
UNIT 1 REACTION MECHANISM

— INTRODUCTION

Structure

- 1.1 Introduction
 - Objectives
- 1.2 Types of Mechanism
- 1.3 Types of Reagents
 - Nucleophiles
 - Electrophiles
 - Free Radicals
 - Radical Ions
- 1.4 Types of Reactions
 - Substitution Reactions
 - Addition Reactions
 - Elimination Reactions
 - Rearrangements
 - Oxidation and Reduction Reactions
- 1.5 Summary
- 1.6 Terminal Questions
- 1.7 Answers

1.1 INTRODUCTION

As mentioned in the Block Introduction, reaction mechanism involves an understanding of the detailed description of stepwise progress of a reaction as the reactants are converted into products. A knowledge of reaction mechanism is of utmost importance in devising synthesis of new molecules. These find applications in medicine, industry, textiles, household appliances, defence, space research, etc., in fact, practically in every sphere of modern life.

Study of reaction mechanism is very interesting as it gives us an opportunity to have a feel of the fantastic world of atoms and molecules, their nature and their reactions. If the fundamentals of reaction mechanism are clear, it is easy to understand the mechanism of any particular reaction. In this unit you will study the basic types of reaction mechanism, the types of reagents and types of reactions. Thermodynamic and kinetic aspects of reaction mechanism would be discussed in the next unit.

Objectives

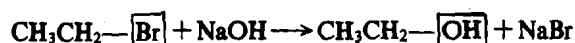
After studying this unit you should be able to :

- explain the general types of reaction mechanism,
- define the terms, nucleophile, electrophile, free radical and radical ion with examples,
- differentiate a nucleophile from a base, nucleophilicity from basicity, and
- define and categorise a reaction as substitution, addition, elimination, rearrangement or oxidation-reduction.

1.2 TYPES OF MECHANISM

There are two features which, in general, characterise the reactions of organic compounds. One of these is the relative slowness of most organic reactions compared to many familiar inorganic reactions. For example, the reaction between hydrochloric acid and sodium hydroxide is instantaneous, whereas the esterification of acetic acid by ethyl alcohol takes hours and occurs only if the reaction mixture is heated with a catalyst such as sulphuric acid. Even then the reaction hardly ever goes to completion. The other characteristic feature of organic reactions is that, in general, the greater part of the reacting molecule remains relatively unchanged during the course of a reaction. Thus you may recall that most organic reactions

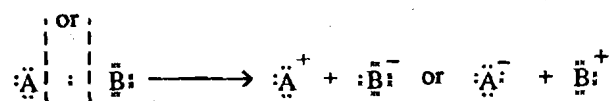
occur at the site of functional groups which leave the rest of the molecule intact. For example, in the reaction between bromoethane and aqueous sodium hydroxide,



the hydrocarbon part of the molecule, i.e., CH_3CH_2 is retained as such and the bromo functional group is replaced by the hydroxy one.

The slowness and the relative stability of the molecule in reactions are due to the type of bonding that exists in organic compounds. We know that atoms in organic compounds are covalently bonded. When reactions involving organic compounds take place one or more of these bonds may be broken and atoms (or groups) originally attached may be replaced by other atoms (or groups) or may be lost altogether. The type of mechanism followed by the reaction is determined by the way the bond breaks. The cleavage of a covalent bond may take place in one of the following ways :

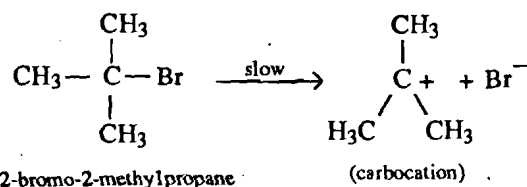
- i) **Bond heterolysis** : When a bond breaks in an unsymmetrical way, such that both the bonding electrons remain with either of the fragments, then it is called bond heterolysis.



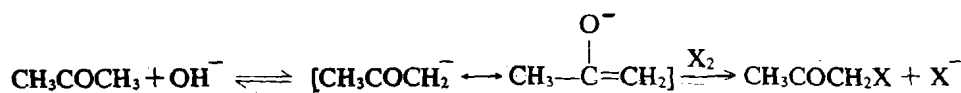
Bond heterolysis

In heterolytic cleavage of a bond, the resulting species are charged. Depending upon the site of cleavage, either of the resulting species can be positively or negatively charged as shown above.

If the species resulting from heterolytic cleavage has a carbon atom bearing positive charge, then it is called a **carbocation** or **carbonium ion**. For example, the hydrolysis of 2-bromo-2-methylpropane to 2-methyl-2-propanol follows a two step mechanism, the first step being the slow heterolytic cleavage forming a carbocation.



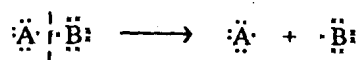
On the other hand, reaction of propanone with halogens in the presence of a base proceeds by a different mechanism :



We see that here we get a species having a carbon atom bearing a negative charge, such a species is called a **carbanion**.

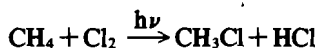
In bond heterolysis, which fragment would carry the pair of bonding electrons is determined by the electronegativity of the constituent atoms of the bond in question. The more electronegative atom retains the electrons and gives rise to a negatively charged ion. Since carbon has very low electronegativity, very often, in the event of heterolytic cleavage, it loses its share in the bond and becomes a part of the positively charged fragment. Therefore, while carbocations are very common as intermediates, carbanions are rare. You would learn about these in later units when we talk about nucleophilic and electrophilic substitution reactions in detail. As these reactions involve charged species, these are said to follow **ionic** or **polar** mechanism.

- ii) **Bond homolysis** : If a bond cleaves in a symmetrical way, such that either fragment of the molecule gets one electron, then it is referred to as bond homolysis.

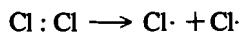


Bond homolysis

For example, in photochlorination of methane,

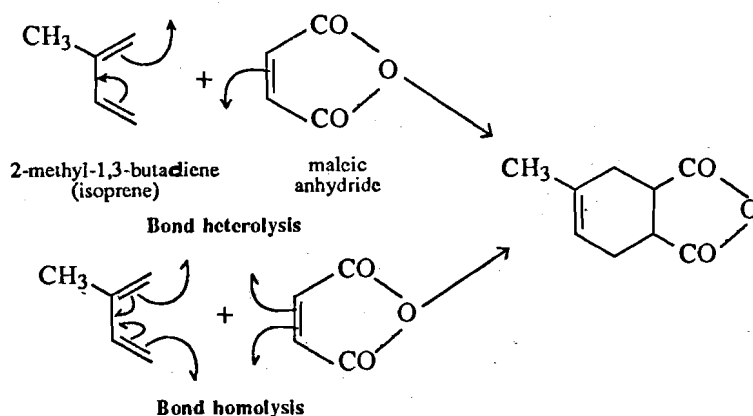


which is a multistep reaction, the first step is homolysis of Cl_2 molecule as,



The resulting species have got an unpaired electron each and are referred to as **free radicals**. Chlorine free radical, same as chlorine atom, has got seven valence electrons. It means, therefore, that a chlorine radical is a neutral species. In fact, it is true of any free radical. Further, due to the presence of unpaired electrons, free radicals are very reactive. Reactions involving the formation of free radicals are said to follow **free radical mechanism**.

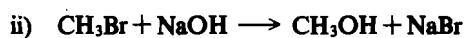
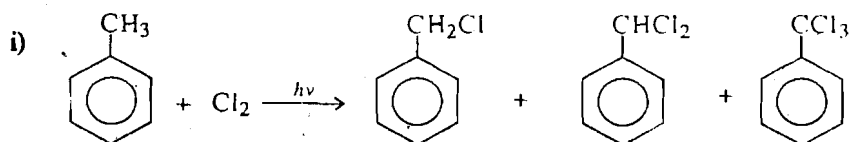
- ii) **Pericyclic mechanism** : In certain cases it is difficult to ascertain whether the reaction involves bond homolysis or heterolysis. In such reactions both types of bond cleavages are possible and lead to the same product. For example, in the case of Diels-Alder reaction, the two possibilities are as shown below :



Here the reaction is said to proceed in a concerted manner, i.e., bond making and bond breaking is simultaneous. These reactions are said to follow pericyclic mechanism. Many photochemical reactions which you would study in detail in Unit 12 of this course follow this kind of a mechanism.

SAQ 1

Indicate the probable mechanism type-ionic or radical for the following reactions.



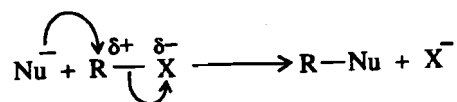
1.3 TYPES OF REAGENTS

In the previous section, we have tried to focus our attention only on a single molecule and attempted to visualise the process of bond breaking. You would have noticed that organic reactions often involve two reactants : one is the organic molecule which is referred to as the **substrate** and the other is called the **reagent**. You may recall in the reaction between bromoethane and sodium hydroxide, the former is a substrate and the latter is a reagent. Since these reagents are the ones which bring about changes in organic molecules it is important to know more about their types and their nature.

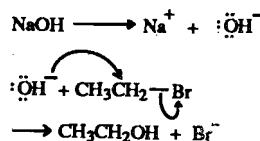
On the basis of their electronic structure, reagents can be broadly classified into the following types.

1.3.1 Nucleophiles

These are electron rich reagents possessing at least one nonbonded pair of electrons. These are attracted towards an electron deficient site in the substrate. Nucleophiles are thus "nucleus loving" and tend to donate electrons. Most of the nucleophiles are negatively charged or negatively polarised. However, a few of them are also neutral molecules with at least one lone pair. A reaction initiated by a nucleophile is called nucleophilic reaction. A nucleophilic reaction is represented in the following manner :



You would recall that as per convention, movement of an electron pair is depicted by the use of a curved arrow. For example, the reaction between bromoethane and sodium hydroxide can be represented as :



A list of nucleophiles with corresponding nucleophilic atoms is given in Table 1.1. A nucleophile with a negative charge is stronger than its conjugate acid. For example, OH^- is a stronger nucleophile than H_2O and NH_2^- than NH_3 .

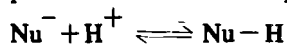
Table 1.1 : List of some common nucleophiles

Nucleophilic atom	Nucleophile
Halogen, X = F, Cl, Br, I	X^-
Oxygen	OH^- , RO^- , $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$, H_2O , ROH , RCOOH
Sulphur	SH^- , RS^- , H_2S , RSH
Nitrogen	NH_3 , RNH_2 , R_2NH , R_3N
Carbon	$-\text{CN}^-$, $\text{RC}\equiv\text{C}^-$

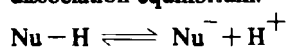
The nonbonded pair of electrons in a nucleophile is provided by C, N, O, S or a halogen atom. The strength of a nucleophile depends upon a number of factors like the nature of the electron donating atom, its position in the periodic table, its polarisability, size and the nature of the solvent, etc. The relative strength of nucleophiles is measured in terms of their **nucleophilicities**. As nucleophiles donate electrons, these are bases according to Lewis definition. Different nucleophiles would have different basic strength, i.e., **basicity**. It is reasonable to expect that strong bases are good reagents for nucleophilic substitution reactions. This is generally true but there are some deviations also. For example, the iodide ion (I^-) is a good nucleophile but a very weak base. It is worthwhile to understand the difference between the two closely related terms, viz., nucleophilicity and basicity.

Basicity and Nucleophilicity

Basicity is a measure of a reagent's ability to accept a proton in an acid-base reaction. It pertains to the acid-base equilibrium,



which is characterised by an equilibrium constant, K_b . It is customary to treat this as an acid dissociation equilibrium.



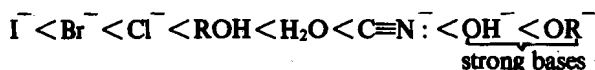
$$pK_a = -\log K_a$$

with an equilibrium constant, K_a which is characterised as pK_a . The magnitude of pK_a serves as an index of basicity. The basicities of two nucleophiles are compared in terms of the pK_a values of their respective conjugate acids. A higher value of pK_a indicates a weaker conjugate acid or a strong base, i.e., a strong nucleophile. A list of pK_a values of the conjugate acids of common nucleophiles is given in Table 1.2.

Table 1.2 : List of common nucleophiles with pK_a values of their conjugate acids

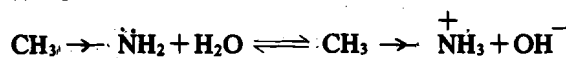
Nucleophile	Conjugate acid	pK_a
I^-	HI	-10
Br^-	HBr	-9
Cl^-	HCl	-7
CN^-	HCN	9.2
RS	RSH_1	10-11
R_3N	R_3NH^+	10-11
R_2NH	$R_2NH_2^+$	11
OH	H_2O	15.7
$CH_3CH_2O^-$	CH_3CH_2OH	16
RCHCN	RCH ₂ CN	25
$HC\equiv C^-$	$HC\equiv CH$	25
NH_2^-	NH_3	38
$CH_2=CH^-$	$CH_2=CH_2$	44
CH_3^-	CH_4	48
$(CH_3)_2CH^-$	$(CH_3)_2CH_2$	51

The increasing order of basicity of some reagents is,



Let us recall here the two important structural features affecting the basicity of a molecule. These are :

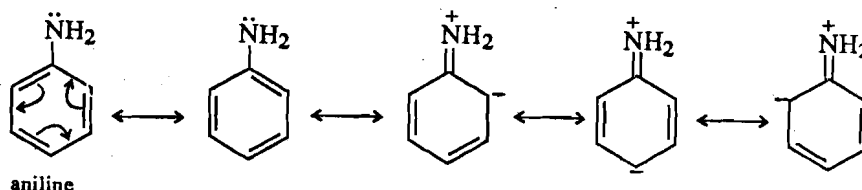
- i) **Inductive effect** : In general, the substituents having +I effect, i.e., electron releasing effect increase basicity. For example, in the case of amines an alkyl group on nitrogen increases basicity by dispersing the positive charge in the cation which is stabilised relative to the free amine.



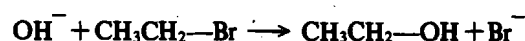
Therefore base strength increases in the series,



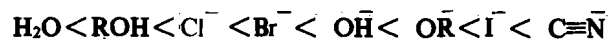
- ii) **Resonance** : Resonance effects the base strength of an amine. For example, cyclohexylamine is a far stronger base than is aniline. The reason is that the availability of lone pair in case of aniline will be reduced due to the delocalisation of the lone pair over the ring as shown in the resonance structures below.



In contrast to basicity, nucleophilicity is a measure of a reagent's ability to cause substitution at a carbon atom. The relative nucleophilicities of a series of reagents are determined by their relative rates of reaction in a substitution reaction, e.g., substitution reaction with bromoethane,



the increasing order of nucleophilicity of some reagents is,



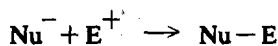
The order of nucleophilicity can be rationalised in terms of polarisability and solvation of nucleophiles and the nature of the solvent. Steric considerations are also associated with

It is important to note here that while basicity is a thermodynamic property (measured by equilibrium constant) nucleophilicity is a kinetic phenomenon.

nucleophilicity. These aspects would be taken up later in Unit 3 when we talk about nucleophilic substitution reactions in detail.

1.3.2 Electrophiles

Electron-deficient reagents which tend to accept electrons and are "electron loving" are called electrophiles. These reagents attack electron rich centres or nucleophiles and form a bond during the reaction.



Since electrophiles can accept an electron pair or get attracted towards a negative centre, they also act as Lewis acids. Electrophiles are of two types, positively charged and neutral. A list of electrophiles is given in Table 1.3.

Table 1.3 : List of some electrophiles

Positively charged	Neutral
H^+	$\text{I}-\text{Cl}, \ddot{\text{C}}\text{Cl}_2$
M^+, MX^+	$\begin{array}{c} \text{O} \\ \\ \text{RC}-\text{Cl} \end{array}$
Br^+, Cl^+	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{array}$
$\text{NO}_2^+, \text{NO}^+, \text{NH}_4^+$	CO_2, SO_3
H_3O^+	$\text{BF}_3, \text{ZnCl}_2, \text{AlCl}_3, \text{FeCl}_3,$
$\text{R}_3\text{C}^+, \text{Ar}-\text{N}^+\equiv\text{N}, \text{RCO}^+$	

1.3.3 Free Radicals

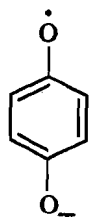
Two types of reagents that we discussed earlier, i.e., electrophiles and nucleophiles, need not necessarily be added reagents. They can be transient species formed during the course of a reaction. Free radicals, the third type, produced as a result of homolytic cleavage of a covalent bond, are essentially reaction intermediates. These are important because of their high reactivity. A free radical is any atom or group that possesses one or more unpaired electrons; because of this and an incomplete octet, it is highly reactive. You will read more about radical intermediates in Unit 9 of Block 3 of this course. Table 1.4 gives a list of some free radicals.

Table 1.4 : Some free radicals

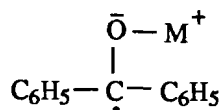
hydrogen	$\text{H}\cdot$
chlorine	$\text{Cl}\cdot$
silver	$\text{Ag}\cdot$
sodium	$\text{Na}\cdot$
oxygen	$\ddot{\text{O}}-\ddot{\text{O}}$ (diradical)
carbon	$-\text{C}\cdot$
alkoxy	$-\text{CO}\cdot$
nitroxide	$-\text{N}\cdot-\text{O}\cdot$

1.3.4 Radical Ions

We should also briefly refer to another type of reagents which are encountered during reactions as intermediates. These are the radical ions. Radical ions possessing both an odd electron and charge are known. These may carry a positive or negative charge along with an odd electron and are correspondingly known as radical cations or radical anions respectively. The semiquinone anion (I) and the metal ketyl (II) produced by donation of an electron by a metal atom to a ketone are well known examples of radical anions. An example of a radical cation is aminium radical ion (III).



I



II

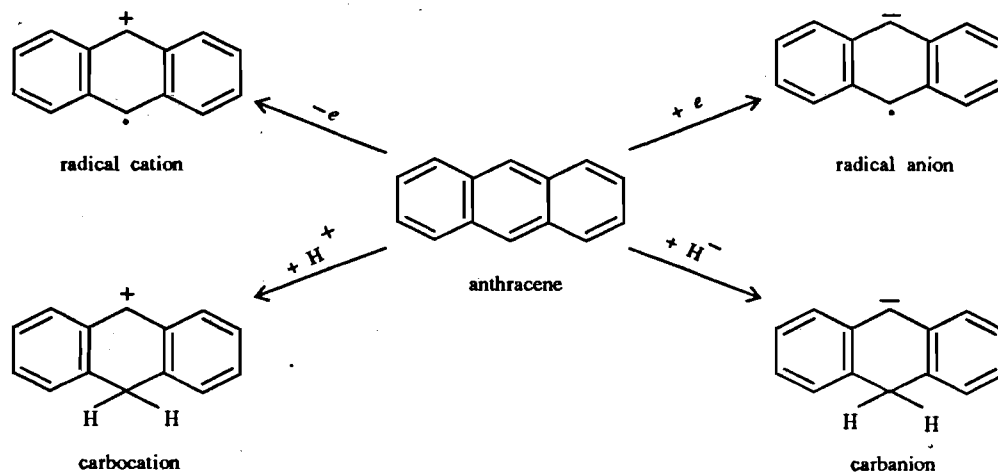


III

The relation between the structures of carbocation, carbanions, radical cations and radical anions can be best illustrated by considering the reaction of anthracene with different reagents. Under suitable reaction conditions, anthracene can produce any one of these four species, as it can,

- add an electron to produce a radical anion (sodium in liquid ammonia will accomplish this);
- add hydride ion to produce a carbanion (lithium aluminium hydride is expected to do this but a very high temperature is required to reduce anthracene with this reagent);
- remove an electron to form a radical cation (a good one-electron oxidising agent such as Mn^{3+} produces this species);
- add a proton to form a carbocation (a nonoxidising acid such as HF can do this).

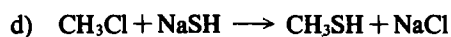
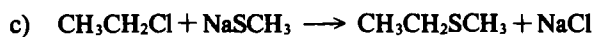
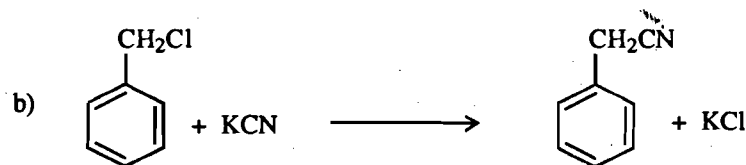
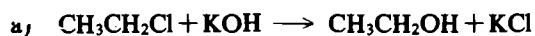
These reactions of anthracene are summarised in the following scheme :



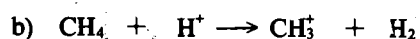
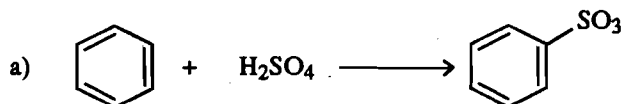
In the case of the radical ions above, the charge and/or the odd electron can be distributed over the rings by resonance.

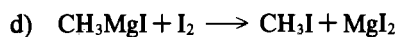
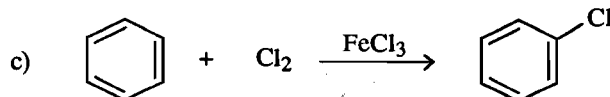
SAQ 2

- i) Pick up the nucleophiles in the following reactions.



- ii) Pick up the electrophiles in the following reactions.





Having understood what reaction mechanism is, the different ways in which the covalent bond of organic molecules can break leading to different kinds of mechanism, the different types of reagents bringing about organic reactions; we would now study the different types of organic reactions. Here you would learn to classify these reactions depending upon the kind of mechanism operating in them and the reagent used.

1.4 TYPES OF REACTIONS

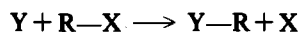
In your previous course, you must have studied classification of organic compounds. You would have noticed that it becomes very easy to understand the nature of organic compounds by categorising them according to the structural types and functional groups. Similarly, it becomes very easy to understand organic reactions if these are categorised into different types which also helps to frame a series of rules pertaining to each type. However, you should remember that products obtained in a reaction depend upon conditions under which the reaction is carried out. Depending upon the substrate, reagent and reaction conditions, sometimes very different and unexpected products are formed.

Let us study the five main types of organic reactions which essentially involve bond making and bond breaking processes at carbon atoms of a substrate. Each of these types will be dealt with in detail in the following units.

1.4.1 Substitution Reactions

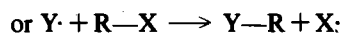
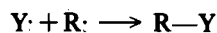
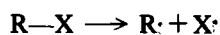
When an atom or group provided by the reagent replaces an atom or group of the substrate molecule, the reaction is called a **substitution reaction**. It can take place in a number of ways.

Consider, for example, the following substitution reaction,



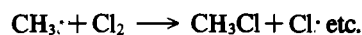
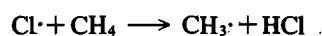
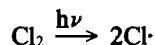
Where R—X and Y—R are both covalent molecules.

i) This reaction may involve a homolytic fission as shown below,

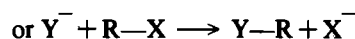
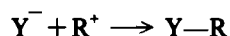


where the free radicals are produced first and later they combine with other free radicals to give substitution products. This is called a **free radical substitution**.

Photochemical chlorination of methane is an example.

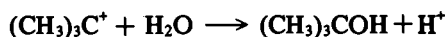
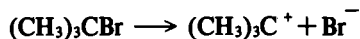


ii) Another way in which the above substitution reaction can take place is represented as :



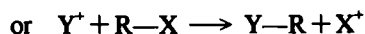
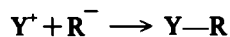
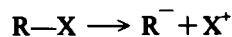
In a substitution reaction, the attacking species of one type (nucleophilic, electrophilic or radical) replaces a similar species.

This occurs when the reaction involves heterolytic fission. The reagent Y is a nucleophile (nucleus-loving) and it seeks a centre of electron deficiency or an electrophilic (electron-loving) centre. The electron deficient centre here is a carbocation. Since the attacking reagent is a nucleophile, the substitution is called **nucleophilic substitution**. You are familiar with nucleophilic substitution reactions of alkyl halides, like, hydrolysis of 2-bromo-2-methylpropane,

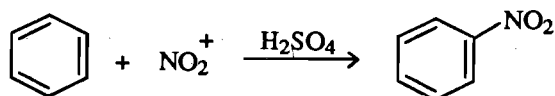


Nucleophilic substitution reactions can proceed by more than one type of mechanism. The mechanistic details of these would be dealt with in Unit 3 of this course.

- iii) There is yet another way in which a substitution reaction can take place. Here also the heterolytic fission of the molecule R—X takes place.



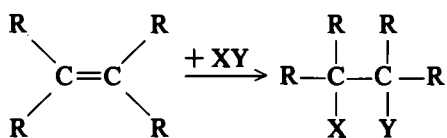
The reagent Y^+ is an electrophile. It seeks a reaction centre which has a high electron density, a carbanion here. Attacking reagent being an electrophile in this case, the substitution is called **electrophilic substitution**. This type of substitution is most common in aromatic compounds, like, nitration of benzene.



You will study this type of substitution in detail in Unit 4 of this course.

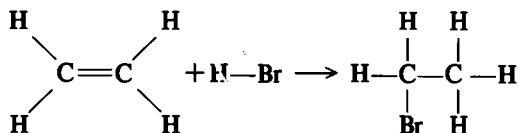
1.4.2 Addition Reactions

Addition is the most characteristic reaction of alkenes and alkynes. In addition reactions, two atoms or groups are added to a molecule containing a double or a triple bond.

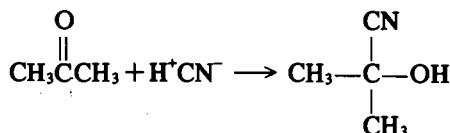


In most of these reactions, the addendum is an electrophile and the alkene, a nucleophile. The reactions are called **electrophilic addition reactions**. Free radicals being electron deficient species, even **free radical additions** can be classified as electrophilic attacks.

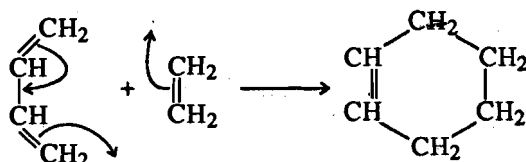
A simple example of an addition reaction is the addition of HBr to ethene to give bromoethane.



Electrophilic and free radical addition reactions are common with alkenes and alkynes while **nucleophilic addition reactions** are encountered in double bonds with hetero atoms, e.g., with carboxyl compounds. The formation of a cyanohydrin by the reaction between propanone and HCN is a common example.

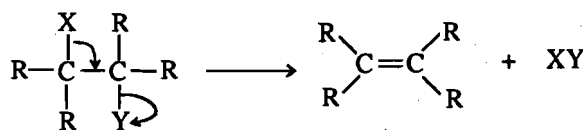


When bond breaking and addition to the double bond take place simultaneously as shown below, it is referred to as **pericyclic addition**.

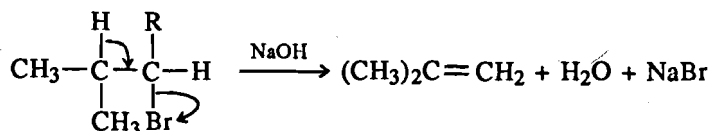


1.4.3 Elimination Reactions

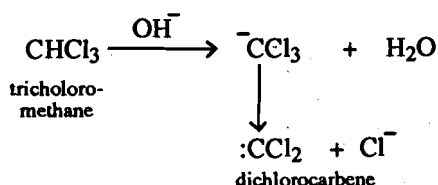
These are reactions that involve the loss of two groups or atoms, commonly from adjacent carbon atoms, introducing a double bond.



For example,



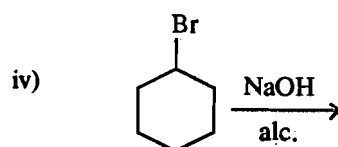
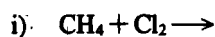
Since the above elimination involves two groups (or atoms) on adjacent carbon atoms, it is called a 1, 2 or β -elimination. When elimination involves loss of two atoms or groups from the same atom, it is called (1, 1) or α -elimination. For example,



The hypovalent neutral species $:CCl_2$ is called a carbene. It is an unstable intermediate about which you will study in detail in Unit 9.

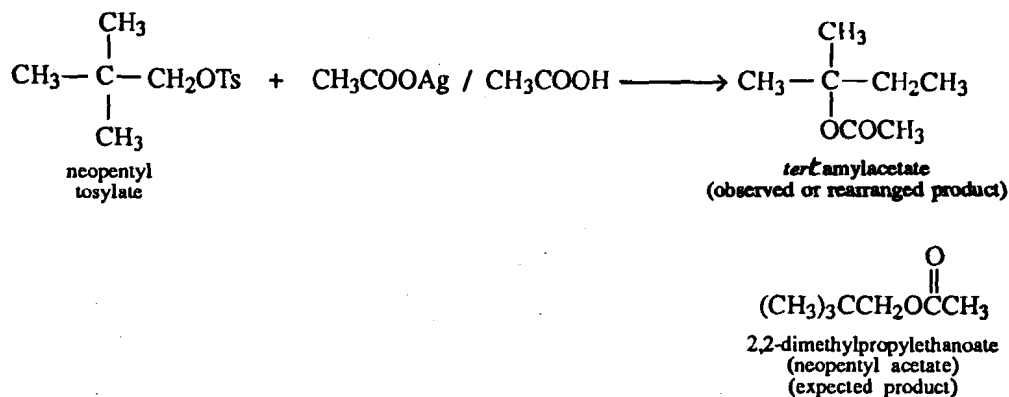
SAQ 3

Write the products of the following reactions and categorise them as substitution, elimination or addition reactions.



1.4.4 Rearrangements

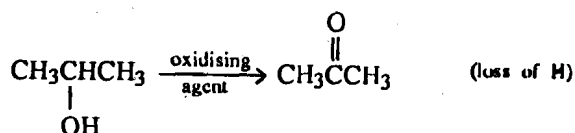
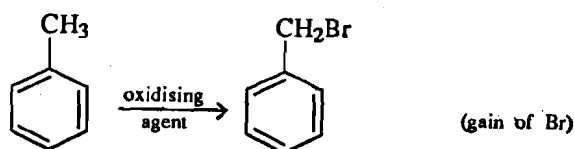
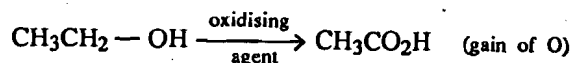
As said before, most of the reactions of organic compounds take place at a functional group while the rest of the molecule does not undergo any change. There are some organic reactions wherein this "intact" part also takes part in the reaction. These are rearrangement reactions in which an atom or a group moves from one position to another within the molecule. In other words, if in a reaction, instead of getting the expected product, an isomerised product is obtained due to the migration of an atom or group it is called a rearrangement. For example, the rearrangement of 2, 2-dimethylpropyl-4'-methylbenzenesulphonate (neopentyl tosylate) to 1, 1-dimethylpropylethanoate (amyl acetate) is given below.



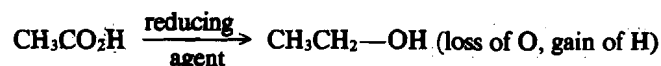
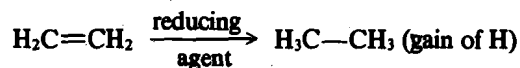
1.4.5 Oxidation and Reduction Reactions

It is difficult to define oxidation or reduction as applied to organic compounds. You might recollect that in Inorganic Chemistry, oxidation is defined as either loss of electrons or increase in oxidation number. Conversely reduction is defined as gain of electrons or decrease in oxidation number. Thumb rules to determine whether an organic compound has been oxidised or reduced are :

- i) If a molecule gains an electronegative element (nitrogen, halogen or oxygen) or loses hydrogen it is oxidised, e.g.,



- ii) If a molecule loses an electronegative element (nitrogen, halogen or oxygen) or gains hydrogen it is reduced, e.g.,



Another way to determine whether an organic molecule is oxidised or reduced is to arrange a series of functional groups in order of increasing oxidation state (Table 1.5) and define oxidation as the conversion of a functional group in a molecule from one category to a higher one. The opposite is true for reduction. You know that oxidation states or oxidation numbers enable us to follow the paths of electrons during a reaction and tell which substances were oxidised and which reduced. Oxidation numbers can be positive or negative. The oxidation

number of carbon in the series representing oxidation of methane to carbon dioxide is as follows:



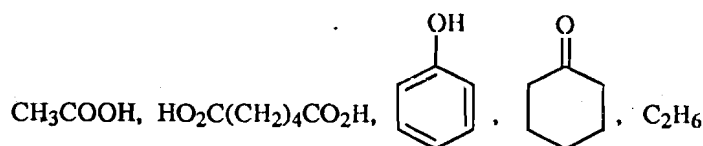
Table 1.5 : Functional groups arranged according to increasing oxidation state

Approximate Oxidation number	-4	-2	0	+2	+4
FUNCTIONAL GROUPS			OXIDATION		
	*RH	--C=C--	$\text{R--C}\equiv\text{C--R}$	RCO_2H	CO_2
		ROH	$\text{R--}\overset{\text{O}}{\parallel}\text{C--R}$	$\overset{\text{O}}{\parallel}\text{RCNH}_2$	CCl_4
		RCl	>CCl_2		
FUNCTIONAL GROUPS		RNH ₂	$\text{Cl--}\overset{\text{R}}{\underset{ }{\text{C}}}\text{--}\overset{\text{R}}{\underset{ }{\text{C}}}\text{--Cl}$	--CCl_3	
			$\text{R--}\overset{\text{OH}}{\underset{ }{\text{C}}}\text{--}\overset{\text{OH}}{\underset{ }{\text{C}}}\text{--R}$		
			REDUCTION		

*R = alkyl group : where not indicated substituent is H.

SAQ 4

Arrange the following in order of increasing oxidation state.



1.5 SUMMARY

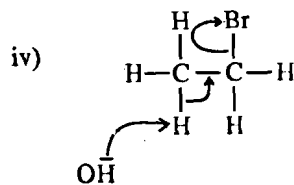
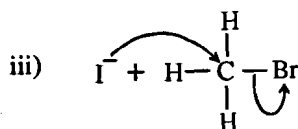
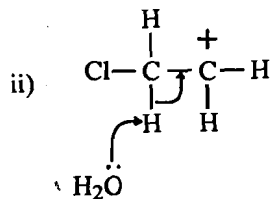
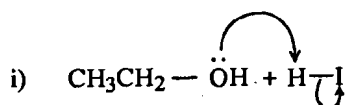
Let us summarise the important aspects of reaction mechanism we have studied in this unit.

- The detailed description of how a reaction occurs is called reaction mechanism. All reactions involve bond breaking and bond making. Depending upon the way a bond is broken, mechanism of organic reactions can be broadly classified into homolytic, heterolytic or pericyclic types.
- The reagents generally used in organic reactions are nucleophiles, attracted towards a positive centre; electrophiles, attracted towards a negative centre; free radicals with unpaired electrons on them and radical ions which are radicals with positive or negative charges.
- It becomes easy to understand the large number of organic reactions if categorised into different types. When a group or atom in an organic molecule is replaced by another group or atom, it is called a substitution reaction. Depending upon the reagent, substitution reactions can be nucleophilic, electrophilic or free radical type. When two atoms or groups are added to a double or a triple bond, it is called an addition reaction. This can also be classified into nucleophilic, electrophilic and free radical type. Elimination reactions are those in which two atoms or groups are removed from a molecule, usually from adjacent carbon atoms leading to unsaturation in the molecule.

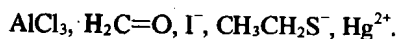
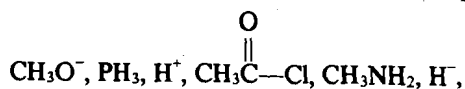
Rearrangement reactions are the ones where in an atom or group shifts to another position in the same molecule. Nucleophilic and electrophilic rearrangements are more common than the free radical types. Another type of organic reactions may involve any of the above four types. These are oxidations and reductions which again can take place in the presence of a number of reagents.

1.6 TERMINAL QUESTIONS

- 1) In the following reaction, reactants and arrows showing the flow of electrons are indicated. Write the products of the reactions.



- 2) Why is iodide ion a good nucleophile but a weak base?
3) Categorise the following species into electrophiles and nucleophiles.



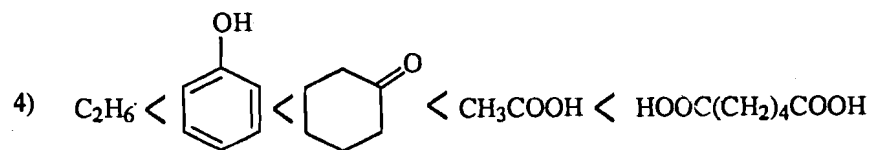
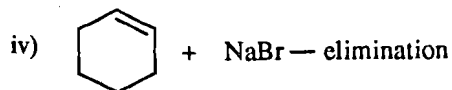
- 4) What type of reaction must be carried out to convert,
i) an alcohol to a carboxylic acid.
ii) an alkyl chloride to an alkyl bromide.
iii) an alkene to an alkane.
iv) a haloalkane to an alkene.

1.7 ANSWERS

Self Assessment Questions

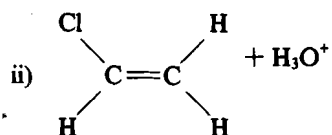
- 1) i) Radical mechanism
ii) Ionic mechanism
iii) Ionic mechanism
- 2) i) Nucleophiles — OH^- , CN^- , SCH_3 , SH^-
ii) Electrophiles — SO_3 , H^+ , Cl^+ , I^+

- 3) i) $\text{CH}_3\text{Cl} + \text{HCl}$ — substitution
 ii) $\text{CH}_3\text{CH}_2\text{Cl}$ — substitution
 iii) $\text{CH}_3\text{CH}_2\text{Br}$ — addition



Terminal Questions

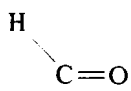
- 1) i) $\text{CH}_3\text{CH}_2\text{—I} + \text{H}_2\text{O}$



- iii) $\text{CH}_3\text{I} + \text{Br}^-$

- iv) $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O} + \text{Br}^-$

- 2) Iodine has a large atom and the outer electrons in it being farther from the nucleus are less tightly held. The outer electrons are, therefore, more easily distorted by attraction to a positive centre and can attack a partially positive carbon atom readily. However, it does not easily accept a proton from an alkyl halide and thus act as a good nucleophile and a weak base.

- 3) Electrophiles : H^+ , $\text{CH}_3\text{C}(=\text{O})\text{—Cl}$, AlCl_3 , Hg^{2+} , 

Nucleophiles : CH_3O^- , PH_3 , H^- , I^- , $\text{CH}_3\text{CH}_2\text{S}^-$, CH_3NH_2

- 4) i) oxidation reaction
 ii) substitution reaction
 iii) addition or reduction reaction
 iv) elimination reaction