I.G.N.O.U. *Based*

NEERAJ®

C.H.E.-6

ORGANIC REACTION MECHANISM

By: *Shashi Gupta*

Question Bank Cum Chapterwise Reference Book
Including **Many Solved Question Papers**

NEERAJ
PUBLICATIONS
(Publishers of Educational Books)
(An ISO 9001 : 2008 Certified Company)

Sales Office:
1507, 1st Floor, Nai Sarak, Delhi - 6
Ph.: 011-23260329, 45704411,
23244362, 23285501
E-mail: info@neerajbooks.com
Website: www.neerajbooks.com

MRP ₹ 280/-

Published by:

NEERAJ PUBLICATIONS

Sales Office : **1507, 1st Floor, Nai Sarak, Delhi-110 006**
E-mail: **info@neerajbooks.com**
Website: **www.neerajbooks.com**

Reprint Edition with Updation of Sample Question Paper Only | Typesetting by: **Competent Computers** | Printed at: **Novelty Printer**

Notes:

1. *For the best & up-to-date study & results, please prefer the recommended textbooks/study material only.*
2. *This book is just a Guide Book/Reference Book published by NEERAJ PUBLICATIONS based on the suggested syllabus by a particular Board/University.*
3. *The information and data etc. given in this Book are from the best of the data arranged by the Author, but for the complete and up-to-date information and data etc. see the Govt. of India Publications/textbooks recommended by the Board/University.*
4. *Publisher is not responsible for any omission or error though every care has been taken while preparing, printing, composing and proof reading of the Book. As all the Composing, Printing, Publishing and Proof Reading, etc. are done by Human only and chances of Human Error could not be denied. If any reader is not satisfied, then he is requested not to buy this book.*
5. *In case of any dispute whatsoever the maximum anybody can claim against NEERAJ PUBLICATIONS is just for the price of the Book.*
6. *If anyone finds any mistake or error in this Book, he is requested to inform the Publisher, so that the same could be rectified and he would be provided the rectified Book free of cost.*
7. *The number of questions in NEERAJ study materials are indicative of general scope and design of the question paper.*
8. *Question Paper and their answers given in this Book provide you just the approximate pattern of the actual paper and is prepared based on the memory only. However, the actual Question Paper might somewhat vary in its contents, distribution of marks and their level of difficulty.*
9. *Any type of ONLINE Sale/Resale of "NEERAJ IGNOU BOOKS/NEERAJ BOOKS" published by "NEERAJ PUBLICATIONS" on Websites, Web Portals, Online Shopping Sites, like Amazon, Flipkart, Ebay, Snapdeal, etc. is strictly not permitted without prior written permission from NEERAJ PUBLICATIONS. Any such online sale activity by an Individual, Company, Dealer, Bookseller, Book Trader or Distributor will be termed as ILLEGAL SALE of NEERAJ IGNOU BOOKS/NEERAJ BOOKS and will invite legal action against the offenders.*
10. *Subject to Delhi Jurisdiction only.*

NEERAJ PUBLICATIONS
(Publishers of Educational Books)
(An ISO 9001 : 2008 Certified Company)
1507, 1st Floor, NAI SARAK, DELHI - 110006
Ph. 011-23260329, 45704411, 23244362, 23285501
E-mail: **info@neerajbooks.com** *Website:* **www.neerajbooks.com**

CONTENTS

ORGANIC REACTION MECHANISM

Question Bank – (Previous Year Solved Question Papers)

S.No. **_Chapterwise Reference Book_** *Page*

BASIC CONCEPTS AND SUBSTITUTIONS

ADDITION AND ELIMINATION

REACTION INTERMEDIATES AND MOLECULAR REARRANGEMENTS

PHOTOCHEMISTRY AND SYNTHETIC METHODS

❐❐

Sample Preview
of the
Solved
Sample Question
Papers

Published by:

NEERAJ
PUBLICATIONS
www.neerajbooks.com

QUESTION PAPER

(June – 2019)

(Solved)

ORGANIC REACTION MECHANISM

Time: 2 Hours] *[Maximum Marks: 50*

***Note:** Answer all the **five** questions. All questions carry **equal** marks.*

Q. 1. (a) Write the mechanism of the hydrolysis of ethyl acetate in presence of Base. Discuss the role of isotopic labelling in establishing its mechanism.

Ans. $C_2H_5\ COOCH_3 + H_2\ {}^{18}O \rightarrow CH_3COO^{18}H + C_2H_5OH$

Also Ref.: See Chapter-2, Page No. 13, 'Isotopic Studies' and 'Isotopic Labelling'.

***(b)* Taking suitable examples, differentiate between stereospecific and stereoselective reactions.**

Ans. Ref.: See Chapter-2, Page No. 14, 'Stereospecific and Stereoselective Reactions'.

Q. 2. *(a)* Write the mechanism of the following using suitable example for each case.

***(i)* Wittig reaction**

Ans. Ref.: See Chapter-6, Page No. 58, 'Wittig Reaction'.

***(ii)* Hydroboration**

Ans. Ref.: See Chapter-5, Page No. 47, 'Concerted Addition Reaction' (Hydroboration).

***(iii)* Knoevenagel reaction**

Ans. Ref.: See Chapter-6, Page No. 59, 'Knoevenagel Condensation'.

***(b)* Distinguish between Addition and Condensation polymerisation with the help of suitable examples.**

Ans. Ref.: See Chapter-15, Page No. 158, 'Addition and Condensation Polymers'.

Q. 3. *(a)* Write the mechanism of the following reactions:

***(i)* Backmann rearrangement**

Ans. Ref.: See Chapter-11, Page No. 103, 'Backmann Rearrangement'.

***(ii)* Benzil-Benzilic acid rearrangement**

Ans. Ref.: See Chapter-11, Page No. 101, 'Benzil-Benzilic Acid Rearrangement'.

***(iii)* Wagner-Mearwein rearrangement**

Ans. Ref.: See Chapter-11, Page No. 97, 'Wagner-Mearwein Rearrangements'.

***(b)* Classify dyes on the basis of their application and give one example of each class.**

Ans. Ref.: See Chapter-16, Page No. 169-170, 'Classification of Dyes'.

Also Add: Classification of Dyes Based on methods of Application Acid Dyes.

Q. 4. *(a)* Draw resonating structures of the intermediates formed by *ortho*, *meta* and *para* attack of the electrophile on nitrobenzene. Explain why is *meta* attack favourable.

Ans. Ref.: See Chapter-4, Page No. 32-33, 'Orientation and Reactivity in Aromatic Electrophilic Substitution'.

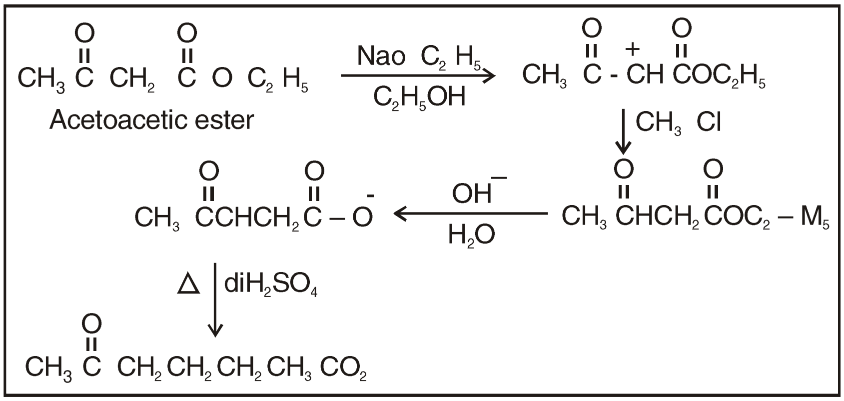
***(b)* Identify the alkene which on reaction with ozone followed by further reaction with Zn/ H_2O, gives a mixture of butanone and ethanol. Write the reactions and explain.**

Ans. Ref.: See Chapter-5, Page No. 48, 'Ozonolysis'.

Q. 5. ***(a)*** **How will you convert:**

(i) **Acetoacetic ester into 2-hexanone**

Ans.



$$CH_3\overset{O}{\overset{\|}{C}}\ CH_2\ \overset{O}{\overset{\|}{C}}\ O\ C_2H_5 \xrightarrow[C_2H_5OH]{Nao\ C_2H_5} CH_3\ \overset{O}{\overset{\|}{C}}-\overset{+}{C}H\ \overset{O}{\overset{\|}{C}}OC_2H_5$$

Acetoacetic ester

$$\downarrow CH_3\ Cl$$

$$CH_3\ \overset{O}{\overset{\|}{C}}CHCH_2\overset{O}{\overset{\|}{C}}-\overset{-}{O} \xleftarrow[H_2O]{OH^-} CH_3\ \overset{O}{\overset{\|}{C}}HCH_2\overset{O}{\overset{\|}{C}}OC_2-M_5$$

$$\Delta \downarrow diH_2SO_4$$

$$CH_3\ \overset{O}{\overset{\|}{C}}\ CH_2CH_2CH_2CH_3\ CO_2$$

(ii) **Malonic ester into adipic acid**

Ans. Adipic acid can be obtained by treating malonate ion with 1,2-dibromoethane followed by hydrolysis and decarboxylation.

$$2\ \overset{+}{Na}\ \overset{-}{C}H\ (COO\ C_2H_5)_2 + Br\ CH_2CH_2Br \xrightarrow{1)\ KOH \quad 2)\ HCl/\Delta} HOO(CH_2)_4COOH$$

Methanal Adipic acid

(iii) **1-Butanol into butanal**

Ans. Oxidation of alcohols yield carbonyl compounds. Alcohols with λ-hydrogen takes place. Primary alcohols hydrogens takes place. Primary alcohols undergo direct oxidation to give carboxylic acid via the corresponding aldehyde by losing two hydrogen actoms.

$$CH_3CH_2CH_2CH_2OH \xrightarrow[r_2so_4]{[O]} CH_3CH_2CH_2CHO$$

1 - Butanol 1 - Butanol

(b) **What are Benzynes? With its reference explain 'cine substitution'.**

Ans. Ref.: See Chapter-9, Page No. 81, 'Benzynes'.

Q. 6. ***(a)*** **What are different methods of generation of free radicals? Give one example for each method.**

Ans. Ref.: See Chapter-10, Page No. 87, 'Generation of Free Radicals'.

(b) **Predict the product formed in the addition reactions of HBr with** ***(i)*** **propene and** ***(ii)*** **2-propenenitrile. Write the mechanism of both the reactions.**

Ans. Ref.: See Chapter-5, Page No. 43, 'Electrophilic Addition Reaction of Alkenes' and 'Alkynes Addition of Hydrogen Halides'.

Q. 7. ***(a)*** **Why do electrophilic substitutions generally take place at 2 and 5 positions in pyrrole? Explain.**

Ans. Pyrrole undergoes electrophilic substitution at 2-position rather than 3-position. Due to its high reactivity and for the fact that pyrrole tends to polymerise in acidic solutions, electrophilic substitution at 2-position takes place because of stabilization by resonance.

Sample Preview
of
The Chapter

Published by:

NEERAJ
PUBLICATIONS
www.neerajbooks.com

ORGANIC REACTION MECHANISM

BASIC CONCEPTS AND SUBSTITUTIONS

1

Reaction Mechanism–Introduction

INTRODUCTION

In chemistry, a reaction mechanism is the step-by-step sequence of elementary reactions by which overall chemical change occurs. A chemical mechanism describes in detail exactly what takes place at each stage of an overall chemical reaction. It also describes each reactive intermediate activated complex and transtition state and which bonds are broken and which bonds are formed. So a complete mechanism must also account for all reactants used. The function of a catalyst, stereo chemistry, all products formed and the amount of each. It also describes the rate equation for the overall reaction. Reaction intermediates are chemical species. Often unstable and short lived, which are not reactants or products of the overall chemical reaction, but are temporary products and reactants in the mechanism's reaction steps. Reaction intermediates are often free radicals or ions. A knowledge of reaction mechanism is very important as these find applications in medicine, industry, textiles, household appliances, defence, space research etc.

CHAPTER AT A GLANCE

TYPES OF MECHANISM

There is no limit to the number of possible organic reactions and mechanisms. Although certain general patterns are observed that can be used to describe many common reactions. Each reaction has a stepwise reaction mechanism that explains how it happend. The detailed description of steps is not always clear organic reactions can be organized into several basic types. Most of the organic reactions are very slow as compared to inorganic reactions. For example, the reaction between hydrochloric acid and sodium hydroxide is instantaneous while the esterification of acetic acid by ethyl alcohol is a consuming reaction. This reaction takes place only if the reaction mixture is heated with a catalyst like sulphuric acid. Secondly, in organic reaction most of the part of reaction remains unchanged during reaction. So, we can say organic reaction takes place at the site of functional groups such as bromethane, or sodium hydroxide which leave the rest of the molecule intact. e.g.

$$CH_3CH_2-\boxed{Br}+NaOH \rightarrow CH_3CH_2-\boxed{OH}+NaBr$$

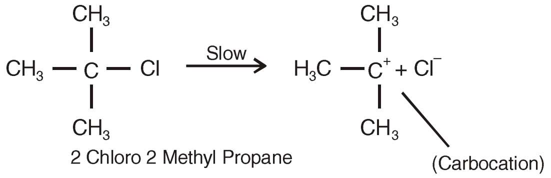
The stability of organic compounds is due to the existence of type of bonds. As organic compounds are covalently bounded and when reaction takes place these bonds may be broken and groups or atoms attached originally may be replaced by other groups. The cleavage of covalent bond may take place as follow:

(i) **Bond heterolysis:** When a covalent bond joining two atoms A and B breakes in such a way that both the electrons of the covalent bond are taken away by one of the bonded atoms. The mode of bond cleavage is called heterolysis.

$$:\ddot{\underset{\cdot\cdot}{A}}\cdot\;\cdot\ddot{\underset{\cdot\cdot}{B}}: \longrightarrow\; :\ddot{\underset{\cdot\cdot}{A}}^{+} + :\ddot{\underset{\cdot\cdot}{B}}:^{-} \text{ or } :\ddot{\underset{\cdot\cdot}{A}}:^{-} + :\ddot{\underset{\cdot\cdot}{B}}^{+}$$

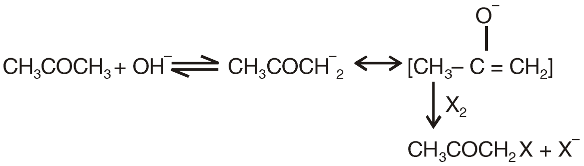
Heterolytic cleavage results in the formation of charged species. That is positively charged - cations and negatively charged anions.

Chemical species bearing positive charge on carbon and carrying six electrons in its valence shell are called carbocation or carbonium ions. These are formed by heterolytic cleavage of the covalent bonds in which the leaving group takes away with it the shared pair of electrons. e.g.



$$(CH_3)_3C-Cl \xrightarrow{\text{Slow}} (CH_3)_3C^+ + Cl^-$$

But reaction of propanone on the other hand with halogens in the presence of a base takes place in different mechanism:



$$CH_3COCH_3 + OH^- \rightleftharpoons CH_3COCH_2^- \leftrightarrow [CH_3-\overset{O^-}{\overset{|}{C}}=CH_2] \xrightarrow{X_2} CH_3COCH_2X + X^-$$

In this mechanism we get a species in which carbon atom bearing a negative charge and this species is called a carbanion.

In bond heterolysis, bonding electrons are determined by electronegativity of the constituent atoms. As carbon has very low electronegativity, so in hetrolytic cleavage, it loses its share in the bond and thus become a part of the positively charged fragment. So, as an intermediates carbocations are very common while carbaninons are rare.

***(ii)* Bond homolysis:** If a covalent bond breaks in such a way that each atom takes away one electron of the shared pair. It is called bond homolysis.

$$:\ddot{A}\cdot|\cdot\ddot{B}: \longrightarrow :\ddot{A}\cdot + \cdot\ddot{B}:$$

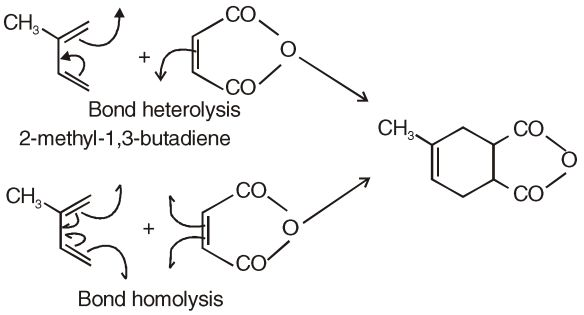
For example,

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$Cl:Cl \longrightarrow Cl\cdot + Cl\cdot$$

The neutral chemical species which contain an odd or unpaired electron and which are produced by homolytic break of covalent bonds and are called as free radicals. Therefore, chlorine radical is a neutral species. Homolytic break-up usually occurs in non-polar bonds and also favoured by high temperature ultraviolet (UV) radiations and by the presence of radical initiators. Because of the presence of unpaired electrons, free radicals are very reactive and these reactions which involve the formation of free radicals are said as free radical mechanism.

***(iii)* Pericyclic mechanism:** In some reactions both bond cleavages are possible and form the same product. In such cases it is difficult to know whether it is heterolysis cleavage or homolytic cleavage. For example,



In this reaction, bond formation and bond breakage, both takes place simultaneously. These reactions are said to follow pericyclic mechanism.

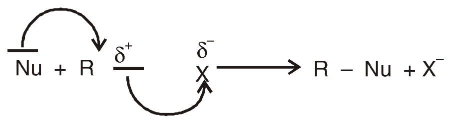
TYPES OF REAGENTS

In an organic reaction, the organic compound called the substrate reacts with a suitable attacking species called the reagent to form product. So organic reactions involve two reactants. An organic reaction substrate is that reactant which supplies carbon for the formation of a new bond while the other is reactant is called the reagent. If both the reactants supply carbon to the new bond, then it is impossible to know from where carbon atom come. During an organic reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed.

On the basis of their electronic structure reagents can be broadly classified into the following types– nucleophiles which are attracted towards a positive centre, electrophiles which are attracted towards a negative centre free radicals with unpaired electrons on them and radical ions which are radicals with positive or negative charges.

Nucleophiles

Nucleophiles are nucleus loving chemical species. Because the nucleus of any atom is positively charged, therefore nucleophiles must be electron rich chemical species containing at least one lone pair of electrons. These are attracted towards an electron deficient site in the substrate nucleophiles may be either negatively charged or neutral with at least one lone pair of electrons. Thus nucleophilic reaction is one which is initiated by a nucleophile.



$$\bar{Nu} + \overset{\delta^+}{R}-\overset{\delta^-}{X} \longrightarrow R-Nu + X^-$$

A nucleophile with negative change is stronger than its conjugate acid like OH^- is a stronger nucleophiles than H_2O and NH_2^- is stronger than NH_3.

As both negative charged and neutral nucleophiles contain at least one unshared pair of electrons they have a strong tendency to donate this pair of electrons to electron deficient species as Lewis basis. Nucleophiles always attack the substrate molecule at the site of lowest electron density. Different nucleophiles have different basicity therefore strong bases are good reagents for nucleophilic substitution reactions. Reagents' ability to accept a proton in an acid-base reaction is its basicity measure.

$$Nu^- + H^+ \rightleftharpoons Nu - H$$

which is characterized by an equilibrium constant, K_b

$$Nu - H \rightleftharpoons Nu^- + H^+$$

The increasing order of basicity of some reagent is

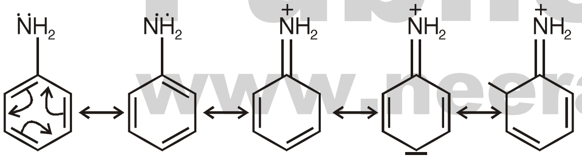
$$I^- < Br^- < Cl^- < ROH < H_2O < C \equiv N^-$$
$$< OH^- < OR^-$$

There are two important structural features affecting the basicity of a molecule:

(i) **Inductive effect:** It effect of substituent or electron releasing effect increase basicity

$$CH_3 \rightarrow NH_2 + H_2O \rightleftharpoons CH_3 \rightarrow NH_3^+ + OH^-$$

(ii) **Resonance:** It effects the base strength of an amine, because the availability of lone pair in case of aniline will be reduced due to the delocalization of the lone pair over the ring.



Electrophiles

These are electron loving chemical species. Their attraction for electron is due to the presence of an electron deficient atom in them. Electrophiles may be either positively charged or electrically neutral chemical species. These reagents attack electron rich centres or nucleophiles and form a bond during the reaction.

$$Nu^- + E^+ \rightarrow Nu - E$$

Since both positively charged and neutral electrophiles are short by a pair of electrons they have a strong tendency to attract electrons from other sources and behaves like a Lewis acids.

Free Radicals

Third type of reagent is free radicals which are formed during the course of a reaction. They are produced by homolytic cleavage of a covalent bond. Free radicals have high reactivity. Any atom or group that possesses one or more unpaired electrons are free radical because they have an incomplete octet.

Radical Ions

Radical ions are another type of reagents. Radical ions possesses odd electrons which may carry a positive or negative charge with an odd collection. So, these are known as radical cations or radical anions.

TYPES OF REACTIONS

Depending upon the substrate, reagent and reaction conditions very unexpected and different products are formed. Involving bond making and bond breaking processes on carbon atoms of a substrate five main types of organic reactions takes place.

Substitution Reactions

A substitution reaction is that which involves the direct replacement of an atom or group of atoms of an organic molecule by another atom or group of atoms that are provided by the reagent without change in the remaining part of the molecule. The product obtained as a result of substitution is called the substitution product. Let us see the following reaction:

$$Y + R - X \rightarrow Y - R + X$$

where R – X and Y – R are covalent molecules.

(i) **Free radical substitution:** Substitution reactions brought about by free radicals are called free radical substitution reaction.

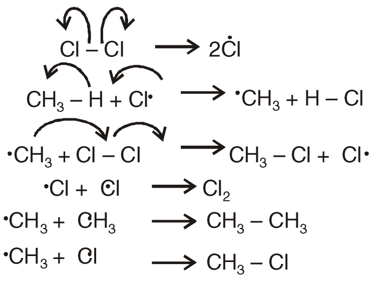
Firstly, the free radicals are produced and then they combine with other free radical to give substitution product.

$$R - X \rightarrow R^\bullet + X^\bullet$$
$$Y^\bullet + R^\bullet \rightarrow R - Y$$
$$\text{or} \quad Y^\bullet + R - X \rightarrow Y - R + X^\bullet$$

For example,

$$CH_3 - H + Cl_2 \rightarrow CH_3Cl + HCl$$

the reaction occurs by a free radical mechanism which involves the following steps:



(ii) **Nucleophilic Substitution Reaction:** Substitution reactions which are brought about by nucleophiles are called nucleophilic substitution reactions.

$$R - X \rightarrow R^+ + X^-$$

$$Y^- + R^+ \rightarrow Y - R$$

or $$Y^- + R - X \rightarrow Y - R + X^-$$

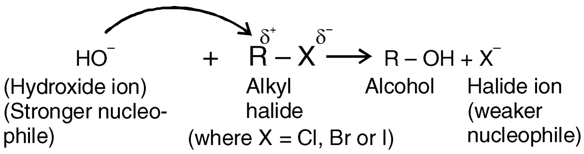
where reagent Y is a nucleophile and go to electron deficient element.

For example,

$$(CH_3)_3\ CBr \rightarrow (CH_3)_3\ C^+ + Br^-$$

$$(CH_3)_3C^2 + H_2O \rightarrow (CH_3)_3\ COH + H^+$$

Mechanism is as follow:



In these reactions, a stronger nucleophile displaces a weaker nucleophile. These reactions are typical of alkyl halides.

(iii) **Electrophilic Substitution Reaction:** Substitution reactions which are brought about by electrophiles are called electrophilic substitution reactions. These reactions are typical of arenes and other aromatic compounds.

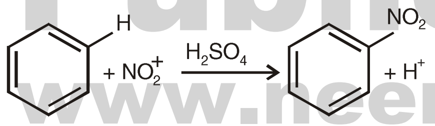
$$R - X \rightarrow R^- + X^+$$

$$Y^+ + R^- \rightarrow Y - R$$

or $$Y^+ + R - X \rightarrow y - R + X^+$$

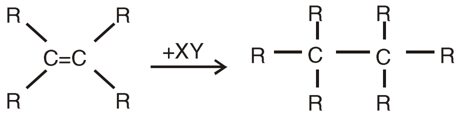
The reagent Y is an electrophile which has a high electron density.

$$HNO_3 + H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + NO_2^+$$



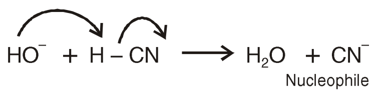
Addition Reactions

Reactions which involve combination between two reacting molecules to give a single molecule of the product are called addition reactions. Such reactions are typical of compounds containing multiple either double or triple bonds. These reactions mostly takes place in alkenes and alkynes.

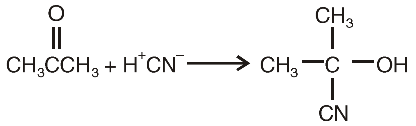


Depending upon the nature of the reagent, that is electrophile, nucleophile or free radical addition reactions are of different types.

For example,

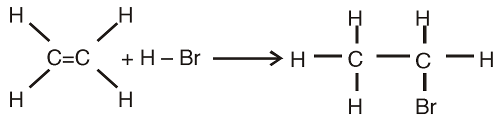


$$HO^- + H - CN \longrightarrow H_2O + \underset{\text{Nucleophile}}{CN^-}$$

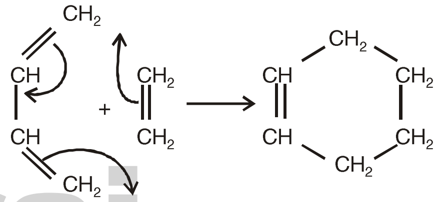


$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + H^+CN^- \longrightarrow CH_3 - \overset{CH_3}{\underset{CN}{C}} - OH$$

Nucleophilic addition reactions takes place in double bond molecules with hetro atoms.

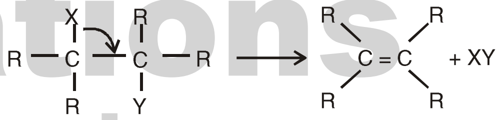


Electrophilic addition reactions and free radical reactions takes place in alkenes and alkynes, when bond breaking and addition to the double bond takes place simultaneously, this type of addition reaction is known as pericyclic addition, e.g.

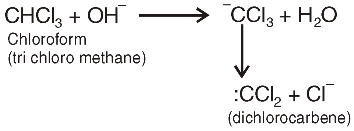


Elimination Reactions

An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple either double or triple bond.



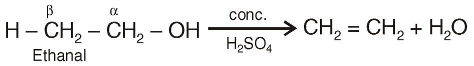
When in the reaction, the loss of two atoms or groups occurs from the same atom of the substrate molecule, it is called (1, 1) or α-elimination.



$$\underset{\substack{\text{Chloroform}\\\text{(tri chloro methane)}}}{CHCl_3} + OH^- \longrightarrow {}^-CCl_3 + H_2O \longrightarrow \underset{\text{(dichlorocarbene)}}{:CCl_2 + Cl^-}$$

Dichlorocarbene is the reactive and an ustable intermediate.

When in the reaction the loss of two atoms or groups occurs from the adjacent atoms of the substrate molecule, it is called (1, 2) or β-elimination.



$$H - \underset{\text{Ethanal}}{\overset{\beta}{CH_2}} - \overset{\alpha}{CH_2} - OH \xrightarrow[H_2SO_4]{\text{conc.}} CH_2 = CH_2 + H_2O$$

e.g.,