do or do not know. Research evidence in this area (Metacognition) is rather scanty. As Lester (1982) pointed out, it has been largely *ignored due to a belief that metacognition is* either unimportant or unresearchable. Though such an exercise may mean additional burdens on the teachers, if it is properly carried out, the results, and the use to which they could be put are worth the trouble.

(e) Teachers should avail themselves of opportunities for exchanging professional ideas through conferences, symposia and workshops, from which the experiences of the teachers in the field and curriculum planners in the offices could be pooled together. Such a reservoir of experiences could form a valuable basis for appraising the state of curriculum design and implementation and the formulation of future directions. The main body that seems to fulfil this role at the moment is the Science Teachers' Association of Nigeria, which caters for the interests of all science teachers. The establishment of a similar body that caters for specific interests of chemical educators should be given serious consideration.

12.4.3 Implications for the curriculum planners

(a) The Schools of Basic Studies syllabus in organic chemistry should be structured and organized around bond-types, which tend to bring the discussions of different compounds that share similar chemical reactions under the same umbrella, rather than on the basis of families of organic compounds, as it now stands, which separate into different conceptual categories compounds whose chemical behaviour shares essential similiarities.

(b) The aims and objectives of the course contents embodied in the syllabus should be clearly spelt out in behavioural terms. Also, the educational outcome and skills expected of the students, after instruction should be unambigiously indicated. This is grossly inadequate at the moment. It is only when this is done that instruction and assessment of chemical knowledge assume meaningful direction.

(c) The Schools of Basic Studies syllabus should be reviewed with a view to closing the gap between the students' prior knowledge and the conceptual demands of the new materials that they are expected to learn. For example, such concepts as covalent bonding, molecular structure representation, chemical symbols and formulae, hitherto taken for granted as constituting part of the students' pool of prior knowledge should be revised with a view to teaching them specifically as basis for subsequent learning in organic reactions.

(d) The syllabus operated by the schools appears over-loaded with some chemical concepts that can be safely shedded. For example, the first sectin dealing with purification of organic compounds, detection and determination of elements, calculations of molecular formula should be dropped or merged with the laboratory instructions where they appear more

appropriate, if their continued retention is desirable.

(e) There should be greater articulation of the various facets of the curriculum: the aim, implementation of aim, assessment of implementation and necessary adjustments via feed back. That means closer liaison and collaboration between the various agents involved in chemical education. These include the curriculum planners, the teachers in the field and the examination boards.

12.4.4 Implication for the examination board

(a) The pattern of assessments undertaken by the board should reflect the aims and objectives underlying the design of the curriculum.

(b) The structure of the tests should have in-built flexibility that would make them suitable in diagnosing the students' difficulties, while at the same time pursuing the broad aim of identifying their general capabilities. One approach would be to diversify the pattern of the tests (examinations) to include multiple-choice items, short questions and free-response problems - all structured in some sort of conceptual hierarchy.

(c) The grading schemes designed by the examination board or its chief examiners should seek to define the meaning and explain the utility of the conventional symbols:

(✓) to show a correct response and (X) to show an incorrect solution. Some pertinent questions in this regard are:

(i) Does the symbol "X" show a lack of ability on the part of the student?

(ii) Is the student awarded "✓" significantly more capable than that scoring "X"?

One method of doing this is by designing schemes that do not focus only on products of thought but also on the process.

12.5 Limitations

This study suffers from a number of limitations. The measurement of problem solving ability is influenced by a number of factors that the paper-and-pencil method used could not take into account. These include language and reading abilities, students' general attitude to, and mood during test-taking, effort etc. Thus the results obtained from the measurements necessarily suffer the limitation of the imperfect match between problem solving ability and the tests designed to reveal them.

The verbalizations used in the "thinking aloud" method to reveal underlying thought-processes also have their shortcomings. They are, at best, overt approximations of the covert processes occurring in the solver. In addition, the scope of generalization that can be made from the results obtained from the technique is constrained by the

limited number of subjects called for by the nature of the method.

The method used for obtaining initial information about the students' difficulties involved their examination scripts or results. These, by nature were not designed with the aim of revealing students' difficulties, but their achievements. It is, however, expected that the reports and comments of the chief examiners of IJMB included made up for this limitation.

The remedial programme, which employed the "printed text" method cannot fully answer the question: Can problem solving be taught? The scope of the method was necessarily narrow due to practical constraints of time, funds and, of course the overall aim of the study. Thus, while the students' problem solving capability significantly improved following remediation, it is not clear that the acquired skills can be effectively transferred to solve problems of different nature and context, or indeed increased the students' capability to solve every day, open problems that do not generally conform to particular theoretical models or heuristics. Thus, the results though of significant importance, are limited in that sense.

12.6 Conclusions

Some of the difficulties that the students of Schools of Basic Studies in Nigeria face in solving problems of mechanistic organic chemistry have been revealed in this study. In a sense, they show the

students' learning difficulties in that area of chemistry.

For classroom teachers to improve their methods of instruction, they need to know, not only the aptitudes and achievements of the students, but equally of importance, the sort of difficulties that confront them in the task of learning chemical concepts. This study has attempted to provide some information in that direction. It has been shown that the students' limited understanding of both the chemical content and the problems posed, constrained their capability in solving the problems. Some of the areas of chemical knowledge that presented difficulty to the students were discussed. Their difficulties in problem solving strategies or procedures were also indicated. The study also attempted to provide information about the mental processes that underlie the students' problem solving behaviour. Their conceptual frameworks, and some of the chemical misconceptions typical of their thought processes were revealed. All these put together constitute revelations about the students' problem solving difficulties which the study set out to investigate.

The methods employed in both parts of the study are simple and adaptable to classroom situations. They can be replicated or modified by teachers for carrying out small-scale research for purposes of improving the general process of pedagogy.

Curriculum planners also require feedbacks not only from achievement tests, but also from research conducted to reveal the difficulties that attend the learning of the course contents. The results from this study provide such feedback which can be used as basis for reviewing and appraising the effectiveness of curriculum design, and to provide some direction for improvement.

12.7 Suggestions for further research

Curriculum development and implementation are dynamic processes. Findings from one research often raise further questions for investigation. Based on the findings from this study the following suggestions are offered for further investigations:

(a) The sort of study reported here should be extended to the universities, with a view to finding out if the same kind of difficulties are typical of the universities which are higher in the educational structure.

(b) Further research should be conducted into how students construct understanding of problems involving organic reactions, and the factors that affect the process. The knowledge of this will provide a theoretical basis for designing instruction for teaching problem solving.

(c) Research should be carried out to identify, in some specific terms, the role of teachers in the process of developing problem solving skills in students. The results will be

useful in focusing and directing teachers' efforts.

(d) The role of metacognition i.e the knowledge of cognition, which includes awareness of self-capabilities and limitations, in problem solving success or failure should be investigated.

(e) The effects of such factors as interest, attitude, career prospects on problem solving success should be investigated in view of their link with motivation.

(f) Research should be carried out, with a view to providing answers to the questions:

(i) Can problem solving be taught?

(ii) If so, what are the theoretical instructional models involved?

(iii) How can such instruction be most effectively designed?

(g) The role of sex differences in problem solving success should be further investigated with a view to spelling out those sex-related factors that are involved, and how they function to produce the effects ascribed to them.

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APPENDICES

APPENDIX 1.1



■ Schools of Basic Studies

*■ Schools that participated in the Study

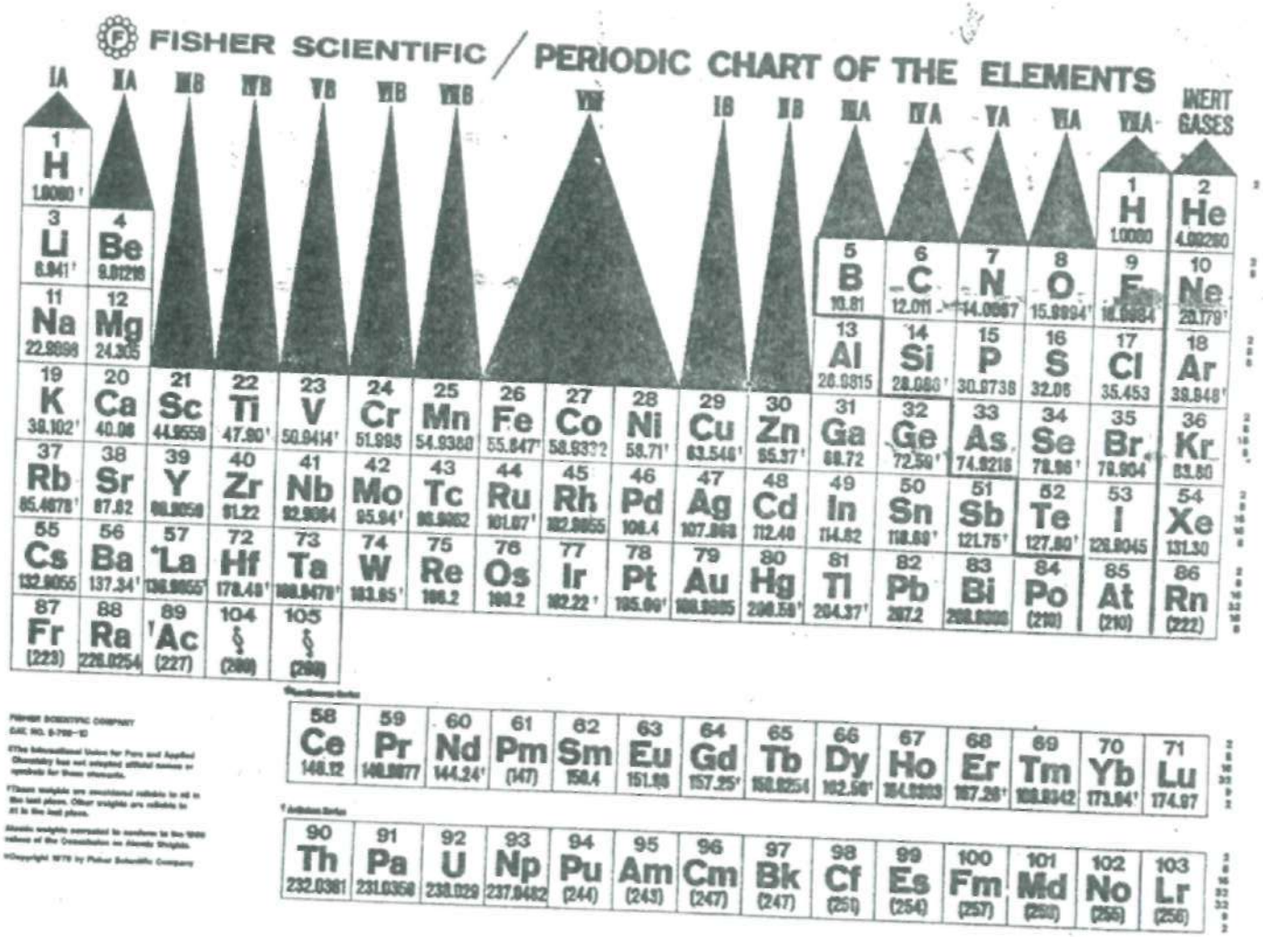
A P P E N D I X 1 . 2

INTERIM JOINT MATRICULATION BOARD
INSTITUTE OF EDUCATION
AHMADU BELLO UNIVERSITY
Z A R I A

CHEMISTRY SYLLABUS
(S. I. Units to be Used)

This syllabus compares very well with that for the A - Level Chemistry of the West African Examinations Council. Provisions have however been made for greater depth in certain areas in order to facilitate transition from the College course to the Part I Chemistry programme in a University.

EFFECTIVE



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©The International Union for Pure and Applied Chemistry has not adopted official names or symbols for these elements.

†These weights are considered reliable to ±1 in the last place. Other weights are reliable to ±1 in the last place.

Atomic weights corrected to conform to the 1969 values of the Commission on Atomic Weights.

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AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA.

I.J.M.B CHEMISTRY EXAMINATION FORMAT BEGINING FROM 1984

There will be TWO Papers - I and II

Paper I This will be made up of TWO SECTIONS A and B and it will be for 3 hours.

Section A
(Time - 1hour) This section will consist of TEN (10) structured questions drawn from General, Physical and In-organic Chemistry. Each question carries FIVE marks giving a total of 50 marks for this section.

Section B
(Time - 2 hours) This section will consist of six (6) essay questions in the areas of Chemistry as in section A. Candidates will be required to answer FOUR (4) questions. All QUESTIONS in this section carry equal marks. Section B carries 100 marks.

Paper I carries a total of 150 marks.

Paper II is made up of two sections - A and B and it will be for 2 hours.

Section A
(Time - 1 hour) This section will consist of TEN STRUCTURED QUESTIONS drawn from organic and from Practical Chemistry. Each question carries equal marks. Section A carries 50 marks.

Section B

(Time - 1 hour) This will be made up of FOUR (4) essay type questions in organic Chemistry. Candidates will be required to answer TWO (2) questions; all questions carry equal marks. This section carries a total of 50 marks.

Paper II carries a total of 100 marks.

The score from the IJMB Final Examination shall constitute 70% of the Final score.

Continous assessment will constitute 30% of the Final score. The continous assessment shall be made up as follows:

20% from practical exercises
10% from monthly and Terminal tests of the theory component of the syllabus.

Note IT IS A CONDITION THAT A CANDIDATE MUST SCORE AT LEAST A MINIMUM PASS MARK IN BOTH THE CONTINOUS ASSESSMENT AND THE FINAL EXAMINATION TO BE ABLE TO QUALIFY FOR AN OVERALL PASS.

Records for the continous assessment should be kept up-to-date so that the question paper and the marks obtained in the continous assessment can be periodically checked by the moderator.

Terminal or Monthly Test should be conducted under Examination conditions. Corrected Examination scripts may not be given to the students.

A. GENERAL CHEMISTRY

1 ATOMS, MOLECULES, ELEMENTS AND COMPOUNDS

(a) Atoms, molecules, elements and compounds
Definitions and inter-relation with one another.

(b) The Law of conservation of matter, the law of constant proportions, the Law of multiple proportions, the Law of combining volumes, Dalton's atomic theory, Avogadro's hypothesis;
Definitions, experimental verifications and calculations.
Limitations of above Laws.

(c) Atomic mass scale: ^{12}C as the standard, Determination of the relative atomic and molecular masses by mass spectrometry (Details of mass spectrometry or calculations involved in mass spectrometry are not required). Comparison with Labcratory methods for the determination of these quantities.

(d) Relative densities and relationship with relative molecular mass Determination of molecular mass by victor Meyer method. Use of the simple gas Law, $P.V = nRT$, to determine relative molecular mass.

(e) Avogadro number; the mole as a fundamental unit in Chemistry. Application of the mole concept in volumetric analysis should be stressed; molarity and molality; relationship between the two.

NOTE:-

Students are expected to be able to prepare solutions of definite concentration and or to calculate the concentration of unknown solutions from prepared standard solutions.

2. GROSS FEATURES OF ATOMIC STRUCTURE

(a) Electrical nature of atom - electron, proton, and neutron from the works of Faraday, Goldstein, Thomson, Millikan, Becquerel (natural radioactivity) Moseley and Rutherford.

IJMB Chemistry Syllabus (cont'd)

Mathematical treatment of these experiments are not required. Qualitative treatment only.

(b) Atomic number, mass number, neutron number, Isotopes (detection and uses)
Convention: In writing nuclear symbols mass number and atomic number are to be written on the top left hand corner and bottom left hand corner, respectively

e.g. $^{235}_{92}U$ $^{16}_{8}O$

(c) Models of the atom: Qualitative descriptions:-

(i) Rutherford's atomic model; Electronic energy Levels - evidence from emission spectra (qualitative treatment only)

(ii) Bohr's atomic theory (only qualitative treatment of the basic postulates required) Arrangement of the electrons in the energy levels: Main Levels, sub-levels, orbitals; electron spin. Quantum numbers-principal, subsidiary, magnetic and spin. Shape and symmetry of S.P and d orbitals. Energy level diagrams. Aufbau principle, Pauli exclusion principle, Hund's rule and electronic configuration. Degeneracy of atomic orbitals and filling of orbitals.

(d) The periodic Law and Periodic Table
The Periodicity of electronic configuration Leading to periodicity of properties such as atomic radius, ionization energy, electronegativity electron affinity.
Classification into S,P,D, and f block elements
Horizontal, vertical and diagonal relationships to be mentioned.
(Periodic table giving symbol, atomic number and atomic mass
shall be provided to students at the time of examination).

IJMB Chemistry Syllabus:

3 CHEMICAL BONDING

Use of Lewis structures (electron - dot - formulae) to discuss

(a) Electrovalent (Ionic) bonds:

Importance of octet rule in explaining valencies, importance of ionization potential, electron affinity and electronegativity in predicting bond types.

Energy factor in the formation of ionic compounds; The Born-Haber cycle.

(b) COVALENT BONDS:

Comparison of electron dot structures for ionic, partially ionic, and covalent bonds. Valence bond description: Electron sharing and potential energy diagram; single, double and triple bonds, polar covalent bonds.

Eg: H_2S, H_2O, HCl etc.

Prediction of bond types using Fajan's rules and properties associated with bond types. The concept of resonance to rationalise the possible existence of multiple structures.

(c) COORDINATE COVALENT BONDS

Examples with Cu Salts, ammonium chloride, hydronium ion, ammonia/boron trifluoride complex.

(d) METALLIC BOND.

General properties of metals and explanation for them in terms of ' electron cloud' structure; eg.: metallic lustre, ductility, malleability, conductivity, cation formation. Brief comparison of electrons in atoms, molecules and metals in terms of energy levels.

(e) HYDROGEN BOND

Especially using hyrides of Groups V to VII: explanation of molecular association for H_2O and HF. Brief comparison with dipole/dipole effect on acetone/butane.

(f) VAN DER WAAL FORCES

Explanation in non polar molecules Eg: Helium. Relationship between strength of Van der Waal forces and Phase change temperature Eg. b.p. of inert gas and hydrogen halides; iodine and chlorine.

(g) MOLECULAR ORBITAL THEORY - QUALITATIVE DESCRIPTION

Comparison with valence bond theory: combination of atomic orbitals for hydrogen and helium to give bonding and antibonding orbitals; non-existence of Be_2.
Existence of N_2, O_2 & F_2. Introduction of p-orbital overlap and rules for electron distribution applied to second period molecules: Bond order calulations.

(h) DIPOLE MOMENTS

Qualitative determination and comparison for some molecules. Bond dipoles and molecular dipoles. No numerical problems to be given.

(i) SHAPE OF MOLECULES

Use of molecular dipole moments in predicting and/or rationalising molecular shapes e.g. CO_2 (linear) SO_2 (non-linear); The concept of bond angles and bond lengths (effect of atomic No., bond type, nature of group). Electron pair repulsion model: basic assumptions. Eg: Octet molecules:- CH_4, NH_4^+, H_2O, H_3O^+. non-Octet molecules: BF_3, $SnCl_2$, $HgCl_2$,

Reasons for deviation in bond angles from expected values.

4 STOICHIOMETRY, OXIDATION - REDUCTION - REACTIONS

Electronic concepts, half reactions. Oxidation number

Note:
Candidates will be expected to use the concept of oxidation numbers and of half-reaction equations to balance oxidation-reduction reactions.

5. CONCEPTS OF ACIDS AND BASES

Theories of Arrhenius, Lowry-Bronsted and Lewis. Water as solvent, strengths of acids and bases; hydration, hydrolysis and concept of strong and weak electrolytes.

B. PHYSICAL CHEMISTRY

1 STATES OF MATTER:

(a) Gases -Ideal

Boyle's Law, Charles' Law and the Absolute Temperature Scale-Dalton's Law of Partial Pressures, Graham's Law, General Gas Equation, Gay Lusac's Law of combining volumes; Arogadro's Law. The concept of molar volume . Value of Gas constant $R=8.31JK^{-1}\ mol^{-1}$

KINETIC MOLECULAR THEORY
Derivation of the expression $PV = 1/3\ nmc^2$ from the postulates of this theory and its application to gas laws.

REAL GASES
Qualitative account of deviations from ideal behaviour. Introduction of Van der Waal' equation (qualitative account)

(b) LIQUIDS

(i) Liquid as intermediate between gases and solids. Changes of state, Phase diagrams of one component system; cooling and heating

curves, supercooling. Vapour pressure and boiling point. Effect of nature of bonds on the variation of boiling point.

(ii) Solutions: Solution terminology; solubility of substances; vapour pressure of solutions, Raoults Law. Separation of Liquid mixtures by distillation or by cooling.

Colligative properties: Effect of non-volatile solutes on phase diagrams of pure solvents eg. E Elevation in boiling in boiling point, molal freezing point depression constant, and related calculations; Osmotic pressure.

Use of the expressions

(i) $\Delta T = K.\ m$

Where m = Molality

K = a constant; details of the constant K to be given

(b)

(ii) $\pi V = nRT$

No derivation of either equation is required.

NOTE

Deviation from Raoult's Law should be mentioned but no detailed study is required.

(c) SOLIDS

Atomic radii (Van der Waal's radii, covalent radii, metallic radii). Variation of atomic radii in groups and periods in the Periodic Table. Ionic radii - variation of ionic radii in groups and periods in the Periodic Table. Structure of ionic solids. Limiting radii ratios.

CRYSTALS Isomorphism, unit cell lattice energy, Born Haber cycle and related calculations. Lattice structure, super lattice and Lattice defects. Seven types of crystal systems with

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IJMB Chemistry Syllabus ('B' 1 cont'd)

(ii) (c) cont'd

examples - cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic. Classification of solids by the units that occupy the lattice points. Eg: Molecular, Ionic, Covalent and metallic. Students will not be required to carry out calculations involving molecular geometry.

2 THERMOCHEMISTRY

(a) Relationship between chemical energy and thermal energy. Exothermic and endothermic reactions. Effect of physical state on heat of reaction: Laboratory determination of heats of reactions and heats of formation. Thermochemical equation.

(b) Heat (or enthalpy) of formation, combustion, neutralisation, solution (including the effect of lattice energy on the heat of solution and the difference between integral heat of solution and heat of solution at infinite dilution), dilution, hydration, reaction and change of state.

(c) Hess's Law and its application.

(d) Bond disssociation energy and calculation of enthalpy with particualr reference to certain bonds. Eg. C - C, C=C, C≡C C-H, C=O, O-H

(e) The use of energy level diagrams for starting materials, transition states, intermediates, and products.

(f) Inadequacy of enthalpy data alone to predict spontaneity of a reaction. Entropy as a driving force in chemical reaction. Introduction of the idea of structural stability and thermal stability of products. Concept of free energy, enthalpy and entropy. Use of the derivation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ as a predictor of spontaneity.

IJMB Chemistry Syllabus ('B') 2 cont'd)

3 CHEMICAL KINETICS

(a) Overall reaction and elementary processes.

(b) Order and molecularity concept.

(c) 1st order rate Law. Analysis of experimental results for 1st order reactions

(i) for gaseous reactions when pressure measurements are observed

(ii) for homogeneous Liquid phase reactions e.g. acid hydrolysis of an ester.

(iii) for reactions in solution when a physical property is used. e.g. use of polarimeter to measure the angle of rotation.

(d) 2nd order rate law. Analysis of experimental results for 2nd order reactions.

(i) for gaseous reactions.

(ii) for reactions in solution.

(e) Reaction of any order - Analysis of experimental results. Differential method for analysis [illegible] - log Rate = log K + n log C.) - As a general relationship for use in various physical - chemical systems.

(f) Factors influencing the rate of reaction

(i) Concentration - Determination of rate Law by observing the effect of concentration on rate and related calculations.

(ii) temperature
Use of simple Collision theory to explain the effect of consentration and temperature.

(iii) Catalysis - qualitative treatment of types of catalysts and mode of action.

(g) Activation energy. Introduction of Arrhenius equation and the plotting of log K vs T^{-1} values obtained from experiment.

(h) Application of chemical kinetics in predicting mechanism of a reaction.

4. CHEMICAL EQUILIBRIUM

(a) Equilibrium Law and equilibrium constant. The general equilibrium expression as an experimental result. K should be expressed both in terms of pressure K_p, and in terms of concentration, K_c, Relationship between K_c and K_p. (no derivation required).
Dynamic nature of equilibrium, when $\Delta G_i = 0$. Determination of equilibrium concentration from known equilibrium constant of simple reaction.

Eg: $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
$CO + Cl_2 \rightleftharpoons COCl_2$; $H_2 - I_2 \rightleftharpoons 2HI$ etc

$\Delta G^\circ = -RT \ln K$ (no derivation required).

(b) Altering the position of equilibrium: Efect of changing concentration, temperature and pressure: Le Chatelier's principle. Examples to illustrate the principle.

(c) Dissociation constant Ka and Kb for weak acids and bases, Dissociation of water and ionic product of water, Kw; pH, POH, pKa and pKb; the relation PKa + pKb = pKw. Buffer solution - Mixtue of a weak acid and its salt and or weak base and its salt.
Derivation and application of Henderson - Hasselbrch equation.

$pH = pKa + \log \frac{salt}{Acid}$ and $POH = pKb + \log \frac{salt}{Base}$

Titration, and theory of acid-base indicators. Hydrolysis of salts. The relation $Kh = \frac{Kw}{Ka}$ and $Kh = \frac{Kw}{Kb}$
(Problems involving the above constants should be treated).

(d) Solubility product and common ion effect in relation to qualitative analysis. Determination of solubility of sparingly soluble salt in water and in presence of common ion.

IJMB CHEMISTRY SYLLABUS CONTINUES

5. ELECTROCHEMISTRY

(a) Explanation of oxidation - reduction reactions in terms of (i) oxidation number and (ii) electron transfer.

(b) Metallic conduction, electrolytic conduction; Electrolysis of some molten and aqueous salts. Electrolysis of molten NaCl, aqueous Na_2SO_4, molten cryolite and aqueous copper suphate using inert electrodes:
Electrolysis of aqueous copper sulphate using copper anode.

(c) Faraday's Laws of Electrolysis. Application to simple systems. Solutions of problems relating mass and current.

(d) Chemical changes to generate electric energy. galvanic cells. Study of some galvanic cells- Daniell Cell, Dry cell, storage cell; fuel cell Reduction potential and electrochemical series (Sign convention $Li^+ + e = Li - 3.06V$)

(e) Variation of change of free energy (ΔG) with concentration. Graphical explanation of the relationship $\Delta G = \Delta G^\circ + RT \ln K$, derivation of Nernst equation $E = E^\circ - \frac{0.059}{n} \log K$, hence

variation of cell potential with concentration, solution of problems. Determination of e.m.f of a cell when concentrations are not unity. Spontaneity of a cell reaction; $\Delta G = - EnF$ Calculation of free energy change (ΔG°) and equilibrium constant of a cell reaction.

(f) Corrosion of metals treated from the stand point of electron transfer. Prevention of corresion.

6. NUCLEAR CHEMISTRY

Stability of nucleus: Half - life as a measure of stability of nucleus; stability belts, types of radioactivity - natural and artificial radioactivity; radioactive alpha and beta particles, gamma rays, radioactive carbon dating, other uses, nuclear energy, nuclear fission, fusion, nuclear reactors as a means

of thermal power generation (General discussion, no details)

Simple nuclear reactions - nuclear x equations to be balanced in terms of both mass numbers and atomic numbers.

C. INORGANIC CHEMISTRY

INTRODUCTION

Emphasis should be placed throughout this part of the course on the application of the chemical concepts studied under General Chemistry (Section A) rather than on the presentation of the mass of facts on specific elements and their inorganic compounds. More specifically, the gradation of physical and chemical properties within the periods and groups of the periodic table should be stressed and explained in terms of such parameters as electronic structure ionization potential, electron affinity, electro-negativity, atomic or ionic size, and type etc.

HYDROGEN

Variable position of hydrogen in the Periodic Table. Occurrence; preparation of hydrogen from acid and water using active metals. Large scale preparation of hydrogen from water gas (only the outline). Atomic hydrogen and isotopes of hydrogen. Heavy water and its physical properties compared with ordinary water.

ALKALI AND ALKALINE EARTH METALS.

Position in the periodic Table.
Occurrence and electronic configurations. Their properties with emphasis on comparison within the groups in the light of physical and chemical properties. Nature of their compounds - oxides, hydrides, halides, carbonates and bicarbonates.
Extraction of the metals (only principles)

BORON AND ALUMINIUM GROUP

Occurrence, electronic configuration, their general properties. Simple treatment of their oxides, hydrides (only borane and diborane for boron) and halides.

CARBON GROUP

Occurrence and electronic configuration, group comparison with emphasis on metallic and non metallic character and also differences between carbon and silicon on one side and germanium, tin and lead on the other side. The unique properties of carbon. e.g. Catenation-ionization

potential method or inert-pair effect or both could be used to explain the unique character of carbon. Simple treatment of oxides, hydrides, halides and sulphides. Differences between diamond and graphite. Differences in structure and hence in properties between carbon dioxide and silicon dioxide.

5. General comparison of oxygen, nitrogen and halogen groups to bring out similarities and differences in the chemical and physical properties.

Relationship of the properties in the formation of oxides, nitrides, halides should be restricted to compounds of period II and III elements. Interhalogen compounds may be mentioned but no details are required.

6. The first transition metal series:

Electronic structure, and relationship to variable oxidation states of the elements, colour, metallic properties and complex formation. Examples are to be given using their hydrides, halides, and oxides wherever possible. Differences in the reactivities of members of the group should be related to their electronic structures and comparisons made wherever possible to the elements of periods II and III studied earlier.

D. ORGANIC CHEMISTRY

Mechanisms should be discussed whenever applicable and IUPAC system of nonmenolature should be used.

1. (a) Introduction to organic chemistry
   - brief review of the development of organic chemistry

   (b) Molecular compounds (aliphatic, aromatic, cyclic, unsaturated and saturated)

   (c) Purification of organic compounds
   - purity and the physical characteristic
   - Determination of melting and boiling points.
   - Crystallization and recrystallization
   - Simple distillation
   - Fractional distillation (e.g. benzene-toluene)
   - Other distillation techniques (steam and vacuum)
   - Liquid extraction & - Sublimation

IJMB CHEMISTRY SYLLABUS (Cont'd)

- Chromatographic separation: paper and thin layer

(d) Detection and determination of elements (C,H,N,S and halogens except F)
- qualitative (sodium fusion text)
- quantitative (carius and Dumas methods; experimental details not required)
- calculation of empirical formula

(e) Calculation of molecular formula, when molecular mass or vapour density is given or calculated from depression of freezing point, from a Volumetric method, combustion experiment or Victor Meyer's method.

(f) IUPAC nomenclature-Introduction

2. Electronic concepts in organic compounds

(a) - hybridization-sp, sp^2, sp^3
- characterisation bond types in H_3C-CH_3, $H_2C=CH_2$ and $HC\equiv CH$
- covalent bonding, σ and π bonds.

(b) Effect of structure on reactivity.
- polarity of bonds; dipole moments
- molecular association: H-bonding
- Inductive effect
- elecromeric effect
- steric effect.

3. Use of concepts in (2) to discuss reactivity of, and mechanism of reaction in various organic compounds.

(a) Aliphatic Hydrocarbons
ALKANES
- nomenclature
- homologous series - general formula
- alkyl groups (up to pentyl)
- structural isomerism (up to pentane)
- physical properties (gradation)
- chemical properties

IJMB CHEMISTRY SYLLABUS (cont'd)

(i) reactivity-explanation for inertness
(ii) mechanism of chlorination of CH_4
(iii) nitration
(iv) oxidation-combustion

- Preparation of alkanes

(i) from CO, CO_2 and H_2
(ii) from alkenes and alkynes - reduction
(iii) from metallic carbides
(iv) from alkyl halides and Grignard reagents
(v) from carboxylic acids.

- Crude oil as main source of hydrocarbons
- Simple cycloalkanes: general properties (cyclopropane to cyclohexane) shapes and stereochemistry of molecules.

Alkenes

- nomenclature (dienes and trienes, too)
- physical properties
- geometric isomerism: cis-trans influence on the properties
- preparation of alkenes

(i) by removal of H_2O from alcohols
(ii) byremoval of HX from alkyl halides
(iii) by removal of halogen from dihalides
(iv) Kolbe method on succinic acid
(v) cracking of petroleum

- Chemical properties

differences in reaction involving alkenes and alkenes related to the nature of single and double bonds:

(i) mechanism of addition reaction of alkenes e.g. bromination
(ii) Markonikoff's rule
(iii) oxidation with O_2, H_2O2, $Cr_2O_7^{2-}$, OsO_4, MnO_4^-
(iv) ozonization - ozonide formation
(v) hydrogenation
(vi) polymerisation (brief introduction)

Alkynes

- nomenclature
- physical properties
- preparation from dihalides and tetrahalides
- properties

metallic deriyatives: acetylide formation

(Cu, Ag and Na acetylides)

- Ethyne (acetylene)
  - properties
  - reactions
  - (i) mechanism of addition of water
  - (ii) mechanism of addition of H_2 and HX
  - (iii) Reduction
  - conversion of ethyne to benzene

(b) AROMATIC - Hydrorabons

- Structure and names of simple aromatic compounds
  - benzene and functional dertivatives
  - naphthalene and anthracene
- Benzene
  - physical properties
  - Chemical properties
  - isomerism (1:2, 1:3, 1:4 isomers)
  - Contrasting benzene with aliphatic unsaturated compounds
  - Aromaticity
- Resonance
  - orbital model of benzene
  - comparison with hypothetieal cyclohexatriene
  - resonance energy
  - difference between aromatic and unsaturated compounds
  - rules for resonance
  - resonating structures of bezene and directive influence of functional groups.

4. TYPES OF ORGANIC REACTIONS

(a) Substitution reactions

- mechanism of SN_1
- mechanism of SN_2
- structural effects of alkyl substituents
- effect of leaving groups
- nucleophilic reagents
- solvent effect

IJMB CHEMISTRY SYLLABUS (Cont'D)

(b) Elimination reaction

- mechanism of E_1
- mechanism of E_2
- elimination versus displacement

(c) Addition reactions

- nucleophilic addition to polar double bonds
- electrophilic addition to non polar double bonds.

(d) Rearrangement reactions

- Brief mention only.

5. ALKYL HALIDES

- nomenclature
- preparation
  - (i) alkene + HCl
  - (ii) alcohol + HCl
  - (iii) alcohol + PCl_5 or PCl_3

Properties

- (i) nucleophilic substitution reaction with Grignard reagent, Ag_2O/H_2O Aqueous KOH, $AgNO_3$, $AgNO_2$, KCN, KSH, NH_3
- (ii) Elimination reaction with alcoholic potash

- halogen derivatives of unsaturated hydrocarbons (allyl derivatives)
- Name and structure of $CHCl_3$, and CHI_3,
- Mention and use of fluorochloromethanes
- Halogen derivatives of aromatic compounds (e.g. chloro derivative of benzene and toluene)
  - physical properties
  - preparation
  - chemical properties
    - (i) Grignard
    - (ii) Wurtz-Fittig
    - (iii) Ulmann
    - (iv) Aryl lithium
    - (v) Reactions with amines

IJMB CHEMISTRY SYLLABUS (Cont'd)

6. HYDROXY COMPOUNDS

Alcohols
- Introduction - primary, secondary, tertiary
- nomenclature
- properties of hydroxyl groups
- physical properties (hydrogen bonding)
- preparation

(i) from alkenes
(ii) from carbonyl compounds
(iii) from carboxylic acids
(iv) by Grignard from carbonyl cpds
(v) by hydrolysis of alkyl halides
(vi) Industrial methods of preparation of ethanol by fermentation.

- Chemical properties
  (i) Ether formation
  (ii) Williamson synthesis
  (iii) Est er formation
  (iv) formation of alkenes
  (v) reaction with alkyl halides (alcoholysis)
  (vi) oxidation
  (vii) Acidic and basic properties (alkoxide and alkoxonium ion)
- Unsaturated alcohols (allyl alcohols): Just mention
- polyhydroxy alcohols - glycol and glycerol (mention only the source)
- phenols: comparison of the properties of alcohols with those of phenol.

7. CARBONYL COMPOUNDS

- polarisation of carbonyl compounds
- Structure and nomenclature
- Aldehydes
  - Preparation
    (i) oxidation of alcohol
    (ii) ozonolysis of alkenes
    (iii) Reduc tion of acids
    (iv) Addition of H_2O to alkynes

- Ketones
  - Preparation
    - (i) Oxidation of sec. alcohol
    - (ii) from carboxylic acids
    - (iii) from aldehydes
    - (iv) Ozonolysis of alkenes
    - (v) Decarboxylation of calcium salts
    - (vi) direct oxidition of hydrocarbons
  - Physical properties of aldehydes and ketones
    - homologous series
  - Chemical properties of aldehydes and ketones
    - Addition reactions with Grignard, HCN, $NaHSO_3$, NH_2, alcohol and the reaction mechanism
    - condensation reactions with methyl amine, hydrazine, hydroxyl amine, phenyl hydrazine
    - aldol condensation
    - polymerisation of aldehydes (para formaldehyde, metaldehyde)
    - oxidation of carbonyl compound with $KMnO_4$.
    - Reduction of carbonyl compounds
      - (i) to alcohols by H_2, $NaBH_4$, $LiAlH_4$
      - (ii) to hydrocarbon (Clemenson)
    - Canizzaro reaction
    - tautomerism
    - Tests for aldehydes and ketones
      - Tollens, Fehling, Haloform reaction
  - Aromatic aldehydes and ketones
    - Comparison of benzaldehyde and benzophenone with the aliphatic analogue.

8. ACIDS

- Structure and nomenclature
- physical properties (hydrogen bonding)
- Resonance effect-acidity. Comparison with the alcohols.
- Preparation
  - (i) oxidation of alcohols& aldehydes
  - (ii) hydrolysis of nitriles
  - (iii) Grignard + C_2
- Chemical properties
  - (i) Esterification
  - (ii) Refuction with $LiAlH_4$.

IJMB CHEMISTRY SYLLABUS (Cont'd)

(iii) decarboxylation of acids
(iv) kolbe electrolysis
-Acid Derivatives
- Acyl halides
- Anhydries
- Amides
- nitriles
- Esters
methods of preparation and chemical reactions)
- Dicarboxylic acid (oxalic, malonic, maleic and fumaric)
- aromatic acids (benzoic, salicylic, phthalic)
- fatty acids-fats
- (only brief mention of the above three groups)

9.AMINES

- Structure and nomenclature
- physical propertics (Hydrogen bonding)
- basicity of amines
- methods of preparation
(i) $RX + NH_3$
(ii) alcohols + NH_3 + $ZnCl_2$
(iii) Hoffman degradation
(iv) Curtius rearrangement
(v) Beckmann rearrangement
(vi) Reduction of nitro & cyano compounds
- Chemical properties
(i) with HNO_2
(ii(acylation
(iii) salt formation
(iv) oxidation
- Method to distinguish the types of amines
(any of the three methods)
- distinction between aniline and aliphatic amine

10. CARBOHYDRATES

- Structure and nomenclature
(only straight chain structure is required)
- monosaccharides: glucose and fructose
reducing reactions and osazone formation
- disaccharides: sucrose
- polysaccharides: starch and cellulose

IJMB CHEMISTRY SYLLABUS (Cont'd)

11. AMINO ACIDS & PROTEINS

- Short introduction to amino acids and proteins.
- Behaviour of amino-acids and proteins in an electricfield; zwitterions

12. POLYMERS

- Nature and examples of natural and synthetic polymers, (cellulose, rubber, nylon, polythene etc); Sources of monomers for various polymeric materials. Uses of Polymers.

IJMB CHEMISTRY SYLLABUS PRACTICAL WORK

1. WEIGHING PRACTICES
2. TITRIMETRIC ANALYSIS
   (a) ACID - Base Titration.
      (i) Preparation of a standard NaOH solution. The use of this solution in standardising a given solution of dilute strong acid e.g. dil H_2SO_4
      (ii) Standardisation of a given oxalic acid solution using a standard sodium hydroxide solution
      (iii) Determination of the amount of NaoH and Na_2CO_3 in a given mixture - the use of two indicators.
      (iv) Determination of the concentrations of $NaHCO_3$ and Na_2CO_3 in a given mixture - the use of two indicators.
   (b) REDOX TITRATIONS
      (i) Standardisation of iron II) solution using solutions of $KMnO_4$ and standard Oxalic acid solution-Double titration.
      (ii) Standardisation of $MKrO_4$ solution using Oxalic acid and standard sodium hydroxide solution.
      (iii) Estimation of Oxalicacid and sodium Oxalate in a given mixture.
      (iv) Standardisation of given sodium thiosulphate solution using standard KIO and determination of number of moles of water of crystallisation in the hydrated sodium Thiosulphate.

IJMB CHEMISTRY SYLLABUS (Cont'd)

(v) Determination of percentage purity of an impure sample of copper sulphate ($CuSO_4 \cdot 5H_2O$) solution using sodium thiosulphate and standard potassium permanganate solution.

3. Determination of Enthalphy of reaction e.g. neutralisation
4. Partition coefficient of Iodine between water and another solvent. e.g. CCl_4
5. CHEMICAL KINETICS
   (i) Rate of hydrolysis of an ester e.g. methyl acetate.
   (ii) Rate of reaction between sulphite and Iodate ion (Clock experiment)
   (iii) Determination of activation energy for the reaction.
   $BrO^-_3 + 5Br^- + 6H_3O^+ \longrightarrow 3Br_2 + 9H_2O$
6. Depression of Freezing point in binary mixtures (e.g. Rast's method)
7. Determination of the solubility of a sparingly soluble salt (e.g. $Ca(OH)_2$)
8. Distillation (simple and steam distillation)
9. Qualitative in-organic analysis-Group analysis of In-organic salts.
   (a) In-organic anions
   CO_3^{2-}, HCO_3^-, S^{2-}, NO_2^-, Cl^- Br^-, I^-, NO_3^-, SO_4^{2-}
   (b) Inorganic Cations
   Ag^+ Pb^{2+} Hg^+ Hg^{2+} Cu^{2+} Cd^{2+} Sn^{2+} Sn^{4+}
   Fe^{2+} Fe^{3+} Al^{3+} Cr^{3+} Ni^{2+} Co^{2+}, Zn^{2+}
   Mn^{2+} Ba^{2+} Ca^{2+} Mg^{2+} Na^+ K^+ (NH_4^+)
10. Qualitative tests of the Functional groups mentioned in the theory.
11. Preparation of simple transition metal complex
12. Acetylation and Benzoylation.

APPENDIX 3.1

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TEST A

PROBLEM-SOLVING IN ORGANIC REACTION MECHANISM

STUDENT'S INDEX NUMBER _____

SCHOOL _____

SEX _____

AGE _____

Dear Student,

This booklet consists of fifty multiple-choice questions. Part I consists of questions 1-12 and Part II, questions 13-40. The format of Part I is slightly different from Part II, but the underlying principle for both is the same.

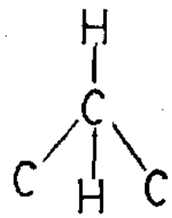
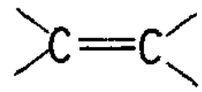
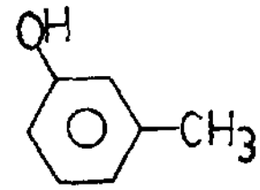
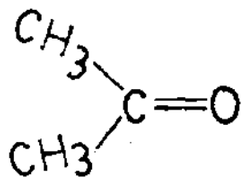
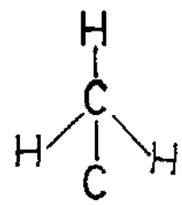
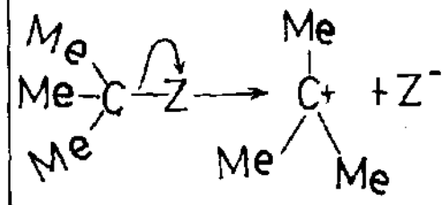
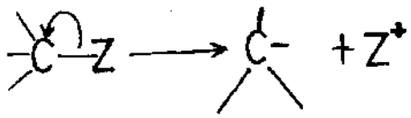
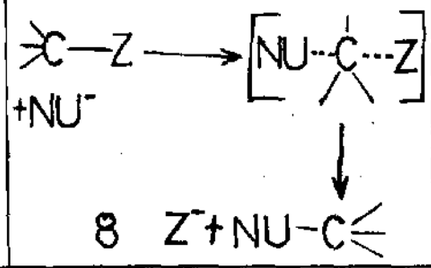
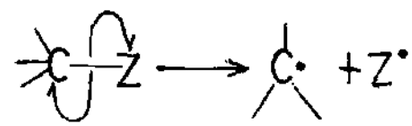
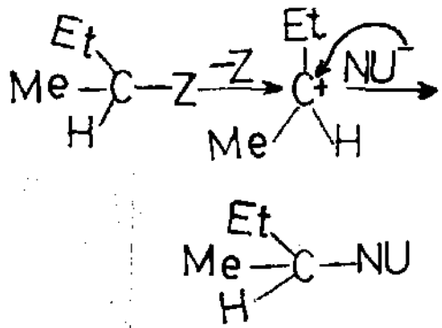
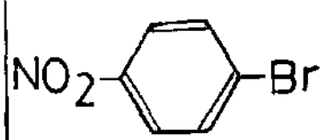
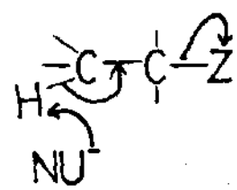
For each question, you have a choice of answers, only one of which is correct. You have to decide which that is. You are provided with a separate answer sheet on which to enter all answers.

Attempt all questions, and ensure that you make your entries very clearly.

Thank you.

A.A.M. Shaibu

TABLE 1: TO BE USED FOR QUESTIONS 1-12

 1	 2	 3
 4	 5	 6
 7	 8	 9
		 12

SECTION A

PART I: TIME ALLOWED: 30 minutes

Questions 1-12 are based on the information given on Table I. Select the box from the table that most appropriately answers each question, and put "X" in the corresponding box provided in the answer sheet. You can mark only one box for each question.

e.g. In which box do you find an aromatic compound with an electron releasing group?

The answer is box 3 which is marked thus:

1	2	3	4	5	6	7	8	9	10	11	12
		X									

Now continue in the same way, using the answer sheet provided.

In which box do you find:

1. a compound that is likely to undergo electrophilic addition across a non-polar double bond?
2. a secondary group?
3. a homolytic dissociation process?
4. an elimination process?
5. a primary group?
6. a compound that is likely to undergo nucleophilic addition across a polar double bond?
7. an S_N^2 reaction mechanism?
8. an aromatic compound with meta-substituent?
9. a tertiary carbonium ion?
10. a carbanion?
11. an aromatic compound that can undergo nucleophilic aromatic substitution reaction?
12. an S_N^1 reaction mechanism?

AHMADU BELLO UNIVERSITY
KASHIM IBRAHIM

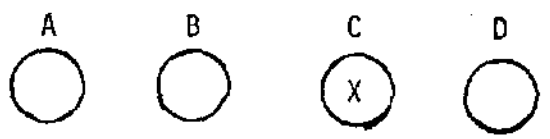
PART II

Each of the questions 13-40 has four options as answers. Only one of these is correct. Select the correct one and put "X" in the circle immediately below the letter on the answer sheet that corresponds with your choice. Here is an example for you to follow:

Which of the following elements are present in cyclopropane?

(A) carbon and oxygen
(B) hydrogen and oxygen
(C) carbon and hydrogen
(D) carbon, hydrogen and oxygen

On the answer sheet you will find:



The correct answer is C, so an "X" is put in the circle immediately below it as shown above.

Now attempt the questions in the same manner:

13. The electrophile that is responsible for nitration of benzene in concentrated sulphuric acid medium is normally:

(A) NO^+
(B) NO_2^+
(C) NO_3^+
(D) $N_2O_3^+$

14-16. For these three reactions, indicate which reagent is required to carry out the conversion.

14. $C_6H_5COOH \longrightarrow C_5H_5COCl$

(A) HCl
(B) NaOCl
(C) Cl2/CCl4
(D) SOCl2

15. $C_6H_6 \longrightarrow C_6H_5NO_2$

(A) HNO_2/conc. HCl

(B) HNO_3/conc. HCl

(C) HNO_2/conc. NH_3

(D) HNO_3/conc. H_2SO_4

16. $C_6H_5CH_2CH_2Br \longrightarrow C_6H_5CH{=}CH_2$

(A) Conc. H_2SO_4

(B) Alcoholic NaOH

(C) Alcoholic NH_3

(D) Alcoholic $K_2Cr_2O_7$

17. By what name is the following reaction usually known?

$$C_6H_6 + RCOCl \xrightarrow{AlCl_3} C_6H_5COR + HCl$$

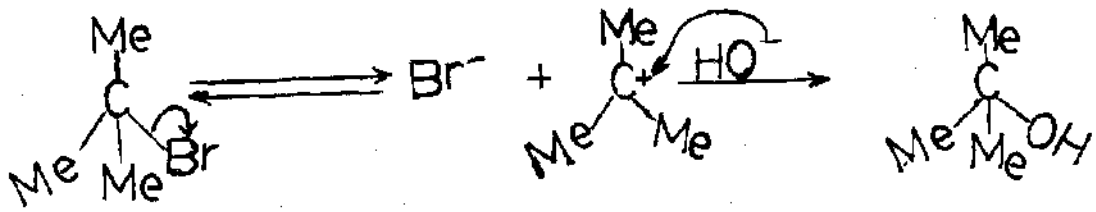
(A) Hofmann reaction

(B) Friedel-crafts alkylation

(C) Friedel-crafts acylation

(D) Ulmann reaction

18. Consider the reaction below, following the mechanism indicated:



Addition of KBr to the aqueous reaction system will:

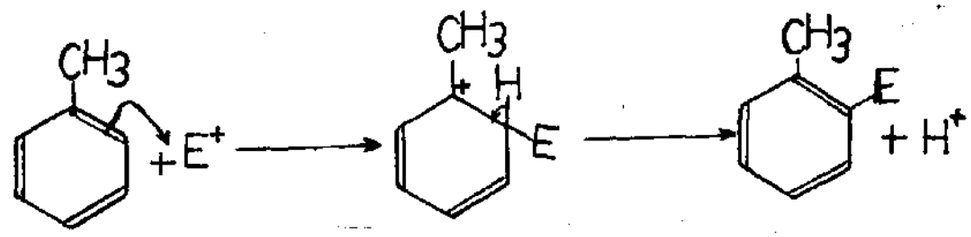
(A) increase the rate of reaction

(B) decrease the rate of reaction

(C) leaves the rate of reaction unaffected

(D) makes the rate of reaction impossible to determine.

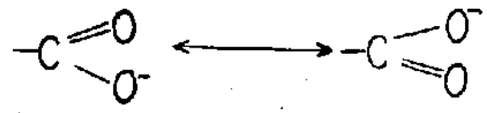
19.



The above reaction is an example of:

(A) rearrangement reaction
(B) electrophilic addition
(C) nucleophilic addition
(D) electrophilic substitution

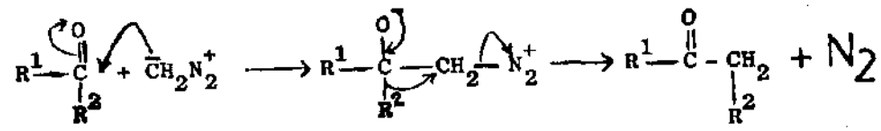
20.



The representation of molecular structures by more than one molecular structural forms as shown above is usually described as:

(A) conformation
(B) migration
(C) mesomerism
(D) isomorphism

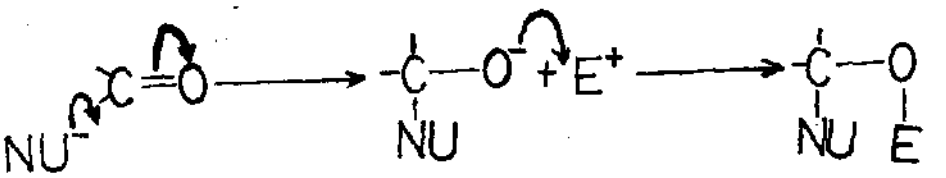
21.



Consider the above reaction, it is an example of:

(A) rearrangement
(B) substitution
(C) addition
(D) elimination

22.



The above reaction is an example of:

(A) electrophilic addition

(B) nucleophilic substitution

(C) electrophilic substitution

(D) nucleophilic addition

23. In which of the following compounds can the carbon atom said to be SP^3 hybridised?

(A) CH_2O

(B) CH_2N_2

(C) $CHCl_3$

(D) CO_2

24. Which of the following statements is true?

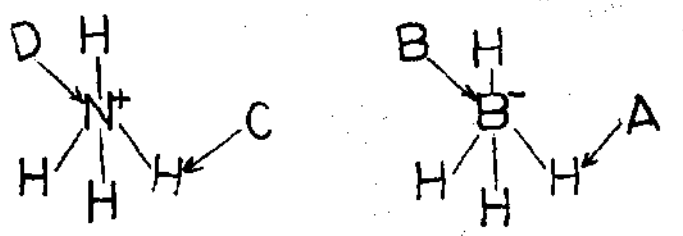
(A) An electrophile reacts by donating an electron pair.

(B) All Lewis acids are nucleophiles

(C) All electrophiles are cationic

(D) A nucleophile reacts by donating an electron pair

25. Which of the following arrows point to a nucleophilic site?



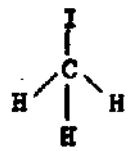
A

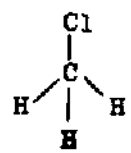
B

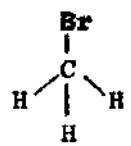
C

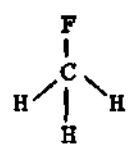
D

26.

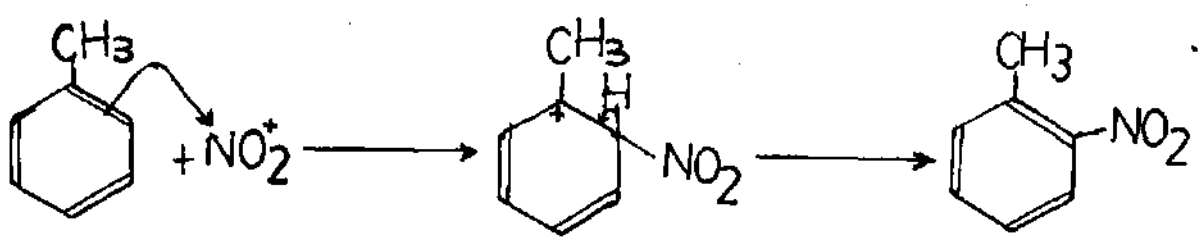
(A) 

(C) 

(B) 

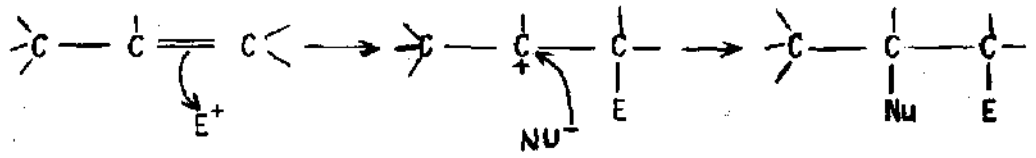
(D) 

In which of the above compounds does the carbon atom have the highest electron density?

27. 

The above reaction is an example of:

(A) nucleophilic addition
(B) electrophilic addition
(C) nucleophilic substitution
(D) electrophilic substitution

28. 

The reaction shown above is an example of:

(A) electrophilic substitution
(B) electrophilic addition
(C) elimination reaction
(D) nucleophilic addition

29. 

The above reaction is an example of:

(A) rearrangement

(B) nucleophilic addition

(C) electrophilic addition

(D) nucleophilic substitution

30. R^1COR^2 : R^1 and R^2 are alkyl groups.

The molecule shown above is an example of:

(A) an ester

(B) an ether

(C) a ketone

(D) an anhydride

Questions 31 and 32 refer to Fig. I



Fig. I

31. Fig. I represents the molecular structure of:

(A) butyne

(B) butene

(C) butadiene

(D) cyclobutane

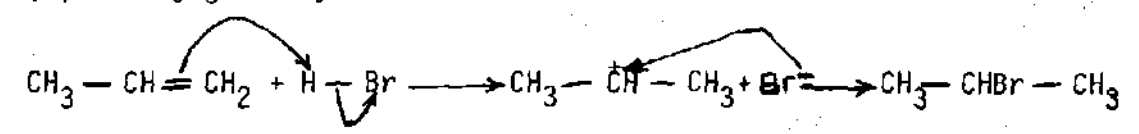
32. Compounds with molecules of the structure shown in Fig. I are said to have:

(A) an aromatic system

(B) a heterocyclic system

(C) a hyperconjugated system

(D) a conjugated system.

33. 

The above reaction is an example of:

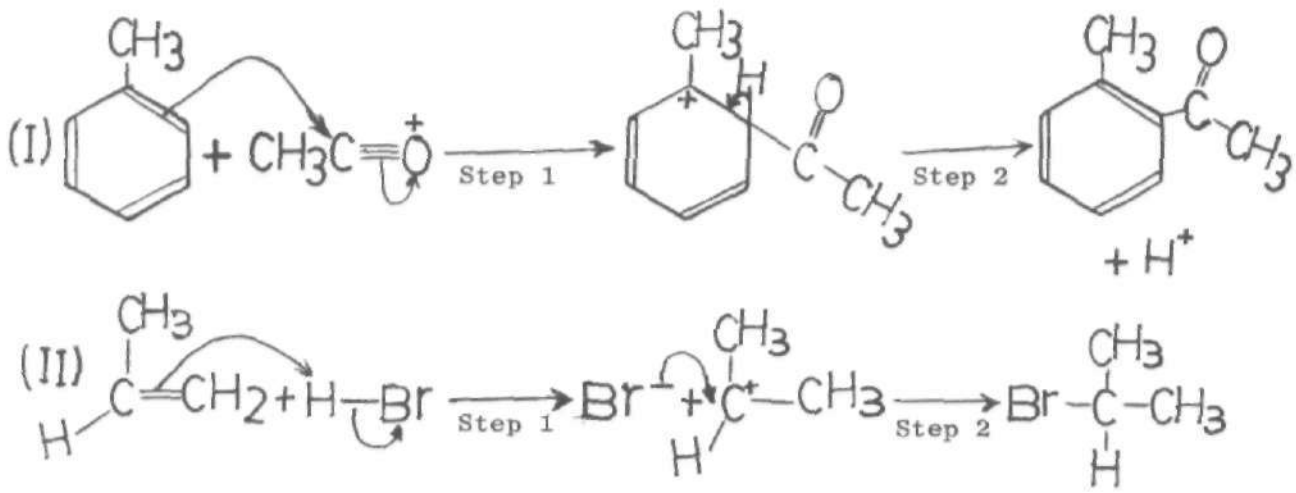
(A) electrophilic addition

(B) nucleophilic addition

(C) nucleophilic substitution

(D) elimination reaction

Questions 34 and 35 refer to reactions I and II



34. In reaction I and II shown above, step 1 in each reaction is:

(A) an electrophilic attack on the hydrocarbon
(B) a rearrangement of the hydrocarbon
(C) a nucleophilic attack on the hydrocarbon
(D) *none of the above*

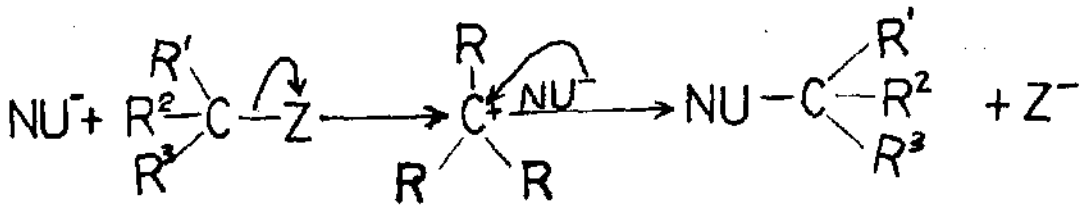
35. Step 2 in reaction I is:

(A) a substitution process
(B) an elimination process
(C) *an addition process*
(D) *a rearrangement process*

36. $CH_3 - CH = CH_2$ (1.) $\quad CH_2 = CH_2$ (2.) $\quad CH_2 = CHCl$ (3.)

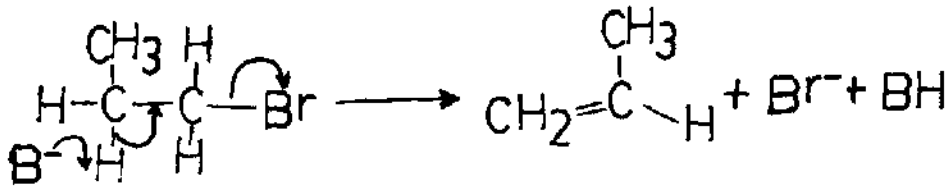
Consider the three compounds above; which box in the table below shows the increasing order of relative ease in which HBr adds under polar conditions to them.

A	B	C	D
1 < 3 < 2	1 < 2 < 3	3 < 2 < 1	2 < 3 < 1

37. 

The reaction mechanism shown above is an example of:

(A) E2
(B) E1
(C) SN^2
(D) SN^1

38. 

The reaction mechanism shown in the above reaction is an example of:

(A) SN^1
(B) SN^2
(C) E1
(D) E2

Questions 39 and 40 refer to Fig. 2

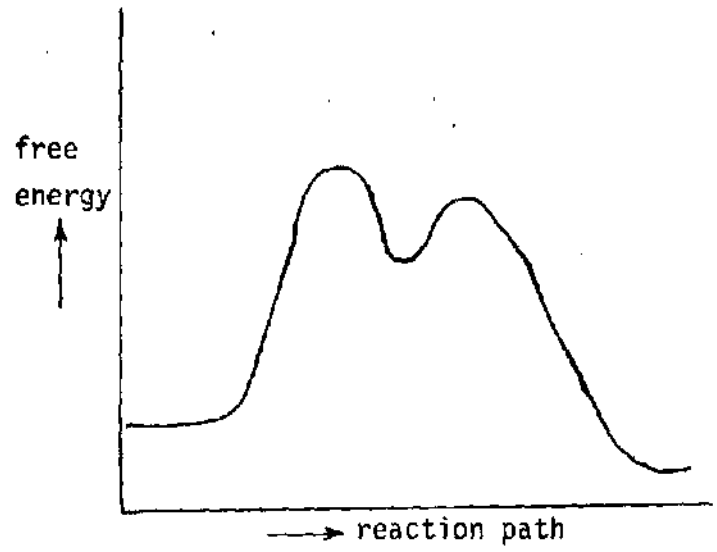


Fig. 2

39. If the above diagram (Fig. 2) represents the energy profile of the reaction:



; then:

(A) first step is rate-limiting
(B) second step is rate-limiting
(C) both steps are rate-limiting
(D) none of the steps is rate-limiting

40. Fig. 2 most likely represents the reaction progress of:

(A) E2 mechanism
(B) SN^2 mechanism
(C) SN^1 mechanism
(D) all of the above

APPENDIX 3.2

ANSWER SHEET

STUDENT'S INDEX NUMBER: _____

SCHOOL: _____

SEX: _____

AGE: _____

QUESTIONS	1	2	3	4	5	6	7	8	9	10	11	12
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												

	A	B	C	D
13.	○	○	○	○
14.	○	○	○	○
15.	○	○	○	○
16.	○	○	○	○
17.	○	○	○	○
18.	○	○	○	○
19.	○	○	○	○
20.	○	○	○	○
21.	○	○	○	○
22.	○	○	○	○
23.	○	○	○	○
24.	○	○	○	○
25.	○	○	○	○
26.	○	○	○	○
27.	○	○	○	○
28.	○	○	○	○
29.	○	○	○	○
30.	○	○	○	○
31.	○	○	○	○
32.	○	○	○	○

	A	B	C	D
33.	○	○	○	○
34.	○	○	○	○
35.	○	○	○	○
36.	○	○	○	○
37.	○	○	○	○
38.	○	○	○	○
39.	○	○	○	○
40.	○	○	○	○

APPENDIX 3.3

University of East Anglia

School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ

Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH

TEST B

PROBLEM-SOLVING IN ORGANIC REACTION MECHANISM

STUDENT'S INDEX NUMBER _____

SCHOOL _____

SEX _____

AGE _____

Dear Student,

The following questions form the second part of the test on organic reaction mechanisms.

Please answer all the questions in the space provided immediately after each question. Show all the steps in your solution as clearly as possible.

Immediately following each question is a four-item questionnaire. Complete it as soon as you have attempted the question.

There is also a six-item questionnaire at the end of the problems; it is required that you respond to them as well.

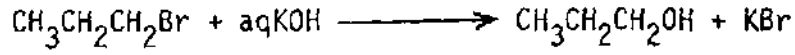
Thank you.

A.A.M. Shaibu

SECTION B

ANSWER ALL QUESTIONS TIME ALLOWED: 2½ hours

1. Considering structural and solvent factors, outline the most probable reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:



QUESTIONNAIRE

Put "X" in the box that corresponds to your opinion.

1. Are you familiar with this problem?

YES	NO

2. How did you find solving the problem?

DIFFICULT	EASY

3. How confident are you that your answer is correct?

CONFIDENT	NOT CONFIDENT

4. If you had difficulties in solving this problem, which <u>one</u> of the followin reasons mostly accounts for your difficulty?

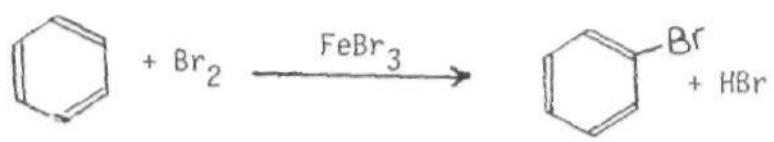
(i)	I do not have the grasp of the basic chemical knowledge	☐
(ii)	I knew the facts, but I did not know how to apply them to arrive at a solution.	☐
(iii)	I cannot understand the question, so I was not able to proceed to solve it.	☐
(iv)	I was never taught this.	☐
(v)	I got mixed up along the way.	☐

If any other reasons, state them briefly.

_____

_____

2. Outline the mechanisms of the reactions of bromine with benzene and with ethene; and briefly explain why a catalyst is needed for the first reaction but not with the second. The reactions are:

(I) 

(II) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

QUESTIONNAIRE

Put "X" in the box that corresponds to your opinion.

1. Are you familiar with this problem?

YES	NO

2. How did you find solving the problem?

DIFFICULT	EASY

3. How confident are you that your answer is correct?

CONFIDENT	NOT CONFIDENT

4. If you had difficulties in solving this problem, which <u>one</u> of the following reasons mostly accounts for your difficulty?

(i) I do not have the grasp of the basic chemical knowledge ☐

(ii) I knew the facts, but I did not know how to apply them to arrive at a solution. ☐

(iii) I cannot understand the question, so I was not able to proceed to solve it. ☐

(iv) I was never taught this. ☐

(v) I got mixed up along the way. ☐

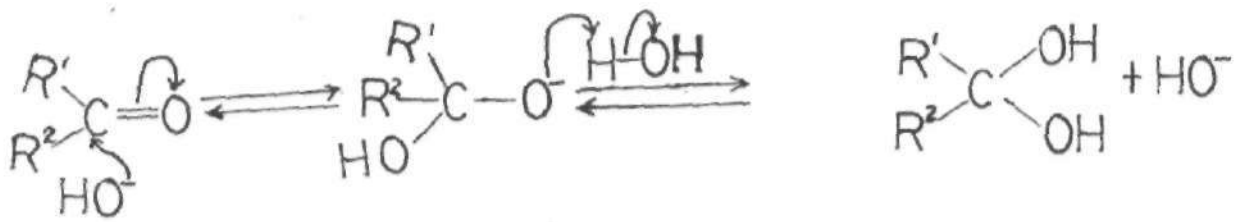
If any other reasons, state them briefly.

_____

_____

_____

3. Hydration of ketones is a reversible reaction resulting in the formation of the hydrate. In alkaline solution, the mechanism is as follows:



The equilibrium is usually in favour of the ketone. Starting from the hydrate, use relevant equation(s) to discuss the mechanism of the reverse process in alkaline solution.

Note: The forward reaction is an example of addition while the reverse reaction is an example of elimination.

QUESTIONNAIRE

Put "X" in the box that corresponds to your opinion.

1. Are you familiar with this problem?

YES	NO

2. How did you find solving the problem?

DIFFICULT	EASY

3. How confident are you that your answer is correct?

CONFIDENT	NOT CONFIDENT

4. If you had difficulties in solving this problem, which <u>one</u> of the following reasons mostly accounts for your difficulty?

(i) I do not have the grasp of the basic chemical knowledge ☐

(ii) I knew the facts, but I did not know how to apply them to arrive at a solution. ☐

(iii) I cannot understand the question, so I was not able to proceed to solve it. ☐

(iv) I was never taught this. ☐

(v) I got mixed up along the way. ☐

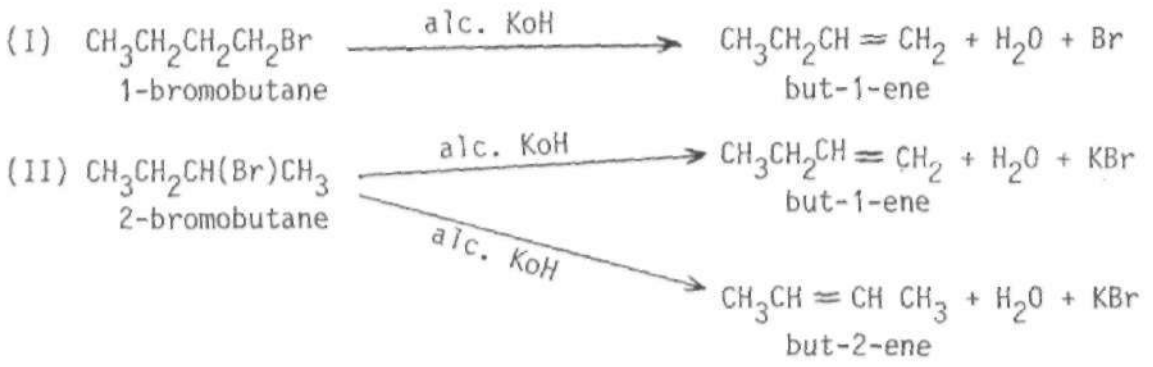
If any other reasons, state them briefly.

_____

_____

4. Using the relevant mechanisms of the respective reactions

(a) Explain why 1-bromobutane forms only one isomer, while 2-bromobutane forms three isomers respectively, when treated with an alcoholic solution of potassium hydroxide. The reactions are as follows



Note: Work out the third isomeric butene from reaction II.

(b) What name is usually given to the mechanism that you have described?

QUESTIONNAIRE

Put "X" in the box that corresponds to your opinion.

1. Are you familiar with this problem?

YES	NO

2. How did you find solving the problem?

DIFFICULT	EASY

3. How confident are you that your answer is correct?

CONFIDENT	NOT CONFIDENT

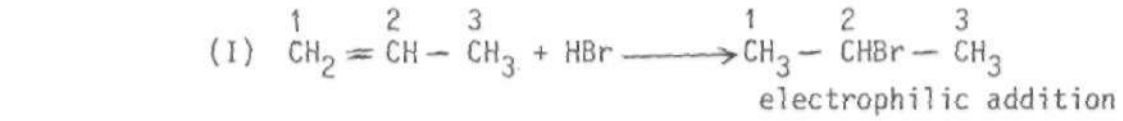
4. If you had difficulties in solving this problem, which <u>one</u> of the followi reasons mostly accounts for your difficulty?

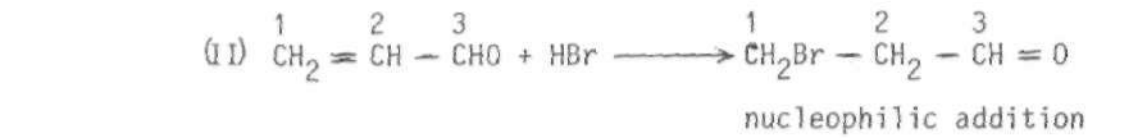
(i)	I do not have the grasp of the basic chemical knowledge	☐
(ii)	I knew the facts, but I did not know how to apply them to arrive at a solution.	☐
(iii)	I cannot understand the question, so I was not able to proceed to solve it.	☐
(iv)	I was never taught this.	☐
(v)	I got mixed up along the way.	☐

If any other reasons, state them briefly.

---

5. Consider reactions I and II below in which HBr adds across the carbon-carbon olefinic bonds:





Outline the mechanisms of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Note: -CHO is an electron withdrawing group.

QUESTIONNAIRE

Put "X" in the box that corresponds to your opinion.

1. Are you familiar with this problem?

YES	NO

2. How did you find solving the problem?

DIFFICULT	EASY

3. How confident are you that your answer is correct?

CONFIDENT	NOT CONFIDENT

4. If you had difficulties in solving this problem, which <u>one</u> of the following reasons mostly accounts for your difficulty?

(i) I do not have the grasp of the basic chemical knowledge ☐

(ii) I knew the facts, but I did not know how to apply them to arrive at a solution. ☐

(iii) I cannot understand the question, so I was not able to proceed to solve it. ☐

(iv) I was never taught this. ☐

(v) I got mixed up along the way. ☐

If any other reasons, state them briefly.

_____

_____

5. Rank the problems in the order of how difficult you found them, putting "1" for the most difficult, "2" for the next most difficult and so on to the easiest.

QUESTION ONE	QUESTION TWO	QUESTION THREE	QUESTION FOUR	QUESTION FIVE

6. How much do you like organic chemistry?

VERY MUCH	NOT MUCH	NOT AT ALL

7. How much to you like learning organic chemistry from a mechanistic approach?

VERY MUCH	NOT MUCH	NOT AT ALL

8. How much is chemistry a necessary requirement for your proposed career?

VERY MUCH	NOT MUCH	NOT AT ALL

9. How much is chemistry (as a subject) boring to you?

VERY MUCH	NOT MUCH	NOT AT ALL

10. How much has your O-level education in chemistry helped to prepare you for your present course?

VERY MUCH	NOT MUCH	NOT AT ALL

APPENDIX 4

University of East Anglia

From Dr. R.A.Y. Jones
Chemical Education Sector

School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ England.

Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH

21st March 1985

The Principal

Dear Sir,

Mr. A.A.M. Shaibu is at present a Ph.D research student in this University. He is a chemistry lecturer at the School of Basic Studies, Ahmadu Bello University, Zaria on secondment here to pursue the course of study.

He is undertaking an investigation of students' problem-solving difficulties in organic reaction mechanisms at the Schools of Basic Studies level. He will be taking samples of Schools across Nigeria for the study and your School is one of those he would like to participate.

I am writing to ask for your kind permission to enable Mr. Shaibu to administer the test to your chemistry students. I should be most grateful for your assistance, and would ask that you give him the cooperation necessary to carry out the exercise which is expected to take place about the beginning of November 1985.

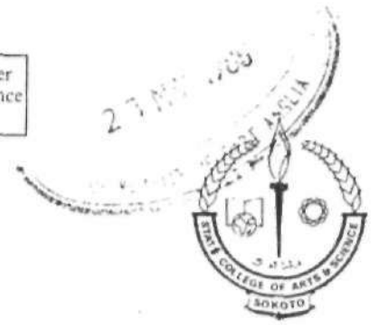
I believe that the results of his findings will be of educational benefit to all the Schools of Basic Studies. I look forward to hearing from you soon and thank you in anticipation.

Yours faithfully,

A.A.M. Shaibu
(Student)

Dr. R.A.Y. Jones
(Supervisor)

In reply please quote reference number and date. Do not address correspondence to Officers by name.



Ref. No. SCAS/CONF/013/II/221

STATE COLLEGE OF ARTS
AND SCIENCE,
P M B 2356,
SOKOTO.

Telegram : SCAS SOKOTO

Telephone: SOKOTO 232301

Date 9th May, 1985

Dr. R. A. Y. Jones,
Supervisor,
School of Chemical sciences,
University of East Anglia,
Norwich NR4 7TJ, England.

Dear Sir,

I am directed to refer to your letter of 21st March, 1985 to inform you that this college has no objection to his coming here to administer test to our chemistry students but we suggest that the test should take place in Feb. 1986 when the college is in session and all the students to be involved in the test are physically present.

We look forward to his coming here.

Yours faithfully,

(BELLO UMARU GWANDU)
P. A. R.

RIVERS STATE SCHOOL OF BASIC STUDIES

(CAMPUSES AT ANDONI, OGBIA AND SAGBAMA)

Felix E. Wigwe, B.Sc.; Ph.D. (Principal)

Rumuola,
P. M. B. 5936,
Port Harcourt.

Our Ref....GC/SBS/61..... .....20th May,.....1985...

Dr. R. A. Y. Jones,
Supervisor,
School of Chemical Sciences,
Chemical Education Sector,
University of East Anglia,
Norwich NR4 7TJ,
ENGLAND.

Dear Sir,

We thank you for your letter dated 21st March, 1985, and wish to confirm that our institution is very willing to accept your test in Chemistry.

We would therefore like to request that the student, Mr. A. A. Shaibu, inform us at least one month before the actual date of commencement of the said test.

Thanking you for your interest in our schools,

Yours faithfully,

A. M. IKURU
Ag. Principal

COLLEGE OF ADVANCED STUDIES ZARIA

27 AUG 1985

Telephones: 32841, 33206, 33031.

Telegram CAS ZARIA

P. M. B. 1061, ZARIA

Your Ref:

Our Ref: KCAST/SEC/146/Vol.I/104

Date 14th Aug. 1985

Dr. R.A.Y. Jones,
University of East Anglia,
School of Chemical Sciences,
University of East Anglia
Norwich NR 4 7TJ

Dear Sir,

RE: MR. A.A.M. SHAIBU'S RESEARCH WORK

With reference to your letter on the above mentioned subject, I am directed to inform you that permission has been granted to your student, namely, Mr. A.A.M. Shaibu to undertake an investigation of our students' problem solving difficulties in organic reaction mechanisms.

Above is in line with your request

Yours faithfully,

T. A. IMAM
Ag. Registrar

TAI/Y.

SCHOOL OF BASIC STUDIES.

P.M.B. 102211, MAKURDI.

Office of the ~~Secretary~~ PRINCIPAL

Principal: T. V. D. IHYUMAN, B.A. [Hons] GRAD. CERT. IN EDUCATION

Secretary: J. K. A. UMARU, B.A. [Hons] ABU, Dip. French Univ. of Dakar.

YOUR REF: .....

DATE 17th January, 1986

OUR REF: PRI/GEN/22/462

Mr. A.A.M. Shaibu,
School of Basic Studies,
Ahmadu Bello University,
Zaria.

PERMISSION TO ADMINISTER TEST

I acknowledge receipt of your letter dated 8th January, 1986 and to inform you that an approval is given for you to administer your test on the 24th February, 1986 as you have requested in your letter.

Thanks.

Yours faithfully,

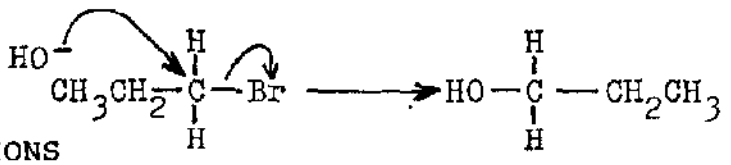
J.B. Abah
for: Principal

APPENDIX 5

APPENDIX 5

SCORING SCHEME FOR TEST B

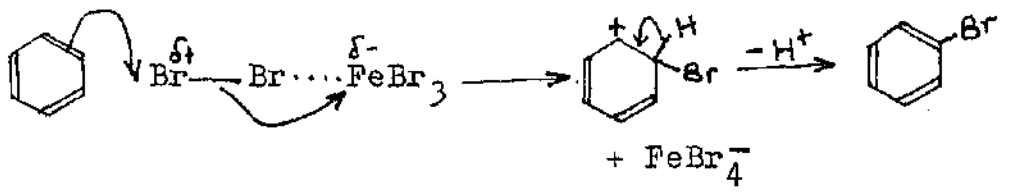
Problem 1:



OPERATIONS	GRADES
Structural representation of bomopropane.	1
Identification of the nucleophilic reagent.	1
Representation of the nucleophilic attack of OH^- on the α - carbon.	1
Representation of the heterolytic cleavage of the C-Br bond.	1
Representation of the C-OH bond in alcohol.	1

Problem 2:

(I)



Generation of the electrophile.	1
Representation of the electrophilic attack on the π system of the benzene ring.	1
Representation of the bonding of Br to the ring carbon.	1
Representation of the Wheland intermediate.	1
Representation of H^+ abstraction or conversion of the intermediate to the product.	1

(II) 

$CH_2Br—CH_2Br$

Identification of the electrophile. 1

Representation of the electrophilic attack of the polarised Br_2 on either of ethene carbon. 1

Representation of the intermediate carbocation. 1

Representation of the nucleophilic attack by the Br^- 1

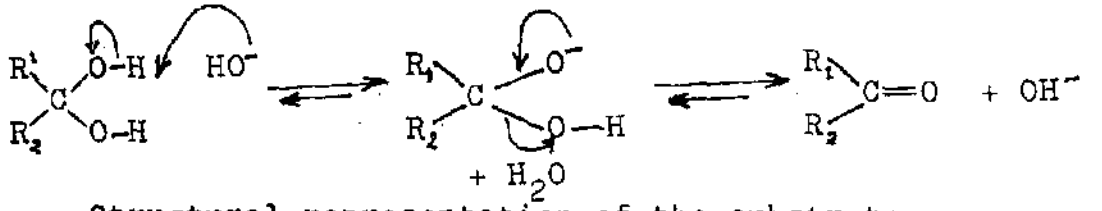
Representation of the C-Br bonds formed in the 1,2-dibromoethane. 1

(III) Benzene is resonance stabilised, ethene is not. 1

This stabilization is lost at the transition state of the reaction, resulting in a relatively wide energy difference between benzene molecule and the activated complex i.e high free energy of activation.

A catalyst provides a reaction path requiring lower activation energy. 1

Problem 3



Structural representation of the substrate molecule. 1

Identification of OH^- as the nucleophile. 1

Representation of the removal of H^+ by the nucleophile. 1

Structural representation of the intermediate. 1

Representation of the elimination of OH^- via the push-pull effects of the electron-pairs. 1

Problem 4

(I) $CH_3CH_2-C(H)-C(H)-Br$ (with HO^- abstracting H) $\longrightarrow CH_3CH_2CH=CH_2 + Br^- + H_2O$

but-1-ene

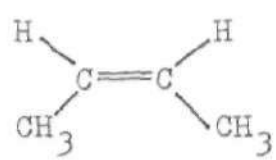
(II) $CH_3CH_2-C(Br)-C(H)-H$ (with HO^- abstracting H) $\longrightarrow CH_3CH_2CH=CH_2 + Br^- + H_2O$

but-1-ene

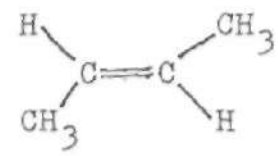
(III) $CH_3-C(H)-C(Br)-CH_3$ (with HO^- abstracting H) $\longrightarrow CH_3CH=CHCH_3 + Br^- + H_2O$

but-2-ene

(IV)



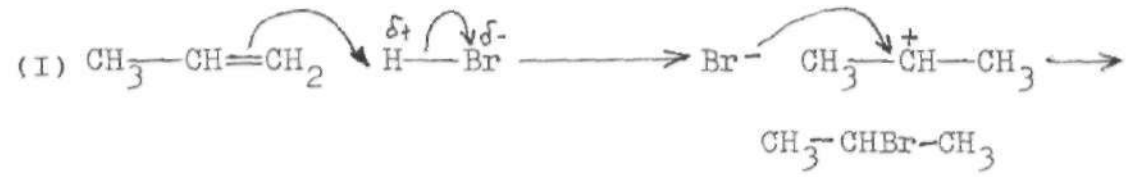
Cis-but-2-ene



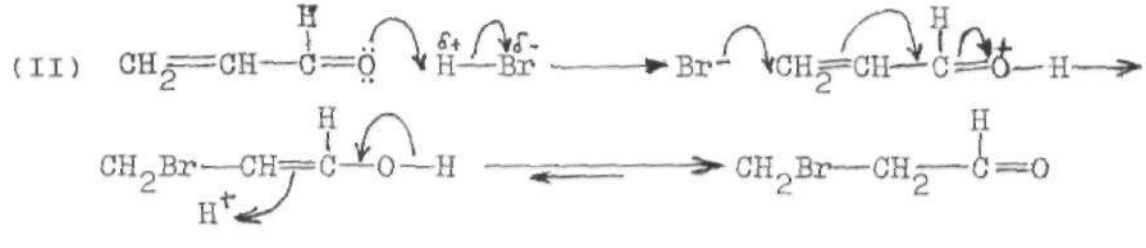
Trans-but-2-ene

Structural representation of 1-bromobutane.	1
Structural representation of 2-bromobutane.	1
Identification of the nucleophile.	1
Representation of the removal of H^+ by the nucleophile.	1
Representation of the C-H bond cleavage	1
Representation of the C-Br bond cleavage	1
Representation of the Cis-but-2-ene.	1
Representation of the trans-but-2-ene.	1
Naming the mechanistic process: 1,2-elimination.	1

Problem 5

(I) 

Identification of the electrophile.	1
Structural representation of the electrophilic molecule	1
Representation of the electrophilic attack on the C=C π system, indicating the preferential attack.	1
Representation of the intermediate carbocation.	1
Representation of the nucleophilic attack by Br^- on the intermediate yielding the 2-bromopropane product.	1

(II) 

Recognition of the non-bonded electron-pairs
of the carbonyl oxygen and its protonation. 1

Representation of the intermediate oxonium ion. 1

Nucleophilic attack of the Br^- on the
β-carbon. 1

Representation of the 1,4-addition product. 1

Equilibration of the enol product to
keto form. 1

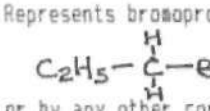
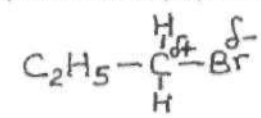
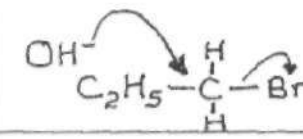
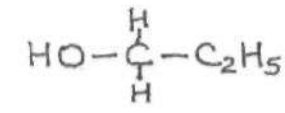
(III) The -CHO group activates the C=C bonds
toward nucleophilic addition by making the
β-carbon become an electrophilic site. 1
This activation become pronouned by the
added mesomeric effects as indicated;

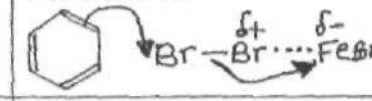
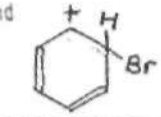
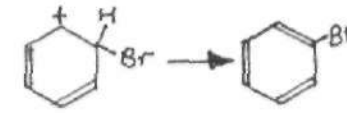
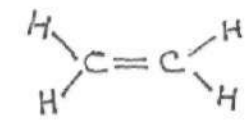
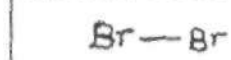
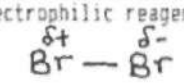
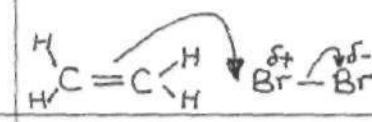
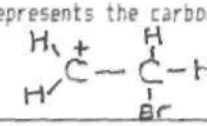
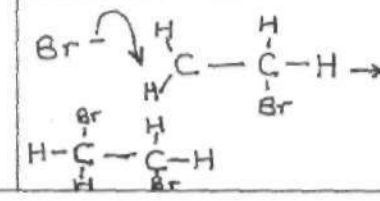
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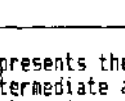
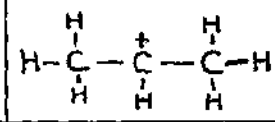
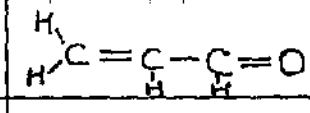
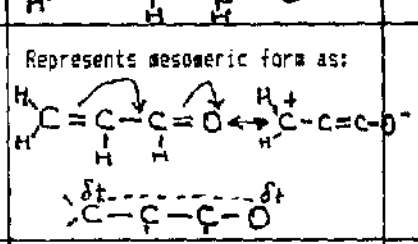
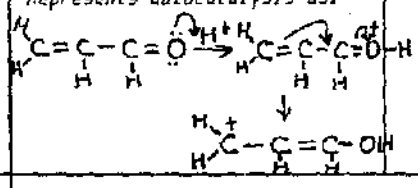
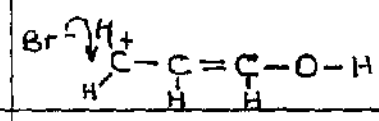
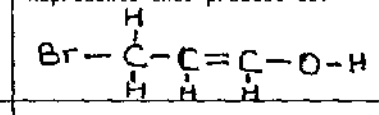
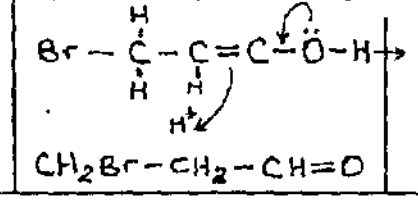
APPENDIX 8.1

APPENDIX 8.1

A SCHEME FOR SCORING THE PROTOCOL

PROBLEM No	CATEGORY	RULE	ACTION	GRADE		
				RULE	ACTION	TOTAL
1	3.1	Bromopropane molecule comprises arrangements of C and H atoms, and a hetero atom - all linked by covalent bonds	Represents bromopropane as:  or by any other correct structural formula			
	3.2	Because of high polarizability and relatively higher electronegativity of bromine compared to α- carbon, the latter constitutes a region of low electron density	Represents bromopropane as: 			
	3.3	KOH is aqueous, thus it is in the form of potassium and hydroxyl ions	Represents the nucleophile as: OH^-			
	3.5	The nucleophile attacks the α- carbon by donating, and sharing with it, a pair of electrons (forming a bond) while bromine atom departs with the pair of bond-electrons leading to cleavage of the C-Br bond	Represents the substrate/ reagent interaction as: 			
	3.7	Hydroxyl group replaces bromine, forming alcohol				
2(I)	3.1 & 3.2	Benzene molecule comprises six C and six H atoms linked by σ and π bonds in a hexagonal structure; generally represented by the Kekule (classical) structures. The cloud of π electrons constitutes a region of high electron density vulnerable to electron-seeking reagents	Represents benzene as: 			
	3.3	Br_2 represents a bromine molecule which comprises two bromine atoms joined by a covalent bond	Represents bromine molecule as: $Br-Br$			
	3.4	Because of resonance stabilization of benzene, Br_2 is not strong enough an electrophile to initiate reaction. Polarization by $FeBr_3$ makes it a stronger electrophilic reagent	Represents generation of the electrophile as: $Br-\overset{\delta+}{B}r\cdots\overset{\delta-}{F}eBr_3$			

PROBLEM No	CATEGORY	RULE	ACTION	GRADE		
				RULE	ACTION	TOTAL
2 (I)	3.5	The electrophile attacks the benzene molecule by accepting electron-pair which is shared to form a σ bond	Represents the substrate/reagent interaction as: 			
	3.6	A positively charged, reactive intermediate is formed	Represents Wheland intermediate as: 			
	3.7	Because of resonance stabilization of benzene, elimination of H (removal by $FeBr_4^-$ as a H^+) is energetically more favourable than addition of a nucleophile; thus forming a substitution product	Represents elimination of H from Wheland intermediate as: 			
2 (II)	3.1 & 3.2	Ethene molecule comprises C and H atoms linked by σ and π bonds. The cloud of π electrons constitutes a region of high electron density that can easily be attacked by electron-seeking reagents	Represents ethene molecule as: 			
	3.3	Br_2 represents bromine molecule comprising two bromine atoms joined together by a covalent bond	Represents Br_2 as: 			
	3.4	Br_2 is easily polarizable; thus inducing an electrophilic site in the molecule	Represents Br_2 as an electrophilic reagent: 			
	3.5	Br_2 accepts a pair of π electrons from ethene, to form a bond with one of the carbon atoms, accompanied by heterolytic fission of the Br—Br bond	Represents the substrate/reagent interaction as: 			
	3.6	A positively charged reactive intermediate is formed	Represents the carbocation as: 			
	3.7	The departed bromine, now a nucleophile (Br-) attacks the intermediate and forms a bond with it by sharing a pair of electron in its valence shell	Represents the nucleophilic addition of Br- as: 			

PROBLEM No	CATEGORY	RULE	ACTION	GRADE		
				RULE	ACTION	TOTAL
5 (I)		Problem 5 (I) follows the same scheme as in problem 2 (II) except for two modifications:				
	3.4	Bromine atom is more electronegative than hydrogen atom. Thus, HBr is a polar, electrophilic molecule	Represents HBr as a dipolar molecule: 			
	3.6	Propene is an unsymmetrical alkene. The positive end of the electrophilic reagent adds to one of the doubly bonded C that already has the greater number of H attached	Represents the reactive intermediate as a secondary carbocation: 			
5 (II)	3.1	The molecule comprises an arrangement of C, H and O atoms joined by single and double bonds	Represents propenal as: 			
	3.2	The carbon-carbon double bonds are conjugated with the C-O double bonds. Resonance is thus a feature	Represents mesomeric form as: 			
	3.3	Because of resonance stabilization, a catalyst is required. This is provided by HBr - an example of acid autocatalysis inducing an electrophilic site	Represents autocatalysis as: 			
	3.5	The bromide ion (nucleophile) shares its electron pair with the positive centre	Represents nucleophilic attack as: 			
	3.6	An enol is formed	Represents enol product as: 			
	3.7	The enolic product quickly tautomerizes into the corresponding, more stable keto form	Represents the proton exchange as: 			

APPENDIX 10.1

STRUCTURED TEXT

IN

ORGANIC REACTION MECHANISMS

INTRODUCTION

The study of organic chemistry is based on two aspects of molecules: their structure and their reactions. Both are interrelated. The approach adopted in this text is based on features and processes of organic reactions. "Features" mean the structural changes that occur in the overall conversion of reactants to products. "Processes" mean the steps involved in the conversion. These are described by reaction mechanisms. The first few topics of this text (topics 1-3) are devoted to the discussion of some basic ideas about the structure of molecules.

This text is designed to help you improve your understanding of the basic principles of organic reactions, and your skill in using chemical ideas to solve problems in organic chemistry.

The text is divided into a number of topics, each treating just one idea or a few related ones. Each topic has four parts. They are:

(i) Introduction: which explains what the topic is about.

(ii) Exercises: These are questions about the topic, for you to check your understanding. Try them before you go on to the next part.

(iii) Lesson Note: This gives you some information about the topic. Pay attention to anything that explains exercises that you have difficulties with.

(iv) Answers: These are the answers to the exercises for you to compare with your own answers. If you get a problem wrong, you should cross-check to find out where and why you are wrong. Read through the lesson note again until you are sure of it.

By the time you have completed this programme, your understanding of organic chemistry, and your ability to use chemical ideas to solve problems in organic reactions will be greatly improved.

Thank you.

A.A.M. Shaibu

TOPIC 1

COVALENT BONDS IN ORGANIC COMPOUNDS

COVALENT BONDS IN ORGANIC COMPOUNDS

1.1 INTRODUCTION

We want to begin by developing some basic ideas that will lead us on to discussing the structure of molecules. This is necessary for our later discussion of reaction mechanisms.

In this topic we shall discuss covalent bonds in organic compounds. We shall focus attention on four aspects:

(i) Electronic nature of covalent bonds.

(ii) Representation of covalent bonds.

(iii) Valence electrons

(iv) Factors affecting covalent bonds.

(v) Breaking of covalent bonds.

By the time you have completed studying this topic you should be able to understand:

(i) the electronic nature of bonds

(ii) how bonds are represented in organic compounds

(iii) some electronic factors affecting bonds

(iv) the processes of bond breaking.

1.2 EXERCISES

(1) From an electronic point of view, what is a covalent bond?

(2) (a) What do you understand by the term "polar bond"?

(b) Are all bonds polar?
If "Yes", why?
If "No", why not?

(3) (a) What do you understand by the term "inductive effect"?

(b) Use the example of a molecule having three carbon atoms and terminal chlorine atom to illustrate inductive effect.

(4) (a) Name two processes by which covalent bonds are broken.

(b) Name the end-products of each process.

(c) Use an equation to illustrate each process.

1.3 LESSON NOTES

1.3.1 Electronic nature of covalent bonds

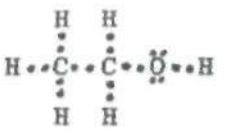
There is a vast number of organic compounds. Their molecules are made up from relatively few elements; most commonly C, H, N, O and the halogens comprising F, Cl, Br and I.

The molecules are composed of atoms held together by covalent bonds. These bonds consist of an electron-pair shared between two atoms. Such mutual sharing of an electron-pair binds the atoms concerned because the negatively charged electrons are attracted to the positive atomic nuclei.

We will find this idea about covalent bonds consisting of an electron-pair useful in understanding our later discussion of reaction mechanisms.

Some examples of covalent bonds in molecules are given below in table 1.1, in which electrons are represented by dots (•).

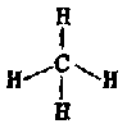
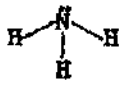
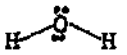
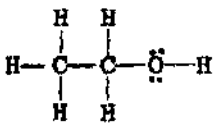
TABLE 1.1

(i) CH_4 Methane 	(ii) NH_3 Ammonia 
(iii) H_2O Water 	(iv) C_2H_5OH Ethanol 

1.3.2 Representation of bonds

In organic chemistry, the symbol generally used to represent bonds is a "dash" (—). Thus the molecules shown as examples above (1.3.1) are represented below:

TABLE 1.2

 Methane	 Ammonia
 Water	 Ethanol

It can thus be understood that each "dash" (—) between atoms represents a bond, which represents a pair of electrons, between two atoms and shared by both.

1.3.3 Valence Electrons

We have discussed in the last two sections that bonding involves sharing of a pair of electrons. The question may be asked: which electrons are used in bonding? They are the valence electrons. Valence electrons are those in the outermost shell of the atom. Some are paired, some are unpaired. Usually the bonding atoms "contribute" their unpaired electrons; but paired ones are also sometimes used, as we shall see in examples following table 1.3 below. It is a scheme of the electronic arrangements within the atoms of elements comprising the first two rows of the periodic table.

TABLE 1.3

Elements	ORBITALS 1S	2S	2Px	2Py	2Pz
*H	↑				
He	↑↓				
Li	↑↓	↑			
Be	↑↓	↑↓			
B	↑↓	↑↓	↑		
*C	↑↓	↑↓	↑	↑	
*N	↑↓	↑↓	↑	↑	↑
*O	↑↓	↑↓	↑↓	↑	↑
*F	↑↓	↑↓	↑↓	↑↓	↑↓
Ne	↑↓	↑↓	↑↓	↑↓	↑↓

↑↓ = paired electrons

↑ = unpaired electrons

* = Elements mostly found in molecules of common organic compounds. F (fluorine) is taken in this table to represent other halogens (Cl, Br, I) in the sense that they all have seven valence electrons, only one of which is unpaired.

All the atoms (except H) have their valence electrons in the outer 2s and 2p orbitals.

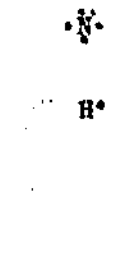
This table should help us to further understand bonding and also give us some insight into the structure of molecules (topic 3).

Let us take NH_3 as an example,

N has three unpaired valence electrons

H has only one valence electron

Thus we have a ratio of 1N : 3H as shown below, in which three pairs of electrons are shared between three hydrogen and one nitrogen atoms.

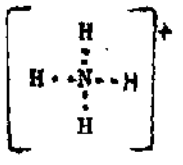


Nitrogen atom showing the valence electrons

H• Hydrogen atom showing the valence electron

Ammonia molecule

Covalent bonds generally involve sharing of unpaired valence electrons as shown in the ammonia molecule above. The paired valence electrons are also sometimes shared with an electron-seeking entity such as hydrogen ion, H^+. A typical example is ammonium ion in which the paired valence electrons of nitrogen are shared with H^+ as shown below:



Atoms are bonded together (by sharing electron pairs) so that each atom in the resulting molecule tends to acquire a closed shell similar to that of the nearest noble gas. Take the example of NH_3 molecule shown above; we see that N tends to acquire an electron shell of neon and H that of helium.

1.3.4 Factors affecting bonds

(a) Polarity of bonds

Some atoms are able to attract electrons more than others. When two atoms of different electron-attracting abilities are bonded together; the bond electrons are not equally shared between them. They are attracted more towards the atom that has the greater attracting ability. When that happens, the bond between them is said to be polarised. The result is that the atoms acquire partial (small) charges; negative for the more electron-attracting atom and positive for the less electron attracting one.

Examples

(i) C—C Bond electrons are equally shared

(ii) H—H No polarity of bond

(i) $\overset{\delta+}{C}—\overset{\delta-}{Br}$ Br attracts the bond electrons more than C and H. The bond is thus polar. Br has a partial negative charge;

(ii) $\overset{\delta+}{H}—\overset{\delta-}{Br}$ C and H have partial positive charge. This is shown as $\delta-$ and $\delta+$ respectively.

The symbol "δ" means "a small amount".

(b) Inductive Effect

Polarisation in one bond may induce polarisation in adjacent bonds. Such a situation is known as inductive effect.

e.g.

$$\underset{3}{\overset{\delta\delta\delta+}{C}}\longrightarrow\underset{2}{\overset{\delta\delta+}{C}}\longrightarrow\underset{1}{\overset{\delta+}{C}}\longrightarrow\overset{\delta-}{X}$$

The arrow ($\longrightarrow$) shows the direction of electron shift.

Usually, inductive effects become insignificant starting from about the third carbon away from the electron-attracting atom i.e. X in the example given above.

1.3.5 Breaking of covalent bonds

We have already discussed that a covalent bond consists of an electron-pair shared between two atoms. Breaking of covalent bonds involve moving apart of the bond-electrons. There are two processes by which bond-breaking occurs. These are as follows:

(a) Heterolytic cleavage

In this process, one of the bonded atoms acquires the pair of bond-electrons. This results in the atom which acquires the electron-pair becoming "richer" by one electron and the other atom becoming deficient by one electron. It leads to formation of ions as shown in the examples given below:

(i) $-\overset{|}{\underset{|}{C}}\cdot\cdot Br \longrightarrow -\overset{+}{C}< + Br^-$

a molecule ions

OR $-\overset{|}{\underset{|}{C}}—Br \longrightarrow -\overset{+}{C}< + Br^-$

(ii) $H\cdot\cdot Br \longrightarrow H^+ + Br^-$

a molecule ions

$\cdot\cdot u^+ + Br^-$

Heterolytic cleavage occurs most commonly between bonded atoms that have different electron-attracting abilities. It is this kind of bond-breaking that we shall be mostly dealing with in our later discussions of reaction mechanisms.

(b) Homolytic cleavage

In this process of bond-breaking, each of the bonded atoms pull apart with one of the bond-electrons. This results in formation of radicals as shown in the examples given below:

(i) $H{\cdot\cdot}H \longrightarrow H^{\bullet} + H^{\bullet}$

a molecule radicals

OR $H{-}H \longrightarrow H^{\bullet} + H^{\bullet}$

(ii) $Cl{\cdot\cdot}Cl \longrightarrow Cl^{\bullet} + Cl^{\bullet}$

a molecule radicals

OR $Cl{-}Cl \longrightarrow Cl^{\bullet} + Cl^{\bullet}$

Homolytic cleavage occurs mostly between atoms of similar electron-attracting abilities.

4 ANSWERS

(1) A covalent bond is a pair of electrons that are shared between two atoms. The mutual sharing of the electron-pair binds the atoms together.

(2) (a) A polar bond is one in which the bond-electrons are not equally shared between the atoms concerned.

(b) No.
Not all bonds are polar because the basis for polarity (i.e. differences in electron-attracting ability) does not exist for all molecules e.g. molecules formed from similar atoms will be non-polar.

(3) (a) Inductive effect is the "transmission" of polarity from one bond to the adjacent ones.

(b) $\overset{\delta\delta\delta+}{-C}\longrightarrow \overset{\delta\delta+}{C}\longrightarrow \overset{\delta+}{C}\longrightarrow Cl$

(4) (a) Homolytic and heterolytic processes.

(b) (i) homolytic cleavage results in formation of radicals.

For example:

$$Cl{\cdot\cdot}Cl \longrightarrow Cl^{\bullet} + Cl^{\bullet}$$

(ii) Heterolytic cleavage results in formation of ions.

For example:

$$-\overset{|}{\underset{|}{C}}{\cdot\cdot}Br \longrightarrow -\overset{|}{\underset{|}{\overset{+}{C}}}(+ Br^{-}$$

TOPIC 2

FUNCTIONAL GROUPS

FUNCTIONAL GROUPS

2.1 INTRODUCTION

Another idea we want to discuss just before we discuss structure of molecules is functional groups. It is possible to study the chemistry of the very large number of organic compounds primarily because they are classified. Functional groups form an important basis for such classification. This makes it possible to talk of compounds in terms of their classes, e.g. carboxylic acids, alcohols, amines, etc. Functional groups are also important in the naming of organic compounds.

In this topic, we shall discuss functional groups in their relation to:

(i) Classification of organic compounds.

(ii) Naming of organic compounds.

By the time you have completed studying this topic, you should be able to:

(i) know the kind of functional groups that characterise organic compounds,

(ii) demonstrate an understanding of "types" of organic compounds based on functional groups,

(iii) know how functional groups are used as a basis for naming organic compounds.

2.2 EXERCISES

(1) Briefly explain the term "functional group".

(2) List the functional groups that characterise the following classes of organic compounds.

(i) carboxylic acids
(ii) ketones
(iii) aldehydes
(iv) esters
(v) acid amides
(vi) amines
(vii) alcohols

2.3 LESSON NOTE

2.3.1 Functional groups and classification of organic compounds

A functional group is an atom or group of atoms that determine the characteristic chemical behaviour of organic compounds. They are thus used to classify organic compounds. Some of the functional groups commonly encountered in organic chemistry are listed in table 2.1 below, showing the class of organic compound characterised by each functional group.

TABLE 2.1

SERIAL No.	FUNCTIONAL GROUP	CLASS OF ORGANIC COMPOUND
1	$-F$, $-Cl$, $-Br$, $-I$	Alkyl halides
2	$-OH$	Alcohols
3	$-OR$	Ethers
4	$>C=O$	Aldehydes and ketones
5	$-C(=O)-OH$	Carboxylic acids
6	$-C(=O)-OR$	Esters
7	$-C(=O)-X$ (X = Cl, Br, I)	Acid halides
8	$-C(=O)-NH_2$	Amides
9	$-C(=O)-O-C(=O)-$	Acid anhydrides
10	$-NH_2$	Amines
11	$=N-$	Imines
12	$-C\equiv N$	Cyanides or nitriles
13	$-SO_2-OH$	Sulphonic acids

/continued

Table 2.1 (Continued)

SERIAL No.	FUNCTIONAL GROUP	CLASS OF ORGANIC COMPOUND
14	$-SO_2-Cl$	Sulphonyl chlorides
*15	$\rangle C=C\langle$	Alkenes
*16	$-C\equiv C-$	Alkynes

NOTE: *These are not strictly functional groups, but they are listed because they behave like functional groups in determining the chemical characteristics of their compounds.

2.3.2 Functional groups and naming of organic compounds

There are many conventions for naming organic compounds. The one presented here is based on the rules of IUPAC; meaning International Union of Pure and Applied Chemistry.

This is presented in table 2.2 below. The table is simplified because we cannot go into too much details during this brief discussion. The table, however, shows a general basis for naming the various "families" of organic compounds and members of each class.

e.g. Aldehydes have the general name alkanals. Members of the group take their names from this, the difference being the number of carbon atoms in the molecule of each member. Thus we have:

$HCHO$: methanal

CH_3CHO : ethanal

CH_3CH_2CHO : propanal

$CH_3CH_2CH_2CHO$: butanal etc.

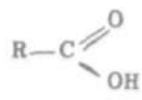
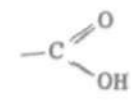
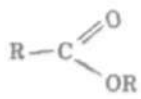
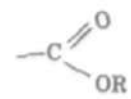
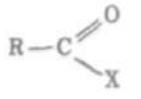
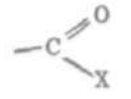
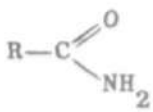
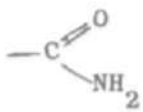
Other groups of compounds follow similarly.

TABLE 2.2

Compound	Formula R = alkyl group	Functional Group	IUPAC Name
Alkanes	C_nH_{2n+2}	Nil	alkane
	e.g. C_2H_6		ethane
Alkenes	C_nH_{2n}	$\rangle C{=}C \langle$	alkene
	e.g. CH_2CH_2		ethene
Alkynes	C_nH_{2n-2}	$-C{\equiv}C-$	alkyne
	e.g. C_2H_2		ethyne
Alcohols	R—OH	—OH	alkanol
	e.g. CH_3CH_2OH $CH_3CH_2CH_2OH$		ethanol propanol
Ethers	R—O—R	—OR	alkoxyalkane
	e.g. $CH_3OC_2H_5$		methoxyethane
Aldehydes	$R\diagdown C{=}O \atop H\diagup$	$\rangle C{=}O$	alkanal
	e.g. CH_3CHO CH_3CH_2CHO		ethanal propanal
Ketones	$R\diagdown C{=}O \atop R\diagup$	$\rangle C{=}O$	alkanone
	e.g. CH_3COCH_3 $C_2H_5COCH_3$		propanone butanone

/continued

Table 2.2 (Continued)

Compound	Formula R = alkyl group	Functional Group	IUPAC Name
Carboxylic acids			alkanoic acid
	e.g. CH_3COOH CH_3CH_2COOH		ethanoic acid propanoic acid
Esters			alkyl alkanoate
	e.g. CH_3COOCH_3 $CH_3COOC_2H_5$		methyl ethanoate methyl propanoate
Acid halides	 [X = Cl, Br, I]		alkanoyl halide
	e.g. CH_3COCl CH_3CH_2COBr		ethanoyl chloride propanoyl bromide
Alkyl halides	R—X [X = Cl, Br, I]	—X	halogenoalkane
	e.g. CH_3Cl CH_3CH_2Br		chloromethane bromoethane
Acid amides			alkanamides
	e.g. CH_3CONH_2 $CH_3CH_2CONH_2$		ethanamide propanamide

/continued

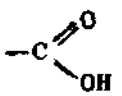
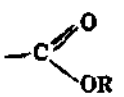
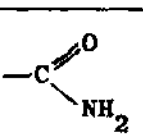
Table 2.2 (Continued)

Compound	Formula	Functional Group	IUPAC Name
Amines	$R-NH_2$	$-NH_2$	aminoalkane
	e.g. CH_3NH_2		aminomethane
	$CH_3CH_2NH_2$		aminoethane
Nitriles	$R-C\equiv N$	$-CN$	alkane nitrile
	e.g. CH_3CH_2CN		propanenitrile
	$CH_3CH_2CH_2CN$		butanenitrile
Sulphonic acids	$R-SO_2-OH$	$-SO_2-OH$	alkanesulphonic acid
	e.g. CH_3SO_2OH		methane sulphonic acid
	$CH_3CH_2SO_2OH$		ethane sulphonic acid
Sulphonyl chlorides	$R-SO_2-Cl$	$-SO_2-Cl$	alkane sulphonyl chloride
	e.g. CH_3SO_2Cl		methane sulphonyl chloride
	$CH_3CH_2SO_2Cl$		ethane sulphonyl chloride

2.4 ANSWERS

(1) A functional group is an atom or group of atoms that determine the characteristic chemical behaviour of groups of organic compounds e.g. alcohols, caboxylic acids, esters, etc.

(2)

	CLASS OF COMPOUND	FUNCTIONAL GROUP
i	Carboxylic acids	
ii	Ketones	
iii	Aldehydes	
iv	Esters	
v	Acid amides	
vi	Amines	—NH_2
vii	Alcohols	—OH

TOPIC 3

MOLECULAR STRUCTURE

MOLECULAR STRUCTURE

3.1 INTRODUCTION

This topic deals with molecular structure. It covers the following:

(i) The components of molecules and the forces that bind them together.

(ii) Representation of molecules.

By the time you have completed studying this topic you should understand:

(i) The idea of molecular structure.

(ii) Different ways used in symbolic representation of molecules.

3.2 EXERCISES

(1) (a) What do you understand by the term "molecule"?

(b) What are the components of molecules?

(2) What do you understand by the term "molecular structure"?

(3) (a) Give the condensed and the structural formulae of the following conpounds:

(i) propanoic acid
(ii) propanal
(iii) propanone
(iv) propanol
(v) methylethanoate

(b) Name the class of organic compounds that each of (i-v) belong to.

(4) (a) Give the structural formulae of the following molecules:

(i) CH_3OH
(ii) CH_3COCH_3
(iii) CH_3COOH
(iv) $CH_3CH_2CH_2Br$
(v) $CH_3CHBrCH_3$

(b) Give the names of the compounds.

3.3 LESSON NOTES

3.3.1 Molecules

Molecules are the smallest units of compounds that are capable of free existence. They are composed of two or more atoms chemically joined together, e.g. CH_4, C_2H_6O, C_2H_7N, etc.

3.3.2 Molecular structure

"Structure" simply means the way in which atoms are arranged within the molecule and how they are bonded to each other. Thus molecular structure concerns:

(i) The component parts of the molecule (atoms)

(ii) The "forces" holding them together (bonds) and the way the atoms and bonds are arranged in relation to each other.

Molecules are composed of atoms held together by covalent bonds, e.g.

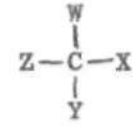


Fig. 3.1

A molecule

Fig. 3.1 is an example of a molecule showing its structure. It consists of atoms W, X, Y, Z, linked by covalent bonds to the central carbon atom. Note that C, W, X, Y, Z represent the symbols of the atoms concerned.

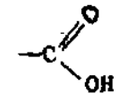
3.3.3 Representation

Molecules are usually represented by formulae. Two types of formulae are commonly used. They are condensed and structural formulae. The Lewis structure is sometimes used; especially to show valence electrons.

(I) Condensed Formulae:

These are representations of molecules which show the kind and number of each atom present and the functional group(s). They give no idea of how the atoms are linked within the molecule. Examples of condensed formulae are given in table 3.1 below:

TABLE 3.1

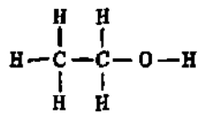
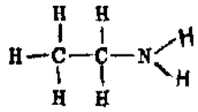
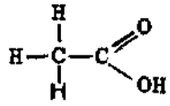
	CONDENSED FORMULA	ATOMS PRESENT	FUNCTIONAL GROUP
i	CH_3CH_2OH	carbon, hydrogen, oxygen	—OH
ii	$CH_3CH_2NH_2$	carbon, hydrogen, nitrogen	$-NH_2$
iii	CH_3COOH	carbon, hydrogen, oxygen	

(II) Structural Formulae:

These show the kind and number of each atom present in a molecule, and the order in which they are joined together.

Let us use the three examples already given above to make it easier for us to compare the two methods of representation:

TABLE 3.2

	STRUCTURAL FORMULA	CONDENSED FORMULA	NAME OF COMPOUND
i		CH_3CH_2OH	Ethanol
ii		$CH_3CH_2NH_2$	Aminoethane
iii		CH_3COOH	Ethanoic acid

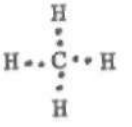
NOTE:

You should note that molecules are not necessarily flat structures as the above structural formulae seem to portray. Thus bond angles and shapes of the molecules are not truly represented by flat diagrams on paper, which show only the order in which atoms are bonded toegher.

(JII) Lewis structure

In topic 1, we showed molecules in which the valence electrons of the bonded atoms are indicated by dots (•). This method of representing molecules is known as Lewis structure.

An example of methane is given below:



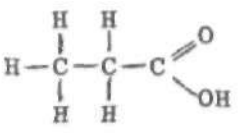
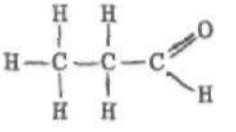
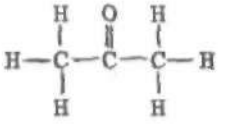
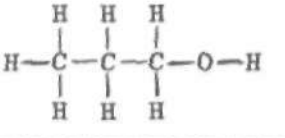
Lewis structure of methane molecule

3.4 ANSWERS

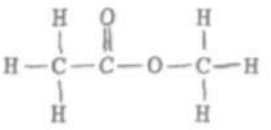
(1) (a) Molecules are the smallest units of compounds that are capable of free existence.

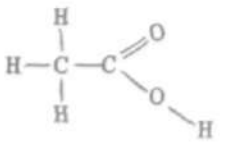
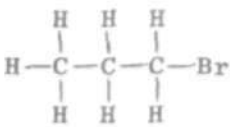
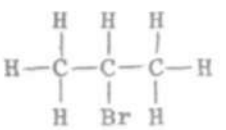
(b) The components of molecules are: atoms and covalent bonds.

(2) "Molecular structure" refers to the way in which atoms are linked and arranged within the molecule.

3(a & b)	Condensed Formula	Structural Formula	Class of Organic Compounds
i	CH_3CH_2COOH		Carboxylic acids
ii	CH_3CH_2CHO		Aldehydes
iii	CH_3COCH_3		Ketones
iv	$CH_3CH_2CH_2OH$		Alcohols

/continued

3(a & b) cont'd	Condensed Formula	Structural Formula	Class of Organic Compounds
v	CH_3COOCH_3		Esters

4(a & b)	Structural Formula	Name
i		Methanol
ii		Propanone
iii		Ethanoic acid
iv		1-bromopropane
v		2-bromopropane

TOPIC 4

CONVENTIONS COMMONLY USED IN ORGANIC REACTION MECHANISMS

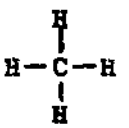
CONVENTIONS COMMONLY USED IN ORGANIC REACTION MECHANISMS

4.1 INTRODUCTION

This topic deals with conventions that are frequently used in organic reaction mechanisms. You will find them being used in later topics. You are therefore expected to know what they mean and be able to use them correctly.

4.2 EXERCISES

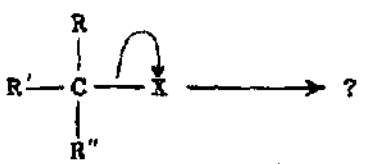
(1)



The structural formula of methane is shown above.

What does each dash represent?

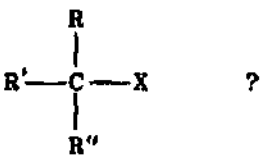
(2)



Examine the above process and answer the following questions:

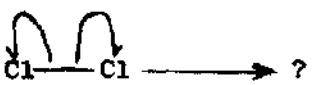
(i) What does the curved arrow (↷) indicate?

(ii) What change(s) will the process produce in the structure:



(iii) Write down the end-products of the process.

(3)

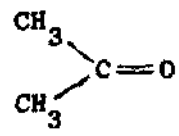


The following question (i-iii) are based on the process represented above.

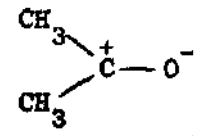
(i) What do the half-headed arrows (↶) indicate?

(ii) What change(s) will the process produce in the structure:
Cl—Cl?

(iii) Write down the end-products of the process.

(4.) 

I



II

Consider structures I and II above.

(i) Draw the usual symbol between them to show that both structures are ways of representing the same molecule (propanone).

(ii) Draw one more example of this use of two different structures to show a single molecule.

(iii) What do we call this type of representation?

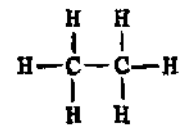
4.3 LESSON NOTE

4.3.1 A dash (—)

This is used to show a 2-electron covalent bond between two atoms.

Recall structural formulae that we discussed in topic 1.

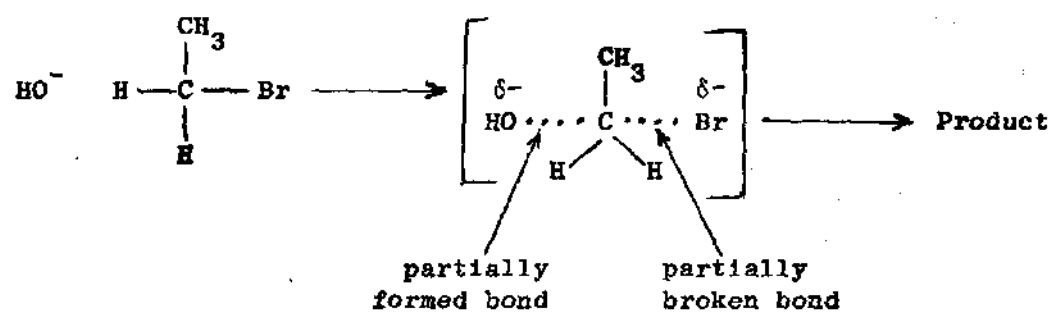
An example of ethane is given below:



A molecule of ethane

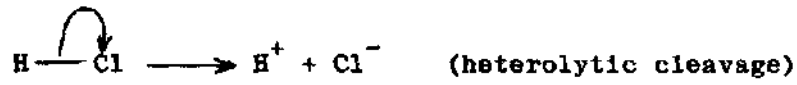
4.3.2 Dotted line (····)

This is used to show partially broken and partially formed bonds, especially at transition states of reactions, e.g.



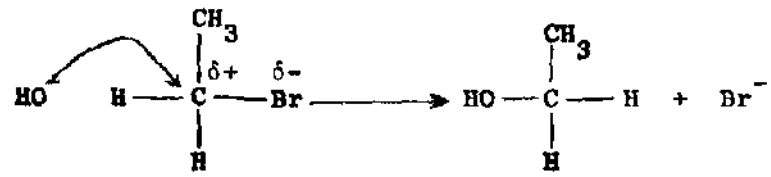
4.3.3 Full-headed curved arrow (↷)

This is used to show the shift of an electron-pair from one position to another. It shows that the direction of the electron-pair movement is from tail to the head of the arrow. It could be within the same molecule or between two reacting molecules. It may be accompanied by breaking existing bonds: e.g.

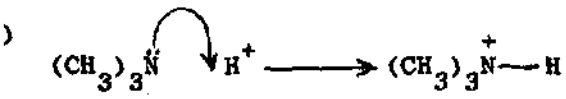


It is also used to show attacking reagents in organic reactions: e.g.

(i)



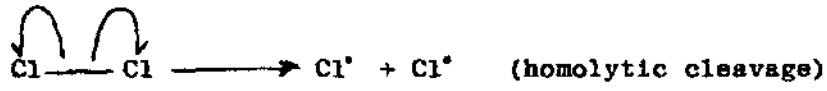
(ii)



The hydroxide (HO^-) is shown "attacking" the partially positive carbon centre in (i) and the nitrogen of dimethylaminomethane a proton H^+ in (ii).

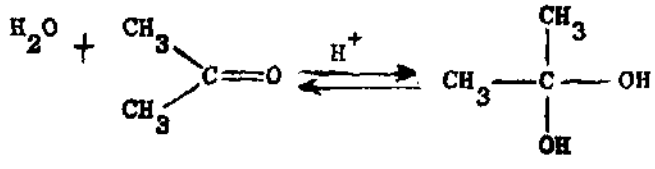
4.3.4 Half-headed curved arrow (↶)

A half-headed arrow (fish-book shape) is used to show the movement of one electron: e.g.



4.3.5 Parallel arrows (⇌)

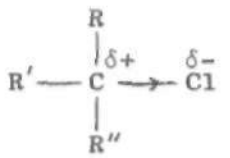
These are used to show a reversible reaction or a reversible step within a multi-step reaction. Many organic reactions involve reversible processes: e.g.



4.3.6 Partial electrical charges

In molecules composed of atoms of different electron-withdrawing abilities, the atom that pulls the bond electrons more towards itself acquires a partial negative charge, and the other, a partial positive charge. These are usually indicated as δ- and δ+ respectively. The symbol "δ" (delta) means " a small amount" (see 1.3.3).

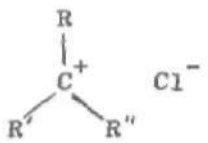
e.g.



(A molecule)

It should be noted that these symbols have different meaning when used without the "δ".

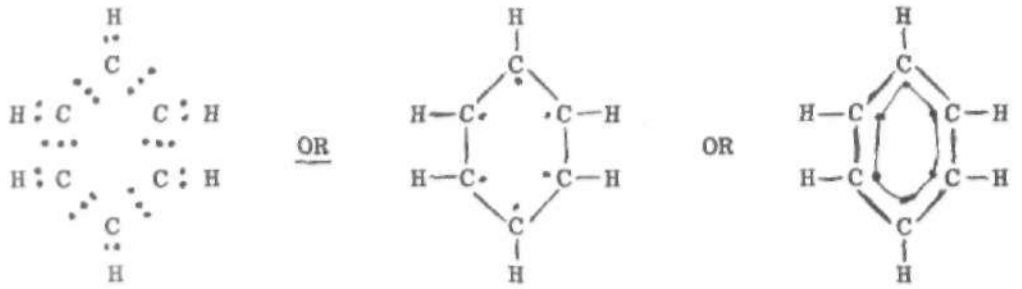
e.g.



These are ions in which Cl^- has one excess electron and C^{+} deficient by one electron compared to their respective nuclear charges.

4.3.7 Double-headed arrow (⟷)

The structure of some molecules cannot be properly represented using 2-electron bond symbols. For example, there are three electrons for every carbon-carbon bond in benzene as shown below:



(a) (b) (c)

One way of showing this is to write two (or more) different structures joined by a double-headed arrow thus:

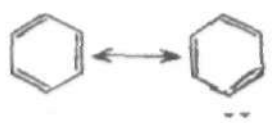


Fig. 4.2 The two structures are referred to as canonical or classical structure of benzene.

This means that the real molecule has a structure partway between the two i.e I and II. (It does <u>not</u> mean that the molecule changes back and forward between them.)

Each carbon-carbon bond is shown as double (four electrons) in one structure and single (two electrons) in the other, averaging to the real value of <u>three</u>.

Benzene is often shown as illustrated in fig 4.3 below:



Fig. 4.3

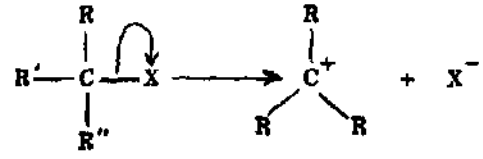
The circle represents the six electrons shared round the six carbon-carbon bonds (see fig 4.1 b and c above).

4.4 <u>ANSWERS</u>

(1) Each dash represents a 2-electron covalent bond.

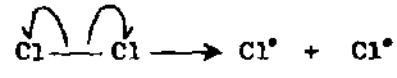
(2) (i) The curved arrow indicates that the <u>pair</u> of bond-electrons between C and X are being shifted to X.

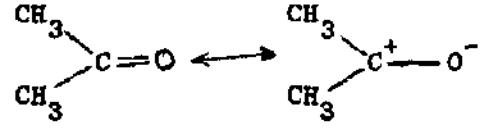
(ii) The bond breaks.

(iii) 

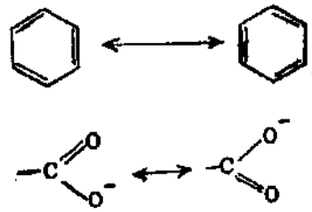
(3) (i) The half-headed arrows indicate that <u>each</u> of the <u>pair</u> of bond electrons between the two chlorine atoms is being shifted to each atom.

(ii) The bond will break.

(iii) 

(4) (i) 

(ii) Further examples include:



(iii) This type of representation is called mesomerism.

TOPIC 5

CLASSIFICATION OF ORGANIC REACTIONS AND INTRODUCTION TO REACTION MECHANISM

CLASSIFICATION OF ORGANIC REACTIONS AND INTRODUCTION TO REACTION MECHANISM

5.1 INTRODUCTION

In the previous topics (1-4) we have been building up the idea of the structure of molecules. In the remaining topics of this text, we shall be using these ideas in describing and discussing reactions of organic compounds. In this topic, we shall discuss the structural basis for the "reaction types" we shall discuss in topics 6-10.

Classification of organic reactions means grouping the vast number of reactions into relatively few categories based on the structural changes that result from the overall process of transforming reactants to products. The advantage of classification of organic reactions in this way is that it becomes possible to study only a few principles which can be applied to the vast number of individual reactions that we come across. This requires some basic abilities (or skills) which are discussed in this topic. They are:

(i) Recognition of structural features.

(ii) Classification of the structural features so recognised.

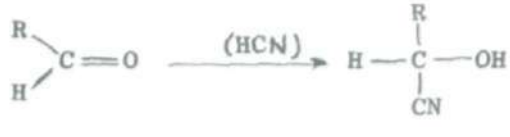
(iii) Recognition of changes in structural features resulting from reactions.

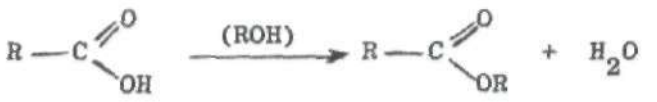
(iv) Classification of such structural changes, which forms the basis for classification of reactions into "reaction types" discussed in later topics.

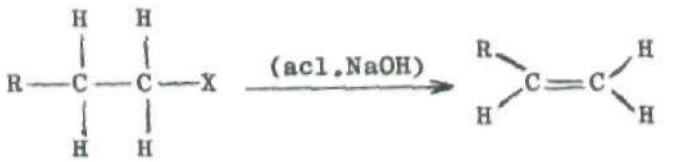
5.2 EXERCISES

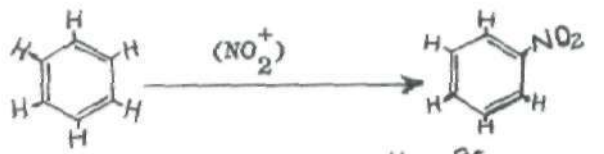
(1) List four basic abilities that you may need as pre-requisites for classifying organic reactions.

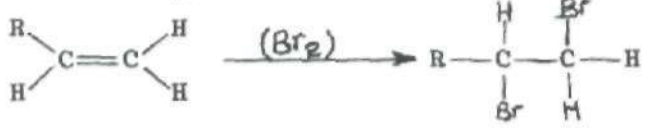
(2) Classify the following reactions according to whether they are substitution, elimination or addition:

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(3) Indicate which of the following molecules have <u>saturation</u> and which have <u>unsaturation</u>:

(i) CH_3CH_3 (ii) CH_2CH_2

(iii) CH_3COCH_3 (iv) CH_3COOH

(v) $CH_3CH_2NH_2$ (vi) CH_3CH_2OH

(4) Which of the following statements is a definition of "reaction mechanism"?

(i) It is a description of how fast a reaction proceeds.

(ii) It is a description of the various classifications of organic reactions.

(iii) It is a description of the processes involved at each step of a reaction, from reactants to products.

(iv) It is a description of how catalysts affect equilibrium of reactions.

5.2 LESSON NOTES

5.2.1 Recognition of structural features

This refers to the <u>recognition</u> and <u>interpretation</u> of the <u>structure of molecules</u>. It involves the recognition of:

(i) The kinds and number of each atom or groups in the molecule.

(ii) Recognition of bonds within the molecule.

(iii) Bond polarity.

Examples: (I) CH_3CH_2Cl These examples will be used in the later sections for illustration

(II) CH_3COCH_3

We have already dealt with these ideas in the previous topics (see topics 1 and 3).

5.2.2 Classification of structural features

The recognition of structural features lead on to their classification. This requires the recognition of:

(i) Functional group(s) within the molecules.

(ii) Saturated or unsaturated bonds within carbon-carbon chain of the molecule.

(iii) Whether the functional group within the molecule contains unsaturation.

(iv) Combination of (5.2.1 and 2) to determine the class of the molecule.

Example I: CH_3CH_2Cl

(i) The functional group is: Cl

(ii) The molecule is saturated.

(iii) Saturated heteroatom is present, i.e. —Cl

(iv) The hydrocarbon group is CH_3CH_2—

Thus the molecule is saturated; belongs to the class of alkyl halides; specifically, it is chloroethane.

Example II: CH_3COCH_3

(i) The functional group is: $\rangle C{=}O$

(ii) The functional group contains unsaturation.

(iii) The hydrocarbon groups are: $\underline{CH_3}$ and $\underline{CH_3}$

The molecule is a ketone; specifically, it is propanone.

A classification flow chart is given below:

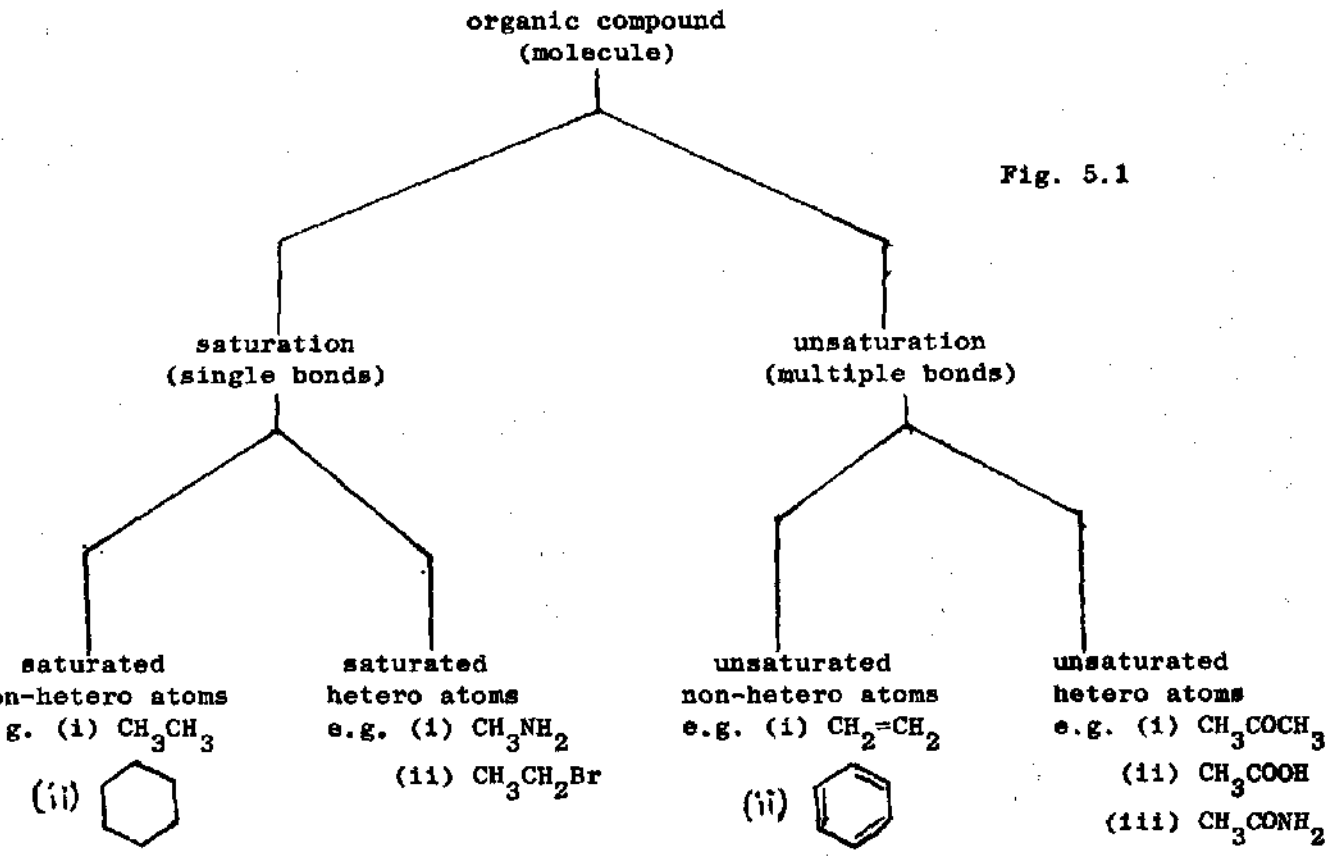


Fig. 5.1

5.2.3 Recognition and classification of changes in structural features resulting from reactions

(a) Recognition of structural changes:

Having identified and classified the structural features (5.2.1 and 2) we are then prepared to recognise the structural changes that result from the overall reaction, as the reactant molecules are transformed into the product molecules.

One of the ways to do this (i.e. recognition of structural changes) is through comparison by careful inspection. This involves "inspection" of the reactant and product molecules, making comparison to "see" what structural difference there is between them.

The recognition of the structural difference helps in the classification of the structural changes that had taken place as a result of the reaction.

(b) Classification of the structural changes: Reaction-types

(i) Substitution:

Let us use example I (CH_3CH_2Cl) to illustrate this:
Suppose it reacted with aqueous NaOH:

$$CH_3CH_2Cl + Na^+OH^- \longrightarrow CH_3CH_2OH + Na^+Cl^-$$

Comparing the reactant and product molecules, we find that one group (-Cl) has been displaced, i.e. substituted by another group (-OH) in the overall reaction.

Thus, all reactions of this kind in which one group (originally present in the reactant molecule) has been displaced by another in forming the product, are grouped together and called substitution reactions.

(ii) Elimination:

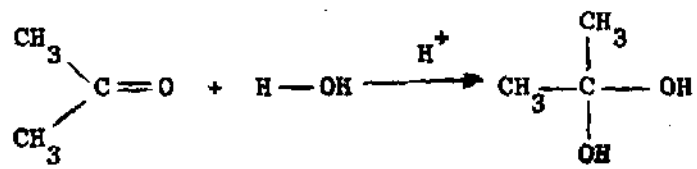
Let us again use example I (CH_3CH_2Cl) to illustrate this:
Suppose it reacted with hot concentrated alcoholic solution of sodium hydroxide:

$$CH_3CH_2Cl + \text{alcoholic NaOH} \longrightarrow CH_2{=}CH_2 + H^+Cl^-$$

Comparing the reactant and the product molecules we see that in the overall process of the reaction, smaller groups, -H and -Cl have been eliminated i.e. ejected from the reactant molecule to yield an unsaturated product in the overall reaction. All reactions of this kind in which some groups are removed, i.e. eliminated from the reactant molecule without subsequent replacement, are called elimination reactions

(iii) Addition:

Let us use example II (CH_3COCH_3) to illustrate this:
Suppose CH_3COCH_3 reacted with H_2O; catalysed by dilute acid:



In this reaction we find that the structural changes that occurred comparing the reactant and product molecules are that:
The groups of one molecule (i.e. H_2O) have been added to the second molecule across a double bond to form a single "bigger" molecule.

All reactions of this kind are called addition reactions.

Thus we can see from the discussions in this topic that the basis for classification of organic reactions into "reaction-types" (substitution, elimination and addition) is the structural changes brought about by the overall reaction when the reactant molecules are compared with the product molecules. Sometimes a complex over-all reaction may fall into more than one of these categories; but even in such cases, the structural differences between the initial reactant and the final product formed may be used as a basis for classification. We shall see an example of this in topic 9.

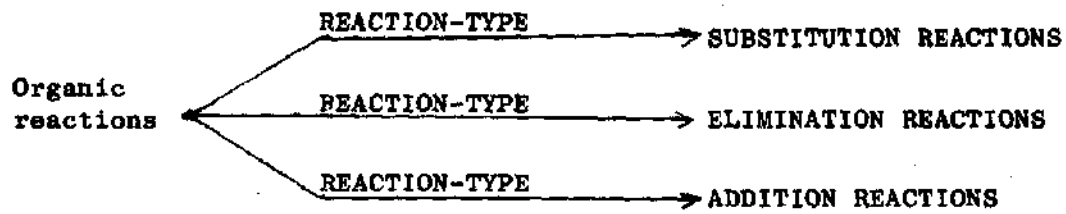


Fig. 5.2

NOTE:
The classification in fig. 5.2 is not exhaustive. Other kinds of reactions, e.g. rearrangements, have not been included. However, most of the organic reactions we come across can be dealt with on the basis of the classification so far discussed.

The mechanisms of substitution, addition and elimination reactions are discussed in topics 6-10.

5.3.4 Organic Reactions and Mechanism

Organic reactions:

(i) involve molecules. Their reactions involve breaking of existing bonds and making of new ones.

(ii) are generally not simple i.e. they involve more than one step in going from reactant to product.

(iii) often involve reversible processes.

Mechanism is the description of the processes involved in each step of a reaction from reactants to products. It describes the timing and sequence of these processes. It also describes the energy, composition and the electronic configuration of the transition state for each step. Thus it forms a basis for the description (and thus understanding) of a few patterns of reaction-types into which we can fit individual reactions.

5.4 ANSWERS

(1) Ability to:

(i) recognise structural features of molecules

(ii) classify such structural features

(iii) recognise changes in the structural features

(iv) classify such changes of structure as molecules react and get transformed.

(2) (i) addition

(ii) substitution

(iii) elimination

(iv) substitution

(v) addition

(3)

SATURATION	UNSATURATION
(i) CH_3CH_3	(ii) CH_2CH_2
(v) $CH_3CH_2NH_2$	(iii) CH_3COCH_3
(vi) CH_3CH_2OH	(iv) CH_3COOH

(4) The correct answer is statement (iii):

Reaction mechanism is a description of the processes involved at each step of a reaction, from reactants to products.

TOPIC 6

NUCLEOPHILIC SUBSTITUTION REACTIONS

SUBSTITUTION REACTIONS

6.1 INTRODUCTION

In the last topic, we classified reactions into substitution, elimination and addition. Each of these classes of reactions is now discussed in greater detail. In this topic and the next we shall discuss substitution reactions.

Substitution reactions can generally be represented as follows:

$$A + C{-}Z \longrightarrow C{-}A + Z$$

where A = the incoming group (reagent)
Z = the leaving group
C = the carbon centre on which substitution occurs.

There are basically three types of substitution reactions, depending on the nature of "A" in the above general equation, and the kind of processes involved in the overall reaction. Where "A" is an electron-rich reagent (i.e. a nucleophile) the reaction is called nucleophilic substitution. Where "A" is an electron-seeking reagent (i.e. an electrophile) the reaction is called electrophilic substitution. Where "A" is an entity having an unpaired electron (i.e. a radical) the reaction is called free radical substitution.

Reactions involving radicals occur widely in the gas phase. A typical example of radical substitution is chlorination of methane, in which the hydrogen atoms of methane are successively displaced by chlorine radicals ($Cl^{\bullet}$) to form a mixture of chloroalkanes. In our discussion, we shall be focussing on nucleophilic and electrophilic substitution reactions.

In this topic, we shall discuss nucleophilic substitution. By the time you have completed studying this topic, you should be able to:

(i) Recognise nucleophilic substitution reactions.

(ii) Understand the mechanisms of nucleophilic substitution reactions.

(iii) Know some of the common factors that influence mechanisms in substitution reactions.

6.2 EXERCISES

(1) Lewis acids react by "accepting" an electron-pair, while Lewis bases react by "donating" an electron-pair.
Are nucleophiles Lewis acids or Lewis bases?

(2) Which of the following reactions (i-v) represent nucleophilic substitution?

(i) $R{-}Cl \xrightarrow{aq\ NaOH} R{-}OH + Na^+Cl^-$

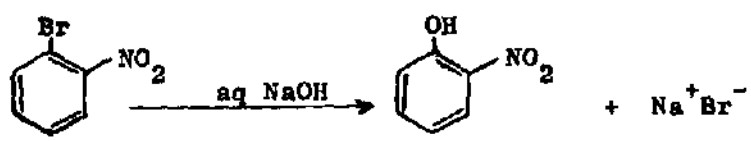
alkyl chloride — alcohol

(ii) $R{-}CHO \xrightarrow[(Ni)]{H_2/catalyst} R{-}CH_2{-}OH$

aldehyde — alcohol

(iii) $R{-}C(=O){-}OH \xrightarrow{R'{-}OH/H^+} R{-}C(=O){-}OR' + H_2O$

carboxylic acid — ester

(iv) 

2-nitrobromobenzene — 2-nitrophenol

(v) $R{-}CH_2{=}CH_2 \xrightarrow{HBr} R{-}CHBr{-}CH_3$

alkene — bromoalkane

(3) Use the reaction between $R{-}CH_2{-}Cl$ (a primary chloroalkane) and aqueous NaOH to illustrate the basic principles of S_N2 mechanism.

(4) Use the hydrolysis of 2-methyl-2-bromopropane $[(CH_3)_3CBr]$ with aqueous NaOH to illustrate the basic principles of S_N1 mechanism.

(5) Name <u>three</u> factors that promote an S_N1 mechanism and <u>three</u> that promote S_N2 .

6.3 LESSON NOTES

6.3.1 Overview

Nucleophilic substitution reactions are those in which an electron-rich, incoming group (a nucleophile) displaces another group from a reactant molecule. The group displaced is called the leaving group. A new bond is formed by an electron pair from the nucleophile. The electron pair from the broken bond leaves with the leaving group.

6.3.2 Nucleophilic Reagents (Nucleophiles)

Nucleophiles are reagents which have an unshared pair of electrons or lone pair of electrons in their outermost shell, which they can share with electron-deficient centres. Nucleophiles are thus Lewis bases. They may be negatively charged species or they may be neutral molecules having a lone pair of electrons.

Examples of some common nucleophiles are given in table 6.1 below:

TABLE 6.1

Charged Nucleophiles	Neutral Nucleophiles
H^-	$H_2\ddot{O}:$
$HOSO_2^-$	$\ddot{N}H_3$
HO^-	$H_2\ddot{S}$
RO^-	
CN^-	

6.3.3 Nucleophilic substitution

We shall give some examples of nucleophilic substitution reactions, examine the features of the reactions and later discuss the mechanism underlying the reactions. In these examples, we shall use halogenoalkanes (alkylhalides) because they are a class of organic compounds about which much is known regarding nucleophilic substitution.

Examples:

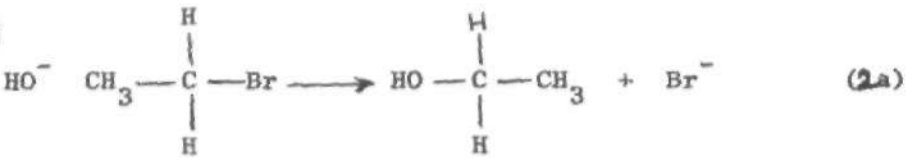
(i) $CH_3CH_2Br + aqNaOH \longrightarrow CH_3CH_2OH + NaBr$ (1a)

(ii) $CH_3CH_2I + CH_3CH_2ONa \longrightarrow CH_3CH_2OCH_2CH_3 + NaI$ (1b)

(iii) $(CH_3)_3CBr + aqNaOH \longrightarrow (CH_3)_3COH + NaBr$ (1c)

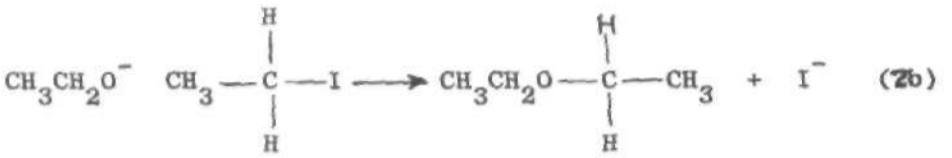
We shall now re-write these examples showing the nucleophiles and the structural formulae of the reacting molecules:

(i)



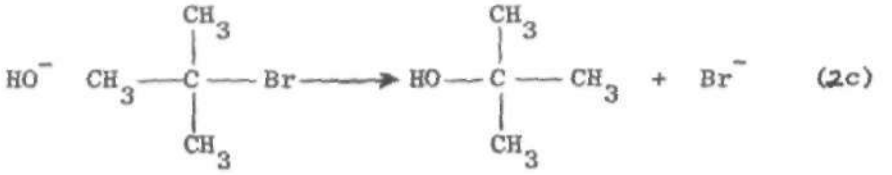
(2a)

(ii)



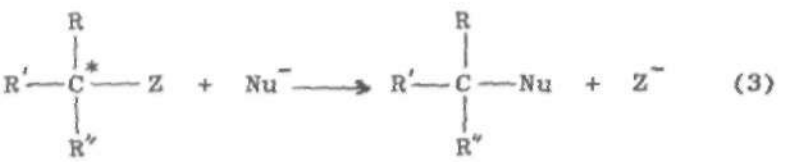
(2b)

(iii)



(2c)

These examples (2a-c) can be represented generally thus:



(3)

where: R = hydrogen or alkyl groups, depending on whether the alkylhalide is primary, secondary or tertiary,

Z = an atom or group, usually a halogen atom called the leaving group,

Nu^- = a nucleophile.

*Shows the carbon centre on which substitution occurred.

The important features we notice from the reactions are:

(i) One atom or group from the reacting molecule has been replaced by another, i.e. the nucleophile:

-Br has been replaced by -OH in (2a)

-I has been replaced by $CH_3CH_2O^-$ in (2b) etc.

(ii) This means that the original C—Z bond in the molecule must break and a new C—Nu bond formed in the overall reaction process.

(iii) The substitution (displacement) occurred on a carbon centre indicated by the asterisk (*). Locate the carbon atoms on which substitution occurred in examples (2a-c).

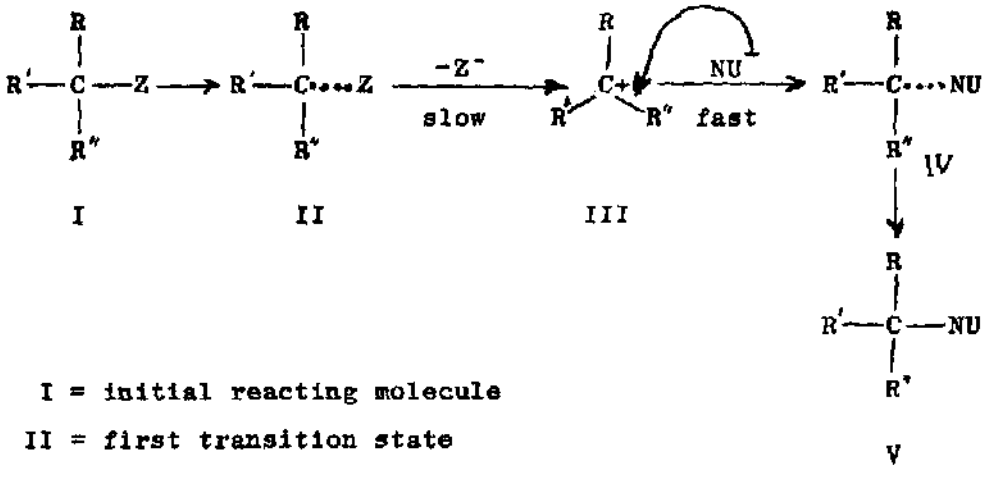
6.3.4 Mechanism

We have already mentioned bond-breaking and bond-making as processes that occur in the overall reaction. The question may be asked: In what order do these chemical events occur?
The answer to this question is related to the mechanism of the reaction. If the old bond C—Z (see equation 3 above) is broken before the formation of the new bond, C—Nu, the mechanism is S_N1. On the other hand if the breaking of the old bond C—Z and the making of the new one C—Nu occur at the same time, the mechanism is S_N2.

We shall now discuss each mechanism, and later discuss factors that favour one mechanism over the other in nucleophilic substitution reactions.

6.3.4.1 S_N1 Mechanism

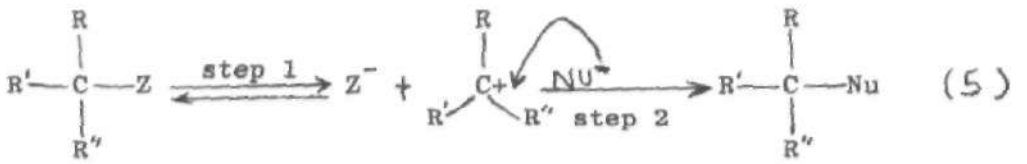
S_N1 means "substitution nucleophilic unimolecular". It is a two-step mechanism involving two transition states and one intermediate.
The general pattern of the S_N1 mechanism is as follows:



(4)

I = initial reacting molecule
II = first transition state
III = the carbonium ion intermediate
IV = the second transition state
V = the substituted product

The first transition state shows the old C—Z bond partially broken.
The second transition state shows the new C—Nu bond partially formed.
Usually these transition states are not shown in writing a reaction sequence.
Thus we have:



(5)

The processes are as follows:

(i) The reacting molecule ionises (heterolytic cleavage of C—Z) to give an intermediate carbonium ion.

(ii) The nucleophile then "attacks" the carbonium ion as shown by the curved arrow, forming the product.

If we examine equations (4) and (5) above, we find that:

(i) Only one entity (molecule) is involved in the transition state of step 1.

(ii) Step 1 is a slow and reversible process. It is called the rate-limiting step. It determines the rate of the overall reaction. One of the implications of (i) and (ii) above is that the rate of reaction (kinetics) that goes by S_N1 pathway is determined by the concentration of only one of the reactants, i.e. the molecule (or entity) present at the first transition state. In the example we have given (see equation 4) rate $\propto [R_3CZ]$. It is independent of the concentration of the nucleophile (Nu^-).

(iii) Step 2 is an irreversible and fast process.

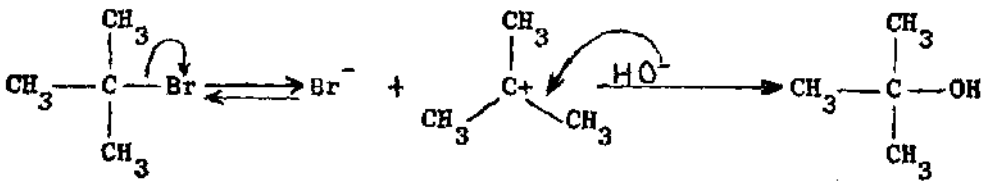
Specific example

Let us now illustrate the S_N1 mechanism using a specific example. Let us consider the hydrolysis of tertiary butyl bromide in aqueous solution of NaOH:

$$(CH_3)_3CBr + aqNaOH \longrightarrow (CH_3)_3COH + NaBr \qquad (6)$$

The nucleophile = hydroxide ion (HO^-)

The mechanism is as follows:



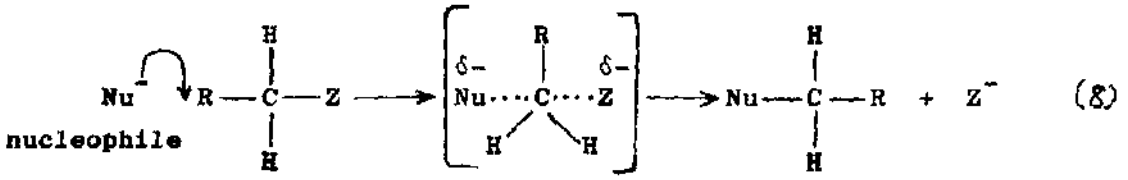
(7)

2-methyl-2-bromopropane tertiary carbonium ion 2-methylpropan-2-ol

6.3.4.2 S_N2 mechanism

S_N2 means "substitution nucleophilic bimolecular". It is a one-step mechanism involving one transition state. The breaking of the existing bond C—Z and the formation of the new bond C—Nu, occur at the same time (see 6.3.4). Such a reaction is said to be concerted.

Let us use a general equation to illustrate the basic principle of S_N2 reactions:



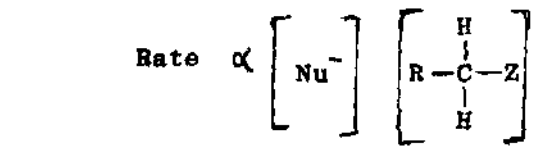
(8)

nucleophile reactant molecule transition state subsitution product

Processes involved in the overall reaction

(i) The nucleophile attacks the alkylhalide from a point opposite to the site of the halogen.

(ii) Two entities (the nucleophile and the reacting molecule) are involved at the transition state. Thus the rate of the overall reaction is determined by the concentrations of both entities, i.e. the reaction is bimolecular.



(9)

(iii) At the transition state, the existing C—Z bond is partially broken and the new C—Nu bond is partially formed. Both are shown by dotted lines [(....) see topic 4].

Specific examples:

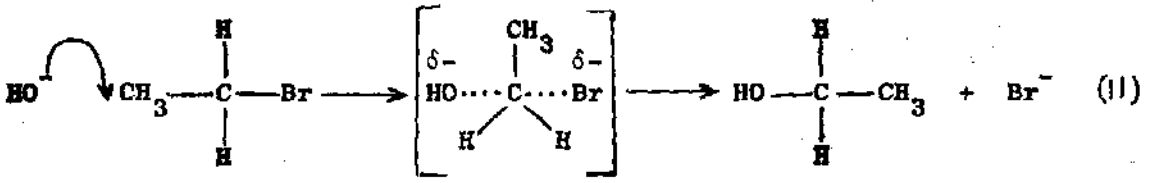
Let us now consider some specific examples of nucleophilic substitution that go by the S_N2 mechanism.

(i) Hydrolysis of bromoethane in aqueous solution of sodium hydroxide.
The overall reaction is:

$$CH_3CH_2Br + aqNaON \longrightarrow CH_3CH_2OH + NaBr \qquad (10)$$

Mechanism:

The nucleophile is the hydroxide ion (HO^-)



(11)

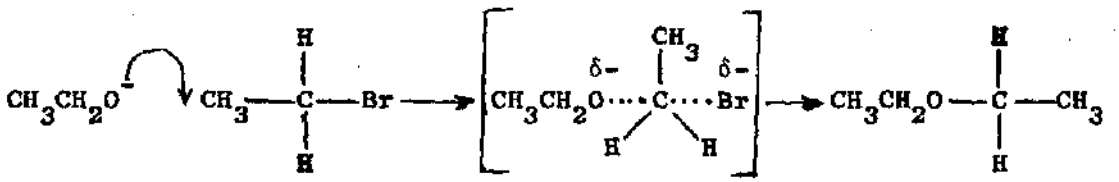
bromoethane transition state ethanol

(ii) Formation of ethers from alkyhalides and sodium alkoxide solution.
(Williamson's ether synthesis)
Equation of the overall reaction is:

$$CH_3CH_2Br + CH_3CH_2ONa \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr \qquad (12)$$

Mechanism:

The nucleophile is the ethoxide anion ($CH_3CH_2O^-$)



(13)

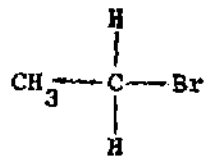
nucleophile bromoethane transition state = $(CH_3CH_2OCH_2CH_3)$ ethoxyethane

6.3.5 Factors affecting mechanism

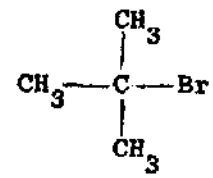
So far, we have outlined the mechanism of the S_N1 and S_N2 reactions. The question might be asked: What makes some reactions follow the S_N1 pathway and others S_N2? We shall discuss three factors:

(a) Structure:

Here we shall consider the "crowdedness" of the reacting molecule. Consider structures I and II below:

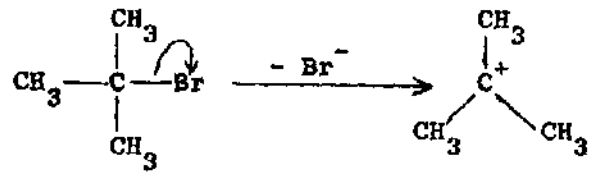


I



II

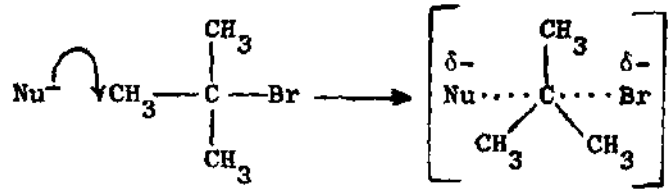
Structure II is more crowded at the central carbon atom than I. The more energetically favourable reaction path for structure II would thus be one in which there will be less "crowding" at the transition state i.e. S_N1:



crowded — less crowded

Is energetically favourable

Compare this to S_N2. For example:

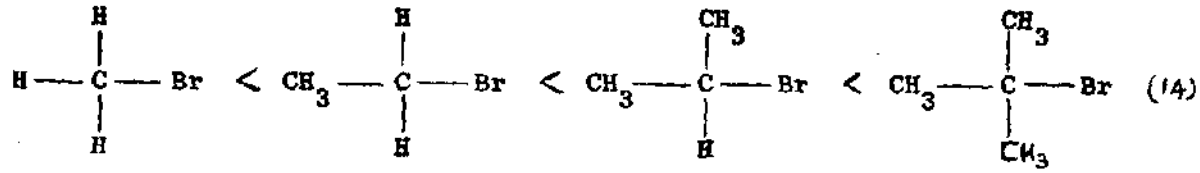


crowded — more crowded

Is energetically unfavourable

Such factors may not be dominant for structure I which reacts by S_N2.

Generally the trend of "crowdedness" is as follows:



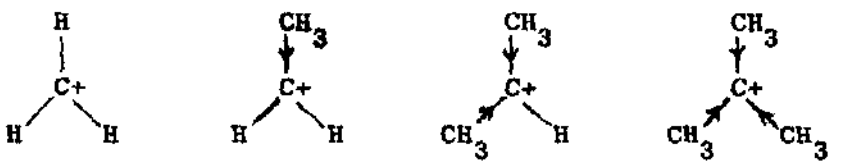
I II III IV

Increasing "crowdedness"

1 Increasing tendency to S_N1 mechanism from I-IV.

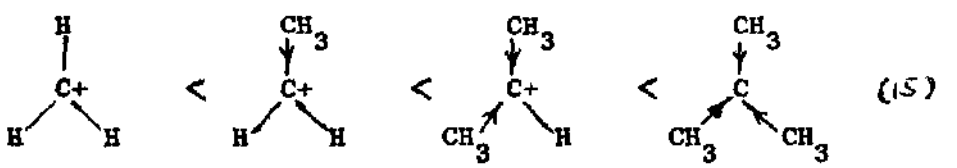
2 Decreasing tendency to S_N2 mechanism from I-IV.

In addition to steric relief effects, the methyl groups attached to the positive carbon atom help to <u>delocalise</u> the charge through <u>inductive effects</u> opposite in direction to that which we discussed in topic 1. This is shown below (see direction of arrows).



I II III IV

This tends to disperse the charge and results in <u>stabilising</u> the carbonium ion. The stabilisation increases with increasing number of attached methyl groups. Thus the <u>order of stability</u> of carbonium ion which parallels its <u>ease of formation</u> increases from I through IV; as shown below:



(15)

<u>Increasing stability of carbonium ion</u> ⟶

1 Increasing tendency to S_N1 mechanism from I-IV.

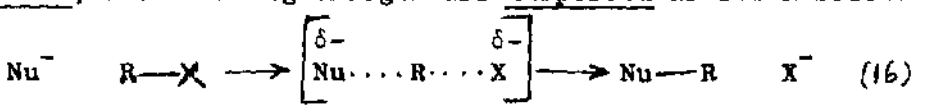
2 Decreasing tendency to S_N2 mechanism from I-IV.

⟶

(b) <u>Solvent effects</u>

Solvents in which reactions are carried out affect mechanisms of the reactions. Polar solvents (e.g. water) promote S_N1; non-polar solvents, S_N2.

Polar solvents interact with the intermediate <u>carbonium ions</u> (solvation) in S_N1, thus <u>stabilising</u> them. The greater the stability of the carbonium ion, the higher the chances of its formation, thus favouring S_N1. In S_N2, new charges are not formed at the <u>transition state</u> relative to the <u>starting material</u>; and existing charges are <u>dispersed</u> as shown below:

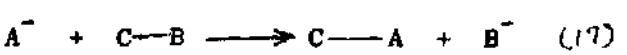


(16)

Thus stabilization afforded by solvating effects of polar solvents are not significant in S_N2 mechanism.

(c) Nature of the incoming nucleophile

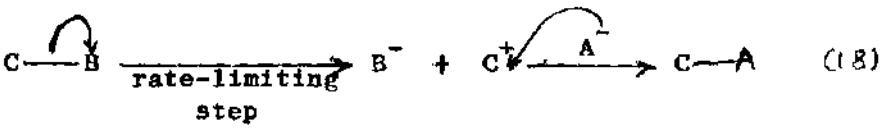
Generally, nucleophilic substitution reactions are of the nature:



$$A^- + C{-}B \longrightarrow C{-}A + B^- \quad (17)$$

(i) S_N1:

In S_N1 mechanism, the nature of A^- (the incoming nucleophile) does not affect the overall reaction. This is because it (i.e. A^-) does not participate in the rate-limiting step of the reaction, as shown below:



$$C{-}B \xrightarrow[\text{step}]{\text{rate-limiting}} B^- + C^+ \xrightarrow{A^-} C{-}A \quad (18)$$

(ii) S_N2:

In S_N2 mechanism, A^- attacks C—B directly and displaces B which leaves as a nucleofuge (B^-) as shown below:



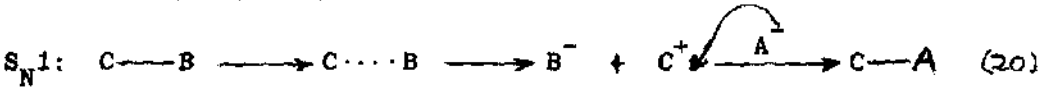
$$A^- + C{-}B \longrightarrow A{-}C + B^- \quad (19)$$

Thus, the more strongly nucleophilic the incoming reagent (A^-) is, the more the reaction will be promoted. Some of the general characteristics of strong nucleophiles include: low electron-attracting ability of the donor atom and high polarisability.

(d) Nature of the leaving group

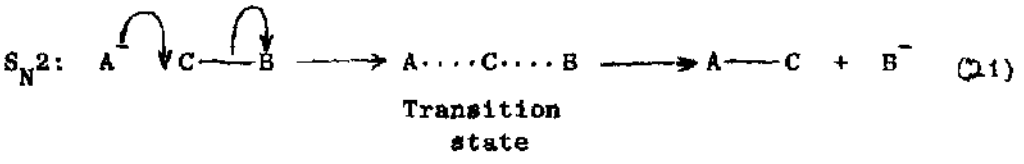
The nature of the leaving group affects both S_N1 and S_N2 mechanisms. This is because breaking of the bond between carbon and the leaving group is involved at the transition state of both mechanisms, as shown below:

(i) S_N1:



$$C{-}B \longrightarrow C\cdots B \longrightarrow B^- + C^+ \xrightarrow{A^-} C{-}A \quad (20)$$

(ii) S_N2:



$$A^- + C{-}B \longrightarrow A\cdots C\cdots B \longrightarrow A{-}C + B^- \quad (21)$$

Where B = the leaving group.

The more easily the C——B is broken, the more easily B can be displaced; thus promoting the reactions. The ease of breaking the C——B bond and hence displacement of B, is determined, amongst other things, by the nature of B. Generally, groups bonded to carbon by relatively small atoms having high electron-attracting abilities and low polarisability are not easily displaced. They are thus generally referred to as poor leaving groups. Examples include: HO^-, RO^-, NH_2^-. Good leaving groups are those that are easily displaced; hence the opposite of poor leaving groups.

The higher halides, Cl^-, and especially Br^- and I^- are typical examples of good leaving groups.

Good leaving groups promote both S_N1 and S_N2 mechanisms. The summary of sections a, b, c and d discussed above is given in table 6.2 below:

TABLE 6.2

	S_N1	S_N2
(a)	Favoured by alkylhalides having "bulky" groups (tertiary alkyl-halides).	Favoured by alkylhalides that do not have "bulky" groups (primary alkylhalides and to some extent secondarys.)
(b)	Favoured by polar solvents.	Favoured by non-polar solvents.
(c)	Nucleophilic "strength" of the incoming group is not a significant factor in the overall reaction.	"Strength" of the incoming nucleophile is important.
(d)	Favoured by good leaving groups.	Favoured by good leaving groups.

6.3.6 Summary

(a) Nucleophilic substitution reactions are those in which an incoming nucleophile displaces an atom (or group of atoms) from a carbon centre.

(b) The mechanism is usually described on the basis of:

(i) The timing of the attack of the incoming nucleophile.

(ii) The sequence of bond-breaking and bond-making.

(iii) The number of molecules (or entities) participating in the rate-limiting transition state.

(c) There are some factors which affect the mechanism of nucleophilic substitutions. They include:

(i) Structure of the reacting molecule.

(ii) Nature of the nucleophilic reagent.

(iii) Nature of the reaction medium.

(iv) Nature of the leaving group.

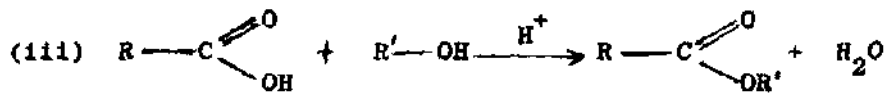
(d) Polarization of the C——Z bond plays an important role in initiating nucleophilic substitutions.

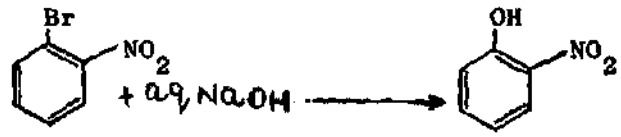
6.4 ANSWERS

(1) Nucleophiles are Lewis bases.

(2) The reactions that represent nucleophilic substitutions are:

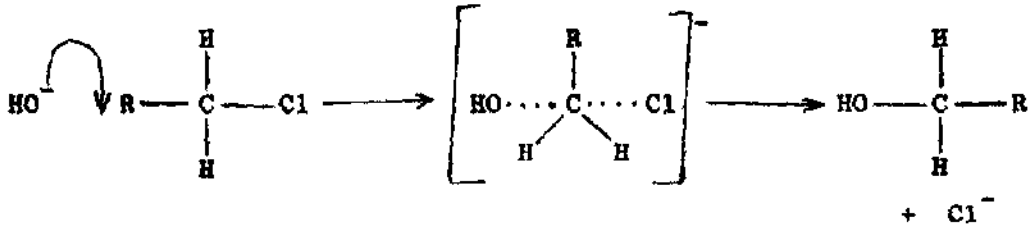
(i) $R—Cl + NaOH \longrightarrow R—OH + NaCl$

(iii) 

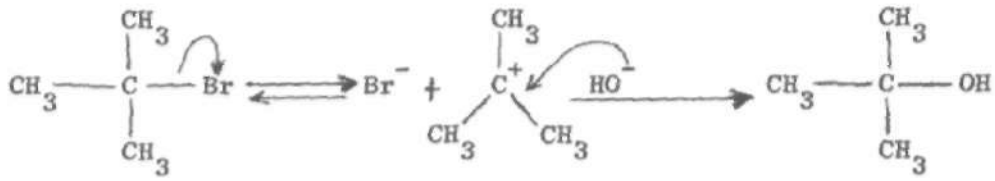
(iv) 

(ii) and (v) are not substitution reactions

(3) In the reaction between $R—CH_2—Cl$ and aqNaOH; the nucleophile is HO^- furnished by the aqNaOH:



(4) The hydrolysis of $(CH_3)_3CBr$ in aqueous NaOH by S_N1 mechanism is as follows:



(5)

	Factors that promote S_N1	Factors that promote S_N2
(i)	"Bulky" substituents on the central carbon atom, e.g. tertiary alkylhalides.	Non-bulky groups on the central carbon atom, e.g. primary alkylhalides.
(ii)	Polar solvents, e.g. water.	Non-polar solvents, e.g. acetone.
(iii)	Easily polarizable groups attached to the central carbon atom (i.e. good leaving groups).	Good leaving groups.

TOPIC 7

ELECTROPHILIC SUBSTITUTION REACTIONS

7.1 INTRODUCTION

In the last topic, we discussed nucleophilic substitution reactions. In this topic, we shall discuss electrophilic substitution reactions. The overall principles of both reactions (i.e. nucleophilic and electrophilic substitutions) are the same. Both involve the displacement of one group by another. Some of the specific differences are:

(i) The kind of organic compounds involved in each reaction.

(ii) The types of reagents involved.

(iii) The processes (mechanisms) involved in the transformation of the reactants to products.

Having studied both topics (6 and 7) you should be able to:

(i) Know the types of organic compounds typically involved in each reaction-type.

(ii) Know the basic principles underlying each reaction-type.

(iii) Relate the principles to see where they are similar and where they differ.

(iv) Apply the principles to specific cases of the reactions.

(v) Use the knowledge of the principles in solving problems in organic reactions.

7.2 EXERCISES

(1) Classify the following compounds according to whether they are aromatic or not.



(i) (ii) (iii) (iv) (v)

(2) (a) Use Lewis structures to show the 6π delocalised bond-electrons in benzene.

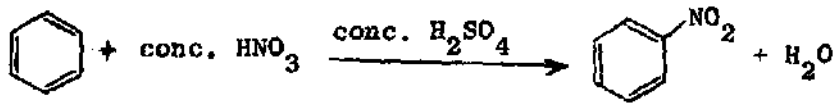
(b) Name one important effect of delocalisation of π electrons on reactivity of benzene.

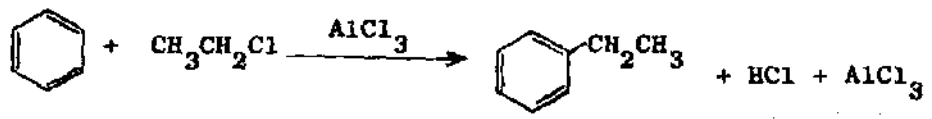
(c) Benzene is 36.0 Kcal/mole more stable than would normally be expected from its classical structure. By what name is this

usually known?

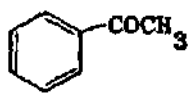
(3) (a) Using a general equation, outline the essential mechanism of electrophilic substitution.

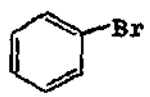
(b) Outline the mechanisms of the following reactions:

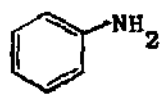
(i) 

(ii) 

(4) Using relevant equations and reagents, show how benzene may be converted to:

(i) 

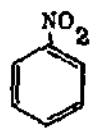
(ii) 

(iii) 

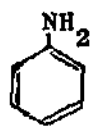
7.3 LESSON NOTES

7.3.1 Overview

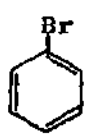
Electrophilic substitution is the characteristic reaction of benzene and its derivatives. The structure of benzene has already been discussed (see topic 4.3.6). Examples of the derivatives of benzene include:

(i) Aromatic nitro-compounds e.g. 

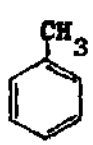
nitrobenzene

(ii) Aromatic amines e.g. 

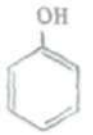
amino benzene

(iii) Aromatic halogen compounds e.g. 

bromo benzene

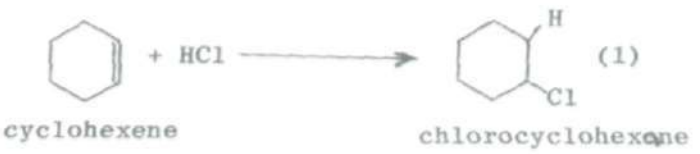
(iv) Alkyl benzenes e.g. 

methylbenzene

(v) Phenols e.g.  hydroxy-benzene etc.

7.3.2 Aromatic character (aromaticity)

Benzene has a system of 6π electrons shared round the six carbon atoms in the ring (see topic 4.3.6). These electrons are said to be delocalised. One of the important effects of this delocalisation is that benzene molecules exhibit an unusual chemical stability in their reactions. For example, HCl easily adds to cyclohexene, but benzene is unreactive towards it:





The expectation is that since benzene is unsaturated it should respond to electrophilic addition reaction which is in fact a characteristic reaction of unsaturated bonds (as we shall see in topic 9), but benzene rarely reacts this way. Instead it reacts by substitution.

This unusual chemical stability of benzene which underlies its chemical behaviour, put together, is referred to as aromatic character of benzene or simply aromaticity.

At least two conditions are required for aromaticity in monocyclic (one ring) compounds. These are:

(i) Presence of 6π electrons.

(ii) Uninterrupted conjugation in the ring atoms of the classical structures representing the molecule.

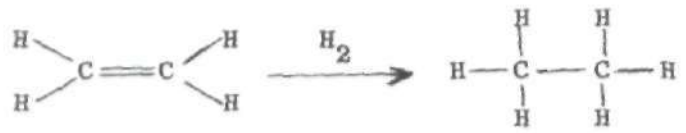
For example, consider structures II and III below compared to benzene (structure I). Can you see why II and III are not aromatic even though their structures contain conjugation and 6π electrons respectively?

AROMATIC	NOT AROMATIC	NOT AROMATIC
		
I	II	III
Benzene	Cyclooctatetraene	cycloheptatriene
(i) 6π electrons (ii) Uninterrupted conjugation (Is aromatic)	(i) 8π electrons (ii) Uninterrupted conjugation (Is not aromatic)	(i) 6π electrons (ii) Interrupted conjugation (Is not aromatic)

7.3.3 Resonance energy in benzene

Resonance energy is sometimes called delocalization energy; both refer to the same idea. Let us discuss some basic ideas that will help us to understand what resonance energy means.

Unsaturated bonds can be hydrogenated to produce saturated compounds e.g. conversion of alkenes to alkanes:



ethene ethane (3)

The process is called hydrogenation.. The heat energy evolved in the process is called heat of hydrogenation.

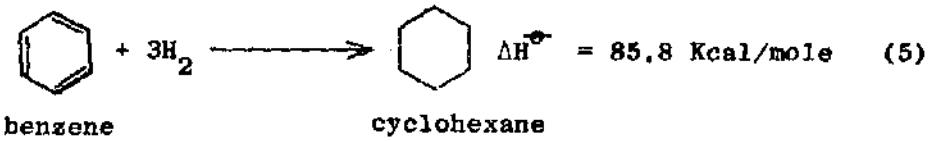
It has been found from experimental studies that when cyclohexene is hydrogenated, 28.6 Kcal of heat is evolved per mole:



ΔH° = -28.6 Kcal/mole (4)

cyclohexene cyclohexane

If one double bond in a cyclic system of this nature produces 28.6 Kcal of heat energy on hydrogenation, we should expect that three double bonds in a similar system should produce 3 x 28.6 (85.8 Kcal/mole) of heat energy, i.e.:



However, it was found that heat of hydrogenation of benzene is 49.8 Kcal/mole, and <u>not</u> 85.8 Kcal/mole, representing a shortfall of 36.0 Kcal/mole. What does this tell us?

It means that benzene molecule is <u>more stable</u> by 36.0 Kcal/mole than would normally be expected. We can say this in another way: benzene molecule is more stable than a hypothetical cyclohexatriene by 36.0 Kcal/mole.

This stability is attributed to the <u>delocalization</u> of the 6π electrons in benzene, and the <u>amount</u> of the stabilization (36.0 Kcal/mole) is known as the <u>resonance energy</u> of benzene. This is illustrated in fig. 7.1:

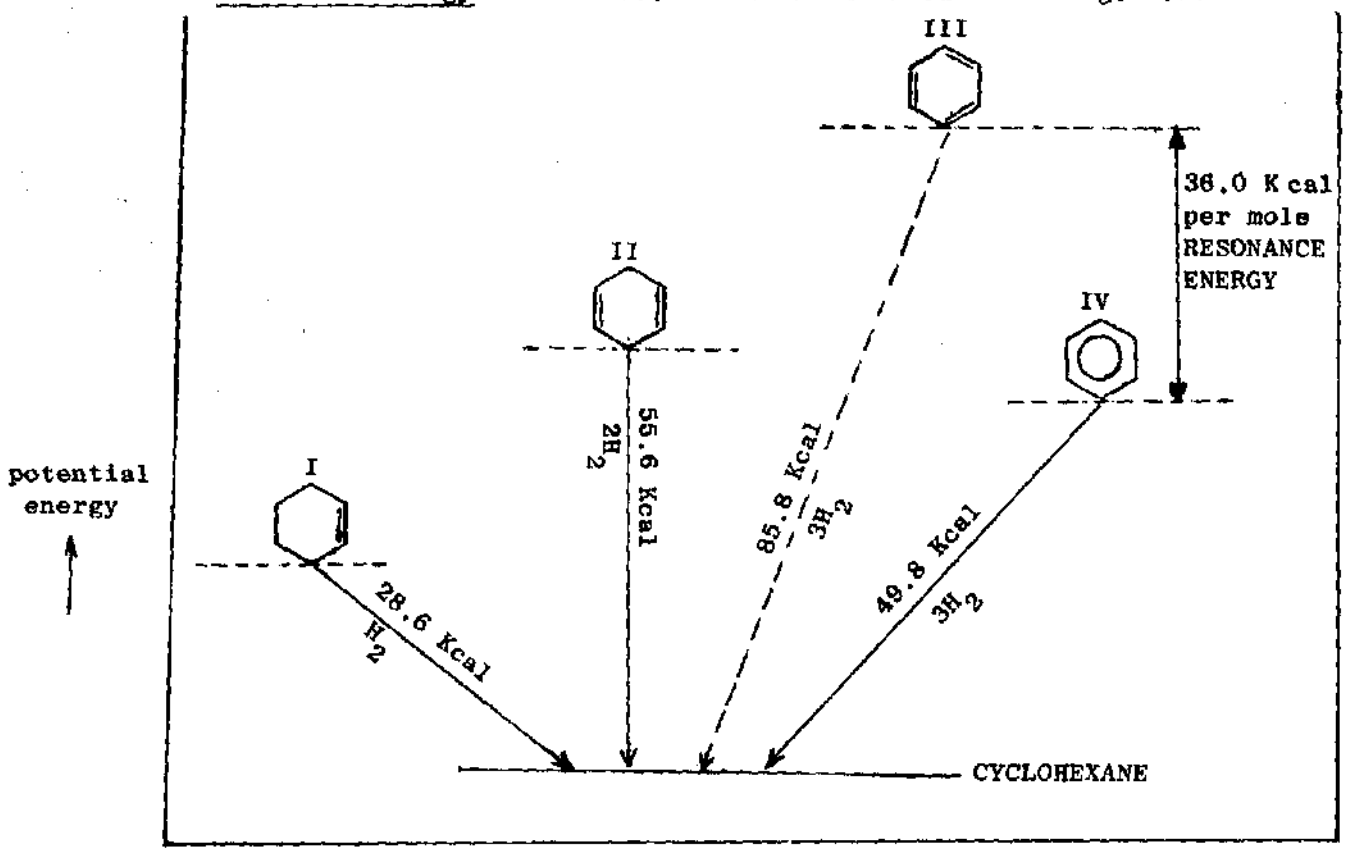


Fig. 7.1

I = cyclohexene
II = cyclohexadiene
III = cyclohexatriene (hypothetical, is not found to exist)
IV = benzene

Fig. 7.1 illustrates the chemical stability of benzene as a consequence of resonance stabilization.

7.3.4 Implication of resonance stabilization in chemical reactions of benzene

(i) Benzene reacts in such a way that its aromatic character is preserved at the end of the reaction (i.e. in the products).

(ii) Its reactions are characteristically those of substitution which preserves the aromatic character, rather than addition which destroys it.

(iii) Its reactivity is relatively low. Thus catalysts are generally used to enhance its reactions.

7.3.5 Electrophilic susbstitution in benzene

Having discussed the background ideas that determine the way in which benzene behaves in chemical reactions, we should now proceed to discuss its reactions, especially their mechanisms.

Reactions of benzene are characteristically electrophilic substitutions. What are the basic principles of electrophilic substitutions? Before we introduce ideas that answer the question, let us discuss electrophiles or electrophilic reagents.

(a) Electrophiles are electron-seeking reagents.
They react by accepting an electron-pair from a donor. Electrophiles are thus Lewis acids. Often, they are positively charged but there are also those that are neutral molecules. A summary of common electrophiles is given below in table 7.1

TABLE 7.1

Charged Electrophiles	Neutral Electrophiles
H^+	$AlCl_3$
H_3O^+	$FeBr_3$
NO_2^+	BF_3
PhN_2^+	SO_3
R_3C^+	Br_2

(b) Mechanism of electrophilic substitution

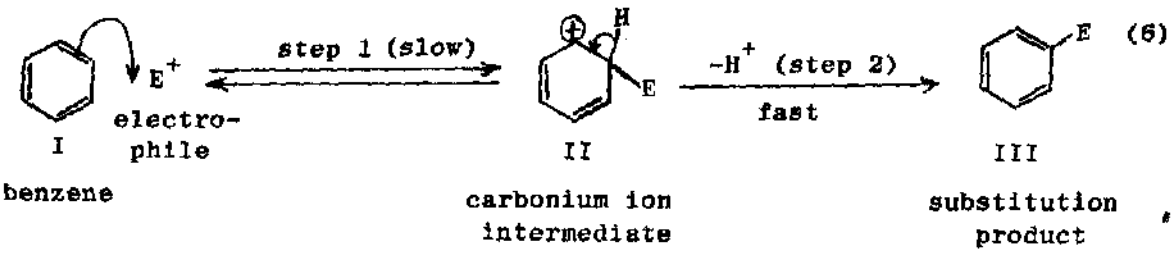


I II III

Structures I and II are known as resonance or classical structures of benzene. Structure III is the "true" structure of benzene molecule. It is a resonance hybrid, i.e. partway between structures I and II.

In discussing the reactions of benzene, the molecule is represented by either of the classical structures; but the "true" structure of the molecule should always be borne in mind.

The basic principles of the mechanism of electrophilic substitution in benzene may be represented as follows:

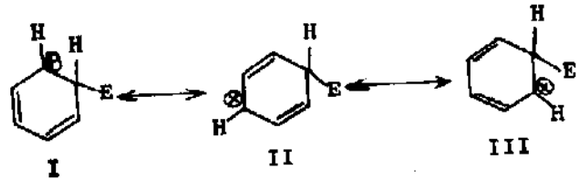


The processes involve:

(i) The attack of an electrophile (E^+) on the π system of the benzene ring; leading to the formation of an intermediate carbonium ion (II) called: Wheland intermediate. The intermediate has lost the aromatic character of the starting benzene molecule (can you see how?). It is thus less stabilised compared to the original benzene molecule. The implication of this is that a significant amount of energy (activation energy) is required to reach the transition state of step 1 which is a slow and rate-limiting step.

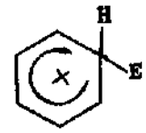
(ii) H^+ is removed from the intermediate to form the substitution product (III) in which the incoming electrophile (E^+) has displaced a hydrogen. (Compare the initial reacting molecule to the product.)

The intermediate carbonium ion formed in equation (6) above is also resonance stablised, but to a lesser extent compared to the reacting benzene molecule. The resonance structures of the intermediate from (6) are shown in (7) below:



I II III (7)

The "true" structure (IV) is partway between structures I, II and II, as shown in (8) below:

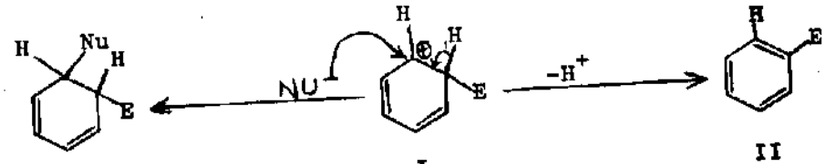


IV (8) (8)

As with benzene, the classical structures are generally used in discussing reactions, but the "true" structure is always borne in mind also.

(c) Substitution versus addition

Let us consider the reaction process shown in (6) a bit more closely at the point of the intermediate. Theoretically, the intermediate could undergo addition reaction by an attack of a nucleophile on the positive carbon (refer S_N1). But if an addition product were formed it would destroy the aromatic character of the benzene and the associated stability, whereas substitution (ejection of H^+) restores it. Thus substitution is energetically more favourable; hence formation of substitution product. This is illustrated in (9) below:



(9)

III
addition product
(non-aromatic)

I
Wheland
intermediate
(non-aromatic)

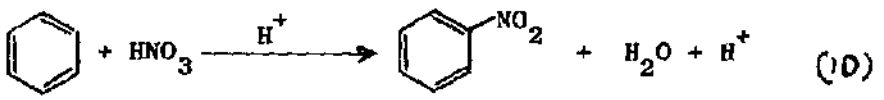
II
substitution
product
(aromatic)

(d) Specific examples

Having discussed the broad principles of electrophilic substitution, let us consider a few specific examples. We shall consider nitration, halogenation and alkylation as examples to illustrate the principle of electrophilic substitution we have already outlined.

I Nitration

Aromatic nitro-compounds are formed by this process. Benzene is reacted with a mixture of concentrated nitric and sulphuric acids.



(10)

Sulphuric acid acts as a catalyst.

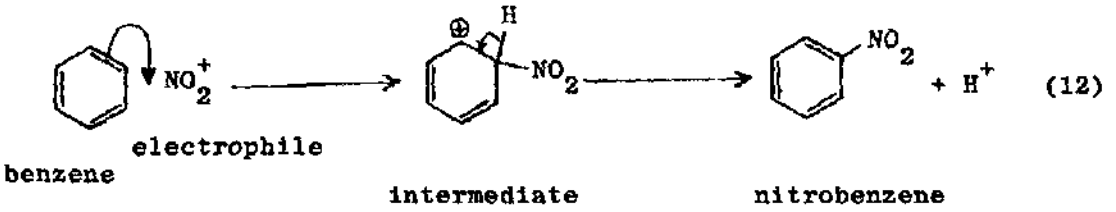
Mechanism:

Two main processes are involved:

(i) Generation of the electrophile (NO_2^+: called nitronium ion); achieved by reaction of the two acids:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \quad (11) \qquad (11)$$

(ii) Reaction of the electrophile with benzene as shown in (12) below:



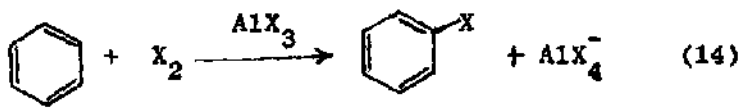
(12)

It is a bi-molecular reaction which is first order with respect to the reagent and first order with respect to the reactant:

$$\text{Rate} \propto [Ar\text{—}H][NO_2^+] \qquad (13)$$

II Halogenation

Halogenation is the reaction of halogens (usually Cl and Br) with benzene in the presence of suitable catalyst to give the corresponding aromatic halogen compound. Catalysts generally used include AlX_3, FeX_3 and $ZnCl_2$ (X = Cl or Br). The general equation of reaction involved in halogenation is shown in (14) below:

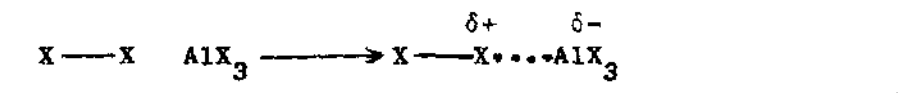


(14)

(X = Cl or Br)

Mechanism:

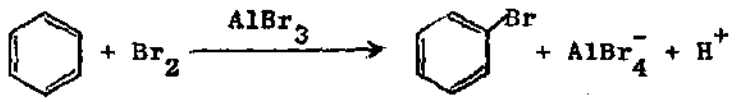
The electrophile in halogenation of benzene is a polarised complex which attacks the π system of benzene molecule to form the substituted product. The polarisation is induced in the halogen molecule by the Lewis acid catalyst. This is shown in (15) below in which there is a partial withdrawal of an electron-pair from the halogen molecule by the aluminium atom of the catalyst:



(15)

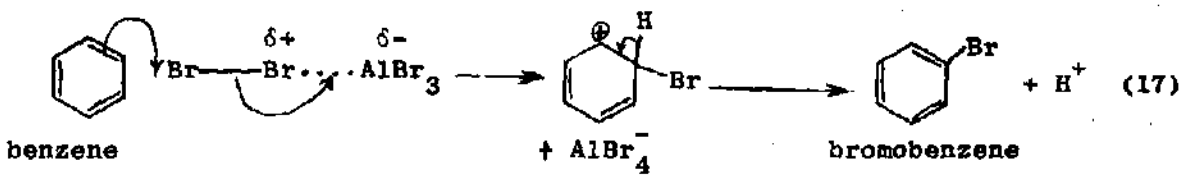
halogen molecule — catalyst — polarised complex (electrophile)

Let us use the reaction of bromine with benzene as a specific example. (Chlorination follows the same principle.) The general equation of the reaction is as follows:



(16)

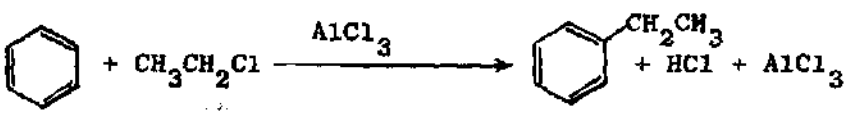
The mechanism is as follows:



benzene — + $AlBr_4^-$ — bromobenzene — (17)

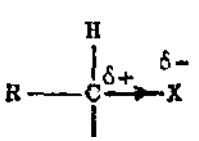
III Alkylation

Alkylation is reaction of alkyl halide with benzene, producing alkyl benzene. Similar catalysts are used as for halogenation. The equation of the overall reaction is as follows:



(18)

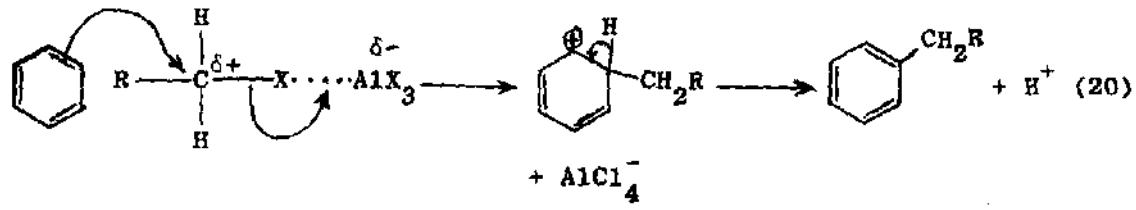
In alkyl halides, the carbon atom bonded to the halogen acquires a partial positive charge as shown below:



(19)

Thus it acts as an electrophile in reaction with benzene. It is however, not sufficiently electrophilic to effect substitution in benzene, hence the requirement for a catalyst. The catalyst acts to increase the C—X polarisation. This results in a polarised complex which attacks the π system of benzene to form a substituted product.

The general mechanism of the reaction is as follows:

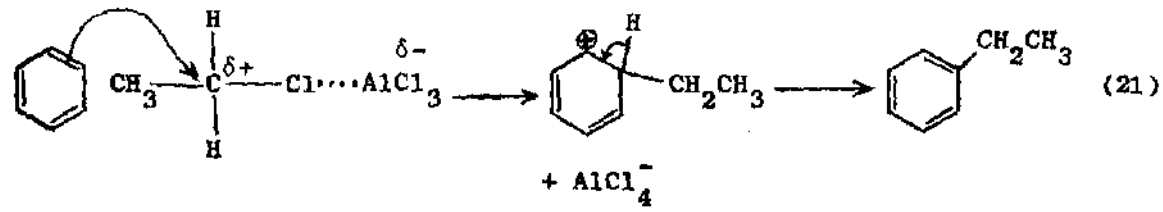


(20)

Where R = an alkyl group

X = a halogen (Cl or Br)

The reaction of benzene with ethyl chloride (chloroethane) is given below as a specific example to illustrate the mechanism:

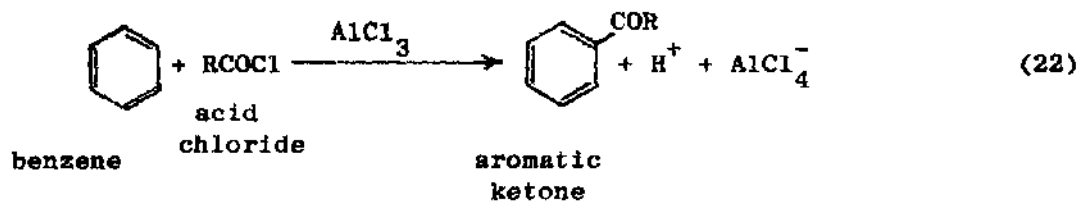


(21)

Note:

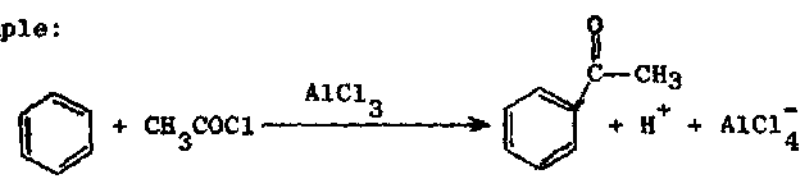
Alkylation and acylation are generally referred to as Friedel-Crafts reactions.

Acylation is the reaction of benzene with acid chlorides to form corresponding aromatic ketones. The general equation of the reaction is as follows:



(22)

For example:



(23)

In acylation, the electrophile is an <u>acylium ion</u> formed from reaction of the acid chloride with the Lewis acid catalyst as shown below:

$$\underset{\text{acid chloride}}{RCOCl} + \underset{\text{catalyst}}{AlCl_3} \rightleftharpoons \underset{\substack{\text{acylium ion} \\ \text{(electrophile)}}}{RCO^+} + AlCl_4^- \qquad (24)$$

Attempt to work out the mechanism of the reaction given in equation (23) above.

7.3.6 <u>Summary</u>

(a) In this topic the general principle of electrophilic substitution is discussed.

(b) Preliminary ideas about electrophilic substitution discussed include:

(i) Electronic nature of aromatic compounds.

(ii) Aromatic character.

(iii) Resonance energy and resonance stabilization.

(iv) Classical and "true" structures of benzene.

(c) The main features of electrophilic substitution are:

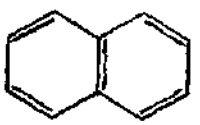
(i) Attack of <u>electrophile</u> on a benzene ring forming a <u>carbocation</u> intermediate which <u>ejects</u> a proton (H^+) to form a <u>substiution product</u>.

(d) Addition products are not formed because the process involved is energetically less favourable than substitution.

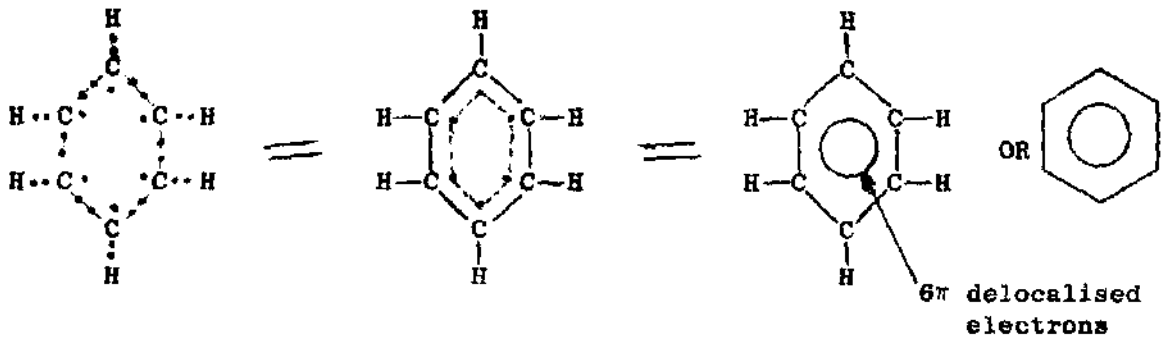
(e) Because of the chemical stability of benzene, catalysts are required to promote its reactions towards electrophilic reagents. The reactions are characterised by a tendency to <u>preserve</u> the aromaticity of benzene.

7.4 ANSWERS

(1)

AROMATIC	NON-AROMATIC
(iii) 	(i) 
(v) 	(ii) 
	(iv) 

(2) (a)

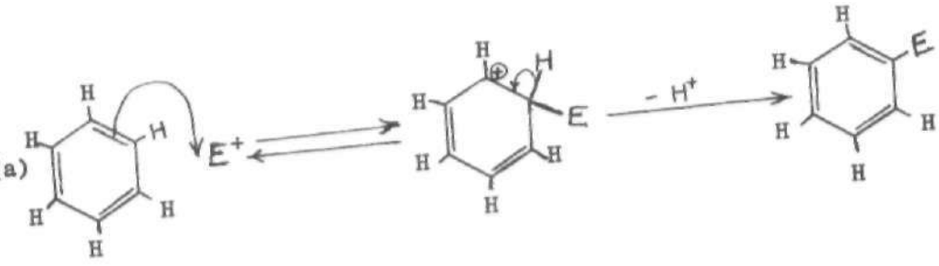


The six dots (•) forming the "inner ring" = the 6π delocalised electrons. Each of the six electrons belong to each of the six carbon atoms. They (the six electrons) are shared round the six carbon atoms.

(b) It makes benzene chemical stable, thus reducing its reactivity.

(c) Resonance energy or delocalization energy.

(3) (a)

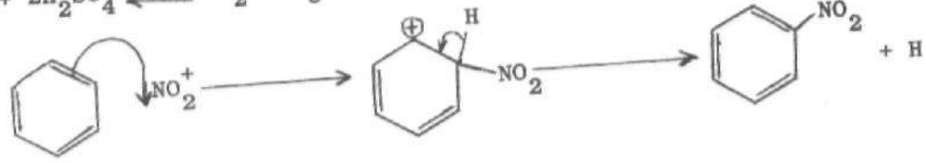


Note:

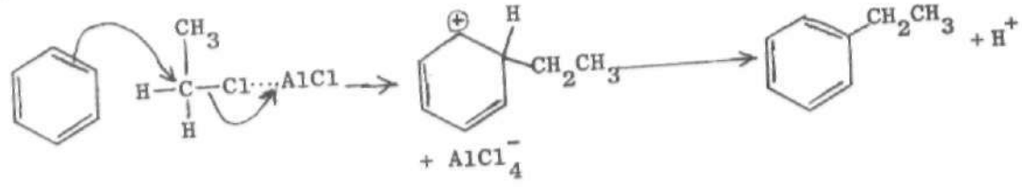
The hydrogens on the ring are shown here as a reminder. They are generally left out in the reactions of benzene. They should however be borne in mind.

(b) $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$

(i)

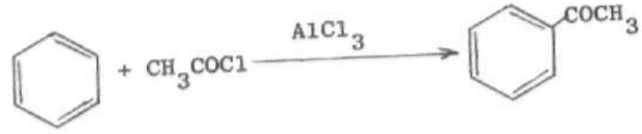


$CH_3CH_2Cl + AlCl_3 \rightleftharpoons CH_3\overset{+}{C}H_2 + AlCl_4^-$

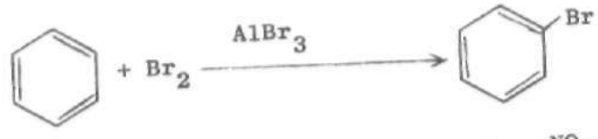


(4)

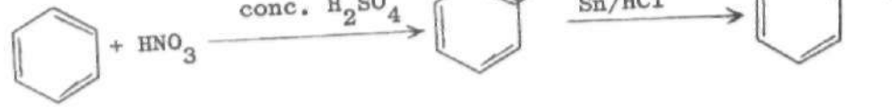
(i)



(ii)



(iii)



TOPIC 8

ELECTROPHILIC ADDITION REACTIONS

ADDITION REACTIONS

8.1 INTRODUCTION

In this topic and the next, we shall discuss addition reactions. The main feature of addition reactions is that they involve the "building" of one molecule into another. Addition reactions occur in:

(i) Compounds which have carbon-carbon multiple bonds in their molecules. These are alkenes and alkynes.

(ii) Compounds having carbon-oxygen double bonds in their molecules. These are aldehydes and ketones. (Recall the classification in topic 5, fig. 5.1.)

Examples of these are shown below:

(i) $\rangle C{=}C\langle$ alkenes

$-C{\equiv}C-$ alkynes

(ii) $\rangle C{=}O$ aldehydes and ketones

Addition reactions occur by three main mechanisms:

(i) Electrophilic addition: This is found in alkenes and alkynes.

(ii) Nucleophilic addition: This is found mostly in carbonyl compounds - aldehydes and ketones.

(iii) Free-radical addition: This is found in compounds having carbon-carbon double bonds, including benzene that is resistant to addition under electrophilic substitution (recall topic 7).

The reaction processes in electrophilic and nucleophilic additions involve heterolytic cleavage of bonds. Those involved in free-radical addition involve homolytic cleavage of bonds.

As for free-radical mechanism, we shall give just one example to illustrate its principles and leave further discussion on it.

In this topic we shall discuss electrophilic addition reactions.

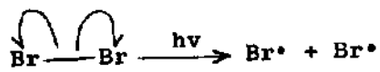
Free-radical addition

Ethene reacts with bromine in the gaseous phase in presence of light:

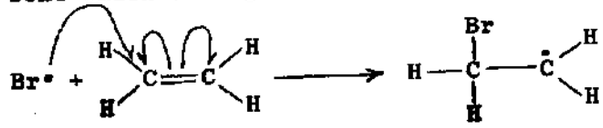
$$CH_2{=}CH_2 + Br_2 \xrightarrow{h\nu} CH_2BrCH_2Br$$

The mechanism involves three main steps:

(i) Homolytic cleavage of Br—Br thus:

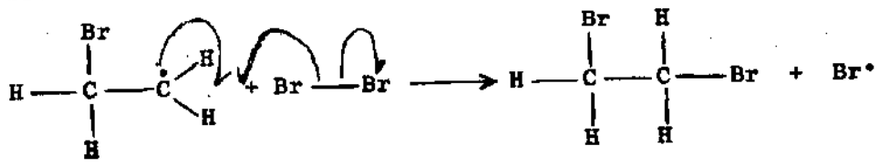


(ii) The second step is the attack of the bromine radical (atom) on the π bond which undergoes homolytic cleavage as shown:



bromoethyl radical

(iii) The third step is the attack of the bromoethyl radical on a bromine molecule:



The Br• generated at the end of step (iii) initiates the process of step (ii) again; and the alternation between steps (ii) and (iii) continues. This is an example of chain reaction.

We shall now proceed to discuss electrophilic addition which is the theme of this topic. By the time you have completed studying this topic, you should be able to:

(i) Recognise electrophilic addition reactions.

(ii) Know the bond-breaking and bond-making processes involved in the overall reaction.

(iii) Demonstrate an understanding of the mechanism of those processes.

(iv) Use knowledge of i-iii to solve problems in organic reactions.

8.2 EXERCISES

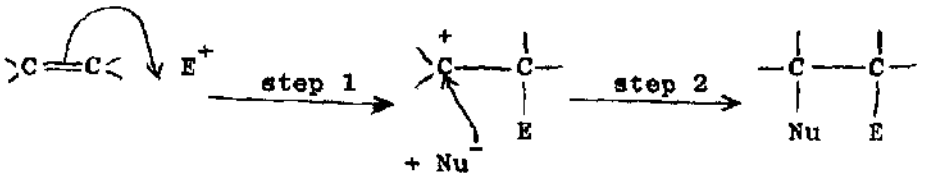
(1) (a) In what class of organic compounds do electrophilic addition reactions occur?

(b) What are the main strucutral features which make such compounds undergo electrophilic addition reactions?

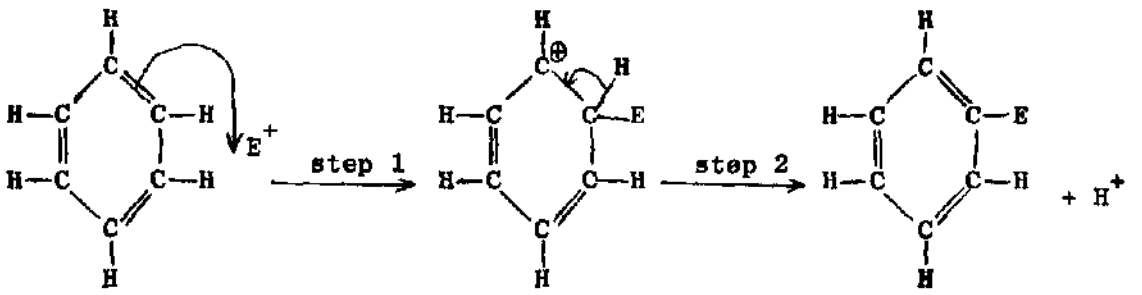
(2) Use the example of the reaction between ethene and hydrogen chloride in a polar solvent to illustrate the general mechanism of electrophilic addition reactions.

(3) Consider reactions (a) and (b) below:

(a)



(b)



a = the general mechanism for electrophilic addition reactions

b = the general mechanism for electrophilic substitution reactions

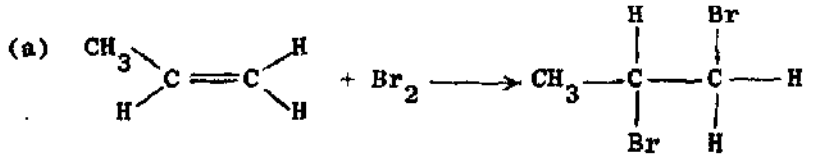
Compare steps 1 and 2 in both reactions:

(i) What is the major difference in the processes of the overall reactions in both cases?

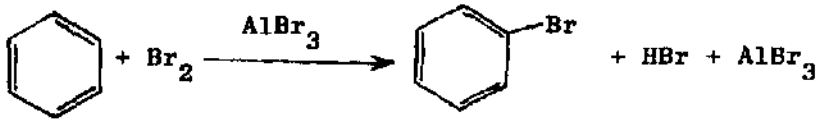
(ii) At what step of the reactions does this difference feature?

(4) Consider reaction (a) and (b) below:

(a)



(b)



(i) Outline the mechanism of both reactions.

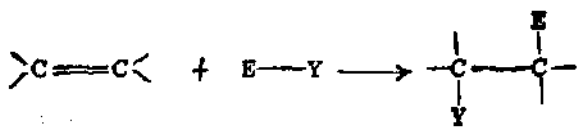
(ii) Why is a catalyst required in reaction (b) and none in reaction (a)?

8.3 LESSON NOTES: ELECTROPHILIC ADDITION REACTIONS

8.3.1 Electrophilic addition:

Electrophilic addition reactions occur in compounds which have carbon-carbon multiple bonds. These are alkenes and alkynes. We shall focus attention on alkenes as the initial addition to alkynes converts them to alkenes.

The main feature of electrophilic addition is the addition of the groups of a molecule across the carbon-carbon double bond; shown in (1) below:

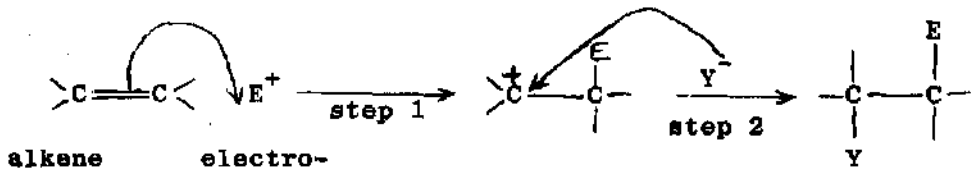


(1)

One of the double bonds (i.e. the more diffused π bond) is broken in the process leading to a saturated product. The reaction is initiated by an electrophile, E^+ (remember electrophilic substitution in benzene?).

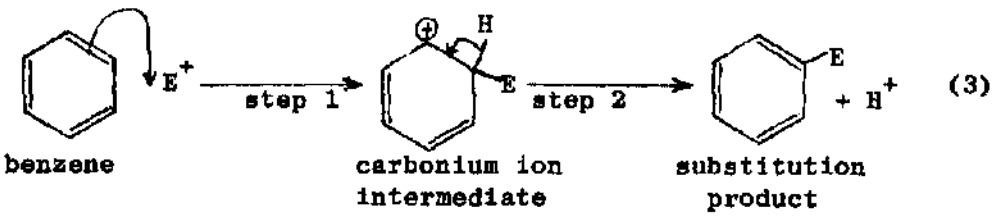
8.3.2 Mechanism:

The mechanism of electrophilic addition involves a two-step process:



(2)

Step 1 is attack of electrophile (E^+) on the π bond. The bond breaks heterolytically and the electron-pair of the π bond is used for bonding between carbon and the electrophile. This process gives an intermediate carbonium ion. The second step involves attack of a nucleophile (usually a conjugate base of the electrophilic reagent) on the carbonium ion leading to formation of the addition product. (Compare the first and second steps in the electrophilic substitution in benzene: what similarities and differences do you observe?)



(3)

8.3.3 Examples of electrophilic addition:

We shall now illustrate the mechanism of electrophilic addition with specific examples. We shall discuss addition of mineral acids and halogens.

(a) Mineral acids

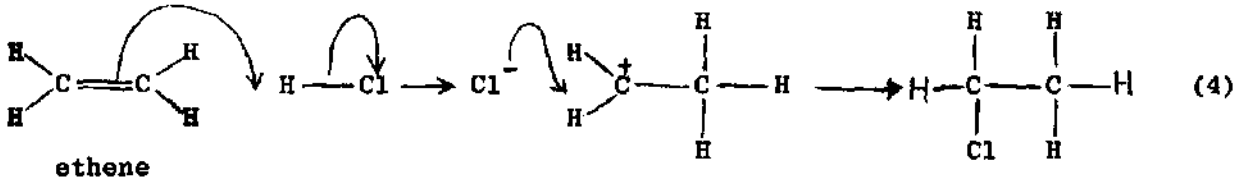
In the addition of mineral acids to alkenes, the electrophile is H^+ from the acid, and the nucleophile is the conjugate-base of the acid:

$$HX \rightleftharpoons H^+ + X^- \qquad (3)$$

acid conjugate base

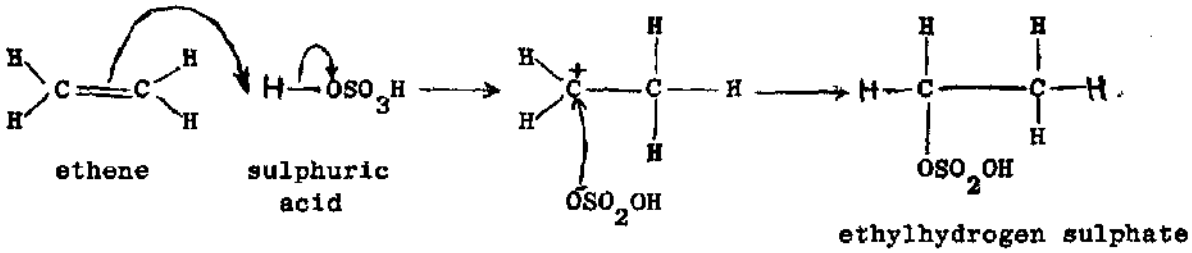
Mineral acids that add to alkenes include: HCl, HBr and H_2SO_4. H_2O also adds to alkenes in the presence of concentrated sulphuric acid as catalyst.

(i) Addition of HCl:



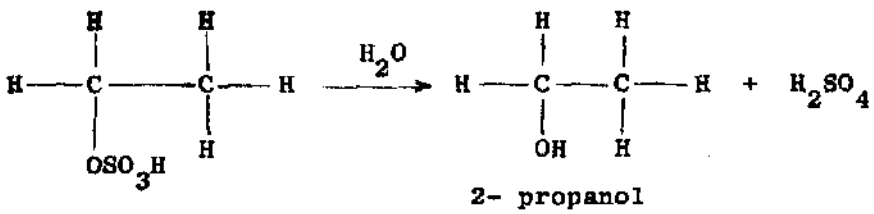
(4)

(ii) Addition of sulphuric acid



(5)

The addition of sulphuric acid to ethene is an important industrial process. The addition product (ethyl hydrogen sulphate) is easily hydrolysed (boiled with water) to give corresponding alcohols.

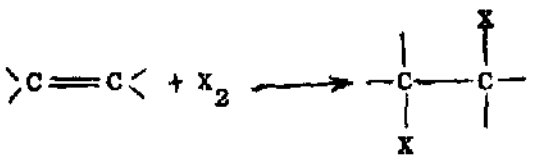


+ H_2SO_4 (6)

Actually, combination of reactions (5) and (6) into a single overall process amounts to addition of water to ethene, using sulphuric acid as catalyst.

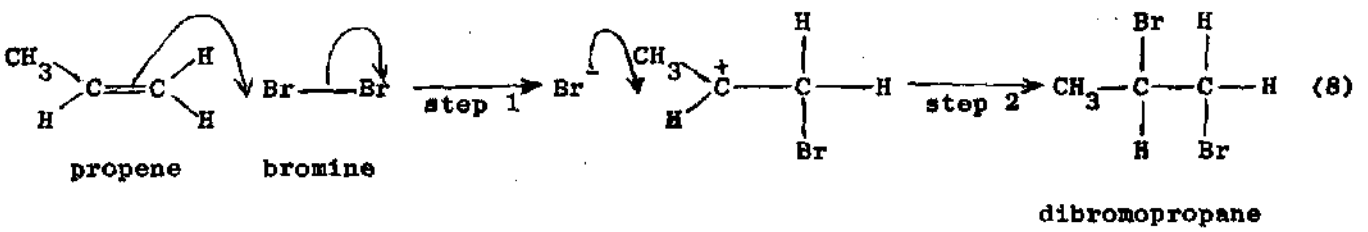
(b) Addition of halogens

Halogens add to alkenes to give the corresponding dihalogeno compounds:



(7)

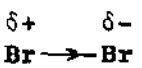
(where X = Br or Cl)



propene bromine dibromopropane (8)

The first step involves attack of an electrophile to form an intermediate carbonium ion. This is accompanied by the heterolytic cleavage of the Br—Br bond.

The electrophile is a polarised bromine molecule with the partially positive end acting as the electrophilic site. This is shown below in (9):



(9)

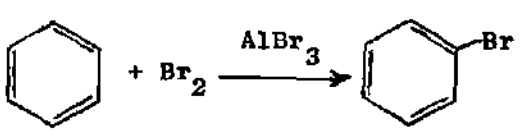
The polarization is induced in Br—Br by the relatively high electron density of alkene π system. Step 2 is attack of the nucelophile (Br^-) on the carbonium ion, leading to formation of the addition product.

Note:

Recall that in bromination of benzene, a substitution product (not addition) was formed. Also, a catalyst is needed for bromination of benzene, but not in addition of bromine to ethene (can you think why?).

Hint:

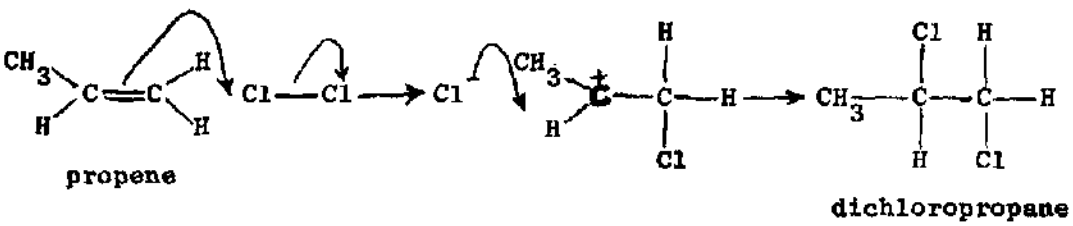
Recall resonance stabilization in benzene which is absent in propene.



(10)

What are your observations of bromination in benzene and in alkenes?

Chlorination follows the same process as bromination:

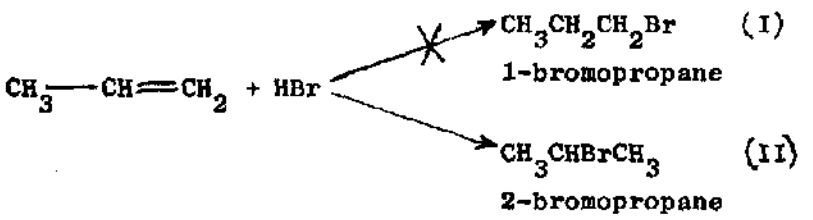


(11)

8.3.4 Orientation of addition: unsymmetrical alkenes

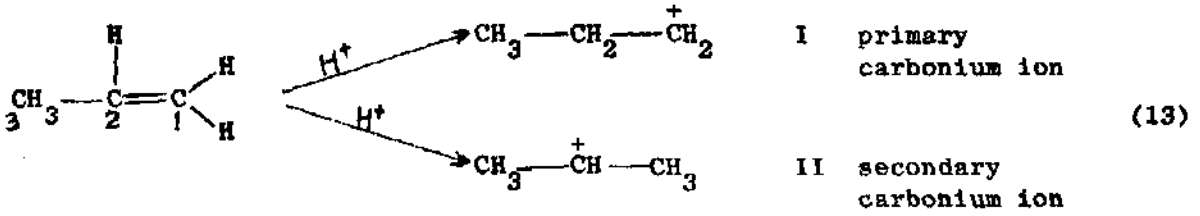
Alkenes may be symmetrical or unsymmetrical. Symmetrical alkenes are those in which the groups on either side of the double bonds are the same e.g. (i) $CH_2{=}CH_2$, (ii) $CH_3CH{=}CHCH_3$. Unsymmetrical alkenes are those in which the groups on either side of the double bonds are not the same e.g. $CH_3{-}CH{=}CH_2$.

In symmetrical alkenes, the two carbon atoms joined by the double bonds are electronically equivalent, and the incoming electrophile bonds with either of them with equal ease. In unsymmetrical alkenes, the two carbon atoms joined by the double bonds are <u>not</u> equivalent. Thus an incoming electrophile joins to the carbon atom that leads to formation of the <u>more stable carbonium ion</u>. The overall process is the formation of one product in preference to the other. This is illustrated in (12) below:



(12)

Addition of HBr to propene could result in the formation of two isomers I and II, but 1-bromopropane (I) is not observed to be formed. This observation can be explained from the mechanism of the reaction as follows:



(13)

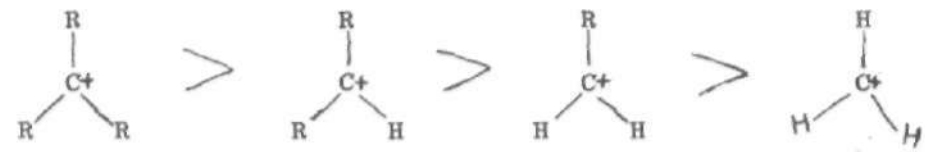
The incoming electrophile H^+ can bond to either C_1 or C_2. A bond to C_2 leads to formation of carbonium ion (I) which is a <u>primary</u> carbonium ion. A bond to C_1 leads to formation of carbonium ion (II) which is a <u>secondary</u>

carbonium ion. It is formed in preference to carbonium ion I because it is more stable. The second step involves the attack of the nucleophile (Br^-) on carbonium ion II, forming product II as shown in equation (12). Product I is not formed. This is because the carbonium ion intermediate that would lead to its formation is not produced in the first place.

The energy required to form carbonium ion II is lower than for carbonium ion I. This explains why product II is formed in preference to product I. This is the basis for Markownikoff's rule which states that the negative part of a reagent adding across an unsymmetrical carbon-carbon double bond goes to the more sustituted carbon atom.

Generally the order of stability of carbonium ions is:

tertiary > secondary > primary > methyl cation

i.e. 

where R = an alkyl group

8.3.6 Summary

(a) Electrophilic addition reactions are initiated by electrophiles, E^+, leading to the formation of intermediate carbonium ion.

(b) This is followed by a nucleophilic attack on the intermediate carbonium ion, leading to formation of the addition product.

(c) Electrophilic additions occur in compounds having carbon-carbon double bonds in their molecules.

(d) If the alkene is unsymmetrical the incoming electrophile attacks the carbon-carbon double bond in such an orientation that will lead to formation of the more stable carbonium ion. This is the basis for explaining Markownikoff's rule.

(e) The first steps in both electrophilic addition and electrophilic substitution involve the same process, i.e. an electrophilic attack. It is the second steps in both reactions that make the difference.

In <u>electrophilic addition</u> the intermediate carbonium ion undergoes a <u>nucelophilic attack</u> to form the addition product. In <u>electrophilic substitution</u>, the intermediate carbonium ion loses a proton H^+ to form a substitution product. This process restores the aromaticity of the benzene molecule.

8.4 ANSWERS

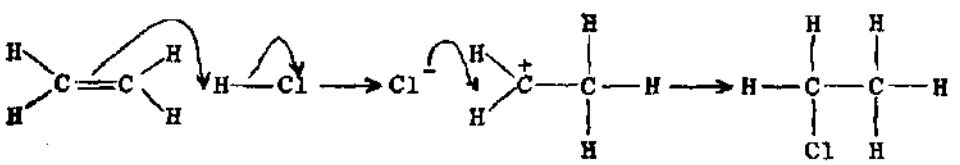
(1) (a) Electrophilic addition reactions occur in:

(i) alkenes : $\rangle C{=}C \langle$

(ii) alkynes : $-C{\equiv}C-$

(b) The main structural features are the carbon-carbon multiple bonds.

(2)



The processes involved are:

(i) An electrophilic attack on the carbon-carbon double bond by H^+, leading to formation of an intermediate carbonium ion.

(ii) A nucleophilic attack on the carbonium ion by Cl^- to form the addition product.

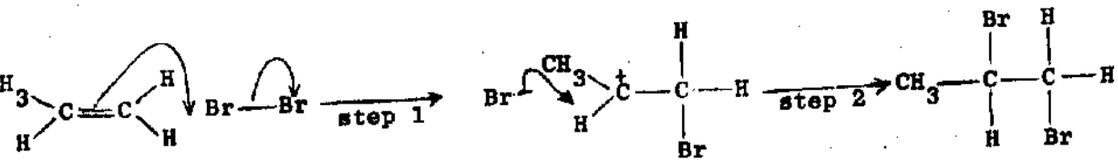
(3) (i) The major difference is that:

In reaction (a) formation of the product involves <u>nucelophilic attack</u> on an intermediate carbonium ion.

In reaction (b) formation of product involves <u>ejection</u> of a proton H^+ by a corresponding carbonium ion intermediate.
Steps 1 in both reactions have the same principle - an electrophilic attack on carbon-carbon π bond.

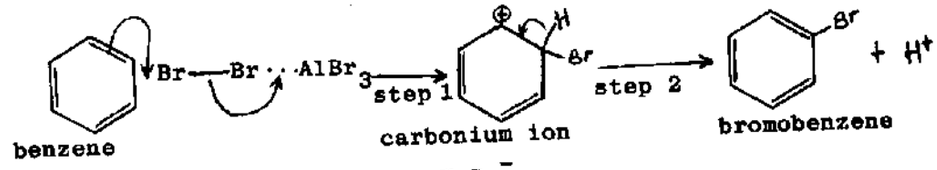
(ii) The difference occurs in step 2 of the respective reactions.

(4) (a)



propene carbonium ion dibromopropane

(b)



benzene carbonium ion + $FeBr_4^-$ bromobenzene

The rate-limiting step in both reactions is step 1 in each case, leading to the formation of the carbonium ions. Benzene is resonance stablised (see topic 7); ethene is not. Therefore benzene is more stable (less reactive) than ethene. Thus, the energy required for step 1 in reaction (b) is much higher than for reaction (a). Using a catalyst in (b) helps to provide a lower energy path for the reaction to occur. This is by making Br—Br sufficiently electrophilic to effect substitution.

TOPIC 9

NUCLEOPHILIC ADDITION REACTIONS

NUCLEOPHILIC ADDITION REACTIONS

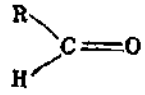
9.1 INTRODUCTION

In the last topic, we discussed reactions in which additions occur across carbon-carbon double bonds, $\rangle C{=}{=}C \langle$. We discussed that the mechanism of such reaction processes is normally electrophilic addition.

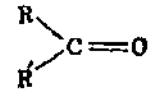
In this topic, we shall discuss another type of additon reaction in which the processes of addition occur across carbon-oxygen double bonds. This is called nucleophilic addition. Compounds containing the $\rangle C{=}{=}O$ group are called carbonyl compounds (see topic 3).

Carbonyl compounds can be classified into two categories as follows:

(a) Those having $\rangle C{=}{=}O$ as the only functional group. These are aldehydes and ketones:



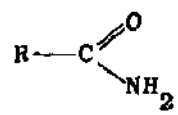
aldehyde

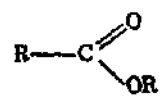


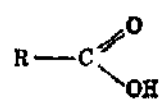
ketone

(b) Those having another group directly attached to the $\rangle C{=}{=}O$ group within their molecules.

These include:

(i)  amides

(ii)  esters

(iii)  carboxylic acids

In our discussion of nucleophilic addition, we shall be considering aldehydes and ketones. The chemical behaviour of the $\rangle C{=}{=}O$ group in compounds of class (b) are sufficiently modified by the presence of the second group that they react somewhat differently.

By the time you have completed studying this topic you should be able to:

(i) Recognise nucleophilic addition reactions.

(ii) Show an understanding of the bond-breaking and bond-making processes involved in the overall reactions.

(iii) Understand the mechanism of these processes.

(iv) Relate nucleophilic addition to other "reaction types" we discussed in topics 7 and 8.

(v) Use knowledge of i-iv to solve problems in organic reactions.

9.2 EXERCISES

(1) (a) What is the most significant structural feature in compounds that undergo nucleophilic addition reactions?

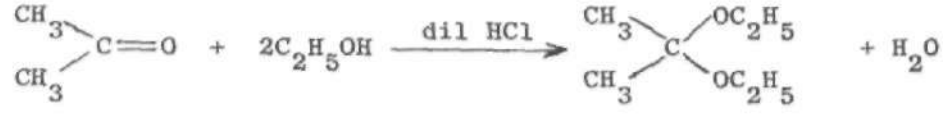
(b) Use a general structural formula of aldehydes and ketones to illustrate this.

(2) Nucleophilic addition reactions involve the addition of a reagent across the $>C{=}O$ double bonds. Illustrate the mechanism of nucleophilic addition using as examples:

(i) Reaction of HCN with CH_3COCH_3

(ii) Hydration of acetaldehyde (CH_3CHO) in the presence of an acid catalyst.

(3) Reaction of acetone with acidic ethanol yields the corresponding acetal:



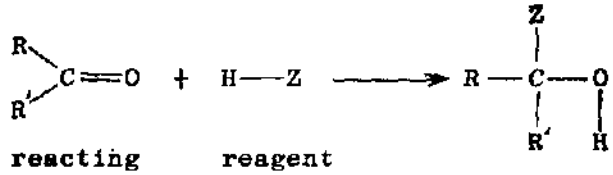
acetone acetal

Use the mechanism of the reaction to show that it represents an example of nucleophilic addition followed by substitution.

9.3 LESSON NOTE

9.3.1 The basic principle of nucleophilic addition

Nucleophilic addition reactions are marked by attack of a nucleophile on the carbonyl carbon followed by co-ordination (linking to) of an electrophile to the carbonyl oxygen. This order may be sometimes altered where acid catalysis is employed. The general principle, however remains the same in the sense that the nucleophile gets attached to the carbonyl carbon and the electrophile to the carbonyl oxygen. The overall process results in saturation of the $\rangle C{=}O$ double bonds. The basic principle of nucleophilic addition is illustrated in (i) below:



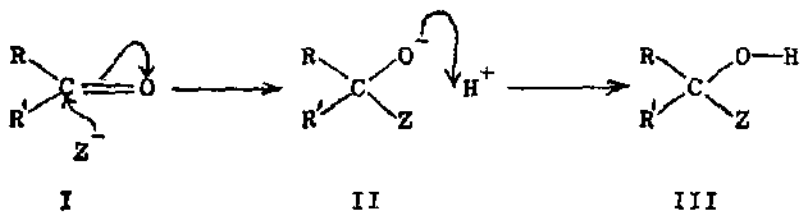
reacting molecule — reagent — addition product (1)

Where Z^- = a nucleophile that adds to carbon

H^+ = an electrophile that adds to oxygen.

9.3.2 Mechanism of nucleophilic addition

The general mechanism of nucleophilic addition is illustrated in (2) below:



I II III (2)

The processes involved are:

(i) Attack of a nucleophile, Z^- (which comes from the reagent, H—Z) on the carbonyl carbon, forming a new bond with it, C—Z. This is accompanied by heterolytic cleavage of the π bond of the $\rangle C{=}O$ double bond leading to formation of a negatively charged intermediate II (an enolate ion).

(ii) The electrophile H^+ attacks the intermediate at the oxygen end, forming a bond with it, using the pair of electrons that come from the heterolytic cleavage of the $\rangle C{=}O$ π bond.

Having outlined the general mechanism, let us now discuss the specific details. Nucleophilic addition reactions can be classified into two categories. These are:

(i) Simple addition reactions.

(ii) Addition reactions followed by further reaction processes.

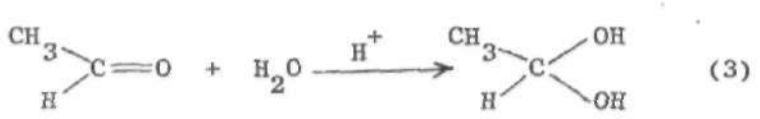
Let us discuss each of these.

9.3.2.1 Simple addition reactions

These are nucleophilic addition reactions in which groups of an incoming reagent add across the reacting molecule, forming an addition product that is not followed by further reaction processes. The overall reaction process results in formation of only the addition product.

We shall use two specific examples to illustrate the mechanism of simple nucleophilic additions:

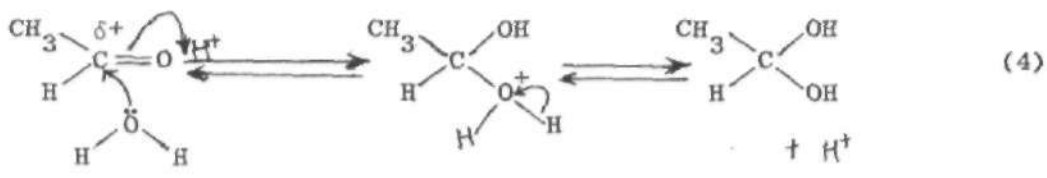
(a) Addition of water to aldehydes: hydration



(3)

acetaldehyde (ethanal) — hydrate

The mechanism is as follows:



(4)

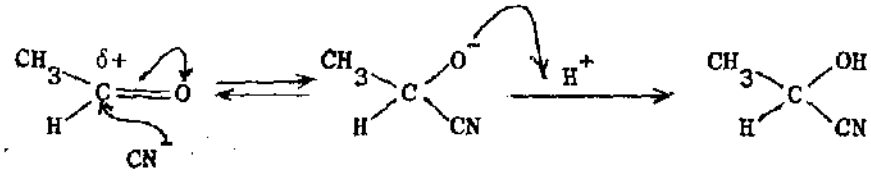
What has effectively happened in the net process is addition of H—OH across the $>C=O$ double bonds. (Can you see how?) H^+ acts as a catalyst.

(b) Addition of HCN

Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. It represents our second example of simple additions.



The mechanism is as follows:



(6)

9.3.2.2 Addition reaction followed by further reaction processes

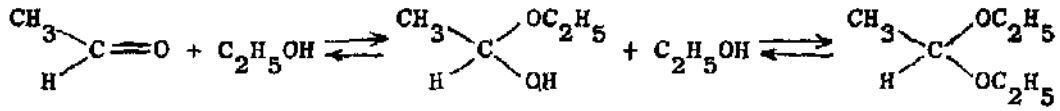
These are nucleophilic addition reactions in which formation of the addition product is followed by other reaction processes, such as substitution or elimination. The net effect is that the addition product is formed, but it is further converted into a final product. We shall use two examples to illustrate these.

(A) Example 1: Addition of alcohols to aldehydes and ketones

In the reaction of alcohols with aldehydes and ketones, hemiacetals are first formed. These represent the addition products; but the hemiacetals undergo further reaction which converts them to acetals by substitution via an intermediate oxonium ion.

Let us use the reaction between acetaldehyde (ethanal) and ethanol to illustrate the mechanism of the processes:

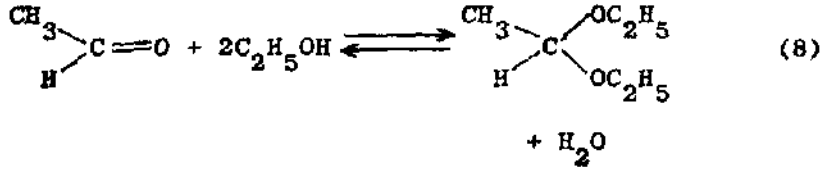
The equation of the reaction is as follows:



(7)

acetaldehyde hemiacetal acetal + H_2O

This can be shown in one step as follows:



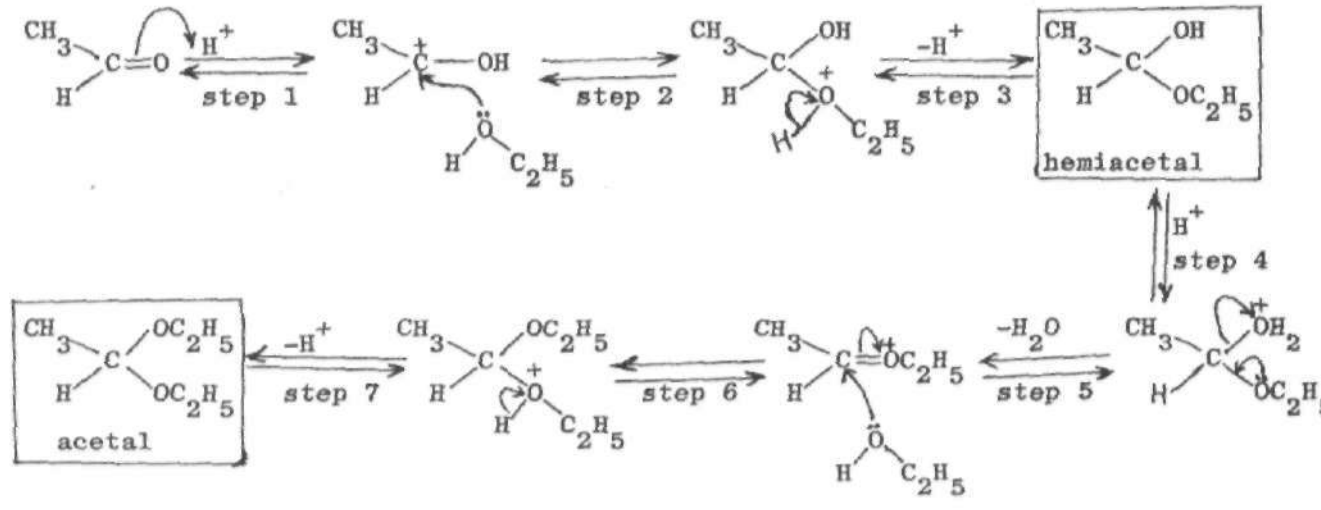
(8)

The mechanism can be viewed as a combination of two major processes:

(i) Formation of hemiacetal

(ii) Conversion of the hemiacetal to acetal

(9)



All the processes of the reaction are reversible. We are interested in the forward process in our discussion:

Step 1 involves an attack of a proton H^+ (from the acid catalyst) on the carbonyl double bond, forming an intermediate carbonium ion. This initial process facilitates the nucleophilic attack of the alcohol on the carbonyl carbon.

Step 2 is a nucleophilic attack of ethanol on the carbonium ion via the lone pair of electrons on oxygen, leading to formation of an intermediate which, in step 3 ejects a H^+ to form the hemiacetal. The H^+ used in step 1 is recovered in step 3, an indication that H^+ is acting as catalyst in the reaction. Up to this point, (i.e. formation of hemiacetal) the reaction is nucleophilic addition.

However, the H^+ which catalyses the processes leading to formation of the hemiacetal also catalyses its conversion to acetal as shown in steps 4-7.

(iii) The H^+ protonates the -OH group of the hemiacetal (step 4) to form an intermediate having a positive charge on oxygen (i.e. an oxonium ion). This process is similar to:

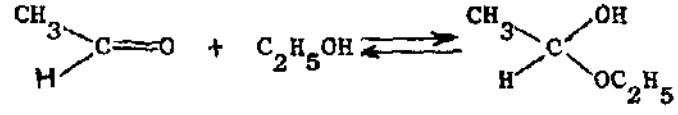


(10)

(iv) The intermediate ejects a molecule of water, helped by the push of electrons from the remaining oxygen atom to form an oxonium ion in step 5. The oxonium ion is then attacked by a second molecule of ethanol (see equation 8: $2C_2H_5OH$ are involved), to form the acetal in two steps: 6 and 7. (In which step was the first ethanol molecule involved?)

The summary of the processes described in steps 1-7 involve just two major chemical events:

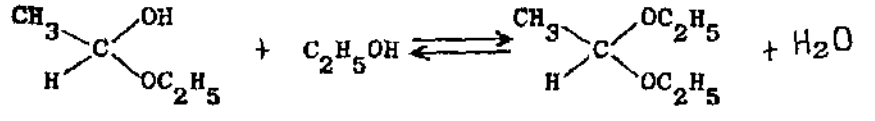
(i) Nucleophilic addition of C_2H_5OH across the $>C=O$ double bond to form a hemiacetal:



(11)

This "chemical event" is described by processes in steps 1-3.

(ii) Nucleophilic substitution, in which the hydroxyl (-OH) group of the hemiacetal is substituted by an ethoxy ($-OC_2H_5$) group to form the acetal:

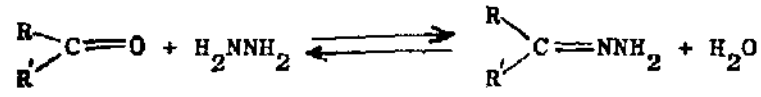


(12)

(B) Example 2: Reaction of amines with aldehydes and ketones

Aldehydes and ketons react with amines to form characteristic compounds. Examples of such amines include:

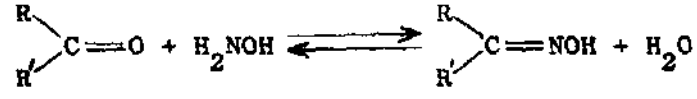
(i) H_2NNH_2 hydrazine



(13)

aldehyde or ketone — hydrazine — a hydrazone

(ii) H_2NOH hydroxylamine



(14)

aldehyde or ketone — hydroxylamine — an oxime

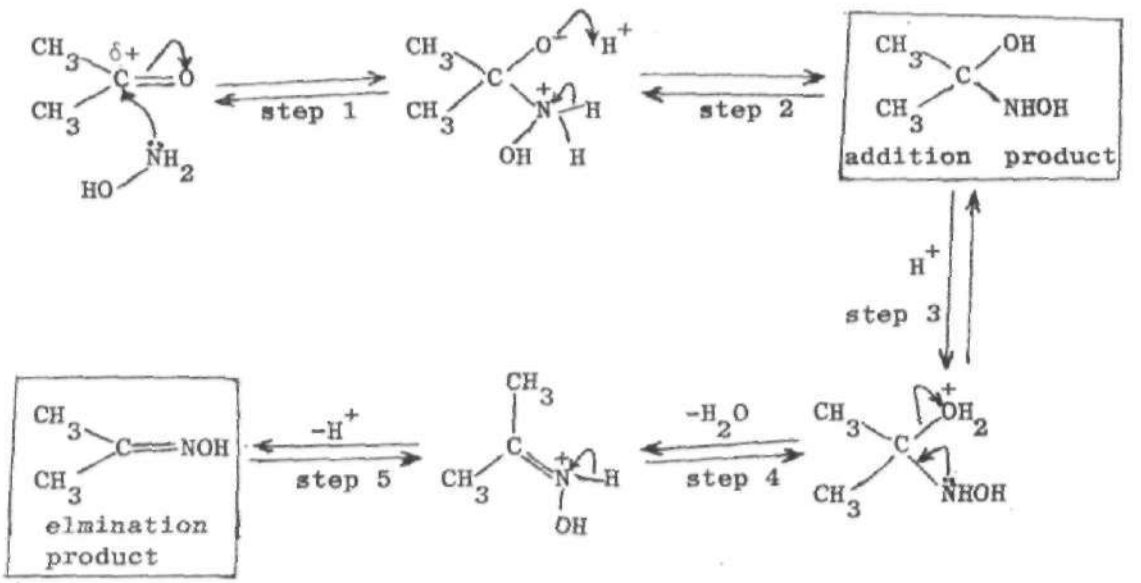
These are examples of nucleophilic addition reactions in which the addition product formed is converted to the final observed product via elimination (refer back to section 9.3.2.2).

Let us use the reaction between acetone (propanone) and hydroxylamine to illustrate the mechanism of this class of reactions.

The general equation of the reaction is:



The mechanism is as follows:



Two major processes are involved:

(i) Nucleophilic addition of H_2NOH to CH_3COCH_3 to form an addition product; steps 1 and 2.

(ii) Further transformation of the addition product via elmination, as shown in steps 3-5. Elimination of water and formation of C=N double bonds occur simultaneously at step 4.

(iii) Steps 3,5 involving elimination of water molecule is acid catalysed as shown.

9.3.3 Summary

(a) The characteristic feature of nucleophilic addition reactions is the addition of an incoming nucleophilic reagent across the >C=O double bond.

(b) Nucleophilic additions generally require the use of catalysts; and the processes of the overall reactions are essentially reversible.

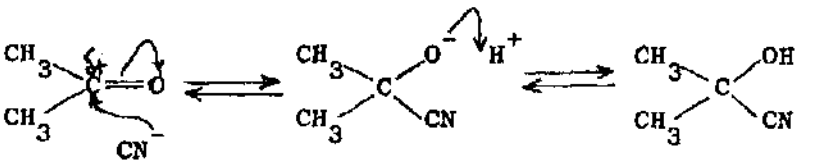
(c) Nucleophilic addition reactions can be classified into simple or complex depending on whether or not the formation of the addition product is followed by further chemical transformations.

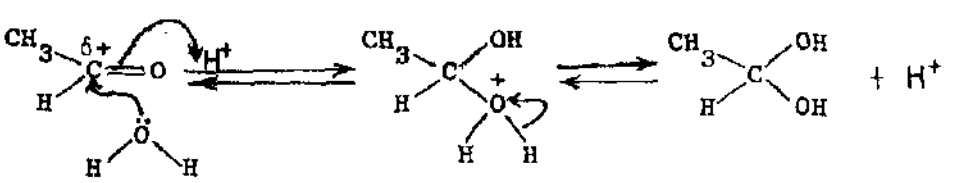
9.4 ANSWERS

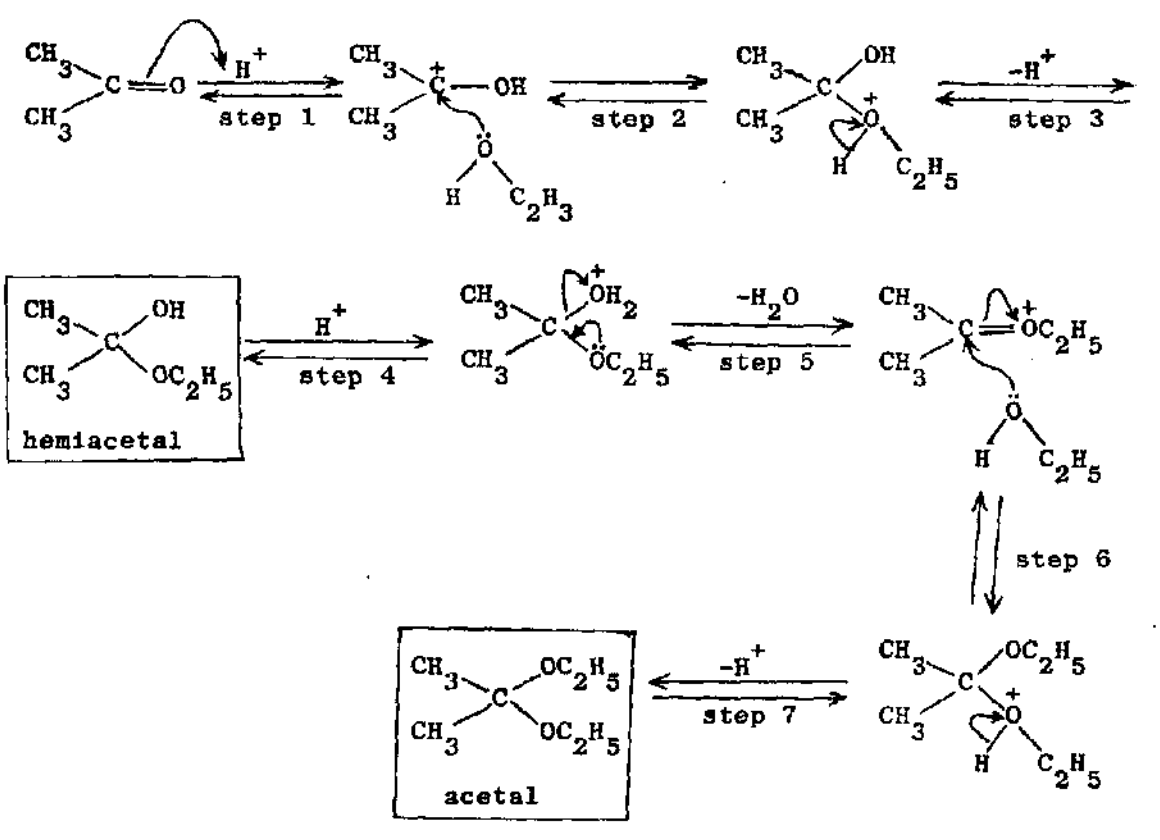
(1) (a) The carbonyl group: $\rangle C{=}O$

(b) 

aldehyde ketone

(2) (i) 

(ii) 

(3) 

Nucleophilic addition reactions are marked by saturation of the $\rangle C{=}O$ double bonds by a nucleophilic reagent to form an addition product.
In addition reactions followed by further processes, the addition product is further converted to another compound. That is what happened in the above reaction in which the addition product, a hemiacetal, is further converted via substitution to acetal. The overall product formed (the acetal) is a substitution product, but its formation follows (comes after) nucleophilic addition processes.

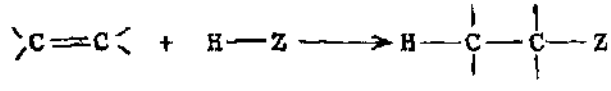
TOPIC 10

ELIMINATION REACTIONS

ELIMINATION REACTIONS

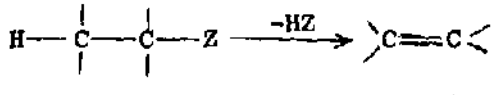
10.1 INTRODUCTION

In topic 8, we discussed addition reactions in which an electrophilic reagent reacts with an unsaturated molecule to form a saturated product. We called these electrophilic addition reactions, i.e.



saturated product (1)

In this topic, we shall discuss elimination reactions. They are reactions which involve removal (elimination) of two groups from a reactant molecule resulting in the formation of unsaturated products as shown in (2) below:



unsaturated product (2)

Elimination reactions can be seen as the opposite of addition reactions.

By the time you have completed studying this topic, you should be able to:

(i) Recognise elimination reactions.

(ii) Understand the processes involved in elimination reactions.

(iii) Demonstrate an understanding of the mechanism of these processes.

(iv) Relate elimination reactions to other reaction-types we have discussed, noting similarities and differences in the basic principles underlying each reaction-type.

10.2 EXERCISES

(1) When chloroethane is treated with hot concentrated alcoholic solution of sodium hydroxide, H and Cl are eliminated and ethene is formed. Write a balanced equation representing the reaction.

(2) (a) Using relevant symbols, show the mechanism of the reaction indicated in (1) above.

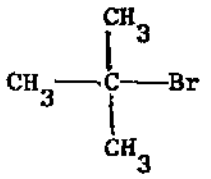
(b) Classify the mechanism you have just used according to whether it is E1, or E2.

(3) (a) Name two reaction factors that form the basis for the mechanisms of elimination reactions.

(b) Use the knowledge of these factors to describe:

(i) E2 mechanism, using reaction of bromopropane with sodium ethoxide as an example.

(ii) E1 mechanism, using reaction of 2-methyl-2-bromopropane with water (hydrolysis) as an example.



2-methyl-2-bromopropane

(4) Use your knowledge of the mechanism of the processes of elimination reactions to predict how many isomeric alkenes would be formed from the reaction of 2-bromobutane with concentrated alcoholic solution of sodium hydroxide:

$CH_3CH_2CHBrCH_3$

2-bromobutane

10.3 LESSON NOTE

10.3.1 Overview

Elimination reactions are those in which the overall process involves the ejection of some groups from the reactant molecule. Compounds that typically undergo elimination reactions are alkyl halides.

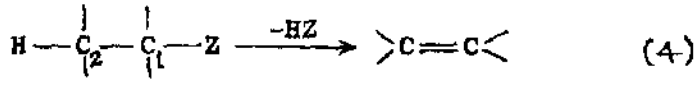
For example, the reaction of bromoethane with hot alcoholic NaOH results in elimination of hydrogen and bromine groups resulting in the formation of ethene (an alkene) as shown in (3) below:

$$\underset{\text{bromoethane}}{CH_3CH_2Br} + \text{alc.NaOH} \longrightarrow \underset{\text{ethene}}{CH_2{=}{=}CH_2} + \underset{\text{ejected groups}}{H^+ \; Br^-} \qquad (3)$$

The commonest of elimination reactions are the 1,2 (or β) eliminations. One of the important features of these kind of eliminations is that the groups removed are bonded to two adjacent carbon atoms in the (original) reactant molecule. Details of this are discussed below in section 10.3.2.

10.3.2 General features of 1,2-elimination reactions

The general feature of 1,2-elimination reactions is as shown in (4) below:



(4)

where Z = a leaving group (usually Cl, Br or I)

C_1 = the carbon atom bonded to the leaving group

C_2 = the carbon atom adjacent to C_1 in the molecules.

As can be seen from (4) above, for elimination to occur, H—C and C—Z bonds must break, and a new C—C bond formed. Two main processes are involved in elimination. These are:

(i) The removal of a β-hydrogen by a nucleophile.
β-hydrogen refers to a hydrogen atom bonded to C_2.

(ii) The removal of the leaving group (Z).

The sequence in which these processes (i and ii above) occur determines the mechanism of the elimination reaction. Details of the mechanisms are explained in section 10.3.4 below.

10.3.4 Mechanism of 1,2-elimination reactions

The mechanism of elmination is explained on the basis of:

(i) The timing of the attack of the nucleophile which removes a β-hydrogen as a proton, H^+.

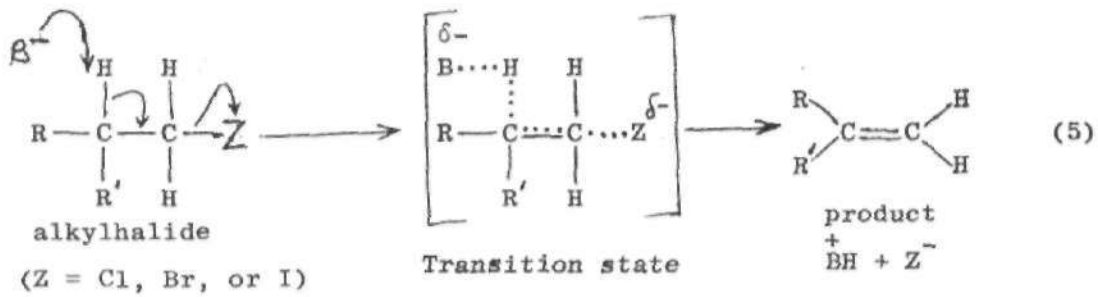
(ii) The sequence of the bond-breaking and the bond-making processes in the overall reaction.

(iii) Where the bond-breaking and bond-making processes occur together, the mechanism is called E2, and where they occur separately (i.e. one after the other), it is called E1. These are discussed below:

10.3.4.1 E2 Mechanism

"E2" means elimination bimolecular. The reaction process is one in which two reacting entities are involved at the transition state of the rate-limiting step. It is thus a bimolecular reaction, involving a one-step mechanism similar to S_N2.

In this mechanism, the bond-breaking and bond-making processes occur simultaneously. A general equation of the mechanism is as follows:



alkylhalide

(Z = Cl, Br, or I)

Transition state

product + $BH + Z^-$

(5)

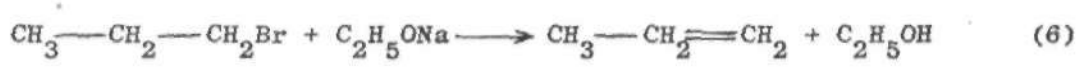
B^- = a nucleophile (Lewis base)

The processes are as follows:

A nucleophile (B^-) approaches a β-hydrogen and progressively co-ordinates with it by removing it as a proton H^+. The original pair of bond electrons of the β-hydrogen and β-carbon shift and gradually form a new bond between the α and β-carbon atoms. At the same time, the C—Z bond is being broken, with Z departing with the pair of bond electrons. In the transition state, the bonds are being made or broken. The final product is an alkene.

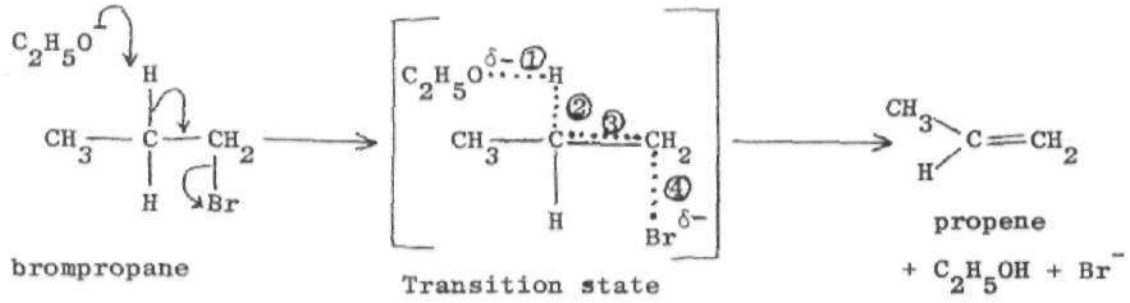
Generally, all alkyl halides undergo elimination by this mechanism.

A specific example is the reaction of bromopropane with sodium ethoxide, forming propene.



(6)

The mechanism is as follows:



brompropane

Transition state

propene + $C_2H_5OH + Br^-$

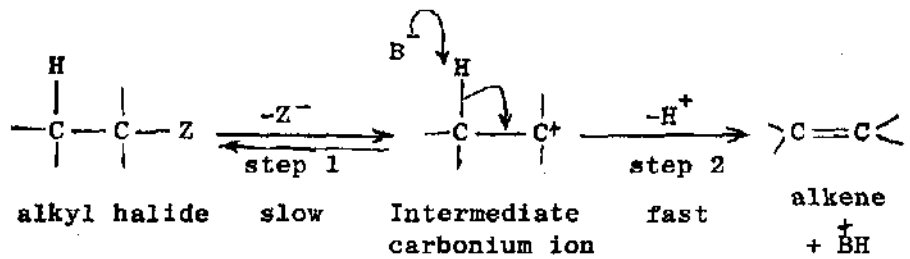
(7)

At the transition state: bonds (1) and (3) are being formed,
bonds (2) and (4) are being broken.

10.3.4.2 E1 Mechanism

"E1" means elimination unimolecular. It is a two-step mechanism involving formation of an intermediate carbonium ion from which a H^+ is removed by an attacking nucleophile. The transition state of the rate-limiting step involves only one reacting entity - the alkyl halide. Its concentration determines the rate of the reaction. E1 mechanism is a similar process to S_N1.

The general equation of the reaction is as follows:



(8)

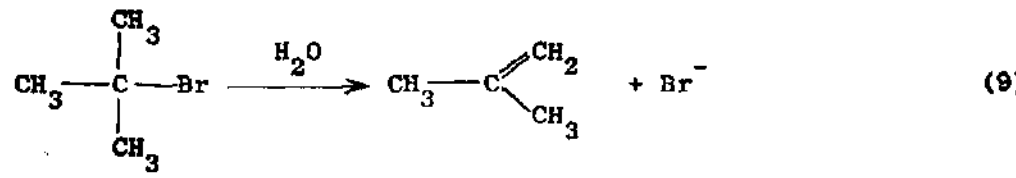
The processes are as follows:

The first step is a heterolytic cleavage of the C—Z bond (ionization of C—Z bond) resulting in the formation of an intermediate carbonium ion.

The second step involves a nucleophilic attack on the carbonium ion in which the nucelophile (B^-) removes a β-hydrogen as a proton H^+. That means that the H—C bond breaks heterolytically, with the pair of bond electrons shifting as shown by the curved arrow to form a new bond between C_1 and C_2 atoms.

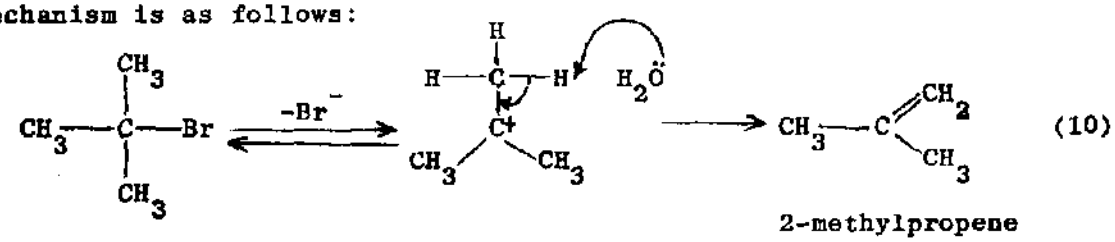
E1 mechanisms are less common than E2. A typical example of E1 is the reaction of 2-methyl-2-bromopropane with water (hydrolysis):

The general equation of the reaction is:



(9)

The mechanism is as follows:



(10)

In E1, the rate of reaction is independent of the concentration of any base employed, but dependent on the concentration of the alkyl halide, i.e.

$$\text{Rate} \propto [RX]$$

Increased concentration of the basic reagent used, shifts the reaction mechanism from E1 to E2, because rate of E2 mechanism is dependent on both reactants:

$$E2 \propto [RX][\text{base}]$$

Thus with added base, for example NaOH in water, the E2 mechanism is dominant.

Steric hindrance does not play as significant a role in the E2 mechanism as it does for S_N2: the bulky groups do not favour E1 over E2 in contrast to substitution where bulky groups favour S_N1 over S_N2. This is because in substitution, nucleophilic attack is on the central carbon atom which becomes shielded when bulky groups are attached; whereas in elimination, attack is on the peripheral hydrogen atom. Consequently, nearly all elimination reactions proceed via the E2 mechanism.

10.3.5 Elimination versus substitution: E1 ~ S_N1 competition

You might have noticed from the discussions we have had so far in this topic that the processes involved in elimination have close similarities with nucleophilic substitution (topic 6).

Considering E1 and S_N1 mechanisms, for example, we find that:

(i) Similar compounds are involved (alkyl halides) as the reacting compounds.

(ii) Both are initiated by nucleophiles, i.e. basic reagents.

(iii) Both E1 and S_N1 mechanisms involve a two-step mechanism.

(iv) The processes that lead to formation of an intermediate carbonium ion in both E1 and S_N1 are the same, i.e. ionization of the halide group.

Because of these close similarities in structure of the reacting molecules and reaction processes, there is often competition between formation of elimination and substitution products. It is this process that is referred to as "elimination versus substitution" which we shall illustrate by E1 and S_N1 reaction processes.

In discussing this point, let us examine <u>two</u> important factors. They are:

(a) Factors that influence E1/S_N1 product ratio. The most important of these factors is the <u>structure of the substrate</u>. Substrates that yield <u>stable carbonium ions</u> promote both E1 and S_N1 mechanisms to varying degrees. This is illustrated in reactions (11) and (12) below.

(b) Factors that influence <u>change</u> of reaction pathway. The most important of these is the <u>nature of basic reagent</u> employed: weak bases promote E1 together with S_N1. Strong bases promote E2 and suppresses formation of substitution products via S_N2.

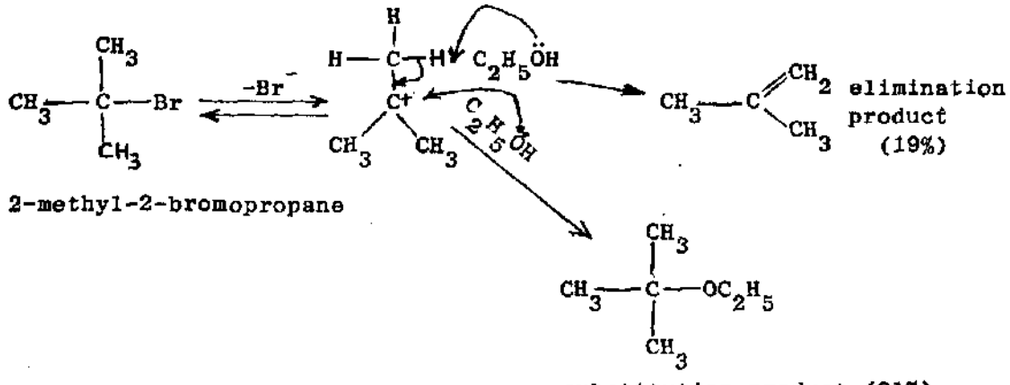
Let us briefly examine each of these:

(a) <u>Substrates</u>

For both E1 and S_N1, the trend in reaction tendency is:

tertiary substrates > secondary substrates > primary substrates

Thus it is tertiary substrates that react by these mechanisms. Considering tertiary substrates, those with more branched substituents tend to yield higher proportions of elimination products. These are illustrated in reactions (11) and (12) below which is reaction of 2-methyl-2-bromopropane in ethanol at 25°C, i.e. solvolysis:

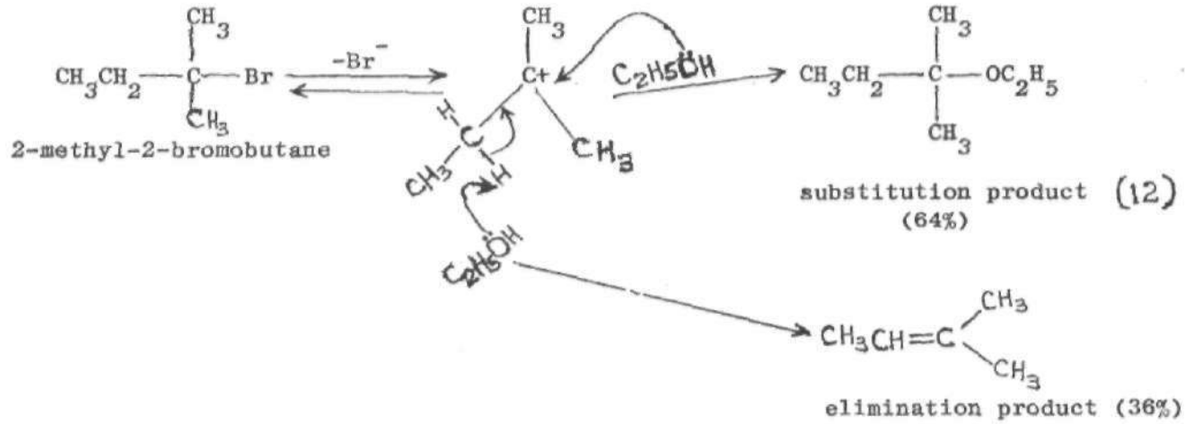


(11)

Elimination/substitution products is approximately in ratio 1:4

This shows that the amount of substitution product in the mixture of products is <u>four times</u> more than elimination product.

If the reaction is carried out with a more substituted alkyl halide, e.g. 2-methyl-2-bromobutane, under similar conditions, we have:



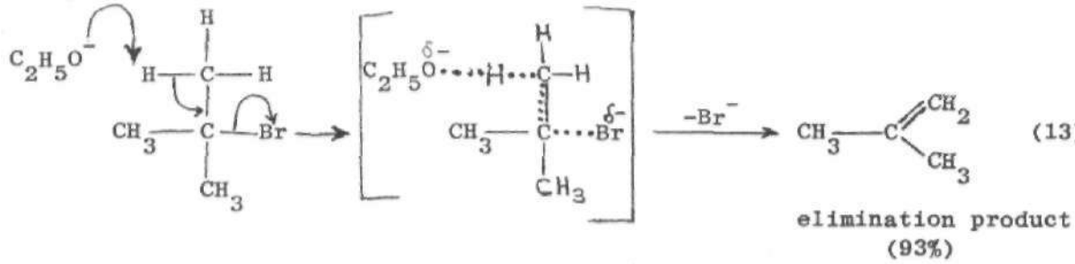
(12)

Elimination/substitution products is approximately in ratio 1:2.

Here we find that the ratio of elimination product is moderately increased by introducing a more substituted substrate. Elimination product is about half substitution product (compare this with reaction 11 above).

(b) Nature of base

This is the most influential factor that serves to tilt the balance of the ratio of elimination/substitution products. This is done through modification of the reaction mechanism as illustrated in reaction (13) below. Let us use the same substrate as in reaction (11) above in which we found that the ratio of elimination/substitution products is 1:4. Let us contrast that with a reaction in which we now use a stronger base, e.g. 2M sodium ethoxide in ethanol, i.e. $C_2H_5O^-$/EtOH. Because the base is a strong one, it attack the substrate directly shifting the mechanism of the reaction from E1 (equation 11) to E2, thereby suppressing S_N1 process that accompany E1. The process is as follows:



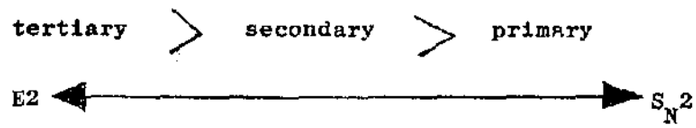
(13)

Comparing this reaction with that shown in equation (11) above, we find that using weak base, i.e. C_2H_5OH with 2-methyl-2-brompropane, yields only 19% of elimination product. Using a stronger base drastically tilts the balance of product formation almost entirely towards elimination (93%). through a change in reaction mechanism.

These are briefly summarised as follows:

(a) Nature of substrate

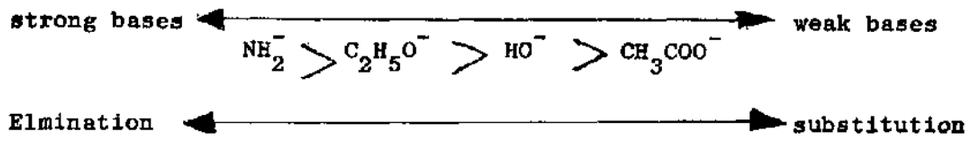
The general trend of carbonium ion stability is:



(b) Nature of base employed

Generally, the more strongly the base employed, the greater the tendency towards elimination via E2 mechanism as seen in reaction (13) forming almost exclusively elimination product.

The trend is as follows:



10.3.6 Summary:

(a) 1,2-eliminations involve ejection of two groups from two adjacent carbon atoms.

(b) Two reaction mechanisms have been discussed in this topic. They are E2 and E1 mechanisms.

(i) E2 mechanism: It is a one-step mechanism. Removal of H^+ and ejection of a leaving group occur together.

(ii) E1 mechanism: It is a two-step mechanism. Ejection of the leaving group precedes the removal of H^+. An intermediate carbonium ion is involved.

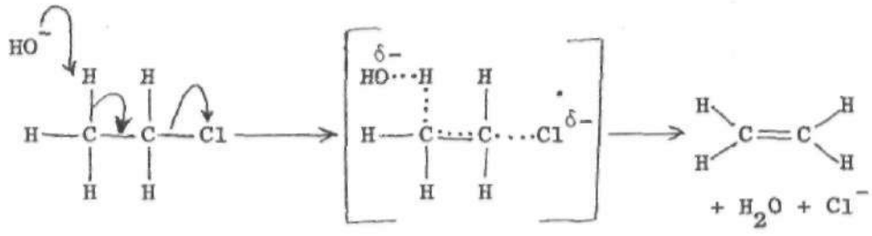
(c) There may be a "competition" between formation of elimination and substitution products, especially with reactions proceeding via E1 mechanism. The product that predominates is determined by such factors as the structure of the substrate and the nature of the base employed.

(d) Our discussion in section 10.3.5 shows that E1 mechanism is not a particularly suitable synthetic route for obtaining alkenes. (Do you know why?)

10.4 ANSWERS

(1) $CH_3CH_2Cl + alc.NaOH \longrightarrow CH_2{=}CH_2 + H_2O + NaCl$

(2) (a)

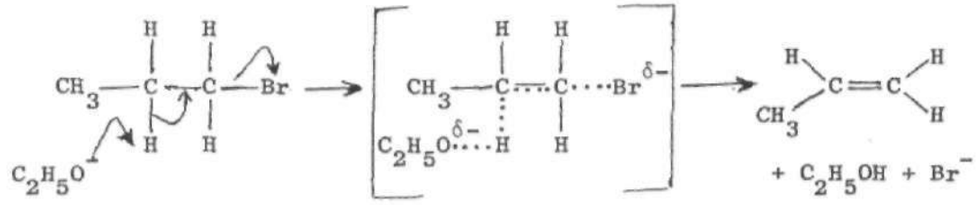


(b) The mechanism is E2. Bromoethane is a primary alkyl halide which undergoes elimination reactions via E2 mechanism.

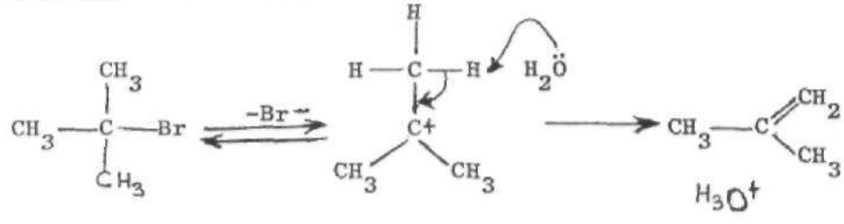
(3) (a) (i) Timing of attack of the nucleophile.

(ii) Sequence of breaking of existing bonds and forming of new ones.

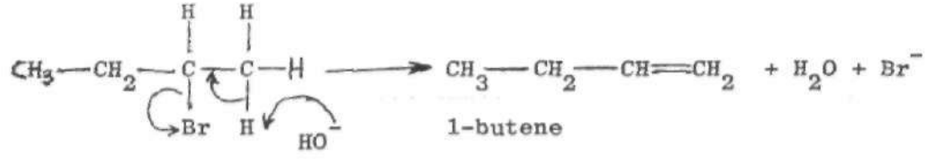
(b) (i) In E2 mechanism, the incoming nucleophile attacks the alkyl halide molecule, removing a H^+. Bond-breaking and bond forming occur together.



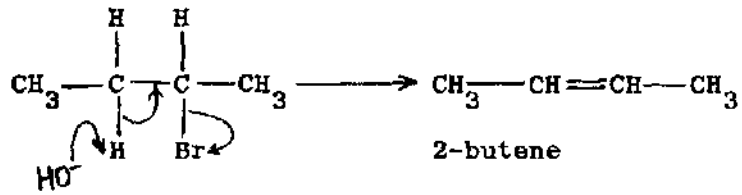
(ii) In E1 mechanism, the incoming nucleophile attacks an intermediate carbonium ion removing a H^+. Bond-breaking precedes bond-making.



(4) (a)

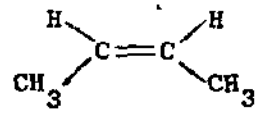


(b)

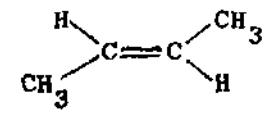


2-butene

There are two isomeric forms of 2-butene: Cis - and trans:



cis-isomer



trans-isomer

Thus a total of <u>three</u> isomers are formed:

(i) 1 - butene

(ii) cis-2-butene

(iii) trans-2-butene

APPENDIX 10.2

QUESTIONNAIRE

This is a questionnaire for you to express your opinion about this course you have just completed. Put a tick (✓) in the appropriate boxes that correspond with your opinion. Your identity is not required. You should therefore feel free to be as honest as possible in your responses.

1. Sex:

MALE	FEMALE

2. How difficult do you normally find studying organic chemistry?

VERY DIFFICULT	MODERATELY DIFFICULT	EASY

3. How did you find reading through this "text on organic reaction mechanism" that you have just completed?

VERY DIFFICULT	MODERATELY DIFFICULT	EASY

4. Having completed this course (i.e. this text), how much has it helped to improve your understanding of organic chemistry?

VERY MUCH	NOT MUCH	NOT AT ALL

5. How much has this text helped to improve your learning or studying of organic chemistry?

VERY MUCH	NOT MUCH	NOT AT ALL

6. Having completed this text, how much would you like to be taught organic chemistry from a mechanistic approach?

VERY MUCH	NOT MUCH	NOT AT ALL

7. On the whole, how would you assess this text considering the extent to which it has helped to reduce your difficulties in organic chemistry?

VERY GOOD	JUST GOOD	POOR

8. Any other comments: _____

_____

_____

_____

CONCLUDING REMARKS AND QUESTIONNAIRE

CONCLUDING REMARKS AND QUESTIONNAIRE

In the "Introduction" to this text we indicated that organic chemistry is about the study of molecules - two aspects of molecules: their structure and reactions.

Reactions of organic compounds involve processes of breaking of existing bonds and making of new ones. Reaction mechanisms describe these processes. Thus the understanding of reaction mechanisms helps us to understand these processes of organic reactions, and thus helps to improve our learning of organic chemistry. This text has been presented on that basis.

The text has not been presented to be additional "facts" of organic chemistry. It is presented as a way through which our learning and understanding of organic chemistry may be improved, based on our understanding of the processes that occur within and between reacting molecules.

It is hoped that the text has helped you in overcoming some of your difficulties in learning and understanding of organic chemistry. You are requested to express your opinion by responding to the attached questionnaire.

Thank you.

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Telegrams UEANOR NORWICH

PROBLEM-SOLVING IN ORGANIC REACTION MECHANISM

STUDENT'S INDEX NUMBER: _____

SCHOOL: _____

SEX: _____

AGE: _____

Dear Student,

The following questions form the second part of the test on organic reaction mechanisms.

Please answer all the questions in the spaces provided immediately after each question. Show all the steps in your solution as clearly as possible.

Immediately following each question is a four-item questionnaire. Complete it as soon as you have attempted the question.

If a question proves difficult for you, don't waste too much time on it. Proceed to the next and then come back to it later.

There is also a six-item questionnaire at the end of the problems; please respond to them as well.

Thank you.

A.A.M. Shaibu

SECTION A

PART I: TIME ALLOWED: 30 minutes

Questions 1-12 are based on the information given on Table 1. Select the box from the table that most appropriately answers each question, and put "X" in the corresponding box provided in the answer sheet. You can mark only one box for each question.

e.g. In which box do you find an aromatic compound with an electron releasing substituent?

The answer is box 3 which is marked thus:

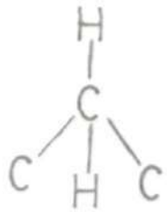
1	2	3	4	5	6	7	8	9	10	11	12
		X									

Now continue in the same way, using the answer sheet provided.

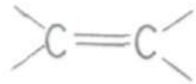
In which box do you find:

1. A compound that is likely to undergo electrophilic addition across a non-polar double bond?
2. A secondary group?
3. A homolytic dissociation process?
4. An elimination process?
5. A primary group?
6. A compound that is likely to undergo nucleophilic addition across a polar double bond?
7. An SN^2 reaction mechanism?
8. An aromatic compound with meta-substituents?
9. A tertiary carbonium ion?
10. A carbanion?
11. An aromatic compound that can undergo a nucleophilic substitution reaction?
12. An SN^1 reaction mechanism?

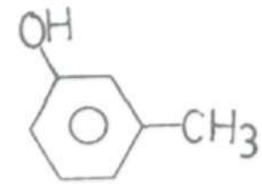
TABLE 1: TO BE USED FOR QUESTIONS 1–12



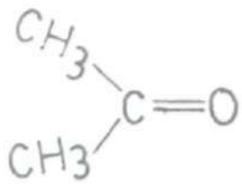
1



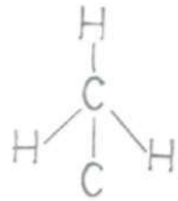
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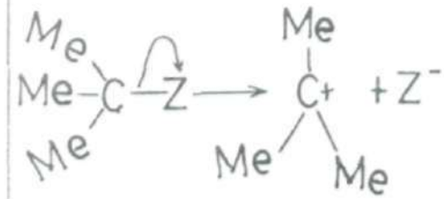
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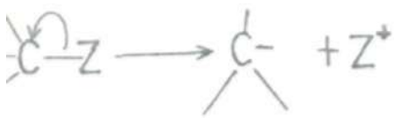
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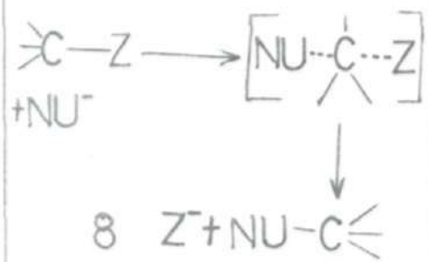
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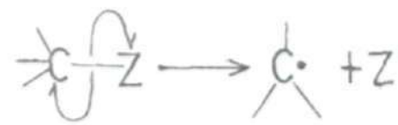
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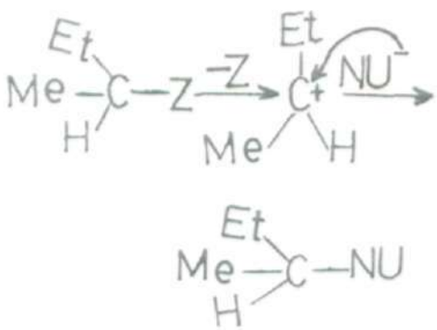
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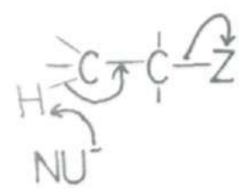
8



9







PART II

Each of the questions 13-50 has four options as answers. Only one of these is correct. Select the correct one and put "X" in the circle immediately below the letter on the answer sheet that corresponds with your choice. Here is an example for you to follow.

Which of the following elements are present in cyclopropane?

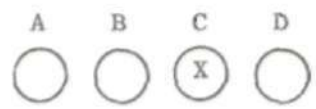
(A) Carbon and oxygen

(B) Hydrogen and oxygen

(C) Carbon and hydrogen

(D) Carbon, hydrogen and oxygen

On the answer sheet you will find:



The correct answer is C, so an "X" is put in the circle immediately below it as shown. Now, attempt the questions in the same manner:

13. Which of the following is an electrophile?

(A) R–C≡C–R

(B) $R-C\equiv\overset{+}{O}$

(C) $R-CH_2-R$

(D) R–NH–R

14. If A and B represent monovalent atoms, in which of the following compounds is the bond polarised?

(A) B–B

(B) $A^+ B^-$

(C) A–A

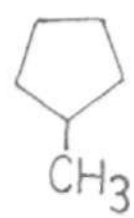
(D) $A^{\delta+}-B^{\delta-}$

15. Which of the following compound is a nucleophile?

(A) 

(B) 

(C) 

(D) 

16. The electrophile that is responsible for nitration of benzene in concentrated sulphuric acid medium is normally:

(A) NO^+

(B) NO_2^+

(C) NO_3^+

(D) $N_2O_3^+$

17-19. For these three reactions, indicate which reagent is required to carry out the conversions:

17. $C_6H_5COOH \longrightarrow C_6H_5COCl$

(A) HCl

(B) NaOCl

(C) Br_2/CCl_4

(D) $SOCl_2$

18. $C_6H_6 \longrightarrow C_6H_5NO_2$

(A) HNO_2 | conc.HCl

(B) HNO_3 | conc.HCl

(C) HNO_2 | conc.NH_3

(D) HNO_3 | conc.H_2SO_4

19. $C_6H_5CH_2CH_2Br \longrightarrow C_6H_5CH{=}CH_2$

(A) Conc. H_2SO_4

(B) Alcoholic NaOH

(C) Solution of Na/EtOH

(D) Alcoholic $K_2Cr_2O_7$

20. By what name is the following reaction usually known?

$$C_6H_6 + RCOCl \xrightarrow{AlCl_3} C_6H_5COR + HCl$$

(A) Cannizzaro reaction

(B) Hofmann reaction

(C) Friedel-crafts acylation

(D) Friedel-crafts alkylation

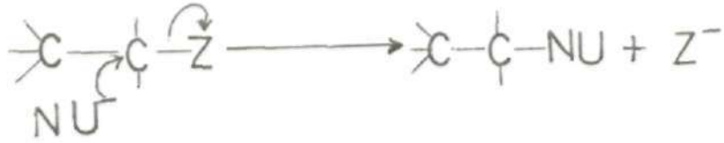
21. An electrophile is an:

(A) Electron pair donor

(B) Electron pair acceptor

(C) Electron pair inhibitor

(D) Electron pair releasing group

22. 

The above reaction is an example of:

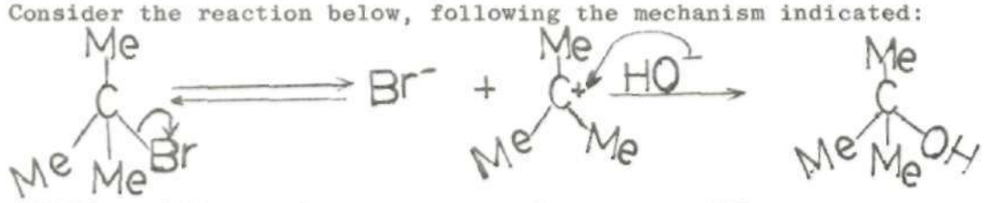
(A) Electrophilic substitution

(B) Nucleophilic addition

(C) Electrophilic addition

(D) Nucleophilic substitution

23. Consider the reaction below, following the mechanism indicated:



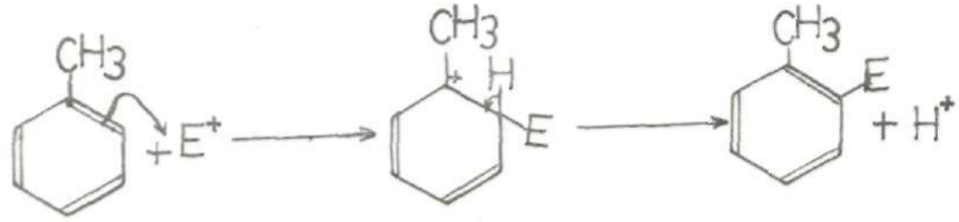
Addition of KBr to the aqueous reaction system will:

(A) Increase the rate of reaction

(B) Decrease the rate of reaction

(C) Leaves the rate of reaction unaffected

(D) Make the rate of reaction impossible to determine

24. 

The above reaction is an example of:

(A) Electrophilic addition

(B) Electrophilic substitution

(C) Nucleophilic substitution

(D) Nucleophilic addition

25. 

The representation of a molecular structure by more than one structure, as shown above, is described as:

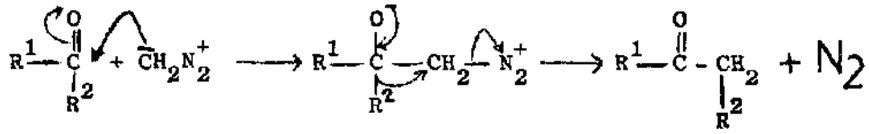
(A) Isomerism

(B) Isomorphism

(C) Mesomerism

(D) Migration

26. Consider the reaction below:



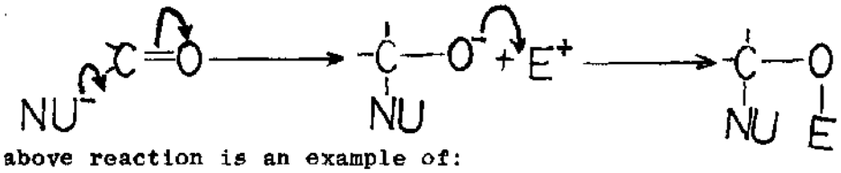
It is an example of:

(A) Rearrangement

(B) Substitution

(C) Addition

(D) Elimination

27. 

The above reaction is an example of:

(A) Nucleophilic addition

(B) Electrophilic addition

(C) Nucleophilic substitution

(D) Electrophilic substitution

28. In which of the following compounds can the carbon atom be described as SP^3 hybridised?

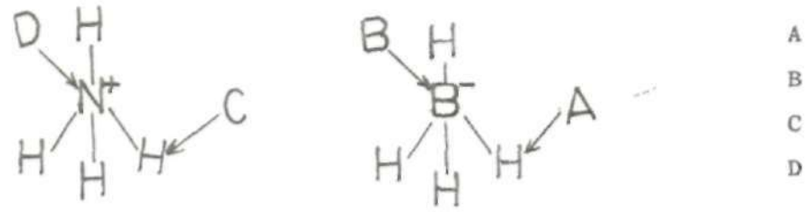
(A) CH_2O

(B) CH_2N_2

(C) $CHCl_3$

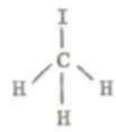
(D) CO_2

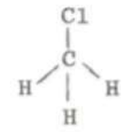
29. Which of the following arrows points to a nucleophilic site?

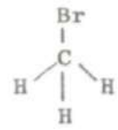


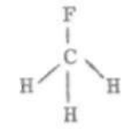
A
B
C
D

30. In which of the following compounds does the carbon atom have the highest electron density?

(A) 

(C) 

(B) 

(D) 

31. Which of the following statements is true?

(A) An electrophile reacts by donating 2 electrons

(B) All Lewis acids are nucleophiles

(C) All electrophiles are cationic

(D) A nucleophile reacts by donating 2 electrons

Use Fig. 1 to answer questions 32 and 33.

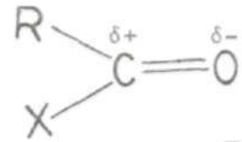


Fig. 1

32. The carbon centre is susceptible to attack by:

(A) Electrophilic reagents

(B) Nucleophilic reagents

(C) Acylating reagents

(D) Dehydrating agents

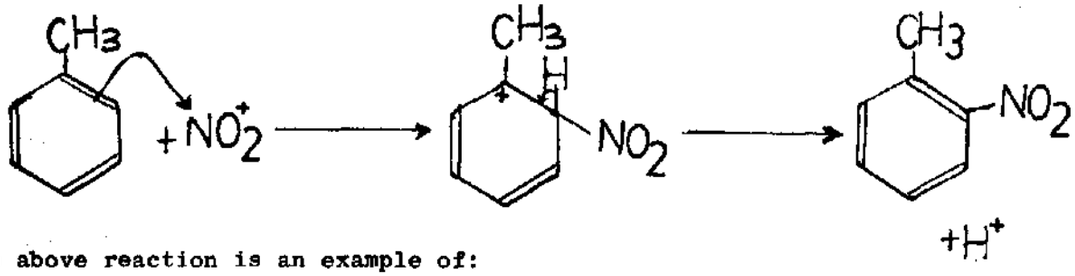
33. Compounds having groups of this nature are most likely to undergo:

(A) Nucleophilic addition

(B) Electrophilic addition

(C) Nucleophilic substitution

(D) Electrophilic substitution

34. 

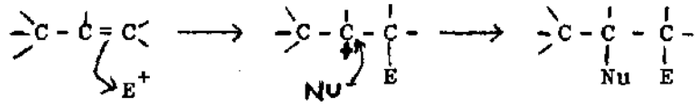
The above reaction is an example of:

(A) Electrophilic addition

(B) Electrophilic substitution

(C) Nucleophilic substitution

(D) Nucleophilic addition

35. 

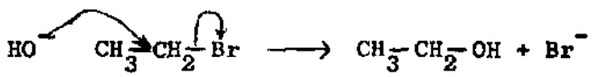
The reaction shown above is an example of:

(A) Nucleophilic addition

(B) Electrophilic substitution

(C) Elimination reaction

(D) Electrophilic addition

36. 

The above reaction is an example of

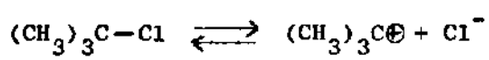
(A) Electrophilic substitution

(B) Nucleophilic addition

(C) Electrophilic addition

(D) Nucleophilic substitution

37. Consider the dissociation indicated below:



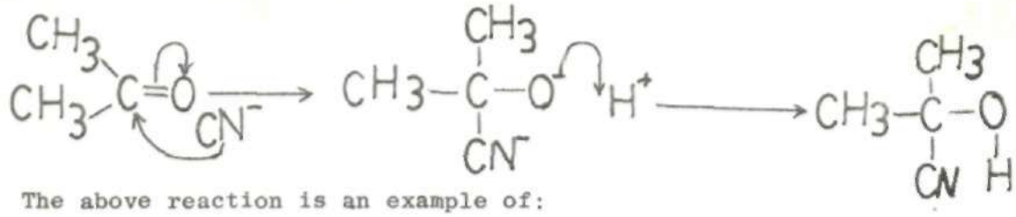
It involves the breaking of the C - Cl bond in which the bonding electrons are acquired by:

(A) Carbon

(B) Bromine

(C) Both carbon and bromine

(D) Neither carbon nor bromine

38. 

The above reaction is an example of:

(A) *Nucleophilic addition*

(B) Electrophilic addition

(C) Nucleophilic substitution

(D) Electrophilic substitution

39. R^1COR^2 : R^1 and R^2 are alkyl groups.

The molecule shown above is an example of:

(A) An ester

(B) An ether

(C) A ketone

(D) An aldehyde

40. R^1COOR^2 : R^1 and R^2 are alkyl groups.

The molecule shown above represents

(A) An ester

(B) An ether

(C) A ketone

(D) An anhydride

Questions 40 and 41 refer to Fig. 2



fig·2

41. Fig. 2 represents the molecular structure of:

(A) Butane

(B) Butene

(C) Butadiene

(D) Cyclobutane

42. Compounds with molecules of the structure shown in Fig. 2 are said to have:

(A) An aromatic system

(B) A heterocyclic system

(C) A hyperconjugated system

(D) A conjugated system

43. $CH_3 - CH = CH_2 + H - Br \longrightarrow CH_3 - \overset{+}{C}H - CH_3 + Br^- \longrightarrow CH_3 - CHBr - CH_3$

The above reaction is an example of:

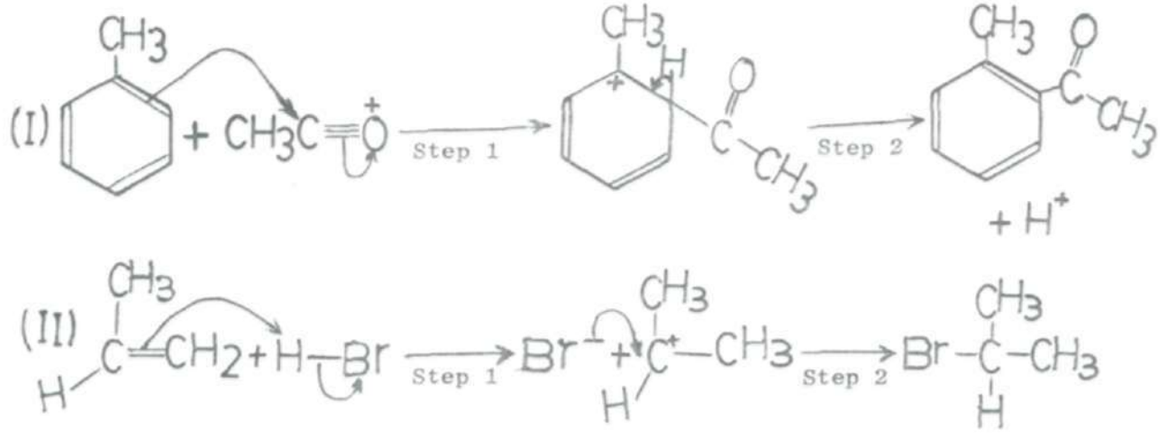
(A) Electrophilic substitution

(B) Nucleophilic substitution

(C) Nucleophilic addition

(D) Electrophilic addion

Questions 44 and 45 refer to reactions I and II



44. In reactions I and II above, step 1 in each case is:

(A) An electrophilic attack on the hydrocarbon

(B) A nucleophilic attack on the hydrocarbon

(C) A rearrangement of the hydrocarbon

(D) None of the above

45. Step 2 in each case is:

(A) A substitution process

(B) A rearrangement process

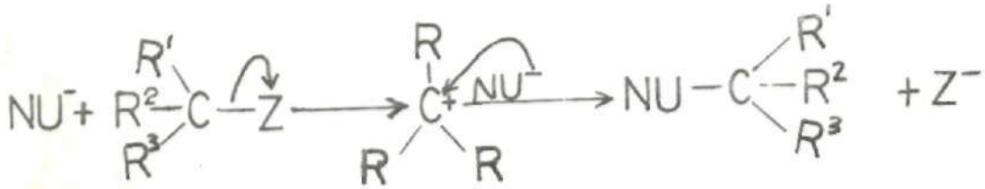
(C) A free radical reaction

(D) None of the above

46. Which box indicates the increasing order of relative ease in which HBr adds under polar conditions to the following three alkenes:

$CH_3 - CH = CH_2$ (1) $CH_2 = CH_2$ (2) $CH_2 = CHCl$ (3)

A	B	C	D
1<3<2	1<2<3	3<2<1	2<3<1

47. 

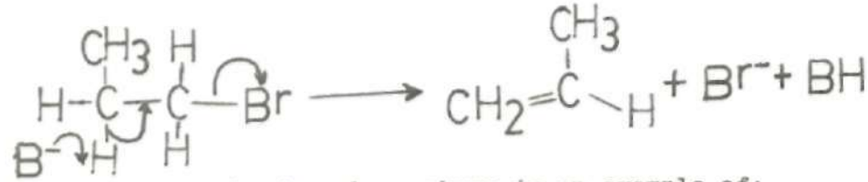
The reaction mechanism indicated above is an example of:

(A) SN^1

(B) SN^2

(C) E1

(D) E2

48. 

The reaction mechanism shown above is an example of:

(A) SN^1

(B) SN^2

(C) E1

(D) E2

49.

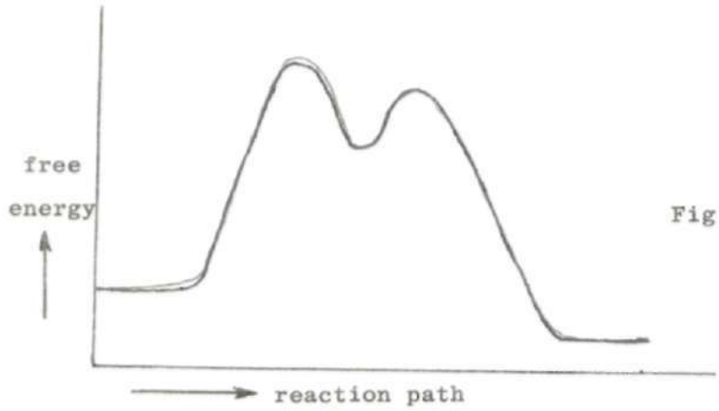


Fig. 3

If the above diagram (Fig. 3) represents the energy profile of the reaction:



then:

(A) First step is rate-limiting

(B) Second step is rate-limiting

(C) Both steps are rate-limiting

(D) None of the steps is rate-limiting

50. The energy profile shown in Fig. 3 on the previous page most likely represents the reaction progress of:

(A) SN^1 reaction

(B) SN^2 reaction

(C) E2 reaction

(D) None of the above

SECTION B

ANSWER ALL QUESTIONS TIME ALLOWED: $2\frac{1}{2}$ hours

1. Considering structural and solvent factors, outline a possible reaction mechanism for the hydrolysis of bromopropane by aqueous potassium hydroxide. The equation of the reaction is:

$$CH_3CH_2CH_2Br + aqNaOH \longrightarrow CH_3CH_2CH_2OH + NaBr$$

QUESTIONNAIRE

Put "X" in the box that most closely corresponds to your opinion:

1. Are you familiar with this problem?

YES	NOT SURE	NO

2. How did you find solving the problem?

DIFFICULT	MODERATE	EASY

3. How confident are you that your answer is correct?

CONFIDENT	MODERATE	DOUBTFUL

4. If you had difficulties in solving this problem, which one of the following reasons mostly accounts for your difficulty?

I do not have the grasp of the basic chemical knowledge. ☐

I knew the facts but I did not know how to apply them to arrive at a solution. ☐

I cannot understand the question so could not proceed. ☐

I was never taught this. ☐

I got mixed up along the way. ☐

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If any other reasons, state them briefly.

---

7. Consider reactions I and II below, in which HBr adds across the carbon-carbon olefinic bonds:

(I) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH_3} + HBr \longrightarrow CH_3 - CHBr - CH_3$

electrophilic addition

(II) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CHO} + HBr \longrightarrow CH_2Br - CH_2 - CH = O$

nucleophilic addition

Outline the mechanism of the reactions; and use it to explain why reaction II behaves differently from reaction I.

Hint: -CHO is an electron withdrawing group.

QUESTIONNAIRE

Put "X" in the box that most closely corresponds to your opinion:

1. Are you familiar with this problem?

YES	NOT SURE	NO

2. How did you find solving the problem?

DIFFICULT	MODERATE	EASY

3. How confident are you that your answer is correct?

CONFIDENT	MODERATE	DOUBTFUL

4. If you had difficulties in solving this problem, which <u>one</u> of the following reasons <u>mostly</u> accounts for your difficulty?

I do not have the grasp of the basic chemical knowledge. ☐

I knew the facts but I did not know how to apply them to arrive at a solution. ☐

I cannot understand the question so could not proceed. ☐

I was never taught this. ☐

I got mixed up along the way. ☐

If any other reasons, state them briefly.

---

6. Using the relevant mechanisms of the respective reactions,

   (a) Explain why 1-butylbromide forms <u>one</u> isomer while 2-butylbromide forms <u>three</u> isomers respectively, when treated with an alcoholic solution of potassium hydroxide.

$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2CH(Br)CH_3$
1-butylbromide	2-butylbromide

   (b) What name is usually given to the mechanism that you have described?

QUESTIONNAIRE

Put "X" in the box that most closely corresponds to your opinion:

1. Are you familiar with this problem?

YES	NOT SURE	NO

2. How did you find solving the problem?

DIFFICULT	MODERATE	EASY

3. How confident are you that your answer is correct?

CONFIDENT	MODERATE	DOUBTFUL

4. If you had difficulties in solving this problem, which one of the following reasons mostly accounts for your difficulty?

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I cannot understand the question so could not proceed. ☐

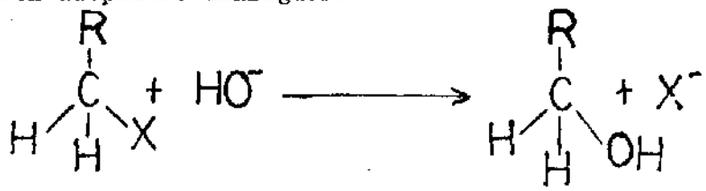
I was never taught this. ☐

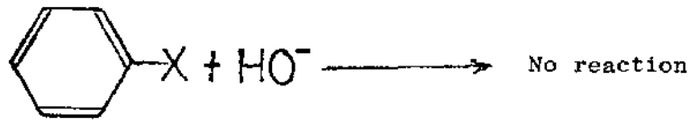
I got mixed up along the way. ☐

If any other reasons, state them briefly.

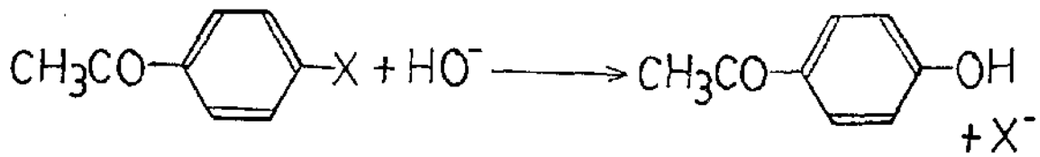
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5. Aryl halides (having a halide group attached directly to benzene ring) do not usually undergo nucleophilic substitution, though this is common with aliphatic analogues:





However, it has been observed that if electron withdrawing groups are attached at ortho or para positions to the halide group, substitution occurs thus:



Suggest a reaction mechanism, showing the role of the electron withdrawing group in the reaction.

QUESTIONNAIRE

Put "X" in the box that most closely corresponds to your opinion:

1. Are you familiar with this problem?

YES	NOT SURE	NO

2. How did you find solving the problem?

DIFFICULT	MODERATE	EASY

3. How confident are you that your answer is correct?

CONFIDENT	MODERATE	DOUBTFUL

4. If you had difficulties in solving this problem, which one of the following reasons mostly accounts for your difficulty?

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I knew the facts but I did not know how to apply them to arrive at a solution. ☐

I cannot understand the question so could not proceed. ☐

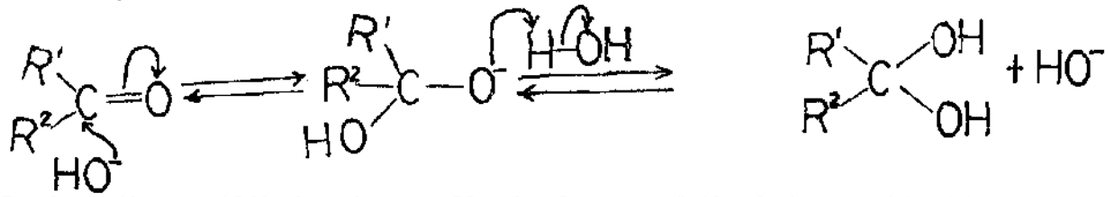
I was never taught this. ☐

I got mixed up along the way. ☐

If any other reasons, state them briefly.

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4. Hydration of ketone is a reversible reaction resulting in the formation of the hydrate. In alkaline solution, the mechanism is as follows:



In fact the equilibrium is usually in favour of the ketone. Starting from the hydrate, discuss the mechanism of the reverse process in alkaline solution.

QUESTIONNAIRE

Put "X" in the box that most closely corresponds to your opinion:

1. Are you familiar with this problem?

YES	NOT SURE	NO

2. How did you find solving the problem?

DIFFICULT	MODERATE	EASY

3. How confident are you that your answer is correct?

CONFIDENT	MODERATE	DOUBTFUL

4. If you had difficulties in solving this problem, which one of the following reasons mostly accounts for your difficulty?

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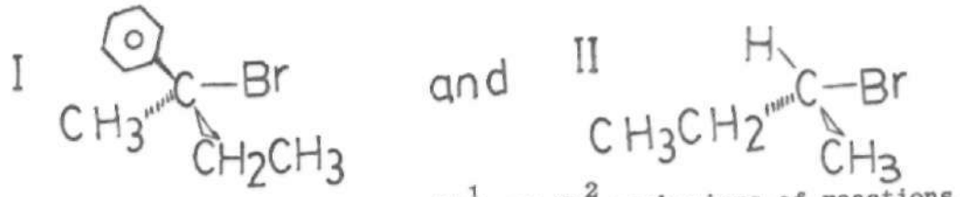
I got mixed up along the way. ☐

If any other reasons, state them briefly.

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3. Considering the mechanisms of the reactions of bromine with benzene and with ethene, explain the following observation:
A catalyst is needed for the reaction of benzene with bromine, but not for the reaction of ethene with bromine.

2. Using as examples, the reactions of CN^- with



show the differences between SN^1 and SN^2 mechanisms of reactions.

QUESTIONNAIRE

Put "X" in the box that most closely corresponds to your opinion:

1. Are you familiar with this problem?

YES	NOT SURE	NO

2. How did you find solving the problem?

DIFFICULT	MODERATE	EASY

3. How confident are you that your answer is correct?

CONFIDENT	MODERATE	DOUBTFUL

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