M.Sc. Final Year

Chemistry, Paper I

ORGANO-TRANSITIONAL METAL CHEMISTRY

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल
MADHYA PRADESH BHOJ (OPEN) UNIVERSITY – BHOPAL

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COURSE WRITERS

Dr. K.S. Tiwari, Former H.O.D. of Chemistry, Christ Church College, Kanpur
N.K. Vishnoi, Retired Professor, N.I.I.T. University, Neemrana, Rajasthan
Units (1.0-1.1, 1.2, 1.2.2, 1.3-1.7, 2.3-2.8, 3.0-3.2.5, 3.4-3.8, 4.3.3)

Dr. Brajendra Singh Chauhan, Professor and Dean, Greater Noida Institute of Technology (G.N.I.T.), Greater Noida (U.P.)
Units (1.2.1, 1.2.3, 2.0-2.2, 3.2.6, 4.0-4.1, 4.2, 4.3, 4.3.1, 4.3.2, 4.3.4, 4.3.5, 4.4-4.8, 5)

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Regd. Office: A-27, 2nd Floor, Mohan Co-operative Industrial Estate, New Delhi 1100 44
• Website: www.vikaspublishing.com • Email: helpline@vikaspublishing.com

SYLLABI-BOOK MAPPING TABLE

Organo-Transitional Metal Chemistry

Syllabi	Mapping in Book
Unit I **Alkyls and Aryls of Transition Metals:** Types, routes of synthesis, stability and decomposition pathways, organocopper in organic synthesis.	**Unit-1:** Alkyls and Aryls of Transition Metals **(Pages 3-20)**
Unit II **Compounds of Transition Metal-Carbon Multiple Bonds:** Alkylidenes, alkylidynes, low valent carbenes and carbynes - synthesis, nature of bond, structural characteristics, nucleophilic and electrophilic reactions on the ligands, role in organic synthesis.	**Unit-2:** Compounds of Transition Metal-Carbon Multiple Bonds **(Pages 21-32)**
Unit III **Transition Metal π-Complexes:** Transition metal π-complexes with unsaturated organic molecules, alkenes, alkynes, allyl, diene, dienyl, arene and trienyl complexes, preparations, properties, nature of bonding and structural features. Important reactions relating to nucleophilic and electrophilic attach on ligands and to organic synthesis.	**Unit-3:** Transition of Metal π-Complexes **(Pages 33-132)**
Unit IV **Transition Metal Compounds with Bonds to Hydrogen:** Transition metal compounds with bonds to hydrogen. **Homogeneous Catalysis:** Stoichiometric reactions for catalysis, homogeneous catalytic hydrogenation, Zeigler-Natta polymerization of olefins, catalytic reactions involving carbon monoxide such as hydrocarbonylation of olefins (oxo reaction), oxopalladation reaction, activation of C-H bond.	**Unit-4:** Transition Metal Compounds with Bonds to Hydrogen **(Pages 133-143)**
Unit V **Fluxional Organometallic Compounds:** Fluxionality and dynamic equilibria	**Unit-5:** Fluxional Organometallic Compounds **(Pages 145-157)**

CONTENTS

INTRODUCTION

NOTES

Organometallic compounds are chemical compounds that contain at least one bond between a metallic element and an organic molecule's carbon atom. Even metalloid elements like silicon, tin, and boron can produce organometallic compounds that are employed in industrial chemical reactions. The quantity of carbon atoms actually bound to the metal and to each other is the main criterion for classifying the compounds. Transition metal organometallic chemistry can be classified based on the type of organic ligands attached to the central metal atom (s).

The book, *Organo-Transitional Metal Compounds*, comprises five units. It discusses various concepts including alkyls, aryls, acetylides, and fluorocarbon complexes, along with olefin, allene, allyl, dienyl and trineyl complexes. It explains the electrophilic and nucleophilic reactions on the ligands and their role in organic synthesis.

This book has been written in the Self-Instructional Mode (SIM) wherein each unit begins with an Introduction to the topic followed by an outline of the Objectives. The detailed content is then presented in a simple and an organized manner, interspersed with Check Your Progress questions to test the understanding of the students. A Summary along with a list of Key Terms and a set of Self-Assessment Questions and Exercises is also provided at the end of each unit for effective recapitulation.

UNIT 1 ALKYLS AND ARYLS OF TRANSITION METALS

NOTES

Structure

1.0 INTRODUCTION

According to the IUPAC definition, 'an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete d sub-shell.' The metals include metals exist in the f-block lanthanide and actinide series and are also known as inner transition metals. In alkyl and aryl derivatives of transition metal complexes, metal atom and alkyl or aryl radical share one electron each to give -electron-2-center Mnormal 2-C σ bonded organometallics. Alkyl or aryl radicals are monohapto (η1) ligands one electron donor(s). Organo-transition metal alkyls and aryls are classified on several bases. This unit will discuss types of alkyls and aryls. In addition, it will explain different routes to synthesis them. Also, it will describe the stability and decomposition pathway and role of organocopper in organic synthesis.

1.1 OBJECTIVES

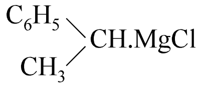
After going through this unit, you will be able to:

- Explain types of alkyls and aryls of transition metals
- Discuss the different routes of synthesis of alkyls and aryls of transition metals
- Analyse the stability and decomposition pathways
- Describe the use of organocopper in organic synthesis

1.2 ALKYLS AND ARYLS

Organometallic compounds may be defined as substances having carbon to metal bonds. A large number of metals , for example, lithium, magnesium, aluminium, lead, tin, zinc, cadmium, mercury, etc., form fairly stable organic compounds. The organic residue is usually an alkyl, alkenyl, alkynyl or aryl group. A few organometallic compounds of different metals are given in Table 1.1:

Table 1.1 *Organometallic Compounds*

Group I **Alkali Metals**	**Group II** **Alkaline Earth Metals**	**Group III**	**Group IV**
CH_3Li Methyl-lithium	C_2H_5MgBr Ethylmagnesium bromide	$(CH_3)_3Al$ Trimethylaluminium	$(C_2H_5)_4Pb$ Tetraethyl lead
$CH_2C{=}CH.Na$ Vinylsodium	 $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>CH.MgCl$ 1-Phenylethylmagnesium chloride		$(CH_3)_2SnCl_2$ Dimethyltin chloride
	$CH_3C{\equiv}CMgX$ Propynylmagnesium halide		
	$C_2H_5OCH_2.MgCl$ Ethoxymethylmagnesium chloride		

Transition Metals			
$(C_2H_5)_2Zn$ Diethylzinc	$(CH_3)_2Cd$ Dimethylcadmium	C_6H_5HgCl Phenylmercury chloride	$(C_2H_5)_2Hg$ Diethylmercury

Metalloids like boron, silicon, germanium and arsenic too form organic compounds which are also regarded as organometallic compounds. Metal-alkyls are metal compounds with alkyl radicals, and on the other hand, metal compounds attached with aryl radicals are termed as metal-aryls.

Organometallic compounds may be substantially ionic as alkylsodium and potassium compounds or essentially covalent as alkylmercury compounds. In general, the more electropositive is the metal, the more ionic is the carbon to metal bond. Compounds like sodium acetate and calcium formate, where the metal is linked to oxygen are largely ionic because of the greater difference in the electronegativity of oxygen and the metal. Such compounds are, therefore, not considered as true organometallic compounds.

The reactivity of organometallic compounds increases with the increase in ionic character of carbon to metal bond. Of special interest are the compounds of intermediate ionic character because of their reactivity and the selective nature of their reactions. By and large, organometallic compounds are obtained directly or indirectly form alkyl halides. They are put to use varying over a wide range. Thus tin, lead, aluminium, boron compounds are of technical importance as fungicide, antiknock compounds, catalysts, whereas compounds of arsenic, antimony, bismuth, mercury, silver are used as war gases, medicinals and pesticides. However, the most important organometallic compounds are those of magnesium, zinc and lithium, which are extensively used in the synthesis of a large number of organic compounds.

1.2.1 Types of Transitions

Organic molecules exhibit $\sigma \rightarrow \sigma*$, $n \rightarrow \sigma*$, $\pi \rightarrow \pi*$, and $n \rightarrow \pi*$ electronic transitions, where σ, π, n and $\pi*$ are σ–bonding, π–bonding, non-bonding, $\sigma*$ antibonding and $\pi*$ antibonding electrons, respectively. On the other hand, transition metal complexes exhibit following four types of transitions.

(i) ***d-d* transitions :** These transition occur between t_{2g} and e_g orbitals of the central metal atom ion of the complexes. These are also known as ligand field spectra. The bands are observed in UV, visible and near IR regions, i.e., from 333 to 1000 nm, E_{max} being in the range 1 to 50. The peaks are of low intensity, the spliting of *d*-orbitals are shown in the Figure 1.1.

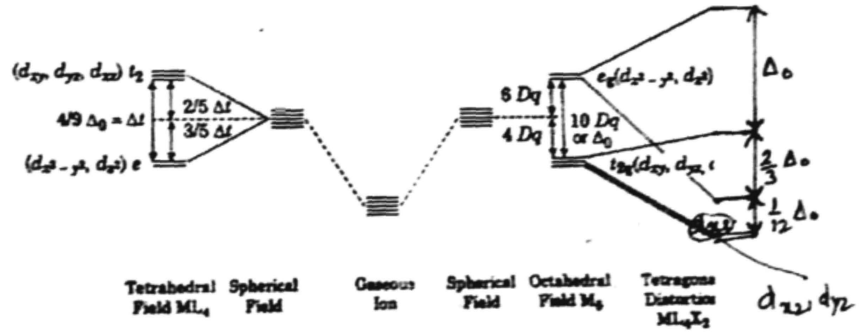


Fig. 1.1 *Splitting of d-Orbitals in Various Fields*

(ii) **Metal to Ligand Charge Transfer Transitions :** These transitions occur when electrons of central metal atom ion present in non-bonding or antibonding orbitals shifts to antibonding orbitals of the ligands. Thus it measures the tendency of the metal ion to reduce the ligand. Generally, these bands occur in the UV region for the metal ions in low oxidation states. These bands have much more intensity ($\varepsilon_{max} \sim$ 1000–10000) as compared to *d-d-* transitions ($\varepsilon_{max} \sim$ 1–50).

(iii) **Ligand to Metal Charge Transfer Transitions :** These transitions occur when the electrons transition takes place from a molecular orbital located primarily on the ligand to a non-bonding or antibonding molecular orbital situated on the metal atom. These transitions show the tendency of the ligands to reduce the metal ion. These transitions also occur in UV region. The position of these bands [occur in (ii) and (iii) transitions] depends on the nature of metal and the ligand.

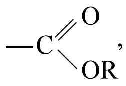
(iv) **Inter-Ligand Transitions :** These transitions occur when an electron transition takes place from one ligand orbitals to another ligand orbitals. These bands occur in UV region and corresponds to $\sigma \rightarrow \sigma*$, and $x \rightarrow x*$ transitions, thus, can be readily separated from M-L charge transfer bands. These bands depend upon the M-L bond strength as well as by coordination.

1.2.2 Routes of Synthesis

In 1899, Barbier used a mixture of alkyl halide and magnesium in ether to prepare a large number of organic compounds. Later in 1900, Grignard, a student of Barbier, prepared alkylmagnesium halide solution and studied its reactions with a variety of compounds. Alkylmagnesium halides are therefore commonly known as *Grignard reagents* after the name of the discoverer. Their general formula is R—Mg—X where R is a univalent hydrocarbon radical, *f*or example, $—CH_3$; $—C_2H_5$; $—CH_2—CH{=}CH_2$; $—C_6H_5$; $C_6H_5CH_2—$ and —X is a halogen. The reaction can be applied to primary, secondary and tertiary alkyl halides. Allylic Grignard reagent can be prepared in the usual manner or in Telra Hydro Furan. However, alkynyl Grignard reagent are prepared by abstraction of a proton from alkyne by alkylmagnesium halide ($RC{\equiv}CH + C_2H_5MgX \longrightarrow RC{\equiv}C.MgX + C_2H_6$).

Alkylmagnesium fluoride can be prepared by refluxing alkyl fluorides with magnesium in presence of suitable catalyst. Grignard reagent from α-halo ethers can be formed only when Telra Hydro Furan or dimethoxymethane is used as solvent at low temperature.

$$C_2H_5OCH_2Cl + Mg \xrightarrow[-35^\circ]{(MeO)_2CH_2 \text{ or THF}} C_2H_5OCH_2MgCl$$

There is some difficulty in preparing aryl and viny lmagnesium halides because of the low reactivity of aryl or vinyl halides. However, this difficulty was overcome by Normant (1953–1957) using Tetra Hydro Furan (THF) in place of ether during preparation of the reagent. The grignard reagent cannot be prepared from alkyl halides containing groups with which it is known to react. Thus only very few groups , for example, R, OR, X may be present in alkyl halide from which Grignard reagent is to be prepared. They cannot be prepared from alkyl halides having groups like — COOH, —OH,—NH_2, $>C{=}O$,$—C{\equiv}N$,  $-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{OR}}$, —$NO_2$,—$SO_3H$ and the like.

Preparation

The Grignard reagent is prepared by the action of magnesium metal on alkyl halide in the presences of alcohol free and dry ether.

$$\underset{\text{Akyl halide}}{R.X} + \underset{\text{Magnesium}}{Mg} \xrightarrow{\text{Ether}} \underset{\text{Grignard reagent}}{R.Mg.X}$$

$$C_2H_5Br + Mg \xrightarrow{\text{Ether}} \underset{\text{Ethylmagnesium bromide}}{C_2H_5MgBr}$$

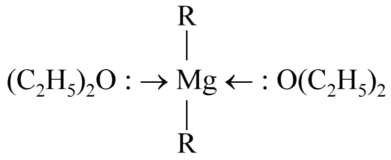
Diethylether is the most common solvent though other ethers like butyl ether, dimethyl- ether of glycol (diglyme) or Tetra Hydro Furan (THF) may also be used. The order of reactivity of various alkyl halides with magnesium is iodides > bromides > chlorides for a given alkyl group, but the yields are in the reverse order. As the number of carbon atoms increases the formation of Grignard reagents becomes more and more difficult and for a given halogen the order or reactivity of alkyl groups is $CH_3 > C_2H_5 > C_3H_7$, etc. It is important that all the reactants must be absolutely dry and pure because the presence of moisture and impurities retards the reaction and results in the formation of other undesirable products.

Let us study the purification of the various reactants

- **Magnesium:** Magnesium turnings or ribbon is rubbed with sand paper and treated with dilute acid to remove the surface film of magnesium oxide. It is then washed with ether and dried immediately before use.
- **Ether:** Diethylether is washed with water to remove any alcohol and then dried over anhydrous calcium chloride for 2–3 days to remove traces of alcohol and moisture. It is then distilled over sodium or phosphorus pentoxide to remove final traces of alcohol and water.
- **Alkyl Halide*:*** Alkyl halide is dried over anhydrous calcium chloride and then distilled over phosphorus pentoxide.

Dry and clean magnesium turnings are suspended in dry and pure ether, in a round bottom flask, fitted with a water condenser carrying a calcium chloride guard tube at the top. Weight of ether taken is about 10 times that of magnesium. Alkyl halide (1 gm mole for every 1 gm atom of Mg.) dissolved in ether is slowly poured through the condenser after removing the guard tube. The flask is then warmed and few crystals of iodine or few drops of ethylene bromide are added to catalyze the reaction. Once the reaction starts, it often becomes brisk and it is sometimes necessary to cool the flask to control the reaction. After the addition of alkyl halide is complete, the flask is heated on water bath till all magnesium dissolves. This solution is used as such for most of the reactions and Grignard reagent is never isolated in solid state for synthetic purposes. The reaction occurs by a free radical mechanism. Alkyl halide is absorbed on the magnesium surface which then transfers an electron to halogen and insertion of magnesium between alkyl groups and halogen gives alkylmagnesium halides.

Structure of Grignard reagents, function of ether and nature of grignard reactions. The structure of Grignard reagent is not understood with certainty. Grignard suggested that the alkylmagnesium halide contains ether of crystallization and can be represented as:



$$(C_2H_5)_2O : \rightarrow \overset{\displaystyle R}{\overset{|}{\underset{\underset{\displaystyle R}{|}}{Mg}}} \leftarrow : O(C_2H_5)_2$$

The electronic configuration of magnesium is $1s^2, 2s^2, 2p^6, 3s^2$. By promoting one of the $3s$ electron to $3p$ orbital and then by the hybridization of these $3s$ and $3p$ orbitals, magnesium atom in organomagnesium compounds exists in sp hybridized state. Overlapping of these orbitals with those of carbon and halogen forms sigma bonds. There are two empty remaining $3p$ orbitals of magnesium due to which it behaves as a Lewis acid and coordinates with two ether molecules. Jolibois in 1912 observed that magnesium is present both in the form of anions and cations and suggested the formula $R_2Mg_2X_2$ for Grignard reagent.

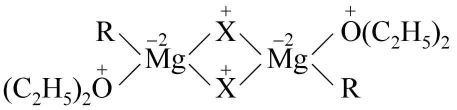
$$R_2Mg_2X_2 \rightleftharpoons R.Mg^+ + R.MgX_2^-$$

Ubbelohde in 1955 suggested that Grignard reagent exists in dimeric form solvated in ether, and following equilibria exists in solution.

$$R_2Mg.MgX_2 \rightleftharpoons R_2.Mg + MgX_2 \rightleftharpoons 2RMgX$$

NOTES

Various physical measurements, NMR studies, etc., favour this dimeric formula for the reagent. However, in solution it exits as a complex of various structures including solvated complexes, such as:



In this text, formula RMgX has been used to represent alkylmagnesium halides. It is thus evident that due to the polarity of alkylmagnesium bond, most of the reactions of Grignard reagent involve an unsymmetrical or heterolytic cleavage of carbon-magnesium bond to form a carbanion and cationic magnesium. Thus:

$$R{-}Mg{-}X \rightleftharpoons \bar{R}: + \overset{+}{M}gX$$

This carbanion possesses an unshared pair of electrons and acts as a nucleophile. Hence, most of the reactions of Grignard reagents are nucleophilic reactions.

Characteristics and uses of Grignard reagents

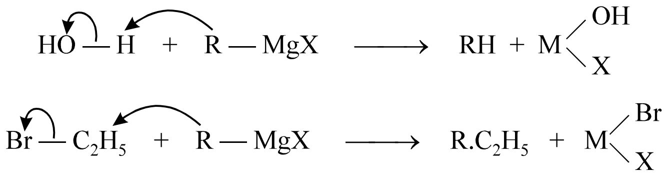
Grignard reagents are colourless, hygroscopic solids. They are fairly stable in air but are never obtained in solid state for chemical reactions in synthesis.

Grignard reagents are highly reactive and enter into reaction with wide variety of substrates yielding many types of organic compounds. Despite their high reactivity they are highly selective also. Thus they add to a carbon-oxygen double bond but do not react with carbon-carbon double bond. Usually the addition of Grignard reagents gives an intermediate addition complex which is hydrolysed by acids or ammonium chloride to give useful products. Alkylmagnesium bromides and iodides, in general react more readily than the corresponding chlorides. Some of the important reactions of Grignard reagents are given below.

(A) Nucleophilic Substitution Reactions

The carbon metal bond is highly polar. Although, the organic group is not a complete anion yet it has a considerable anionic character. Thus carbanion with an unshared pair of electrons acts as a nucleophile. Grignard reagent thus shows nucleophilic addition and nucleophilic substitution reaction.

We shall first take up nucleophilic substitution reaction in which general pattern of mechanism of nucleophilic substitution is as :

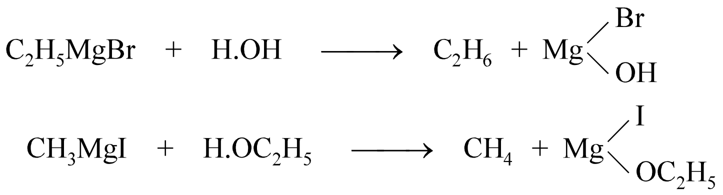


$$HO{-}H + R{-}MgX \longrightarrow RH + Mg\begin{matrix} OH \\ X \end{matrix}$$

$$Br{-}C_2H_5 + R{-}MgX \longrightarrow R.C_2H_5 + Mg\begin{matrix} Br \\ X \end{matrix}$$

1. Reaction with Active Hydrogen Compounds: Formation of hydrocarbons compounds, such as alcohols, water, ammonia, amines, etc., in which hydrogen is attached to highly electronegative atom and can be easily dissociated as a proton, are known as compounds containing active hydrogen. Grignard reagent reacts with such compound, to form hydrocarbons.

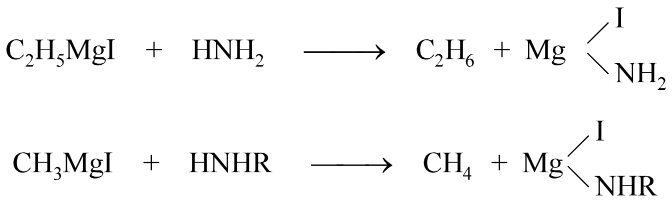
(i)



$$\mathrm{C_2H_5MgBr + H.OH \longrightarrow C_2H_6 + Mg}\Big\langle\begin{matrix}\mathrm{Br}\\ \mathrm{OH}\end{matrix}$$

$$\mathrm{CH_3MgI + H.OC_2H_5 \longrightarrow CH_4 + Mg}\Big\langle\begin{matrix}\mathrm{I}\\ \mathrm{OC_2H_5}\end{matrix}$$

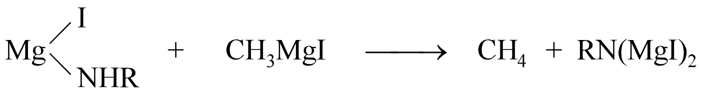
(ii) In case of ammonia and primary amines only one hydrogen atom of a primary amine reacts at room temperature.



$$\mathrm{C_2H_5MgI + HNH_2 \longrightarrow C_2H_6 + Mg}\Big\langle\begin{matrix}\mathrm{I}\\ \mathrm{NH_2}\end{matrix}$$

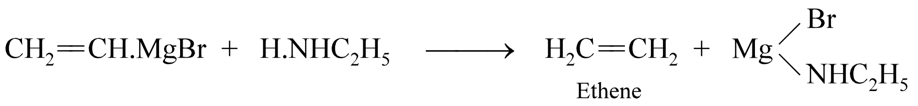
$$\mathrm{CH_3MgI + HNHR \longrightarrow CH_4 + Mg}\Big\langle\begin{matrix}\mathrm{I}\\ \mathrm{NHR}\end{matrix}$$

However, at higher temperature the magnesium derivative of primary amine reacts with another molecule of Grignard reagent.



$$\mathrm{Mg}\Big\langle\begin{matrix}\mathrm{I}\\ \mathrm{NHR}\end{matrix} \mathrm{+ CH_3MgI \longrightarrow CH_4 + RN(MgI)_2}$$

Amines reacting with vinylmagnesium bromide form unsaturated hydrocarbon.



$$\mathrm{CH_2{=}CH.MgBr + H.NHC_2H_5 \longrightarrow \underset{Ethene}{H_2C{=}CH_2} + Mg}\Big\langle\begin{matrix}\mathrm{Br}\\ \mathrm{NHC_2H_5}\end{matrix}$$

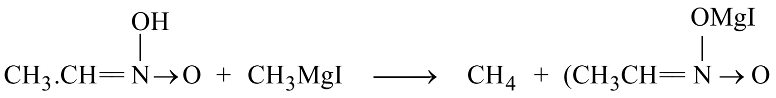
(iii) Both hydrogen atom in acetylene are acidic and therefore when acetylene is passed in ether solution of Grignard reagent both are replaced.

$$\mathrm{HC{\equiv}CH + C_2H_5MgI \longrightarrow HC{\equiv}C.MgI + C_2H_6}$$

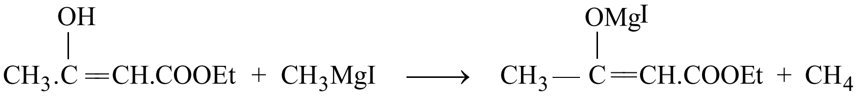
$$\mathrm{HC{\equiv}CMgI + C_2H_5MgI \longrightarrow \underset{Ethynyl\ bis\ (Magnesium\ iodide)}{IMgC{\equiv}C.MgI} + C_2H_6}$$

Jones *et al.*, in 1956 found that second step can be avoided if THF saturated with acetylene is allowed to react with Grignard reagent.

(iv) The enolic form of compounds like nitroethane and acetoacetic ester contain active hydrogen hence reacts with Grignard reagent. The rate of alkane evolved depends upon the rate of conversion to enolic form.



$$\mathrm{CH_3.CH{=}\overset{\overset{\displaystyle OH}{|}}{N}{\rightarrow}O + CH_3MgI \longrightarrow CH_4 + (CH_3CH{=}\overset{\overset{\displaystyle OMgI}{|}}{N}\rightarrow O}$$



$$\mathrm{CH_3.\overset{\overset{\displaystyle OH}{|}}{C}{=}CH.COOEt + CH_3MgI \longrightarrow CH_3{-}\overset{\overset{\displaystyle OMgI}{|}}{C}{=}CH.COOEt + CH_4}$$

When methylmagnesium halide is used, for every active gm atom of hydrogen one mole of methane gas is evolved quantitatively. This reaction is, therefore, used for estimating the groups containing active hydrogens, such as OH, NH_2 and SH in organic compounds and the method is known as *Zerevitinov's* method.

2. Reaction with Alkyl Halides. (**Formation of Alkanes**): Alkyl halides react with Grignard reagents to form alkanes.

$$C_2H_5MgBr + \underset{\text{Ethyl bromide}}{Br.C_2H_5} \longrightarrow \underset{n\text{-Butane}}{C_2H_5.C_2H_5} + MgBr_2$$

3. Reaction with Alkenyl Halides (**Formation of Alkenes):** Alkenyl halides react with Grignard reagent by double decomposition to form alkenes.

$$C_2H_5MgBr + \underset{\text{Allyl bromide}}{Br.CH_2.CH{=}CH_2} \longrightarrow \underset{\text{Pentene-1}}{CH_3.CH_2.CH_2.CH{=}CH_2} + MgBr_2$$

4. **Reaction with Alkynyl Halides** (**Formation of Alkynes**)*:* Alkynyl halides react with Grignard reagent to form alkynes.

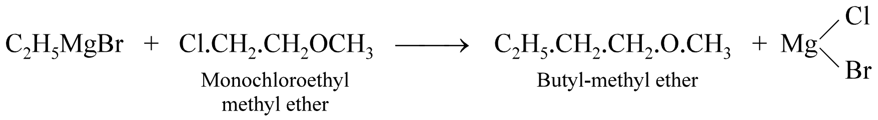
$$CH_3MgBr + Br.CH_2.C{\equiv}CH \longrightarrow \underset{\text{Butyne-1}}{CH_3.CH_2C{\equiv}CH} + MgBr_2$$

Alternatively alkynyl, magnesium halide may be reacted with an alkyl halide to yield alkynes.

$$CH_3.C{\equiv}CH + CH_3MgI \longrightarrow CH_4 + CH_3.C{\equiv}C.MgI$$

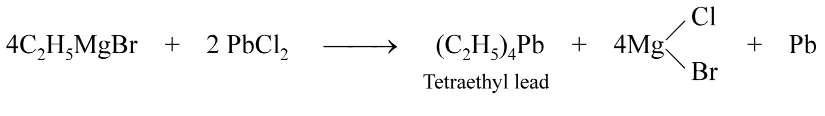
$$\underset{\text{Propynylmagnesium iodide}}{CH_3.C{\equiv}C.MgI} + CH_3I \longrightarrow \underset{\text{Butyne-2}}{CH_3.C{\equiv}C.CH_3} + MgI_2$$

5. Reaction with Monohaloethers (**Formation of Higher Ethers**): Halogen of monochloroethers reacts with Grignard reagents by double decomposition to give higher ethers.

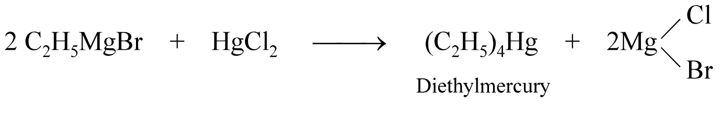


$$C_2H_5MgBr + \underset{\substack{\text{Monochloroethyl}\\ \text{methyl ether}}}{Cl.CH_2.CH_2OCH_3} \longrightarrow \underset{\text{Butyl-methyl ether}}{C_2H_5.CH_2.CH_2.O.CH_3} + Mg\begin{array}{l}\diagup Cl\\ \diagdown Br\end{array}$$

6. Reaction with Inorganic Halides (Formation of Organometallic compounds): Reaction of Grignard reagents with inorganic halides yields different organometallic compounds.

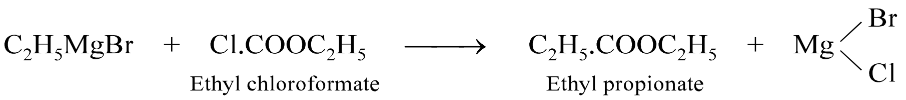


$$4C_2H_5MgBr + 2\,PbCl_2 \longrightarrow \underset{\text{Tetraethyl lead}}{(C_2H_5)_4Pb} + 4Mg\begin{array}{l}\diagup Cl\\ \diagdown Br\end{array} + Pb$$



$$2\,C_2H_5MgBr + HgCl_2 \longrightarrow \underset{\text{Diethylmercury}}{(C_2H_5)_4Hg} + 2Mg\begin{array}{l}\diagup Cl\\ \diagdown Br\end{array}$$

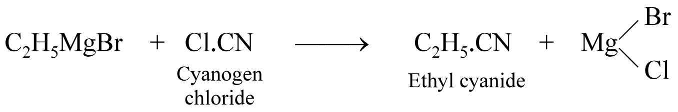
7. Reaction with Chloroformic Esters (**Formation of Esters**): When Grignard reagent is reacted with equimolar amount of chloroformic ester, higher esters are formed.



$$C_2H_5MgBr + \underset{\text{Ethyl chloroformate}}{Cl.COOC_2H_5} \longrightarrow \underset{\text{Ethyl propionate}}{C_2H_5.COOC_2H_5} + Mg\begin{matrix}Br\\Cl\end{matrix}$$

If the Grignard reagent is in excess the ester formed will react with Grignard reagent (nucleophilic addition) to produce ketone and tertiary alcohol.

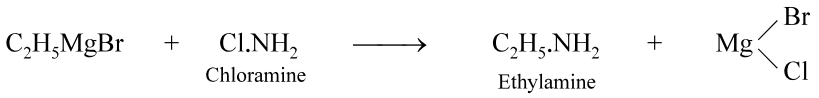
8. Reaction with Cyanogen Chloride (**Formation of cyanides**): Reactive chlorine of cyanogen chloride reacts with the Grignard reagent to yield alkyl cyanides.



$$C_2H_5MgBr + \underset{\text{Cyanogen chloride}}{Cl.CN} \longrightarrow \underset{\text{Ethyl cyanide}}{C_2H_5.CN} + Mg\begin{matrix}Br\\Cl\end{matrix}$$

If Grignard reagent is present in excess, it will react with cyanide (Nucleophilic Addition) to form ketones and tertiary alcohols.

9. Reaction with Chloramine (Formation of Primary Amines). Replacement of reactive chlorine by the carbanion derived from Grignard reagent gives primary amines.

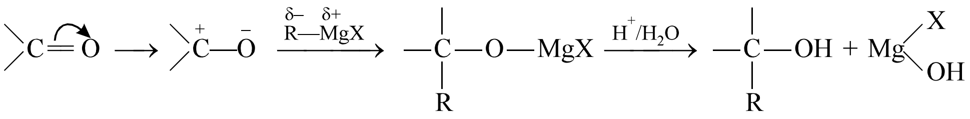


$$C_2H_5MgBr + \underset{\text{Chloramine}}{Cl.NH_2} \longrightarrow \underset{\text{Ethylamine}}{C_2H_5.NH_2} + Mg\begin{matrix}Br\\Cl\end{matrix}$$

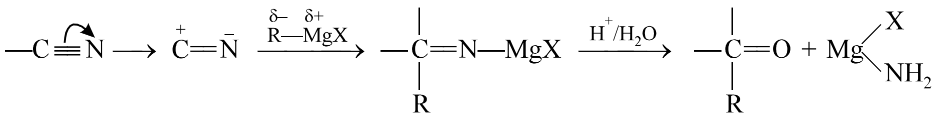
(B) Nucleophilic Addition Reactions

The Grignard reagent reacts with compounds having carbon-oxygen, carbon-sulphur and carbon-nitrogen multiple bonds to give addition products which on hydrolysis give a wide variety of compounds. All such reactions are nucleophilic addition of carbanion (nucleophile) $\bar{R}$, obtained from the heterolysis of Grignard reagent, resulting in the formation of new carbon-carbon bonds.

The general mechanism of nucleophilic addition is as follows:



$$>C{=}O \longrightarrow >\overset{+}{C}-\overset{-}{O} \xrightarrow{\overset{\delta-}{R}-\overset{\delta+}{MgX}} -\underset{R}{\overset{|}{\underset{|}{C}}}-O-MgX \xrightarrow{\overset{+}{H}/H_2O} -\underset{R}{\overset{|}{\underset{|}{C}}}-OH + Mg\begin{matrix}X\\OH\end{matrix}$$

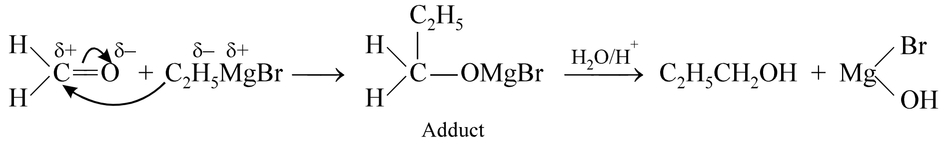


$$-C{\equiv}N \longrightarrow \overset{+}{C}{=}\overset{-}{N} \xrightarrow{\overset{\delta-}{R}-\overset{\delta+}{MgX}} -\underset{R}{\overset{|}{\underset{|}{C}}}{=}N-MgX \xrightarrow{\overset{+}{H}/H_2O} -\underset{R}{\overset{|}{\underset{|}{C}}}{=}O + Mg\begin{matrix}X\\NH_2\end{matrix}$$

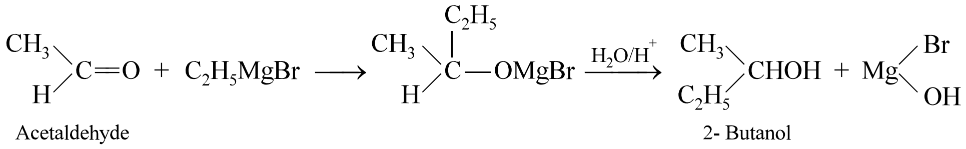
1. Addition to Aldehydes and Ketones

Some of the addition reactions are discussed here.

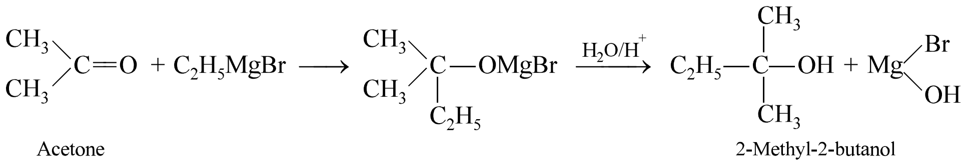
(i) **Addition to Formaldehyde (Formation of Primary Alcohols)**: Grignard reagent adds on to the carbonyl group of formaldehyde to yield an adduct which on hydrolysis with dilute hydrochloric acid forms primary alcohol. The primary alcohol derives its alkyl group from the Grignard reagent.



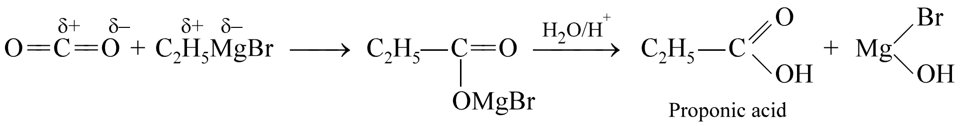
(ii) **Addition to Acetaldehyde (Formation of Secondary Alcohol)**: Addition to aldehydes, other than formaldehyde, gives secondary alcohol in which the alkyl groups come, one each from aldehyde and Grignard reagent.



(iii) **Addition of Ketones (Formation of Tertiary Alcohols)**: Ketones when reacted with Grignard reagent in a similar manner form tertiary alcohols.



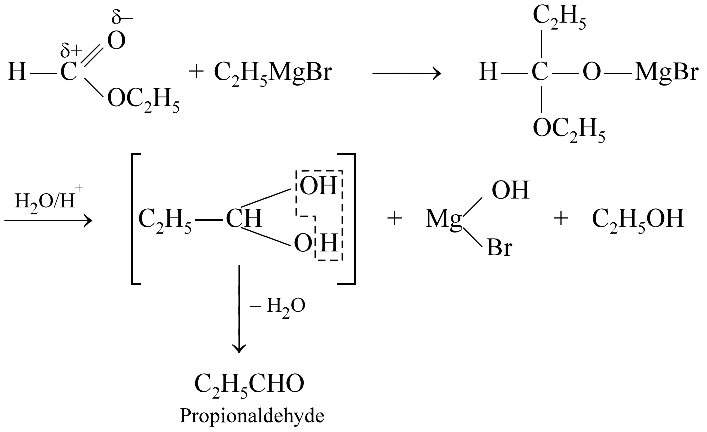
2. Addition to Carbon Dioxide (**Formation of Carboxylic Acid**). Grignard reagent adds on to carbon dioxide (preferably as solid ice) in equimolar amounts and the product formed yields carboxylic acid on hydrolysis.

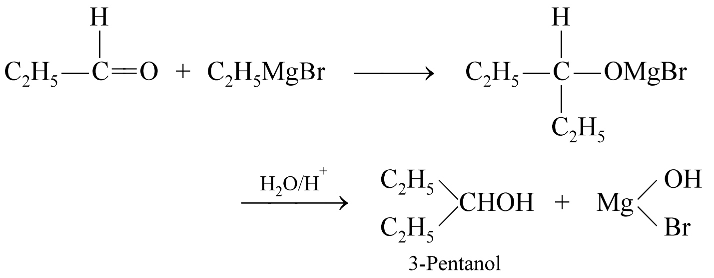


3. Addition to Esters

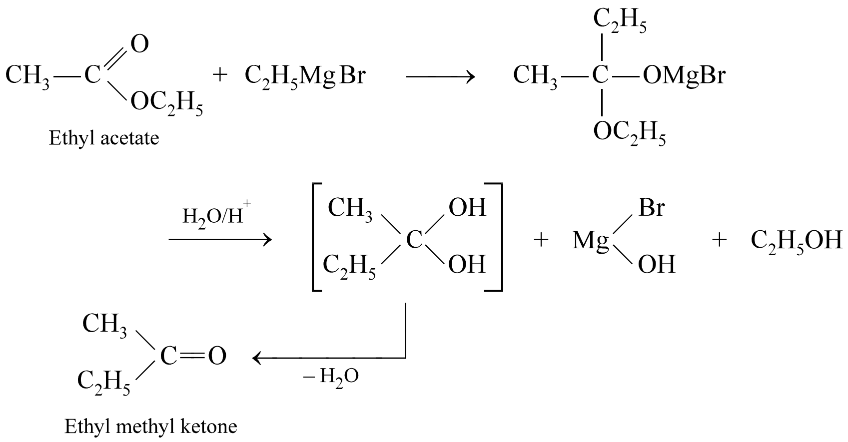
Some of the addition to esters are discussed here.

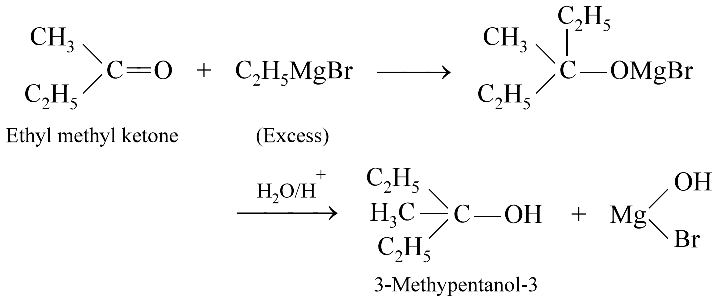
(i) **Addition to Formic Ester (Formation of Aldehydes)**: Reaction of Grignard reagent with equimolar amount of formic ester, first gives aldehyde which then react with further quantity of Grignard reagent to yield secondary-alcohol.



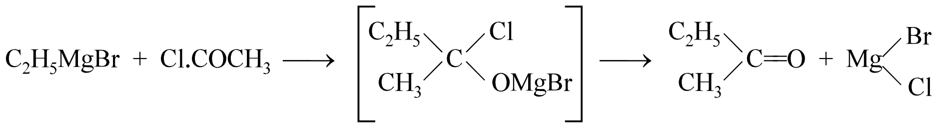


(ii) **Addition to Esters other than Formic Ester (Formation of Ketones)**: Equimolar amounts of ester and Grignard reagent react to form a ketone.



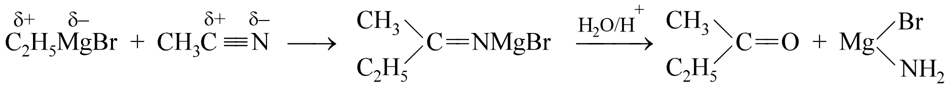


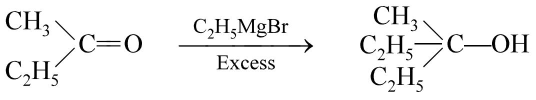
4. Reaction with Acid Halides (Formation of Ketones): The reaction of acid halides (one mole) with Grignard reagent (one mole) yields ketones. As the ketones also react with Grignard reagent it is essential that reaction be carried out under carefully controlled conditions.



If, however, acetyl chloride reacts with two moles of the Grignard reagent the product is a tertiary alcohol. Ketone formed reacts with Grignard reagent to produce tertiary alcohol.

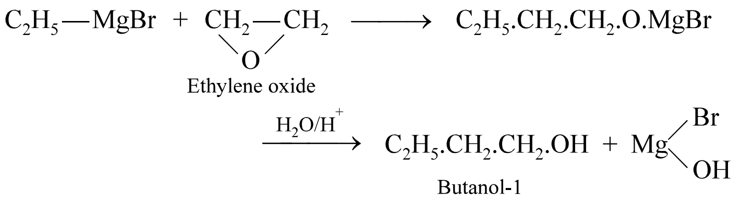
5. Addition of Cyanides (Formation of Ketones): Equimolar amounts of alkyl cyanides react with Grignard reagent to form ketones. If Grignard reagent is in excess tertiary alcohols are obtained as final product of the reaction.





3-Methyl 3-pentanol

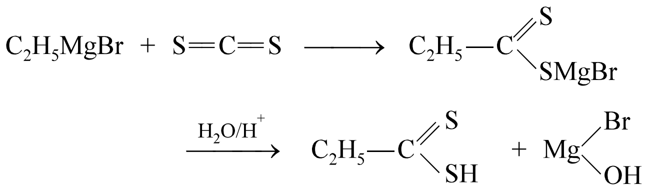
6. Addition to Ethylene Oxide (or Similar Ring Compounds). **(Formation of Primary Alcohols)**: Small ring compounds such as ethylene oxide undergo cleavage at carbon-oxygen bond when treated with Grignard reagent to form primary alcohol with higher number of carbon atoms.



Butanol-1

7. Addition to Carbon Disulphide (Formation of Dithioic Acids):

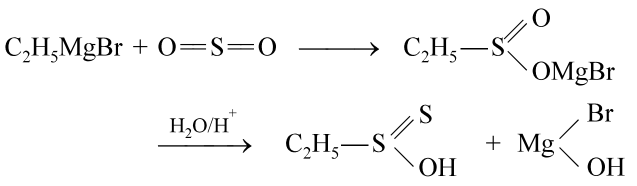
Carbon disulphide reacts with the Grignard reagent to form dithiopropionic acid.



Dithiopropionic acid

8. Addition to Sulphur Dioxide (Formation of Sulphinic Acids):

Sulphur dioxide reacts with the Grignard reagent to form ethane-sulphinc acid.



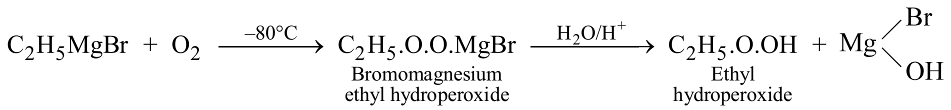
Ethane-sulphinic acid

9. **Addition to Carbon-Carbon Double Bonds**. Grignard reagents do not react with simple alkenes because a carbon-carbon double bond is less susceptible to nucleophilic attack of $\bar{R}$ derived from R.Mg.X. However, in the presence of titanium tetrachloride, alkenes having a terminal double bond react with Grignard reagent to give an olefin exchange reaction.

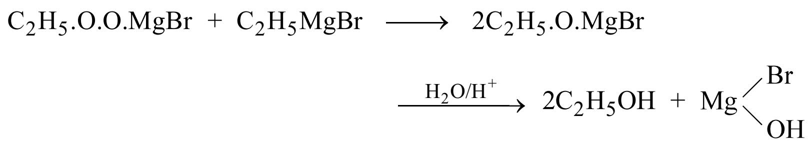
$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Ethylmagnesium bromide}}{C_2H_5MgBr} \xrightarrow{TiCl_4} \underset{\text{New Grignard reagent}}{R.CH_2.CH_2MgBr} + \underset{\text{Ethene}}{CH_2{=}CH_2}$$

(C) Miscellaneous Reactions

1. Reaction with Oxygen (Formation of Hydroperoxides or Alcohols): Grignard reagent reacts with oxygen at –80°C to give the halomagnesium salt of hydroperoxide which further reacts with excess of Grignard reagent at the room temperature to give halomagnesium salt of alcohol which on hydrolysis forms alcohol.



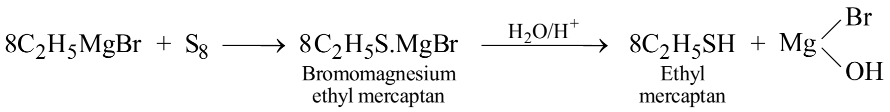
$$C_2H_5MgBr + O_2 \xrightarrow{-80°C} \underset{\text{Bromomagnesium ethyl hydroperoxide}}{C_2H_5.O.O.MgBr} \xrightarrow{H_2O/H^+} \underset{\text{Ethyl hydroperoxide}}{C_2H_5.O.OH} + \mathrm{Mg}\begin{array}{l}\diagup \mathrm{Br}\\ \diagdown \mathrm{OH}\end{array}$$



$$C_2H_5.O.O.MgBr + C_2H_5MgBr \longrightarrow 2C_2H_5.O.MgBr$$

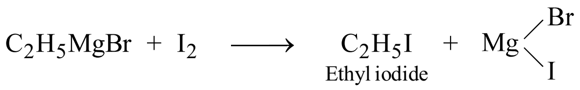
$$\xrightarrow{H_2O/H^+} 2C_2H_5OH + \mathrm{Mg}\begin{array}{l}\diagup \mathrm{Br}\\ \diagdown \mathrm{OH}\end{array}$$

2. Reaction with Sulphur (Formation of Thio Alcohols): Reaction of Grignard reagents with sulphur yields thio alcohols.



$$8C_2H_5MgBr + S_8 \longrightarrow \underset{\text{Bromomagnesium ethyl mercaptan}}{8C_2H_5S.MgBr} \xrightarrow{H_2O/H^+} \underset{\text{Ethyl mercaptan}}{8C_2H_5SH} + \mathrm{Mg}\begin{array}{l}\diagup \mathrm{Br}\\ \diagdown \mathrm{OH}\end{array}$$

3. Reaction with Halogens (Formation of Alkyl Halides): Action of halogens, particularly iodine, on the Grignard reagent give corresponding alkyl halide (Iodides).



$$C_2H_5MgBr + I_2 \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \mathrm{Mg}\begin{array}{l}\diagup \mathrm{Br}\\ \diagdown \mathrm{I}\end{array}$$

It has been observed that if more than one reactive group is present in the compound reacting with Grignard reagent, following order of preference is shown:

Group with active hydrogen > carbonyl group of aldehydes > carbonyl group of ketones > halogen of acid halides > carbonyl group of ester > halogen of an alkyl halide, etc.

Therefore, it is essential that all reactions with Grignard reagent must be carried out under carefully controlled conditions and using proper amounts of the reactants so as to avoid side reactions and formation of undesirable products.

Limitations of the Grignard Reagent

Some of the common limitations of the Grignard reagent are as follows:

1. The high reactivity of the reagent with practically every type of compounds, requires that the reaction mixture must be protected from moisture, air and carbon dioxide. This increases difficulty in handling Grignard reagents.
2. If the Grignard reagent is reacted with a polyfunctional compound mixture of a large number of undesirable products is always present in the final product. Similarly, if the end product has a functional group which can react with Grignard reagent, reaction has to be carried out with controlled amount of reactants but even then side reactions prevail.

However, despite these drawbacks, Grignard reagents are the most important tools used in organic synthesis.

1.2.3 Stability and Decomposition Pathway

There are two types of stability viz. the thermodynamic stability and the kinetic stability for a molecule. If the term "stability" is used without any modification, then it refers to the thermodynamic stability. When we are interested in stability from the thermodynamic point of view, then we must deal with metal-to-ligand bond energies, stability constants and the thermodynamic variables derivable from them. From a thermodynamic point of view, it is more appropriate to speak of complexes as being stable or unstable. If we are interested in stability from the kinetic point of view, then we must deal with the rates and mechanisms of reactions and also with the energies involved in the formation of the activated complex. In the kinetic point of view, it will be more proper to speak of complexes as bt\x\ginert or labile rather than stable or unstable. Very often these two groups of terms are used incorrectly. Stable complexes may be inert or labile and unstable complexes may be labile or inert. For example, CN~ ion forms a very stable complex with Ni^{2+}:

$$[Ni(H_2O)_6]^{2+} + 4\,CN^- \longrightarrow [Ni(CN)_4]^{2-} + 6H_2O$$

Ni^{2+} prefers CN^- rather than H_2O as a ligand. Thus $[Ni(CN)_4]^{2-}$ isthermodynamically more stable than $[Ni(H_2O)_6]^{2+}$. However, when ^{14}C-labelled CN^- ($^{14}CN^-$) is added to the solution, it is almost instantaneously incorporated into the complex:

$$[Ni(CN)_4]^{2-} + 4\ {}^{14}CN^- \longrightarrow [Ni({}^{14}CN)_4]^{2-} + 4CN^-$$

This means that the complex, $[Ni(CN)_4]^{2-}$ is kinetically labile. Thus the stability of this complex does not ensure inertness. $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable in acid solutions. But it can be kept in acid solution for several days at room temperature without noticeable decomposition. This means that this complex is kinetically inert. Thus instability of a complex does not ensure lability.

$[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ have roughly the same bond energy. This means that these two complexes are of equal stability from the thermodynamic point of view. But $[Fe(H_2O)_6]^{3+}$ is labile and exchanges its ligands with other ligands rapidly, whereas$[Cr(H_2O)_6]^{3+}$ is inert and hence exchanges its ligands very slowly. Many such examples may be given. Thus, these two types of stability are related to two different phenomena.

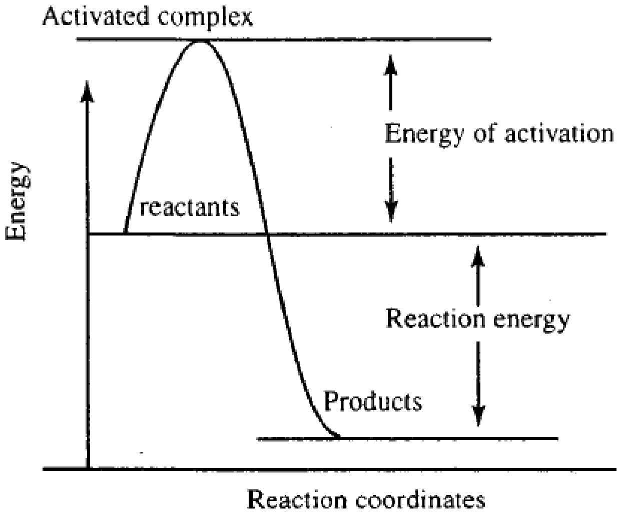
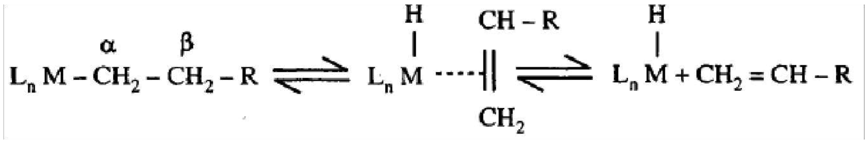


Fig. 1.2 *The relative energies of products, reactants and activated complex of a reaction*

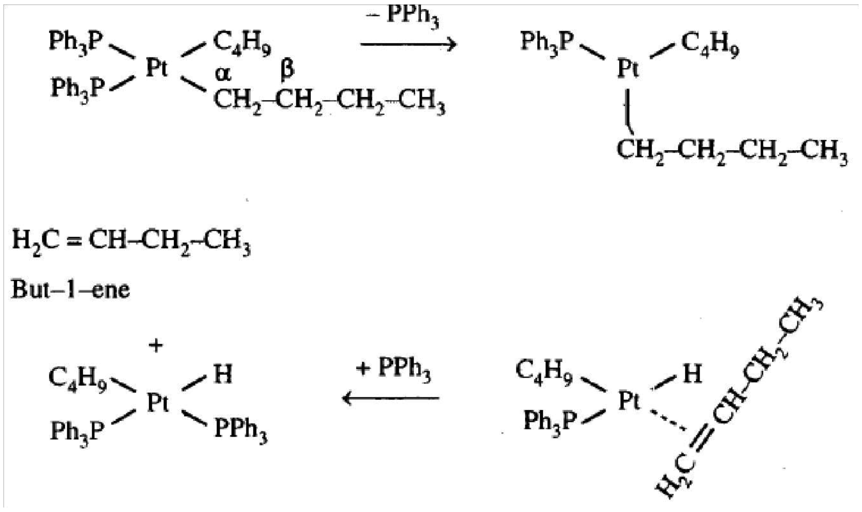
The thermodynamic stability of a complex depends on the difference in energy between the reactants and the products, namely the reaction energy Greater this reaction energy, greater will be the thermodynamic stability. But the kinetic stability of a complex depends on the difference in energy between the reactants and the activated complex, namely the activation energy. Greater this activation energy lesser will be the reaction rate, implying that the complex is inert.

Many transition metal alkyl derivatives are especially unstable with respect to thermal decomposition. The reason for this is not that metal-carbon α bonds are thermodynamically weak, but that one or more pathways for their decomposition are readily available. One such pathway is the so-called β-elimination which involves the elimination of olefin and the formation of the metal hydride. β-elimination is illustrated below:



$$L_n M-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-R \rightleftharpoons L_n\overset{\overset{H}{|}}{M}\cdots\overset{CH-R}{\underset{CH_2}{\|}} \rightleftharpoons L_n\overset{\overset{H}{|}}{M}+CH_2=CH-R$$

β -hydrogen elimination is generally an intramolecular β-hydrogen abstraction by the metal. The best studied example is, $[Pt(PPh_3)_2(n-C_4H_9)_2]$. The probable mechanism is,



This type of fragmentation process is facilitated by the following three conditions:

1. The metal should be capable of increasing its coordination number by one unit. That is, it should be capable of forming a coordinatively unsaturated complex.
2. A substituent attached to the ft atom should be readily transferred to the metal centre and
3. The β atom should be able to form multiple bond with the a-carbon atom.

Factors retarding the β-elimination process

Some of the common factors that inhibit the β-elimination process are as follows:

1. Metal alkyls having less bulky ligands will be coordinatively saturated. Hence they are expected to be more stable and do not undergo this fragmentation.

2. Fragmentation process may also be prevented by designing the alkyl in such a way that the transfer of a fragment group to the metal is no longer feasible. Since the transfer of groups other than hydrogen from the β carbon atom to the metal is very unlikely, alkyl groups having no β-hydrogens will retard this fragmentation process.
3. Multiple bonding between the a and β skeletal atoms may be prevented by the presence of a β -atom having no tendency to π-bond. For example, β -silicon atoms hardly ever participate in multiple bonds and when they have substituents methyl groups, no β -elimination occurs.

   Example, $Cr[CH_2\text{-}Si(CH_3)_3]_4$ does not decompose by this fragmentation.

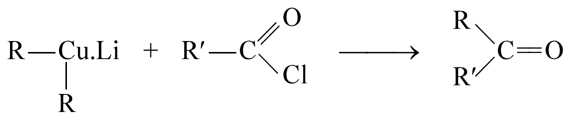
   α-Hydrogen abstraction in which an a-hydrogen of an alkyl ligand is abstracted to give an alkylidene or carbene complex, is much less recognised. A substantial amount of information indicates that this is also a significant decomposition mode for organometallic compounds.

1.2.4 Organocopper in Organic Synthesis

Organoalkyl lithium compounds when treated with cuprous halide from lithium organocuprates.

$$RLi \xrightarrow{Cu_2Cl_2} R_2CuLi$$

Lithium organocuprate reacts with acid chlorides to yield ketones.



$$R\text{—}\underset{|\atop R}{Cu}.Li + R'\text{—}C\overset{O}{\underset{Cl}{\lessgtr}} \longrightarrow \overset{R}{\underset{R'}{>}}C{=}O$$

The acid chloride undergoes nucleophilic substitution, the nucleophilic being the basic alkyl group of organocuprate.

Check Your Progress

1. List the four types of transition.
2. Which compounds were used to prepare a large number of organic compounds by Barbier?
3. How is the common Grignard reagent prepared?
4. What happens when alkynyl halides react with the Grignard reagent?
5. How is lithium organocuprates obtained?

1.3 ANSWERS TO ‘CHECK YOUR PROGRESS’

1. The four types of transitions are d-d transitions, metal to ligand charge transfer transitions, ligand to metal charge transfer transitions and inter-ligand transitions.
2. In 1899, Barbier used a mixture of alkyl halide and magnesium in ether to prepare a large number of organic compounds.

3. Common Grignard reagent is prepared by the action of magnesium metal on alkyl halide in the presences of alcohol free and dry ether.
4. Alkynyl halides react with the Grignard reagent to form alkynes.
5. Organoalkyl lithium compounds when treated with cuprous halide from lithium organocuprates.

NOTES

1.4 SUMMARY

- Organometallic compounds may be defined as substances having carbon to metal bonds.
- The reactivity of organometallic compounds increases with the increase in ionic character of carbon to metal bond.
- In 1899 Barbier used a mixture of alkyl halide and magnesium in ether to prepare a large number of organic compounds.
- Alkylmagnesium halides are therefore commonly known as Grignard reagents after the name of the discoverer. Their general formula is R-Mg-X where R is a univalent hydrocarbon radical, for example, -CH3; -C2H5; - CH2-CH==CH2; -C6H5; C6H5CH2- and -X is a halogen.
- Grignard reagents are colourless, hygroscopic solids. They are fairly stable in air but are never obtained in solid state for chemical reactions in synthesis.
- Diethylether is the most common solvent though other ethers like butyl ether, dimethyl- ether of glycol (diglyme) or TetraHydroFuran (THF) may also be used.
- Grignard suggested that the alkylmagnesium halide contains ether of crystallization.
- The carbon metal bond is highly polar. Although the organic group is not a complete anion yet it has a considerable anionic character.
- Grignard reagent reacts with compounds having carbon-oxygen, carbon-sulphur and carbon-nitrogen multiple bonds to give addition products which on hydrolysis give a wide variety of compounds.
- Alkylmagnesium bromides and iodides, in general react more readily than the corresponding chlorides.
- Organoalkyl lithium compounds when treated with cuprous halide from lithium organocuprates.

1.5 KEY TERMS

- **Transition Metals:** These metals possess unique and useful properties. In the periodic table, they comprise d-block transition elements.
- **Organometallic Compound:** These compounds contain at least one bond between a metallic element and a carbon atom which belongs to an organic group.
- **Alkyl:** This term shows that one hydrogen atom is missing from an alkane.
- **Aryl:** This term refers to any functional group from an aromatic ring, usually an aromatic hydrocarbon.

- **Grignard Reagent:** It is a chemical compound that has the general formula, R–Mg–X. Here, where X is a halogen and R is an organic group, usually an alkyl or aryl.
- **Nucleophilic Substitution Reaction:** It is a reaction in which a functional group within another electron-deficient molecule (known as the electrophile) is replaced by an electron-rich chemical species (known as a nucleophile).
- **Nucleophilic Addition Reaction:** It is an addition reaction in which a reaction takes place between a chemical compound with an electrophilic double or triple bond with a nucleophile, in order to break the bond.

1.6 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Write the organometallic compounds of different metals.
2. Why are compounds like sodium acetate, not considered as true organometallic compounds?
3. How is ether purified?
4. What happens when the Grignard reagent reacts with aldehydes and ketones?
5. List any two limitations of the Grignard Reagent.

Long-Answer Questions

1. Discuss the different types of transitions.
2. Analyse the structure and preparation of the Grignard Reagent in detail.
3. Describe the characteristics and uses of Grignard Reagents.
4. Explain all the nucleophilic substitution reactions of Grignard Reagents.

1.7 FURTHER READING

Ouellette, R. J., Rawn, J. D. 2014. *Organic Chemistry: Structure, Mechanism, and Synthesis*. United States: Elsevier Science.

Adamson, A. 2012. *A Textbook of Physical Chemistry*. United States: Elsevier Science.

Lumb, N. H., McLintock, S., Lyons, C. G. 2016. *A Concise Text-Book of Organic Chemistry:* The Commonwealth and International Library: Chemistry Division. United Kingdom: Elsevier Science.

Rawn, J. D., Ouellette, R. J. 2015. *Principles of Organic Chemistry*. Netherlands: Elsevier Science.

Anthony Hill. 2002. *Organotransition Metal Chemistry*. Wiley: Great Britain.

John F. Hartwig. 2010. *Organotransition Metal Chemistry: From Bonding to Catalysis*. University Science Books: California.

UNIT 2 COMPOUNDS OF TRANSITION METAL-CARBON MULTIPLE BONDS

Structure

2.0 INTRODUCTION

The most widely used method for forming organosilicon compounds is hydrosilylation of carbon-carbon multiple bonds catalysed by transition metal complexes. Several simple and adaptable catalytic systems, including homogeneous and heterogeneous systems, as well as those for asymmetric catalysis techniques, have been created over the previous two decades. The catalytic efficiency, regioselectivity, and stereoselectivity of these transition metal catalysts all has improved. Alkylidenes are produced from an alkane by removal of two hydrogen atoms from the same carbon atom. Alkylidynes are produced from an alkane by removal of three hydrogen atoms from the same carbon atom.This unit will introduce the concepts of alkylidenes and alkylidynes. It will explain the mechanism of low valent carbenes and carbynes. In addition, it will discuss the nucleophilic and electrophilic reactions on ligands and their role in organic synthesis.

2.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain alkylidenes and alkylidynes
- Evaluate low valent carbenes and carbynes
- Analyse nucleophilic and electrophilic reactions on ligands and their role in organic synthesis

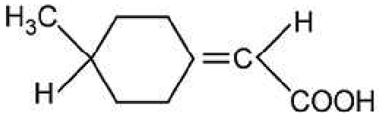
2.2 TRANSITION METAL-CARBON MULTIPLE BOND

NOTES

Transition metals have a strong desire to link with one another and with other metals. Although these bonds have a high degree of covalency, however, it might be oversimplifying to refer them as covalent bonds. Metal-metal bonds can be extremely fascinating.

2.2.1 Alkylidenes and Alkylidynes

Alkylidenes refer to the a class of divalent functional groups that are derived from an alkane by removal of two hydrogen atoms from the same carbon atom, the free valencies being part of a double bond - R2C=. The 1,3 dienes has two exocyclic double bonds and includes alkenation reactions, alkene metathesis, metal mediated coupling reactions and cycloisomerizations. Examples include the metal mediated transformations of acyclic diynes or enzymes into 1, 2 – bis (alkylidene) cycloalkanes. The structure of alkylidene cycloalkane closely resembles that of allenes.



1-Methylcyclohexylidene-4-acetic acid (Alkylidene cvcloalkane)

Fig. 2.1 *Alkylindene Cycloalkane*

The allenes are non-planar molecules due to the two ðð-bonds being formed on almost perpendicular planes as shown below:

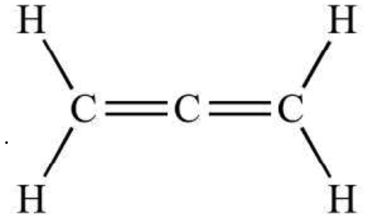


Fig. 2.2 *Non-planar Allene*

2.2.2 Low Valent Carbenes and Carbynes: Synthesis, Nature of Bond and Structural Characteristics

In chemistry, a carbene is a molecule containing a neutral carbon atom with a valence of two and two unshared valence electrons. The general formula is R-(C:)-R’ or R=C: where the R represent substituents or hydrogen atoms.

The term “carbene” may also refer to the specific compound H_2C:, also called methylene, the parent hydride from which all other carbene compounds are formally derived. Carbenes are classified as either singlets or triplets, depending upon their electronic structure. Most carbenes are very short lived, although persistent carbenes are also known. One well-studied carbene is dichlorocarbene Cl_2C:, which can be generated in situ from chloroform and a strong base.

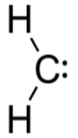


Fig. 2.3 *Methylene, the Simplest Carbene*

Structures and Bondings

The two classes of carbenes are singlet and triplet carbenes. Singlet carbenes are spin-paired. In the language of valence bond theory, the molecule adopts an sp^2 hybrid structure. Triplet carbenes have two unpaired electrons. Most carbenes have a nonlinear triplet ground state, except for those with nitrogen, oxygen, or sulfur atoms, and halides directly bonded to the divalent carbon.

Carbenes are called singlet or triplet depending on the electronic spins they possess. Triplet carbenes are paramagnetic and may be observed by electron spin resonance spectroscopy if they persist long enough. The total spin of singlet carbenes is zero while that of triplet carbenes is one. Bond angles are 125–140° for triplet methylene and 102° for singlet methylene (as determined by EPR). Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous Medium.

For simple hydrocarbons, triplet carbenes usually have energies 8 kcal/mol (33 kJ/mol) lower than singlet carbenes, thus, in general, triplet is the more stable state (the ground state) and singlet is the excited state species. Substituents that can donate electron pairs may stabilize the singlet state by delocalizing the pair into an empty p orbital. If the energy of the singlet state is sufficiently reduced it will actually become the ground state. No viable strategies exist for triplet stabilization. The carbene called 9-fluorenylidene has been shown to be a rapidly equilibrating mixture of singlet and triplet states with an approximately 1.1 kcal/mol (4.6 kJ/mol) energy difference. It is, however, debatable whether diaryl carbenes such as the fluorene carbene are true carbenes because the electrons can delocalize to such an extent that they become in fact biradicals. In silico experiments suggest that triplet carbenes can be thermodynamically stabilized with electropositive heteroatoms such as in silyl and silyloxy carbenes, especially trifluorosilyl carbenes.

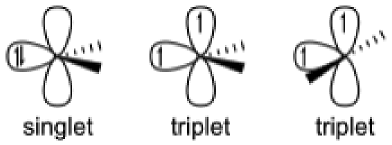


Fig. 2.4 *Singlet and Triplet Carbenes*

Reactivity

Singlet and triplet carbenes exhibit divergent reactivity. Singlet carbenes generally participate in cheletropic reactions as either electrophiles or nucleophiles. Singlet carbenes with unfilled p-orbital should be electrophilic. Triplet carbenes can be considered to be diradicals, and participate in stepwise radical additions. Triplet carbenes have to go through an intermediate with two unpaired electrons whereas singlet carbene can react in a single concerted step.

Due to these two modes of reactivity, reactions of singlet methylene are stereospecific whereas those of triplet methylene are stereoselective. This difference can be used to probe the nature of a carbene. For example, the reaction of methylene generated from photolysis of diazomethane with cis-2-butene or with trans-2-butene each give a single diastereomer of the 1,2-dimethylcyclopropane product: *cis* from *cis* and *trans* from *trans*, which proves that the methylene is a singlet. If the methylene were a triplet, one would not expect the product to depend upon the starting alkene geometry, but rather a nearly identical mixture in each case.

Reactivity of a particular carbene depends on the substituent groups. Their reactivity can be affected by metals. Some of the reactions carbenes can do are insertions into C-H bonds, skeletal rearrangements, and additions to double bonds. Carbenes can be classified as nucleophilic, electrophilic, or ambiphilic. For example, if a substituent is able to donate a pair of electrons, most likely carbene will not be electrophilic. Alkyl carbenes insert much more selectively than methylene, which does not differentiate between primary, secondary, and tertiary C-H bonds.

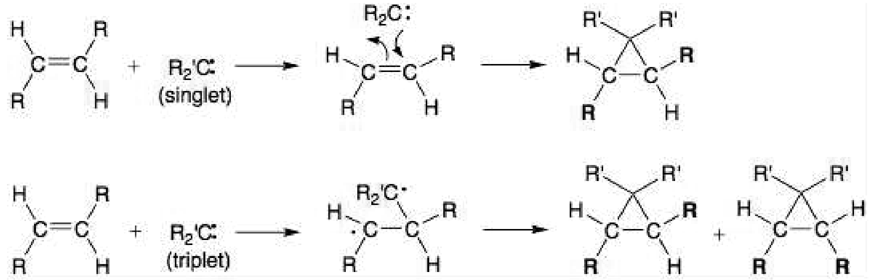


Fig. 2.5 Carbene Addition to Alkenes

Cyclopropanation

Carbenes add to double bonds to form cyclopropanes. A concerted mechanism is available for singlet carbenes. Triplet carbenes do not retain stereochemistry in the product molecule. Addition reactions are commonly very fast and exothermic. The slow step in most instances is generation of carbene. A well-known reagent employed for alkene-to-cyclopropane reactions is Simmons-Smith reagent. This reagent is a system of copper, zinc, and iodine, where the active reagent is believed to be iodomethylzinc iodide. Reagent is complexed by hydroxy groups such that addition commonly happens syn to such group.

Fig. 2.6 Carbene Cyclopropanation

C—H Insertion

Insertions are another common type of carbene reactions. The carbene basically interposes itself into an existing bond. The order of preference is commonly:

(1) X–H bonds where X is not carbon (2) C–H bond and (3) C–C bond. Insertions may or may not occur in single step.

Intramolecular insertion reactions present new synthetic solutions. Generally, rigid structures favor such insertions to happen. When an intramolecular insertion is possible, no intermolecular insertions are seen. In flexible structures, five-membered ring formation is preferred to six-membered ring formation. Both inter- and intramolecular insertions are amendable to asymmetric induction by choosing chiral ligands on metal centers.

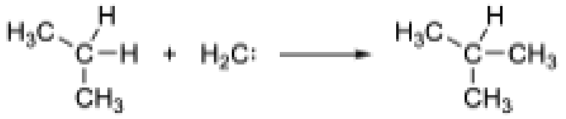


Fig. 2.7 *Carbene Insertion*

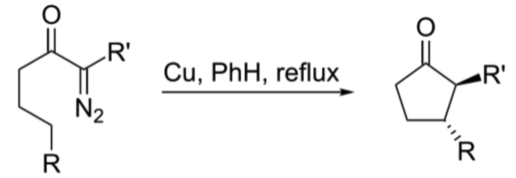


Fig. 2.8 *Carbene Intramolecular Reaction*

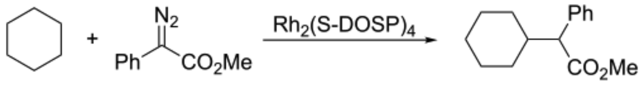


Fig. 2.9 *Carbene Intermolecular Reaction*

Alkylidene carbenes are alluring in that they offer formation of cyclopentene moieties. To generate an alkylidene carbene a ketone can be exposed to trimethylsilyl diazomethane.

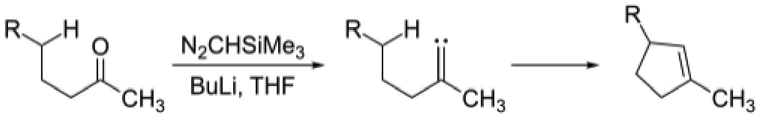


Fig. 2.10 *Alkylidene Carbene*

Generation of Carbenes

A method that is broadly applicable to organic synthesis is induced elimination of halides from gem-dihalides employing organolithium reagents. It remains uncertain if under these conditions free carbenes are formed or metal-carbene complex. Nevertheless, these metallocarbenes (or carbenoids) give the expected organic products.

$$R_2CBr_2 + BuLi ® R_2CLi(Br) + BuBr$$

$$R_2CLi(Br) ® R_2C + LiBr$$

For cyclopropanations, zinc is employed in the Simmons–Smith reaction. In a specialized but instructive case, alpha-halomercury compounds can be isolated and separately thermolyzed. For example, the “Seyferth reagent” releases CCl_2 upon heating.

$$C_6H_5HgCCl_3 \text{ ® } CCl_2 + C_6H_5HgCl$$

Most commonly, carbenes are generated from diazoalkanes, via photolytic, thermal, or transition metal-catalyzed routes. Catalysts typically feature rhodium and copper. The Bamford-Stevens reaction gives carbenes in aprotic solvents and carbenium ions in protic solvents. Base-induced elimination HX from haloforms (CHX_3) under phase-transfer conditions takes place. Photolysis of diazirines and epoxides can also be employed. Diazirines are cyclic forms of diazoalkanes. The strain of the small ring makes photoexcitation easy. Photolysis of epoxides gives carbonyl compounds as side products. With asymmetric epoxides, two different carbonyl compounds can potentially form. The nature of substituents usually favors formation of one over the other. One of the C-O bonds will have a greater double bond character and thus will be stronger and less likely to break. Resonance structures can be drawn to determine which part will contribute more to the formation of carbonyl. When one substituent is alkyl and another aryl, the aryl-substituted carbon is usually released as a carbene fragment. Carbenes are intermediates in the Wolff rearrangement, which is shown in Figure 2.11.

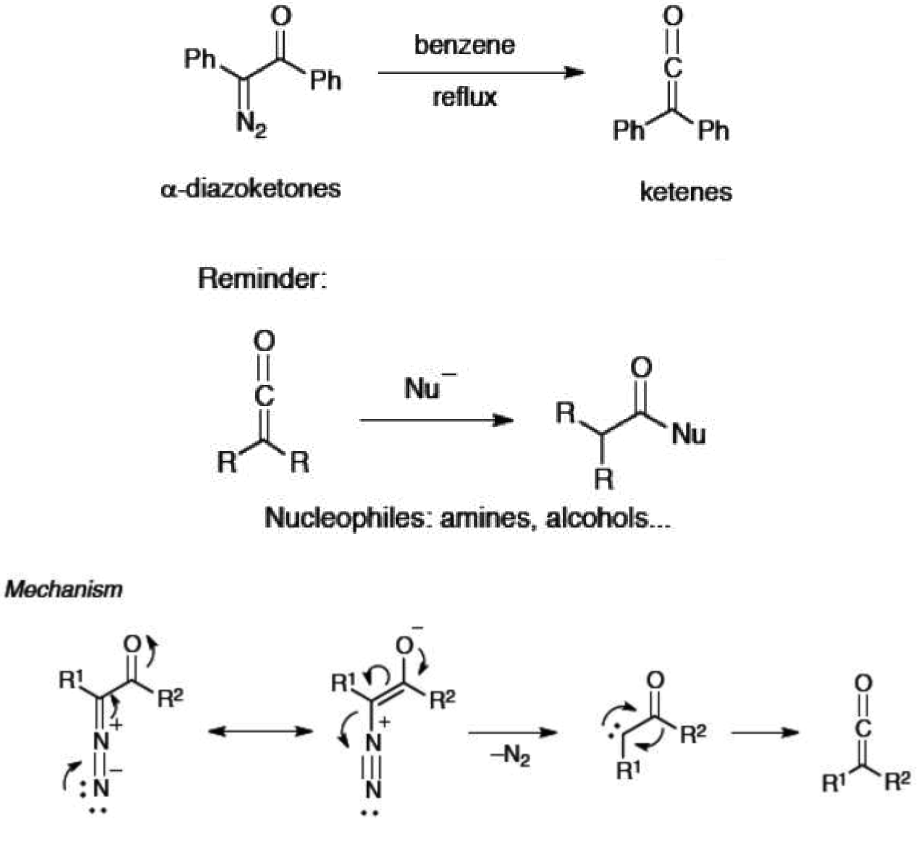


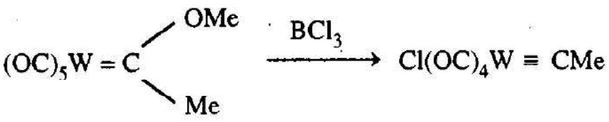
Fig. 2.11 *Walff Rearrangement*

An alkylidyne is a carbene, produced by an alkene by the removal of three hydrogen atoms from the same carbon atom. It has a univalent carbon atom and its generic formula is RC. An MC triple bond, consisting of one bond and two d-p bonds, binds them to the metal. Methylidyne, CH, is the simplest member of this class. The abstraction of an alkoxide group (OR) from a Fischer carbene by BBr_3 is one pathway to methylidynes identified in Fischer's lab. Carbynes can operate as trivalent ligands in transition metal complexes, where the three non-bonded electrons in the $-C^3$ group connect them to the metal. Cl(CO) 4WC-CH 3,[3] WBr(CO)2(2,2'-bipyridine)C-aryl and WBr(CO)2(PPh3)2C-NR2 are examples of coordination compounds.

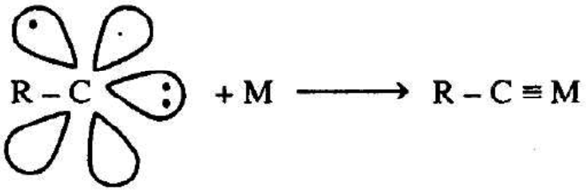
A carbyne complex consists of a metal-carbon triple bond:

M C— **R**

The following reaction indicates the formation of such a complex.



The carbyne ligand is a three-electron donor (similar to NO), with a pair of electrons in an *sp* orbital and one electron in a *p* orbital. The *sp* electron pair forms a π bond, the *p* electron pairing with a metal electron forms a σ bond; the second π bond is formed by the donation of an electron pair from the metal atom to the empty *p* orbital of the ligand.



Carbyne molecules are usually found in electronic doublet states, which means that instead of being a tri-radical, the non-bonding electrons on carbon are arranged as one radical (unpaired electron) and one electron pair, leaving a vacant atomic orbital (the quartet state). The CH radical is the simplest instance, with an electron configuration of 1σ2 2σ2 3σ2 1π.

Check Your Progress

1. Why are allenes non-planar molecules?
2. Write the general formula of a carbine.
3. How much energy do triplet carbenes have?
4. How carbenes form cyclopropanes?

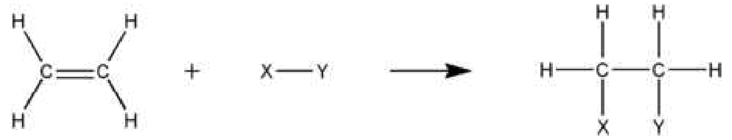
2.3 ELECTROPHILIC AND NUCLEOPHILIC REACTIONS ON LIGANDS AND THEIR ROLE IN ORGANIC SYNTHESIS

Let us study the nucleophilic and electrophilic reaction on ligands and their roles in organic synthesis.

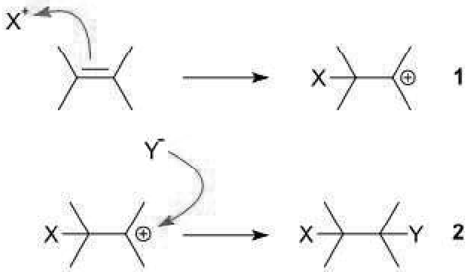
2.3.1 Electrophilic Reaction

In organic chemistry, an electrophilic addition reaction is an addition reaction where, in a chemical compound, a π bond is broken and two new σ bonds are formed. The substrate of an electrophilic addition reaction must have a double bond or triple bond

The driving force for this reaction is the formation of an electrophile X^+ that forms a covalent bond with an electron-rich unsaturated C=C bond. The positive charge on X is transferred to the carbon-carbon bond, forming a carbocation during the formation of the C-X bond.



The overall reaction for electrophilic addition to ethylene.



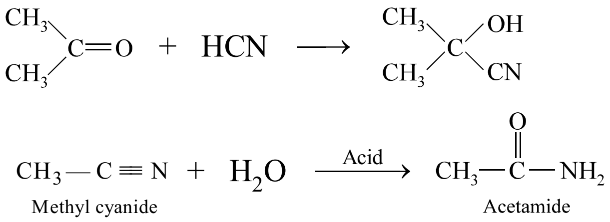
In step 2 of an electrophilic addition, the positively charged intermediate combines with (Y) that is electron-rich and usually an anion to form the second covalent bond.

Step 2 is the same nucleophilic attack process found in an SN_1 reaction. The exact nature of the electrophile and the nature of the positively charged intermediate are not always clear and depends on reactants and reaction conditions.

In all asymmetric addition reactions to carbon, regioselectivity is important and often determined by Markovnikov's rule. Organoborane compounds give anti-Markovnikov additions. Electrophilic attack to an aromatic systems that results in electrophilic aromatic substitution rather than an addition reaction.

2.3.2 Nucleophilic Reaction

In organic chemistry, a nucleophilic addition reaction is an addition reaction where a chemical compound with an electron-deficient or electrophilic double or triple bond, a π bond, reacts with electron-rich reactant, termed a nucleophile, with disappearance of the double bond and creation of two new single, or σ, bonds. The reactions are involved in the biological synthesis of compounds in the metabolism of every living organism, and are used by chemists in academia and industries such as pharmaceuticals to prepare most new complex organic chemicals, and so are central to organic chemistry. Addition reactions require the presence of groups with multiple bonds in the electrophile(due to the fact that double bonds and even triple bonds can both lack electron rich sources): carbon–heteroatom multiple bonds as in carbonyls, imines, and nitriles, or carbon–carbon double or triple bonds. The lack of electron rich sources is due to the fact that these bonds are partially empty, even though they remain connected, the region occupying the orbital is essentially dead. This electrophilic behavior is defined as empty space since everything inside is basically without any source of electricity except from outside the bond, since bonds tend to attract more to themselves (whether this be electric or non-electric, it can differ in most situations). The addition of the nucleophile means the continuous addition of a negative charge throughout the reaction, unless an electrophile also makes itself present to form a complete structure with no charge at all. The negative charge being continuous throughout the reaction until the formation of an intermediate, bearing the charge, thus is the addition reaction we have before us. Once this meets an electrophile, then the intermediate formed with the negative charge can thus be neutralized to form a complete structure via a type of bond.



$$CH_3-C\equiv N + H_2O \xrightarrow{\text{Acid}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Check Your Progress
5. What is the driving force for nucleophilic addition reaction?
6. What does the addition of the nucleophile mean?

2.4 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The allenes are non-planar molecules due to the two ðð-bonds being formed on almost perpendicular planes.
2. The general formula of a carbine is R- (C:)-R' or R=C: where the R represent substituents or hydrogen atoms.
3. For simple hydrocarbons, triplet carbenes usually have energies 8 kcal/mol (33 kJ/mol) lower than singlet carbenes, thus, in general, triplet is the more stable state (the ground state) and singlet is the excited state species.
4. Carbenes add to double bonds to form cyclopropanes
5. The driving force for this reaction is the formation of an electrophile X+ that forms a covalent bond with an electron-rich unsaturated C=C bond.
6. The addition of the nucleophile means the continuous addition of a negative charge throughout the reaction, unless an electrophile also makes itself present to form a complete structure with no charge at all.

2.5 SUMMARY

- Alkylidenes refer to the a class consisting of divalent functional groups that are derived from an alkane by removal of two hydrogen atoms from the same carbon atom, the free valencies being part of a double bond - R2C=.
- An alkylidyne is a carbene. It has a univalent carbon atom and its generic formula is RC.
- The allenes are non-planar molecules due to the two ðð-bonds being formed on almost perpendicular planes.
- A carbene is a molecule containing a neutral carbon atom with a valence of two and two unshared valence electrons.
- Carbenes are called singlet or triplet depending on the electronic spins they possess.
- For simple hydrocarbons, triplet carbenes usually have energies 8 kcal/mol (33 kJ/mol) lower than singlet carbenes, thus, in general, triplet is the more stable state (the ground state) and singlet is the excited state species.
- Singlet carbenes generally participate in cheletropic reactions as either electrophiles or nucleophiles.
- Carbenes can be classified as nucleophilic, electrophilic, or ambiphilic.
- A well-known reagent employed for alkene-to-cyclopropane reactions is Simmons-Smith reagent.
- Alkylidene carbenes are alluring in that they offer formation of cyclopentene moieties. To generate an alkylidene carbene a ketone can be exposed to trimethylsilyl diazomethane.
- In organic chemistry, an electrophilic addition reaction is an addition reaction where, in a chemical compound, a σ bond is broken and two new π bonds are formed.
- In organic chemistry, a nucleophilic addition reaction is an addition reaction where a chemical compound with an electron-deficient or electrophilic double or triple bond, a π bond, reacts with electron-rich reactant, termed a nucleophile, with disappearance of the double bond and creation of two new single, or σ, bonds.
- The addition reactions are the reactions of the double or triple bonds.

2.6 KEY TERMS

- **Alkylidene:** It is a bivalent aliphatic radical formed by removing two hydrogen atoms from the same carbon atom from an alkane.
- **Alkylidyne:** It has a general formula, CH or CR. It is attached to a metal by a triple bond, consisting one σ bond and two *d-p* π bonds.
- **Carbene:** It has a general formula, R-(C**:**)-R′ or R=C**:**. It is a molecule that contains a neutral carbon atom with a valence of two and two unshared valence electrons.
- **Carbyne:** It refers to a molecule that in which the atoms are linked in chains with alternating single and triple bonds.
- **Sigma (σ) Bond:** These bonds are fomed when head-on overlapping between atomic orbitals takes place. These are the strongest type of covalent chemical bond.
- **Pi (π) Bond:** It is formed when sideways overlapping of two parallelly oriented pi orbitals of adjacent atoms takes place.
- **Electrophilic Reaction:** It is an addition reaction in which a double or triple bond in a chemical molecule is broken, resulting in the production of two new bonds.
- **Nucleophilic Addition Reaction:** It is a reaction in which a sigma bond is formed between a nucleophile and an electron deficient molecule.

2.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Why are allenes non-planar molecules?
2. Give the equation to show the Wolff rearrangement.
3. Differentiate between nucleophilic and electrophilic reactions.
4. What is the role of nucleophilic addition reactions in biological synthesis of compounds?

Long-Answer Questions

1. Explain various low valent carbenes and carbynes.
2. Singlet and triplet carbenes exhibit divergent reactivity, Discuss.
3. Analyse the different methods to produce carbenes.

NOTES

2.8 FURTHER READING

Ouellette, R. J., Rawn, J. D. 2014. *Organic Chemistry: Structure, Mechanism, and Synthesis*. United States: Elsevier Science.

Adamson, A. 2012. *A Textbook of Physical Chemistry*. United States: Elsevier Science.

Lumb, N. H., McLintock, S., Lyons, C. G. 2016. *A Concise Text-Book of Organic Chemistry:* The Commonwealth and International Library: Chemistry Division. United Kingdom: Elsevier Science.

Rawn, J. D., Ouellette, R. J. 2015. *Principles of Organic Chemistry*. Netherlands: Elsevier Science.

Anthony Hill. 2002. *Organotransition Metal Chemistry*. Wiley: Great Britain.

John F. Hartwig. 2010. *Organotransition Metal Chemistry: From Bonding to Catalysis*. University Science Books: California.

UNIT 3 TRANSITION METAL π-COMPLEXES

NOTES

Structure

3.0 INTRODUCTION

Transition metal π complexes are cationic, neutral, or anionic entities in which ligands coordinate the transition metal. Transition metals create complexes because their t 2 g orbitals have correct symmetry, allowing them to overlap with the ligands' unoccupied orbitals, producing bonds. Back bonding is the term for this type of connection. As a result, the presence of appropriate symmetry d-orbitals in transition metals allows the creation of p complexes. A metal can also activate a ligand, allowing an external reagent to attack the ligand directly without first binding the reagent to the metal. This unit will discuss transition metal π-complexes with unsaturated organic molecules and their preparation and properties. In addition, it will explain reactions related to nucleophilic and electrophilic attach on ligands and to organic synthesis.

3.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the transition metal π-complexes with unsaturated organic molecules
- Analyse the preparations, properties, nature of bonding and structural features of transition metal π-complexes with unsaturated organic molecules
- Discuss reactions related to nucleophilic and electrophilic attach on ligands and to organic synthesis

3.2 TRANSITION METAL π-COMPLEXES WITH UNSATURATED ORGANIC MOLECULES: PREPARATIONS, PROPERTIES, NATURE OF BONDING AND STRUCTURAL FEATURES

The transition metals have a general configuration of (n-1)d1-10ns1-2(n-1)d1-10ns1-2. Upto ten electrons can be accommodated in the d-orbitals. As a result, they absorb electrons quickly from the pi-orbitals of ligands containing pi-electrons, such as ethylene, benzene, and cyclopentadiene. Since the energies of the d-orbitals and the pi-orbitals are so near to one other, the pi-electrons are easily accepted by the d-orbitals to form the dπ – pπ dπ – pπ bond.

3.2.1 Alkenes

The members of this class of compounds have two hydrogen atoms less than the corresponding alkenes (saturated hydrocarbons). The members of this homologous series are represented by the general formula C_nH_{2n} and are also known as Olefins (Olefiant = oil forming) because lower gaseous members of the series react with chlorine to form oily products. The simplest olefin has the formula C_2H_4 and is commonly known as ethylene. Study of the structure of an olefin reveals that the two hydrogen atoms are lacking at adjacent carbon atoms as compared to saturated hydrocarbons. When two atoms form two covalent bonds with each other, implying the sharing of two pairs of electrons, they are considered to be joined by a double bond. The carbon-carbon double bond is known as olefinic linkage or ethylenic linkage after the name of the first member. In IUPAC system, olefins are termed as alkenes.

The nature of carbon-carbon double bond is best explained terms of molecular orbitals. The hybridization state of carbon atoms united to only three other atoms is sp^2. The three sp^2 hybrid orbitals are planar and are at an angle of 120° to one another. In case of ethylene each carbon atom, forms two C—H bonds by overlap of sp^2 orbital of carbon with 1 *s* orbital of hydrogen and the two carbon atoms are joined by the overlap of sp^2 orbitals of each one of them. All of these bonds are σ-bonds and all bond angles are 120° as shown in Fig. 3.1. The remaining unpaired electron at each carbon atom is in the *p*-orbital which is perpendicular to the plane of the three σ-bonds of the carbon. These two *p*-orbitals can form another bond between two carbon atoms by a parallel or sideways overlap. Such a bond is known as π-bond to distinguish it from σ-bond.

The overlapping of two *p*-orbitals is relatively poor and therefore, a π-bond is less stable than a π-bond. The energy associated with a carbon-carbon π-bond is only 58 kcal whereas, for carbon-carbon σ-bond it is 85 kcal. Thus, the total bond strength of the carbon-carbon double bond is 143 kcal. It is, therefore, stronger than a carbon-carbon single bond and the greater reactivity of the π-bond is because of the tendency to form more stable σ-bonds. Again because of a stronger double bond, the distance between carbon atoms decreases, as compared to singly bonded carbon atoms, so as to allow maximum overlap of *p*-orbitals to form a π-bond. The bond distance of a carbon-carbon single bond is 1.53 Å whereas that of a carbon-carbon double bond is 1.33 Å.

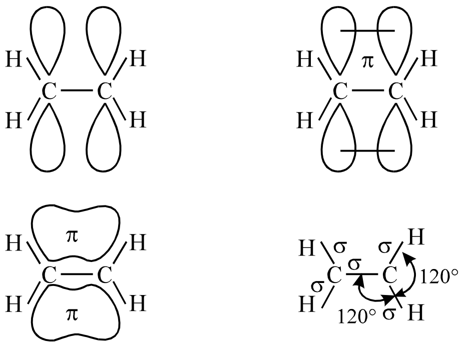


Fig. 3.1 *Formation of a Double Bond in Ethylene Molecule.*

Nomenclature

For naming olefins or alkenes, two systems are prevalent:

1. The common system: The common names of the first four alkenes are derived from the corresponding alkanes by replacement of the '*ane*' of the common name of the saturated hydrocarbon by '*ylene*'. For example,

Table 3.1 *Nomenclature of Alkenes*

	Alkane	*Corresponding Alkene*	*Formula*
C_2H_6	Ethane	Ethylene	$CH_2 = CH_2$
C_3H_8	Propane	Propylene	$CH_3.CH = CH_2$
C_4H_{10}	*n*-Butane	α-Butylene	$CH_3.CH_2CH = CH_2$
C_4H_{10}	*n*-Butane	β-Butylene	$CH_3.CH = CH.CH_2$
C_4H_{10}	Isobutane	Isobutylene	$CH_3—\underset{\underset{CH_3}{\vert}}{C} = CH_2$
C_5H_{12}	*n*-Pentane	α-Amylene	$C_3H_7CH = CH_2$
C_5H_{12}	*n*-Pentane	β-Amylene	$C_2H_5.CH = CH.CH_3$

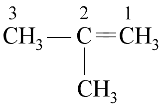
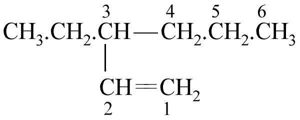
Usually the prefix '*n*' of the alkanes is omitted and isomeric alkenes are distinguished by writing Greek letters α, β, γ etc., as prefixes to indicate the position of double bond at first, second, third...etc., carbon atoms respectively.

The radicals derived from alkenes by removal of a hydrogen are shown below with their common names:

$CH_2 = CH—$	Vinyl	$CH_2 = CH—CH_2—$	Allyl
$CH_3—CH = CH—$	Propenyl	$CH_3—CH = CH—CH_2—$	Crotyl

2. IUPAC system: In this system of nomenclature of alkenes the ending '*ane*' of the corresponding alkane is replaced by '*ene*'. The series is thus known as alkene **series**. The parent alkene is considered to be the one corresponding to the longest chain of carbon atoms containing the double bond. The carbon chain is then numbered from the end nearer to the double bond and its position is indicated by the number of the carbon atom preceding the double bond. The correct and complete name of the alkene is then written according to a set of rules. Some illustrations are given in Table 3.2.

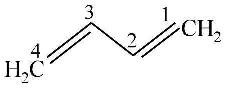
Table 3.2 *Nomenclature of Alkenes*

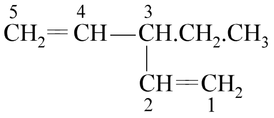
Formula	*IUPAC name*	*Radical derived*	*IUPAC name of the radical*
$CH_2=CH_2$	Ethene	$CH_3=CH—$	Ethenyl
$CH_3.CH=CH_2$	Propene	$CH_2=CH—CH_2—$	2-Propenyl
		$CH_3.CH=CH—$	1-Propenyl
$\overset{4}{CH_3}-\overset{3}{CH_2}.\overset{2}{CH}=\overset{1}{CH_2}$	1-Butene	$CH_3.CH_2.CH=CH—$	1-Butenyl
		$CH_2=CH—CH_2—CH_2—$	3-Butenyl
$\overset{4}{CH_3}-\overset{3}{CH}=\overset{2}{CH}.\overset{1}{CH_3}$	2-Butene	$CH_3—CH=CH—CH—$	2-Butenyl
 $\overset{3}{CH_3}-\underset{\underset{CH_3}{\vert}}{\overset{2}{C}}=\overset{1}{CH_3}$	2-Methyl-1-propene		
 $CH_3.CH_2.\underset{\underset{\underset{2}{CH}=\underset{1}{CH_2}}{\vert}}{\overset{3}{CH}}-\overset{4}{CH_2}.\overset{5}{CH_2}.\overset{6}{CH_3}$	3-Ethyl-1-hexene		

The radicals derived from alkenes by removal of one hydrogen atom are known as alkenyl radicals; the position of double bond being specified by the number of carbon atom preceding the double bond. Their names are obtained by replacing the '*e*' of alkene by '*yl*'. The carbon atom having a free vcalency is always the starting point for numbering. If there are two or more double bonds in the molecule, the ending '*ane*' of alkanes is replaced by '*adiene*' or '*atriene*' or '*apolyene*' respectively to get the name of the hydrocarbon, For example,

$\overset{4}{CH_2}=\overset{3}{CH}-\overset{2}{CH}=\overset{1}{CH_2}$

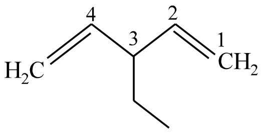
Butadiene#

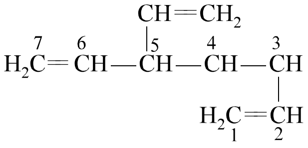




$\overset{5}{CH_2}=\overset{4}{CH}-\underset{\underset{\underset{2}{CH}=\underset{1}{CH_2}}{|}}{\overset{3}{CH}}.CH_2.CH_3$

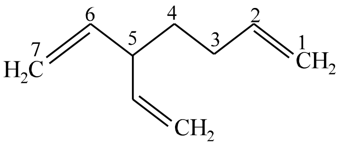
3-Ethyl-1,4-pentadiene
or
3-Ethylpentadiene-1,4

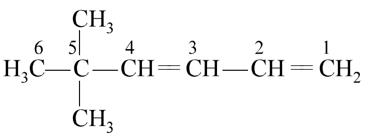




$H_2\overset{7}{C}=\overset{6}{CH}-\overset{CH=CH_2}{\overset{|}{\overset{5}{CH}}}-\overset{4}{CH}-\underset{\underset{H_2\underset{1}{C}=\underset{2}{CH}}{|}}{\overset{3}{CH}}$

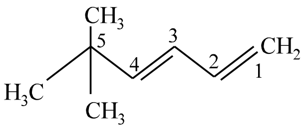
5-Ethenyl-
1,3,6-heptatriene





$H_3\overset{6}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{5}{C}}}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH}=\overset{1}{CH_2}$

5,5-Dimethyl-
1,4-hexadiene



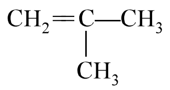
In these line structures $—CH_2$ and $—CH_3$ groups may or may not be written. It makes no difference.

Isomerism

The first two members of this series *viz*., ethene and propene, can have only one structural formula. The next member butene C_4H_8 may be represented by the following structures:

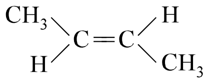
(i) $CH_2=CH—CH_2—CH_3$ 1-Butene

(ii)



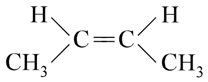
$CH_2=C(CH_3)—CH_3$ 2-Methyl propene

(iii)



trans-2-Butene

(iv)

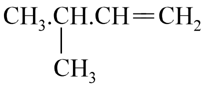


cis-2-Butene

All these isomers are known. Similarly pentene (C_5H_{10}) exists in six isomeric forms; the number of isomers goes on increasing as the number of carbon atoms increases.

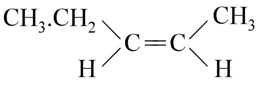
(i) $CH_3.CH_2.CH_2.CH=CH_2$ 1-Pentene

(ii)



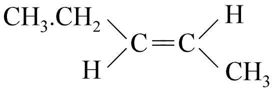
$CH_3.CH(CH_3).CH=CH_2$ 3-Methyl-1-butene

(iii)



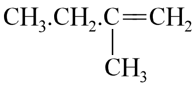
cis-2-Pentene

(iv)



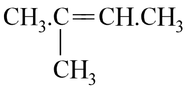
trans-2-Pentene

(v)



$CH_3.CH_2.C(CH_3)=CH_2$ 2-Methyl-1-butene

(vi)



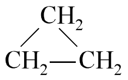
$CH_3.C(CH_3)=CH.CH_3$ 2-Methyl-2-butene

Thus it is clear that alkenes show the following types of isomerism:

- **Chain isomerism:** Alkenes show chain isomerism due to the difference in the nature of carbon skeleton. Thus, for butene it is exhibited by 1-butene and 2-methylpropene and for pentene, 1-pentene, 3-methyl-1-butene and 2-methyl-1-butene are the examples.
- **Position isomerism:** The difference in the position of the double bond in the same formula gives rise to position isomerism. Thus 1-butene and 2-butene; 1-pentene and 2-pentene and 2-methyl-1-butene and 2-methyl-2-butene are position isomers (Formulae given above).
- **Ring-chain isomerism:** Alkenes are isomeric with cycloalkanes; both being represented by the general formula C_nH_{2n}. However, alkenes are open chain or acyclic compounds with a double bond whereas cycloalkanes are cyclic (carbocyclic) compounds without double bonds. For example, propene is isomeric with cyclopropane, butene is isomeric with cyclobutane and so on.

$CH_3.CH{=}CH_2$

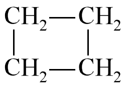
Propene



Cyclopropane or Trimethylene

$CH_3.CH_2.CH{=}CH_2$

1-Butene



Cyclobutane

4. Geometrical isomerism. Alkenes except ethene and propene also exhibit geometrical isomerism. Because of restricted rotation about the double bond two isomers are generally possible; one where the two hydrogens occupy same side of the double bond and the other where these are placed on opposite side of the double bond. For example, 2-butene and 2-pentene exist in isomeric *cis*- and *trans*-forms.

Occurrence of Alkenes

Lower alkenes occur in coal gas but in very small amounts. They seldom occur free in nature due to their reactivity. Ethylene is present in natural gas to the extent of 20%. Alkenes are also produced as products of destructive distillation of organic material.

General Methods of Preparation

Lower alkenes are obtained on a large scale by cracking of petroleum and higher alkenes are prepared by cracking of petroleum or by using Fischer-Tropsch oils under proper pressure and catalyst. Methods of formation of alkenes involve elimination of atoms or groups from adjacent carbon atoms. A few general methods of formation are as follows:

1. Dehydration of alcohols: Alcohols when dehydrated in presence of catalysts give alkenes. The best procedure is to pass the vapours of alcohol over heated alumina.

$$\underset{\text{Alcohol}}{R - CH_2.CH_2.OH} \xrightarrow[350\text{–}450°C]{Al_2O_3} \underset{\text{Alkene}}{R.CH = CH_2} + H_2O$$

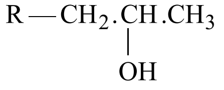
Other substances like P_2O_5, H_2SO_4 (conc.), H_3PO_4 are also used for dehydration. When acids are used the products usually undergo molecular rearrangement to give an isomeric compound. The ease of dehydration of various alcohols is in the order:

Tertiary > Secondary > Primary

However, the reactivity differs if different experimental conditions are employed as shown in the following examples:

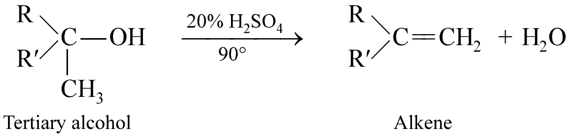
Thus,

$$\underset{\text{Primary alcohol}}{R.CH_2.CH_2.OH} \xrightarrow[140\text{–}170°C]{75\%\ H_2SO_4} \underset{\text{Alkene}}{R.CH = CH_2} + H_2O$$



$$R - CH_2.\underset{\underset{OH}{|}}{CH}.CH_3 \xrightarrow[100°]{60\%\ H_2SO_4} \underset{\text{Alkene}}{R.CH{=}CH.CH_3} + H_2O$$

Secondary alcohol



When ethyl alcohol is reacted with 95%. H_2SO_4 at 170°, ethyl hydrogen sulphate is formed which then decomposes to give ethylene or ethene.

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2.OH} + \underset{\text{Sulphuric acid}}{HO.SO_3H} \longrightarrow \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{CH_3.CH_2.O.SO_3H} + H_2O$$

$$CH_3.CH_2.O.SO_3H \xrightarrow{170°} CH_2{=}CH_2 + H_2SO_4$$

n-Butyl alcohol under similar conditions gives 2-butene as the main product which must, obviously, be formed as a result of a subsequent rearrangement from 1-butene.

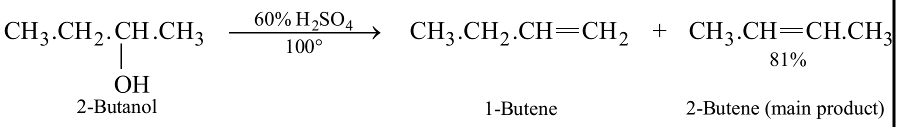
$$CH_3.CH_2.CH_2.CH_2OH \xrightarrow[170°]{75\%\ H_2SO_4} CH_3.CH_2.CH{=}CH_2 \text{ 1-butene}$$

$$\downarrow \text{rearrangement}$$

$$CH_3.CH{=}CH.CH_3$$

2-butene

In the dehydration of secondary and tertiary alcohols, when there is a possibility of the formation of two alkenes, the hydrogen atom is preferentially eliminated from the carbon with fewer number of hydrogens, to give an olefin having maximum number of alkyl groups about the double bond (*Saytzeff Rule*). Thus in the dehydration of 2-butanol, out of the two isomeric olefins possible, 2-butene is formed predominantly.

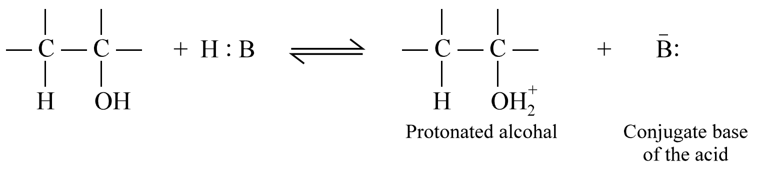


$$\underset{\text{2-Butanol}}{CH_3.CH_2.\underset{\substack{|\\ OH}}{CH}.CH_3} \xrightarrow[100°]{60\%\ H_2SO_4} \underset{\text{1-Butene}}{CH_3.CH_2.CH{=}CH_2} + \underset{\substack{81\%\\ \text{2-Butene (main product)}}}{CH_3.CH{=}CH.CH_3}$$

Mechanism

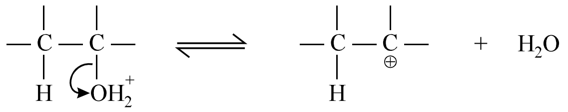
Dehydration of alcohol to alkene is 1 : 2 elimination reaction. The reaction is catalysed by acid and application of heat helps in the reaction as shown above. The acids generally used are sulphuric or phosphoric acids. The reaction proceeds through the following steps:

(i) In the first step an acid base reaction between alcohol and the acid takes place.



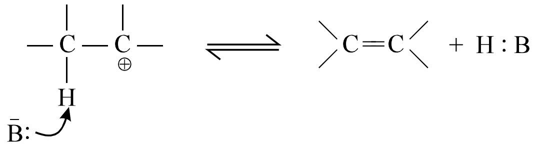
$$-\underset{\substack{|\\ H}}{\overset{|}{C}}-\underset{\substack{|\\ OH}}{\overset{|}{C}}- + H:B \rightleftharpoons \underset{\text{Protonated alcohal}}{-\underset{\substack{|\\ H}}{\overset{|}{C}}-\underset{\substack{|\\ OH_2^+}}{\overset{|}{C}}-} + \underset{\substack{\text{Conjugate base}\\ \text{of the acid}}}{\bar{B}:} \quad \text{... }(i)$$

(ii) In the second step the protonated alcohol undergoes heterolysis to form carbocation and water.



... (*ii*)

(iii) In the last step the carbocation formed loses a proton (accepted by base) to give alkene.



... (*iii*)

Sulphuric acid used gives the proton to produce H_3O^+ which forms the conjugate base water (:B)

$$H_3O^+ \longrightarrow H^+ + H_2O \text{ (Base)}$$

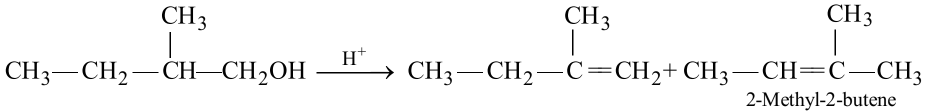
H_2O (base) takes away a proton from carboncation in step (iii) and is reconverted into H_3O^+. Thus acid used in step (i) is regenerated in step (iii). It is therefore clear that the acid used $(H_2SO_4 \rightleftharpoons H^+ + HSO_4^-)$ is not consumed and for the more reactive alcohols only a trace is needed for the reaction.

It should be noted that this 1 : 2 elimination is reversible as we know that the acids catalyse the hydration of alkenes to give alcohols. It is for this reason that in each step of the mechanism reversibility has been shown. However, since the alkene generated in the reaction is volatile the equilibrium in step (*iii*) shifts towards right side of the reaction.

As pointed earlier, the order of the reactivity is 3° > 2° > 1° for alcohols because the stability of the carbocations formed follows the same order. The more stable the carbocation, the faster is its formation and hence faster is the reaction. Since the primary carbocation is least stable, its rate of formation is slow making the overall reaction slower. (Ethylene is formed at a temperature of 170°C with 95% sulphuric acid.)

There is evidence that rate of dehydration depends upon both, steps (i) and (iii) shown above. In true E_1 elimination the rate of the reaction depends only upon the heterolysis step (ii) but here in this dehydration the loss of proton is much faster than regeneration of the substrate. Hence, strictly speaking dehydration is not an E_1 elimination reaction of the protonated alcohol.

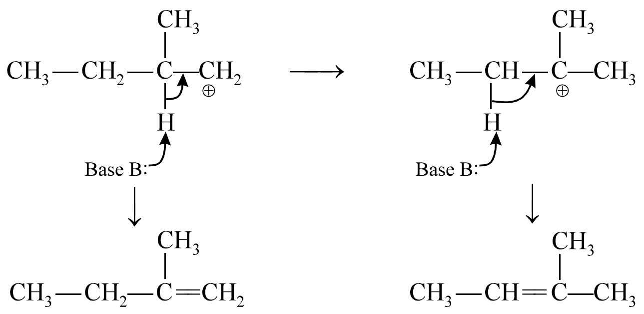
Now look at the dehydration of 2-methyl-1-butanol. Here 2-methyl-2-butene is the main product formed.



$$CH_3—CH_2—\overset{CH_3}{\overset{|}{C}H}—CH_2OH \xrightarrow{H^+} CH_3—CH_2—\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3—CH=\overset{CH_3}{\overset{|}{C}}—CH_3$$

2-Methyl-2-butene
(Main product)

In such cases we assume that the carbocation formed rearranges to a more stable cation. Thus two alkenes are formed; one corresponding to the stable cation and the other corresponding to the less stable one.



Such reactions, as above, which from the point of view of orientation, give exclusively or nearly exclusively one of the several possible isomeric products are called *regioselective* (Latin; *regio* meaning *direction*). The formation of one alkene in greater amount is also according to the Saytzeff rule.

2. Dehydrohalogenation of Alkyl Halides:

Alkyl halides when heated with alcoholic solution of potassium hydroxide eliminate a molecule of hydrogen halide to form olefins. The ease of the dehydrohalogenation is in the order:

Tertiary alkyl halide > Secondary alkyl halide > Primary alkyl halide

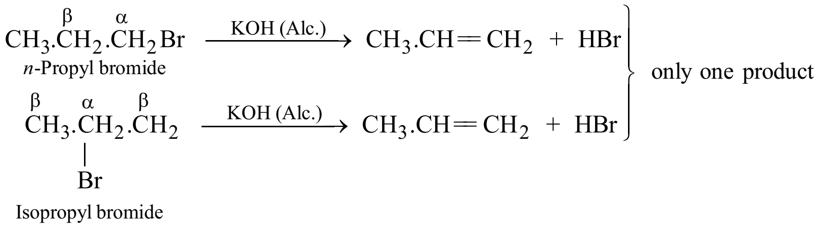
$$\underset{\text{Alkyl halide}}{\text{R.CH}_2\text{.CH}_2\text{X}} \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{\text{Alkene}}{\text{R.CH}=\text{CH}_2} + \text{KX} + \text{H}_2\text{O} \quad (\text{X} = \text{Cl, Br or I})$$

The yields of alkenes are very good in the dehydrohalogenation of tertiary and secondary alkyl halides but only fair or low for primary alkyl halides. In fact, ethyl halide when treated with alc. KOH gives ethene in 1% yield. The reaction is the most important method for introducing a double bond in the organic compound.

The ease of dehydrohalogenation for different halogens is in the order:

Iodine > Bromine > Chlorine

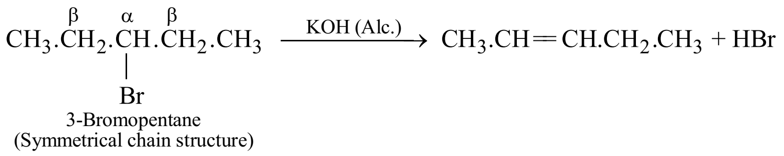
Dehydrohalogenation of alkyl halides is 1 : 2 elimination of the elements of hydrogen halide. The carbon holding the halogen is called α-carbon. The next adjacent carbon atoms on either side of α-carbon (if α-carbon is not at the end) are called β-carbon atoms. Hence this 1 : 2 elimination involves the loss of halogen from α-carbon and hydrogen from β-carbon atom. It is obvious that if α-carbon is not at the end of the chain then generally two different alkenes will be formed (except in some special cases):



$$\underset{n\text{-Propyl bromide}}{\text{CH}_3.\overset{\beta}{\text{CH}_2}.\overset{\alpha}{\text{CH}_2}\text{Br}} \xrightarrow{\text{KOH (Alc.)}} \text{CH}_3.\text{CH}=\text{CH}_2 + \text{HBr}$$

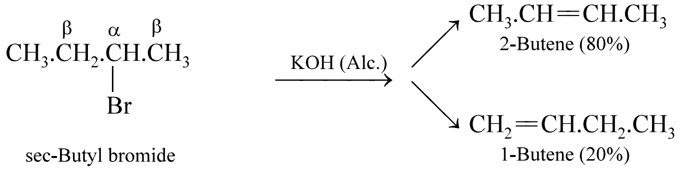
$$\underset{\text{Isopropyl bromide}}{\overset{\beta}{\text{CH}_3}.\underset{\text{Br}}{\overset{\alpha}{\text{CH}}_2}.\overset{\beta}{\text{CH}_2}} \xrightarrow{\text{KOH (Alc.)}} \text{CH}_3.\text{CH}=\text{CH}_2 + \text{HBr}$$

only one product



$$\text{CH}_3.\overset{\beta}{\text{CH}_2}.\underset{\text{Br}}{\overset{\alpha}{\text{CH}}}.\overset{\beta}{\text{CH}_2}.\text{CH}_3 \xrightarrow{\text{KOH (Alc.)}} \text{CH}_3.\text{CH}=\text{CH.CH}_2.\text{CH}_3 + \text{HBr}$$

3-Bromopentane
(Symmetrical chain structure)



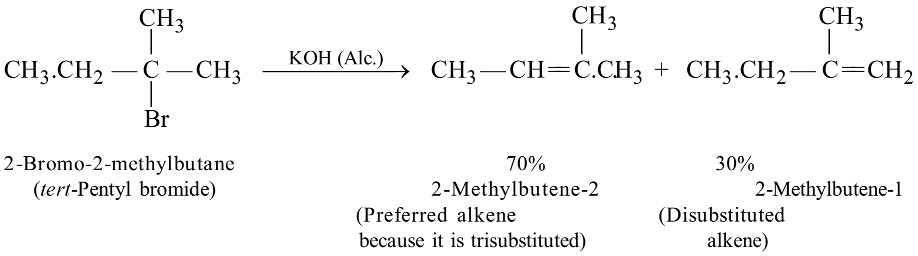
$$CH_3.\overset{\beta}{C}H_2.\underset{Br}{\overset{\alpha}{C}H}.\overset{\beta}{C}H_3 \xrightarrow{\text{KOH (Alc.)}} CH_3.CH{=}CH.CH_3 \; (80\%) + CH_2{=}CH.CH_2.CH_3 \; (20\%)$$

Predominant formation of 2-butene is according to Russian chemist Alexander Saytzeff's rule which states that "In dehydrohalogenation the preferred product is the alkene that has the greater number of alkyl groups attached to doubly bonded carbon atoms." The ease of formation of alkene and the stability follow the same order.

$$\textit{Stability} \longrightarrow$$

$$R.CH{=}CH_2 < RCH{=}CHR\,;\; R_2C{=}CH_2 < RCH{=}CR_2 < R_2C{=}CR_2$$

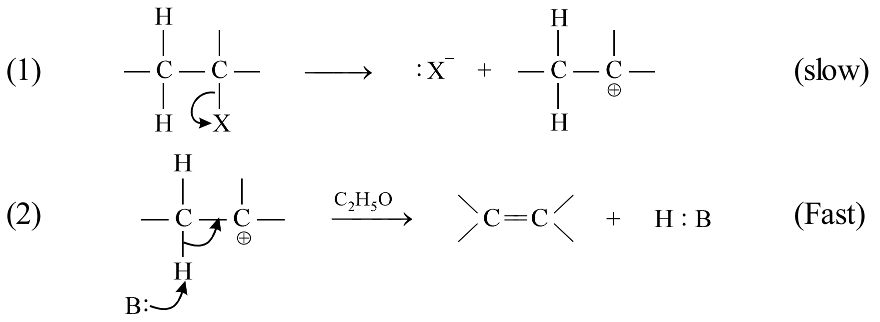
$$\textit{Ease of formation} \longrightarrow$$



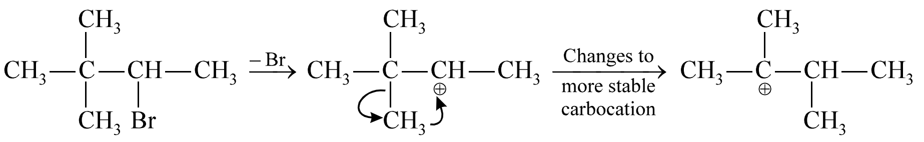
$$CH_3.CH_2-\underset{Br}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{KOH (Alc.)}} CH_3-CH{=}\overset{CH_3}{C}.CH_3 + CH_3.CH_2-\overset{CH_3}{C}{=}CH_2$$

In these examples you can see that trisubstituted alkene formation is preferred over disubstituted which in turn is preferred over monosubstituted alkene. For E_2 elimination reaction the order of reactivity of alkyl halides is 3° > 2° > 1°. An alkoxide base like ethoxide $C_2H_5O^-$ can also be used.

In E_1 elimination also the bond breaking and bond making are same but they take place in two steps instead of one as in case of S_N1. In E_1 elimination the first step involves the hydrolysis of the alkyl halide to a halide ion and a carbocation. This is also a rate-determining step. In the second step carbocation loses a proton to form an alkene.



In E_1 elimination also the reactivity order of alkyl halides is 3° > 2° > 1°. Here also the preferred alkene is formed according to Saytzeff's rule. However, where the structure permits the first order eliminations are accompanied by rearrangement of the cations to more stable ones.



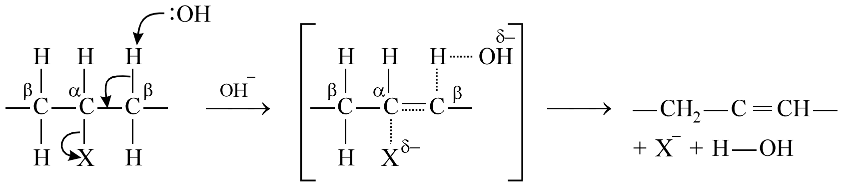
(Secondary) (Tertiary)

NOTES

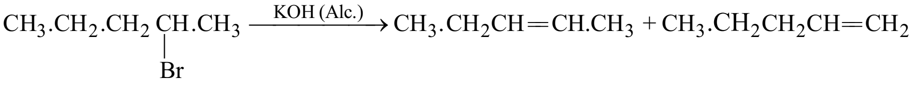
The ease of formation and stability give another definition to Saytzeff's rule: "In dehydrohalogenation the faster an alkene is formed the more stable it is." Predominant formation of the more stable alkene among its isomer is called Saytzeff's orientation.

Mechanism. For dehydrohalogenation both E_2 and E_1 elimination have been proposed depending upon the conditions of the reaction and nature and concentration of the reagent.

E_2 Elimination. If stronger base is used in the reaction and its concentration is greater than the chances of *E_2 elimination* are greater. When the base approaches the proton at β-carbon the proton starts leaving towards base and leaves behind its electron pair, which starts forming a π bond between α and β carbon atoms and at the same time the halogen at α-carbon starts leaving away as halide ion. The π bond formation supplies energy for breaking carbon-halogen bond. Thus a transition develops which results in simultaneous removal of halogen and formation of π bond for alkene.



It should be noted that the hydrogen may be abstracted from other β-carbon also. The proportion of the formation of two alkenes depends upon the ease with which the hydrogen at β-carbon is selected by the base for removal. The orientation of elimination is according to Saytzeff's rule.

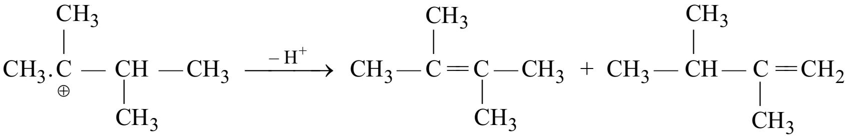


$$CH_3.CH_2.CH_2\underset{\substack{|\\ Br}}{CH}.CH_3 \xrightarrow{\text{KOH (Alc.)}} CH_3.CH_2CH{=}CH.CH_3 + CH_3.CH_2CH_2CH{=}CH_2$$

2-Bromopentane
(Isopentylbromide)

70%
2-Pentene
(Preferred alkene
because it is disubstituted)

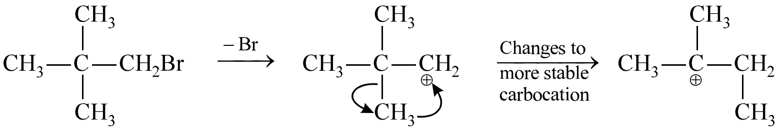
70%
1-Pentene
(Monosubstituted
alkene)



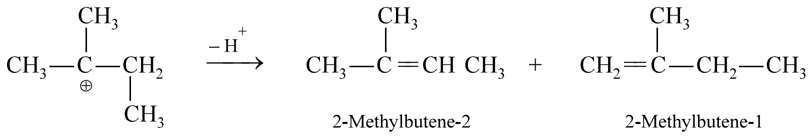
2,3-Dimethyl butene-2
(Preferred product)

2,3-Dimethyl butene-1

This rearrangement to a stable cation can give alkenes from these alkyl halides which do not have β-hydrogen to halogen.



2,2-Dimethyl bromopropane
(Neopentyl bromide)



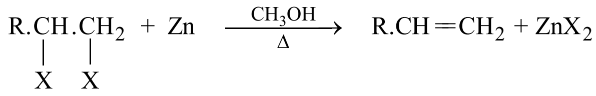
$$\mathrm{CH_3-\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}-\underset{\underset{CH_3}{|}}{CH_2}} \xrightarrow{-\mathrm{H}^+} \mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}=CH\ CH_3} + \mathrm{CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3}$$

2-Methylbutene-2 (Preferred product) 2-Methylbutene-1

Comparison of E_2 and E_1 Elimination

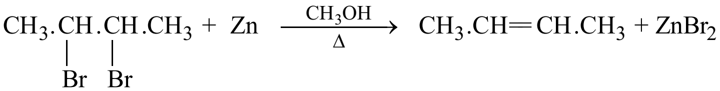
- Reactivity of the alkyl halide follows the same order, 3° > 2° > 1°, in both types, although the reasons are different. In E_2 the reactivity increases due to greater stability of more highly branched alkenes formed whereas in E_1 the reactivity increases due to the more stable carbocation formed in the rate determining step. Primary alkyl halides form carbocation with great difficulty and even they change to 2° or 3° if conditions permit.
- In E_2 elimination base takes part in the rate determining step whereas in E_1 it does not.
- In E_2 the rate depends upon the concentration of the base but the rate in E_1 has nothing to do with it.
- The base comes into play when the carbocation has been formed.
- Generally E_1 elimination is favourable for tertiary and to a lesser extent for secondary alkyl halides with a low concentration of the base. Stronger bases favour E_2 elimination.

3. Dehalogenation of *vic*-Dihalides: *vic*-Dihalides have two halogens on adjacent carbon atoms. When such a compound is heated with zinc dust in alcohol, dehalogenation occurs resulting in the formation of alkene.



$$\mathrm{R.\underset{\underset{X}{|}}{CH}.\underset{\underset{X}{|}}{CH_2} + Zn \xrightarrow[\Delta]{CH_3OH} R.CH=CH_2 + ZnX_2}$$

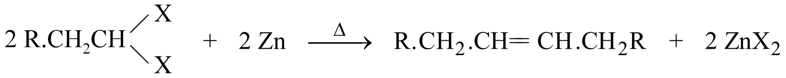
vic-Dihaloalkane Alkene



$$\mathrm{CH_3.\underset{\underset{Br}{|}}{CH}.\underset{\underset{Br}{|}}{CH}.CH_3 + Zn \xrightarrow[\Delta]{CH_3OH} CH_3.CH=CH.CH_3 + ZnBr_2}$$

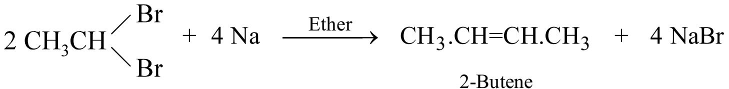
2,3-Dibromobutane 2-Butene

Metallic sodium may also be used in place of zinc. *gem*-Dihalides having two halogens on the same carbon atom usually give a higher alkene.



$$\mathrm{2\ R.CH_2CH}\left\langle\begin{matrix}\mathrm{X}\\\mathrm{X}\end{matrix}\right. + \mathrm{2\ Zn \xrightarrow{\Delta} R.CH_2.CH=CH.CH_2R + 2\ ZnX_2}$$

gem-Dihalide Alkene

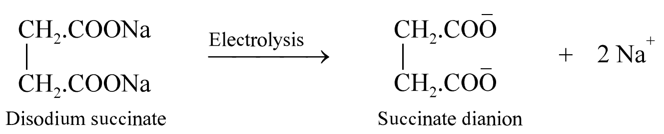


$$\mathrm{2\ CH_3CH}\left\langle\begin{matrix}\mathrm{Br}\\\mathrm{Br}\end{matrix}\right. + \mathrm{4\ Na \xrightarrow{Ether} CH_3.CH=CH.CH_3 + 4\ NaBr}$$

1,1-Dibromoethane
or
Ethylidene bromide

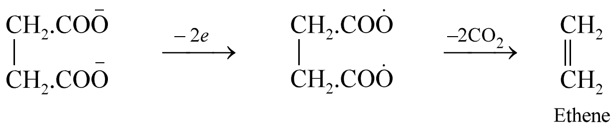
2-Butene

4. Electrolysis of Salts of Dicarboxylic Acids. When sodium or potassium salts of the dicarboxylic acid of the type of succinic acid are subjected to electrolysis in aqueous solution, alkenes are formed.



$$\underset{\text{Disodium succinate}}{\begin{array}{l}CH_2.COONa\\ |\\ CH_2.COONa\end{array}} \xrightarrow{\text{Electrolysis}} \underset{\text{Succinate dianion}}{\begin{array}{l}CH_2.CO\bar{O}\\ |\\ CH_2.CO\bar{O}\end{array}} + 2\,Na^+$$

At anode:



$$\begin{array}{l}CH_2.CO\bar{O}\\ |\\ CH_2.CO\bar{O}\end{array} \xrightarrow{-2e} \begin{array}{l}CH_2.CO\dot{O}\\ |\\ CH_2.CO\dot{O}\end{array} \xrightarrow{-2CO_2} \underset{\text{Ethene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}}$$

At cathode

$$2Na^+ \xrightarrow{+2e} 2\,Na \xrightarrow{2\,H_2O} 2\,NaOH + H_2$$

It is an extension of Kolbe's method for preparation of alkanes.

5. Partial Hydrogenation of Alkynes: The alkynes have a triple bond in the molecule and their controlled hydrogenation by passing the alkyne with hydrogen gas in equimolar ratio over heated catalysts, gives alkenes. The catalyst used may be finely divided platinum, palladium, Lindlar's catalyst or nickel.

$$\underset{\text{Alkyne}}{RC{\equiv}CR} + H_2 \xrightarrow{Pt} \underset{\text{Alkene}}{R.CH{=}CH.R}$$

$$\underset{\text{Propyne}}{CH_3.C{\equiv}CH} + H_2 \xrightarrow{Pd} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

Lindlar's catalyst is palladium poisoned with calcium or barium carbonate and quinoline.

6. Decomposition of Quaternary Ammonium Salts: Quaternary ammonium salts are compounds of nitrogen in which it is joined by four covalent and one electrovalent linkage (quincovalent, unielectrovalent). When these salts are heated, alkenes are formed. For example:

$$\underset{\substack{\text{Tetraethyl ammonium}\\ \text{hydroxide}}}{(C_2H_5)_4N^+OH^-} \xrightarrow{\Delta} \underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Triethylamine}}{(C_2H_5)_3N} + H_2O$$

If two olefins may be fomed by decomposition of a quaternary ammonium salt then the one which is the least substituted around double bond is predominant (*Hofmann rule*).

7. **Pyrolysis or Cracking:** Higher alkanes when heated to a high temperature under pressure decompose to give a mixture of lower alkanes and alkenes.

$$\underset{\text{Alkane}}{R.CH_2.CH_2R} \xrightarrow[\text{200 Atmos.}]{500°C} \underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Alkane}}{R{-}H}$$

$$\underset{\text{Hexane}}{CH_3.CH_2.CH_2.CH_2.CH_2.CH_3} \xrightarrow[\text{200 Atmos.}]{500°C} \underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Propane}}{CH_3.CH_2.CH_3}$$

Sometimes a catalyst is of advantage in this method.

General Physical Characteristics

The physical characteristics of alkenes are in general similar to those of corresponding alkanes. Some of these are as follows:

- First three members of alkene series ethene, propene and butene are gases at room temperature while alkenes having five to fifteen carbon atoms—pentene to pentadecene—are liquids and the higher members are solids.
- Like alkanes they are insoluble in water but unlike them are soluble in certain organic solvents like alcohol, because the greater availability of electrons in the double bond leads to a greater attraction for the positive ends of the solvents.
- They have characteristic smell and burn with luminous flame.
- Unlike alkanes, they show weakly polar properties because a sp^2 hybridized carbon atom is more electronegative than sp^3 hybridized carbon. In unsymmetrical alkenes like propene the bond joining the alkyl group to the carbon involved in double bond formation is slightly polar and the electrons of that bond are held closer to the carbon bonded by the double bond. This results in creation of small dipole having the negative ends towards double bond and the positive pole towards the alkyl group. It is because of this effect that alkyl groups attached to unsaturated carbon cause an electron donating inductive (I) effect. Values of dipole moments for alkenes are pretty close and in the range of 0.35 to 0.40 D. However *trans*-alkenes, ethylene etc., are non-polar and have zero dipole moment.
- They are less volatile than alkanes. Their boiling and melting points and specific gravities are higher than corresponding alkanes and show a regular increase with increase in molecular weight. As a result of higher polarity the *cis*-isomer has higher boiling and melting points and specific gravity as compared to the *trans*-isomer.

  The physical properties of representative alkenes are given in Table 3.3.

Table 3.3 *Physical Properties of Reprsentative Alkenes*

Sl. No.	*Name*	*Formula*	*B.P. °C*	*M.P. °C*	*Sp. Gr. at 20°C*
1.	Ethene	$CH_2{=}CH_2$	– 102	–169	—
2.	Propene	$CH_3.CH{=}CH_2$	– 48	–185	0.514
3.	1-Butene	$CH_3.CH_2.CH{=}CH_2$	– 6.5	–185	0.595
4.	*cis*-2-Butene	*cis*-$CH_3.CH{=}CH.CH_3$	4	–139	0.621
5.	*trans*-2-Butene	*trans*-$CH_3.CH{=}CH.CH_3$	1	–106	0.604
6.	1-Pentene	$CH_3.CH_2.CH_2.CH{=}CH_2$	30	–165	0.641
7.	*cis*-2-Pentene	*cis*-$CH_3.CH_2.CH{=}CH.CH_3$	38	–151	0.656
8.	*trans*-2-Pentene	*trans*-$CH_3.CH_2.CH{=}CH.CH_3$	36	–140	0.648
9.	3-Methyl-1-butene	$(CH_3)_2CH.CH{=}CH_2$	25	–138	0.648
10.	2-Methyl-2-butene	$(CH_3)_2C{=}CH.CH_3$	39	–140	0.660
11.	1-Hexene	$CH_3(CH_2)_3.CH{=}CH_2$	63.5	–140	0.674
12.	1-Heptene	$CH_3(CH_2)_4.CH{=}CH_2$	95	–120	0.697
13.	1-Octene	$CH_3(CH_2)_5.CH{=}CH_2$	122	–102	0.715
14.	1-Nonene	$CH_3(CH_2)_6.CH{=}CH_2$	150	–95	0.732
15.	1-Decene	$CH_3(CH_2)_7.CH{=}CH_2$	171	–87	0.743

Spectroscopic Properties

The electrons of an alkene double bond are designated as π electrons. In UV spectroscopy these π electrons are excited by light of the wavelength 1000-2000 Å (or 100–200 mμ). This region is known as vacuum UV region because substances like air, quartz etc. absorb strongly in this region and is of practically no use. However, when the double bonds are conjugated the wavelength of absorption may shift to higher region *i.e.*, above 2000 Å (or 200 mμ) and can be used to determine the number of double bonds in the molecule.

In case of alkenes exhibiting *cis*-*trans* isomersm, generally the *cis*-form absorbs at a lower wavelength than the *trans*-counterpart and has a lower molar extinction coefficient. This property may be used to distinguish *cis*- and *trans*-isomers. The IR spectra of alkenes show a characteristic stretching vibration absorption band of the carbon-carbon double bond in the region 1680–1620 cm (5.95–6.17μ) besides other C—H stretching and bending vibration absorption band. *cis*-Alkenes show a strong absorption band near 965 cm^{-1} but not the *trans*-isomer. Thus IR spectra may also be used to distinguish *cis-trans* isomers.

In the NMR spectra of alkenes the chemical shift of protons attached to doubly bonded carbon atoms occur at much lower field than those of protons attached to saturated carbon atoms. Vinyl or ethylenic protons generally show an absorption band at 4.8 to 6.2 δ.

General Chemical Characteristics

The alkenes are in general very reactive in contrast to the inert behaviour of alkanes. This high reactivity of alkenes is due to the presence of double bond in the molecule. According to Baeyer's strain theory any deviation from the normal valency angle (109.5°) of the carbon atom results in a strain on the molecule. The greater is the deviation the greater will be the consequent strain. In a molecule having a double bond there is considerable (in fact the bond angle is theoretically reduced to zero) distortion of valency angle which causes a severe strain and therefore such a molecule has a tendency to release the strain by breaking the double bond yielding saturated compound.

The nature and structure of the double bond in terms of molecular orbital concept has already been explained earlier and it can be recalled that formation of a π bond results in the enveloping of the carbon atoms by π electron clouds on either side. Thus a molecule having a carbon-carbon double bond may be considered as a substrate rich in electrons and thus reagents seeking electrons, *i.e.* electrophilic reagents are most likely to react with alkenes. The most important reaction of alkenes will, therefore, be electrophilic reaction.

The π electrons of a double bond are quite mobile and highly reactive because of polarizability brought about by the attacking reagent (**electromeric shifts**).

The molecule of an alkene may be considered to be made up of two units—(i) A double bond and (ii) Alkyl group(s). They will thus show the reactions of both.

(A) Addition Reactions

Alkenes undergo addition at double bond with a large number of reagents to form saturated compounds. These addition reactions are electrophilic addition reactions

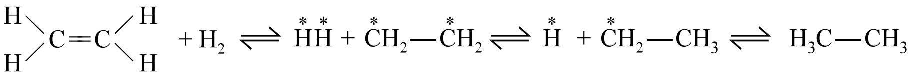
1. Addition of Hydrogen or Hydrogenation: The alkenes when heated with hydrogen gas in presence of catalysts like Ni (*Sabatier-Senderens reduction*), Pt, Pd etc., give alkanes.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + H_2 \xrightarrow[200\text{–}300°C]{Ni} \underset{\text{Alkane}}{R.CH_2.CH_3}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2 \xrightarrow[200°C]{Ni} \underset{\text{Propane}}{CH_3.CH_2.CH_3}$$

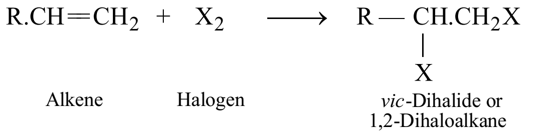
In presence of finely powdered Pt, Pd and Raney nickel[1] the hydrogenation can be affected at room temperature and atmospheric pressure.

The addition of hydrogen to a double or triple bond is known as hydrogenation. The mechanism of catalytic hydrogenation is uncertain. It is widely accepted that alkene and hydrogen get adsorbed at the surface of the catalyst where hydrogen is present as atoms. Smith and coworkers (1942) suggested that addition of the adsorbed hydrogen atoms occurs one at a time and the reaction is reversible.



(Asterisks indicate the adsorbed state at metallic sites)

2. Addition of Halogens: Alkenes react with halogens to form dihalogen derivatives by an addition reaction. The order of reactivity of halogens for a given alkene is Chlorine > Bromine > Iodine.



$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\substack{vic\text{-Dihalide or}\\ \text{1,2-Dihaloalkane}}}{R-\underset{\displaystyle X}{\underset{|}{CH}}.CH_2X}$$

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + Cl_2 \longrightarrow \underset{\substack{\text{Ethylene chloride or}\\ \text{1,2-Dichloroethane}}}{CH_3CI.CH_2CI}$$

$$\underset{\text{Porpene}}{CH_3.CH{=}CH_2} + Br_2 \longrightarrow \underset{\text{1,2-Dibromopropane}}{CH_2.CHBr.CH_2Br}$$

3. Addition of Halogen Acids. Alkenes react with aqueous solution of halogen acids to form alkyl halides. The order of reactivity of the halogen acids is HI > HBr > HCI.

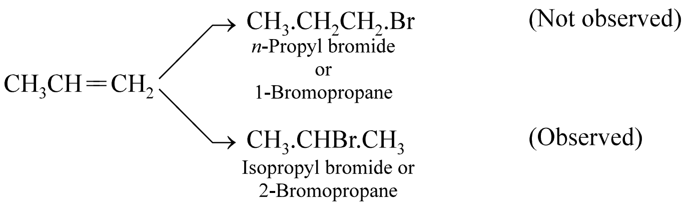
$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\substack{\text{Halogen}\\ \text{acid}}}{HX} \longrightarrow \underset{\substack{\text{Alkyl halide or}\\ \text{Haloalkane}}}{R.CHX.CH_3}$$

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + HCI \longrightarrow \underset{\text{Ethyl chloride}}{CH_3.CH_2.Cl}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + HBr \longrightarrow \underset{\substack{\text{Isopropyl bromide or}\\ \text{2-Bromopropane}}}{CH_3.CHBr.CH_3}$$

NOTES

In the addition reaction of propene it may be noted that because of unsymmetrical nature of alkene two products are theoretically possible. Thus:



Out of these only one is obtained predominantly, *i.e.*, 2-bromopropane. Markovnikov studied a large number of addition reactions of unsymmetrical olefins and gave Markovnikov's rule. This rule states that: In the addition to an unsymmetrical olefin the negative part of the reagent or addendum goes to that carbon constituting the double bond which is poorer in hydrogen. However in the presence of peroxides the addition occurs anti to Markovnikov's rule and in the above example: 1-bromopropane will then be obtained predominantly. This is known as Kharasch peroxide effect.

Regiochemistry

When the alkene is unsymmetric and the adding reagent is also unsymmetric then the regiochemistry (which group adds to which carbon) becomes important. Thus addition of HBr to propene under acidic conditions can give rise to two regio isomeric products of which 2-bromopropane is the main product implying that the reaction is regiospecific.

The additions of HF, HCl and HI are not affected by the presence of peroxides. As the peroxide effect comes from the free radical nature of the reactions, the unusual behaviour of HF and HCl is understandable because the high bond energy prevents the formation of free radicals. On the other hand HI readily dissociates to give iodine free radical but firstly these combine to form iodine molecule and secondly these are insufficiently reactive due to their bigger size.

4. Addition of Hypohalous Acids: Hypohalous acids, *viz*., hypochlorous and hypobromous acids readily add to the double bond of alkenes to give halohydrins.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Hypohalous acid}}{HOX} \longrightarrow \underset{\text{Halohydrin}}{R.CHOH.CH_2X}$$

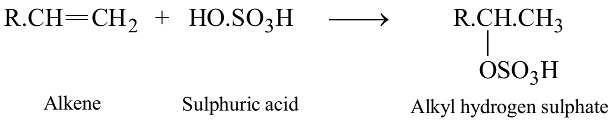
$$\underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Hypochlorous acid}}{HOCI} \longrightarrow \underset{\substack{\text{Ethylene chlorohydrin}\\ \text{or 2-Choloroethanol}}}{CH_2OH.CH_2CI}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + \underset{\text{Hypobromous acid}}{HOBr} \longrightarrow \underset{\text{Propylene bromohydrin}}{CH_3CHOH.CH_2Br}$$

The halogens of the hypohalous acids constitute the positive part with respect to the hydroxyl (—OH) groups and therefore, in the addition of hypohalous acid to unsymmetrical olefins, —OH group goes to carbon poorer in hydrogen. Addition of hypobromous acid to propene, therefore gives 1-bromo-2-propanol and not

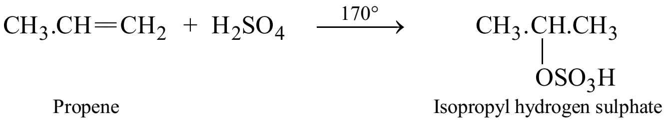
2-bromo-1-propanol. The hypoiodous acid is practically non-reactive in this reaction.

5. Addition of Sulphuric Acid: Alkenes add sulphuric acid at double bond to form alkyl hydrogen sulphates.



$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Sulphuric acid}}{HO.SO_3H} \longrightarrow \underset{\text{Alkyl hydrogen sulphate}}{\underset{\displaystyle OSO_3H}{R.CH.CH_3}}$$

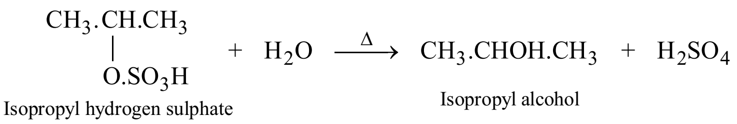
$$\underset{\text{Ethene}}{CH_2{=}CH_2} + H_2SO_4 \xrightarrow{170°} \underset{\text{Ethyl hydrogen sulphate}}{CH_3.CH_2.O.SO_3H}$$



$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2SO_4 \xrightarrow{170°} \underset{\text{Isopropyl hydrogen sulphate}}{\underset{\displaystyle OSO_3H}{CH_3.CH.CH_3}}$$

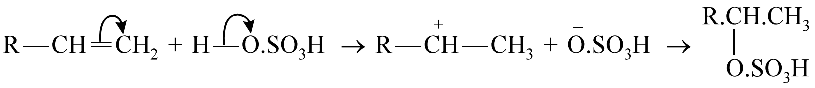
Addition of sulphuric acid to unsymmetrical alkenes, like propene, takes place in accordance with Markovnikov's rule and —SO_3H group adds to the carbon linked to lesser number of hydrogens. These alkyl hydrogen sulphates on boiling with water decompose to give corresponding alcohols.

$$\underset{\text{Ethyl hydrogen sulphate}}{CH_3.CH_2.O.SO_3H} + H_2O \xrightarrow{\Delta} \underset{\text{Ethyl alcohol}}{CH_3.CH_2.OH} + H_2SO_4$$



$$\underset{\text{Isopropyl hydrogen sulphate}}{\underset{\displaystyle O.SO_3H}{CH_3.CH.CH_3}} + H_2O \xrightarrow{\Delta} \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} + H_2SO_4$$

The mechanism of the reaction may be written as:



$$R—CH{=}CH_2 + H—O.SO_3H \rightarrow R—\overset{+}{C}H—CH_3 + \overset{-}{O}.SO_3H \rightarrow \underset{\displaystyle O.SO_3H}{R.CH.CH_3}$$

Alkenes, thus, can be converted to corresponding alcohols on treatment with sulphuric acid and subsequent hydrolysis. Large amounts of ethyl alcohol and isopropyl alcohol are industrially obtained from ethene and propene produced by cracking of petroleum fractions.

6. Addition of Water or Hydration: Alkenes may be hydrated to alcohols by the application of above reaction. However, alkenes having a secondary or tertiary carbon atom may be hydrated directly by boiling with dilute acids or acid acting as catalyst. Isobutylene gives tertiary butyl alcohol under these conditions.

$$\underset{\text{Isobutylene}}{(CH_3)_2.C{=}CH_2} + H_2O \xrightarrow{H^+} \underset{\textit{ter}\text{-Butyl alcohol}}{(CH_3)_3C.OH}$$

The following mechanism has been proposed for hydration

$$H_2O + H^+ \longrightarrow H_3\overset{+}{O}$$

$$(CH_3)_2C{=}CH_2 + H—\underset{+}{O}H_2 \xrightarrow[-H_2O]{\text{Slow}} \underset{t\text{-Butyl carbocation}}{(CH_3)_2\overset{+}{C}.CH_3} \text{ or } (CH_3)_3\overset{+}{C}$$

$$(CH_3)_3\overset{+}{C} + H_2O \xrightarrow{\text{Fast}} (CH_3)_3C—\overset{+}{O}H_2 \xrightarrow[\text{Fast}]{-H^+} \underset{t\text{-Butyl alcohol}}{(CH_3)_3C.OH}$$

NOTES

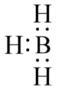
The slow step addition of a proton to alkene gives a carbocation. This carbocation in the fast step adds a molecule of water followed by the elimination of a proton to give addition product, alcohol.

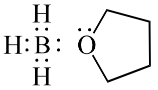
7. Hydroboration-Oxidation: This is another method of hydration of alkenes where hydration takes place anti to Markovnikov's rule. Diborane $(BH_3)_2$ adds to alkene and the trialkyl borane obtained gives alcohol when reacted with alkaline hydrogen peroxide.

$$3\,R—CH{=}CH_2 \xrightarrow{(BH_3)_2} (R.CH_2CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3\,R.CH_2CH_2OH + H_3BO_3$$

The reaction details are given below.

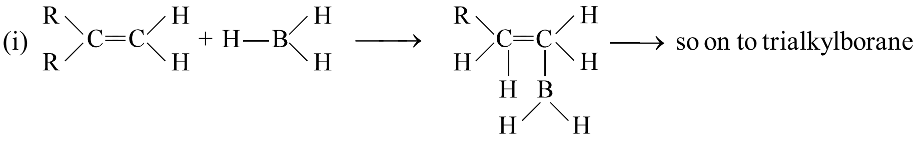
Alkenes react with diborane in ether to undergo hydroboration to yield alkylboranes. It is a case of simple addition of BH_3 to double bond. Diborane is the dimer of the hypothetical BH_3 and in the reaction given below it acts as if it were BH_3. In fact it exists as BH_3 (monomer) in solvents like tetrahydrofuran in the form of acid base complex.





Boron THF complex

Formation of Alkylboranes



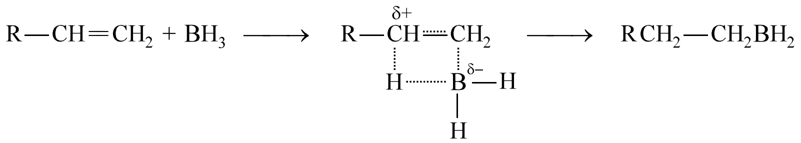
Alkylborane

$$\text{(ii)}\ \underset{\text{Diborane}}{(BH_3)_2} \xrightarrow[\text{ether}]{R.CH=CH_2} R.CH_2CH_2BH_2 \xrightarrow[\text{ether}]{R.CH=CH_2} (R.CH_2CH_2)_2BH$$

$$\text{ether}\ \Big\downarrow\ RCH{=}CH_2$$

$$\underset{\text{Trialkylborane}}{(R.CH_2CH_2)_3B}$$

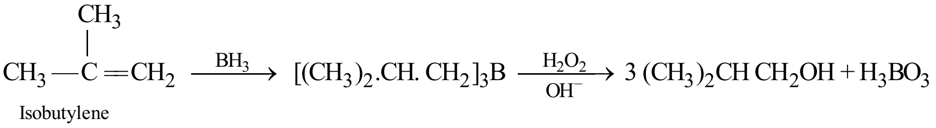
Mechanism. Boron has only six electrons in BH_3 hence it acts as an electrophile. It seeks π electrons of the double bond between two carbon atoms of alkenes. When it approaches alkene it starts attaching itself to carbon with a negative charge but in the meantime the other carbon atom constituting the double bond starts getting a positive charge on losing π electrons. With positive charge developing this carbon begins to take charge of the hydrogen of BH_3 which is near it. Boron which has gained π electrons is willing to part with this hydrogen to acidic carbon atom. Thus a transition state develops which then results in the addition of BH_3 to alkene.



$$R-CH=CH_2 + BH_3 \longrightarrow R-\overset{\delta+}{C}H\cdots CH_2 \,(H\cdots \overset{\delta-}{B}(H)-H) \longrightarrow RCH_2-CH_2BH_2$$

Transition state

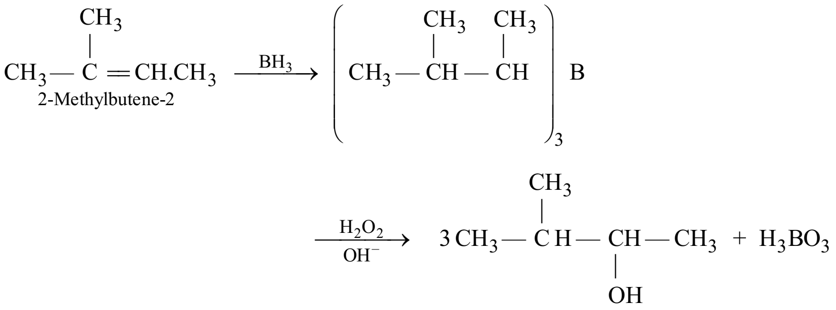
The process goes on till trialkyl borane is formed. Trialkyl boranes are useful because they can be oxidised to alcohol by using alkaline H_2O_2.



$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH_2 \xrightarrow{BH_3} [(CH_3)_2.CH.\,CH_2]_3B \xrightarrow[OH^-]{H_2O_2} 3\,(CH_3)_2CH\,CH_2OH + H_3BO_3$$

Isobutylene

Isobutyl alcohol (1°)



$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH.CH_3 \xrightarrow{BH_3} \left(CH_3-\overset{\overset{\large CH_3}{|}}{CH}-\overset{\overset{\large CH_3}{|}}{CH}\right)_3 B$$

2-Methylbutene-2

$$\xrightarrow[OH^-]{H_2O_2} 3\,CH_3-\overset{\overset{\large CH_3}{|}}{C}H-\underset{\underset{\large OH}{|}}{CH}-CH_3 + H_3BO_3$$

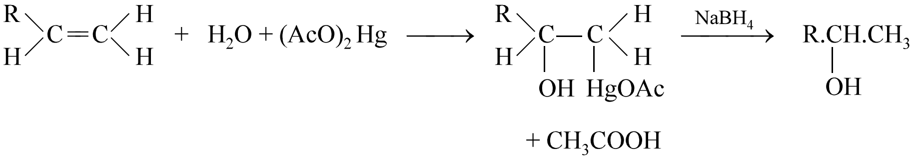
3-Methylbutanol-2 (2°)

Thus hydroboration-oxidation process gives alochol in which water adds in anti-Markovnikov's manner to alkene. Trialkyl boranes can also be used to get alkanes or aldehydes.

$$(R.CH_2CH_2)_3B \xrightarrow[\Delta]{CH_3COOH} R.CH_2.CH_3$$

$$(R.CH_2CH_2)_3B \xrightarrow[\Delta]{H_2Cr_2O_7} R.\,CH_2.CH=O$$

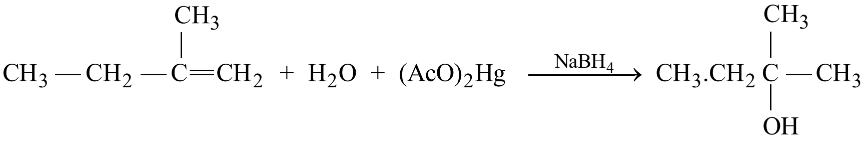
8. Oxymercuration: This is another method of hydration of alkenes where hydration takes place according to Markovnikov's rule. Alkene is added to an aqueous solution of mercuric acetate diluted with tetrahydrofuran at room temperature. The reaction is complete in a very short time. Hydroxy-mercurial compound is first formed which is reduced by sodium borohydride *in situ*.



$$\begin{matrix}R\\H\end{matrix}\!\!>C=C<\!\!\begin{matrix}H\\H\end{matrix} + H_2O + (AcO)_2\,Hg \longrightarrow \begin{matrix}R\\H\end{matrix}\!\!>\underset{\underset{\large OH}{|}}{C}-\underset{\underset{\large HgOAc}{|}}{C}<\!\!\begin{matrix}H\\H\end{matrix} \xrightarrow{NaBH_4} R.\underset{\underset{\large OH}{|}}{C}H.CH_3$$

$$+ CH_3COOH$$

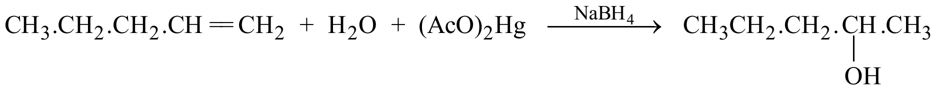
The yields are very good; often over 90%. Oxymercuration is highly regioselective and gives alcohols in accordance with Markovnikov's rule.



$$CH_3-CH_2-\overset{\overset{\large CH_3}{|}}{C}=CH_2 + H_2O + (AcO)_2Hg \xrightarrow{NaBH_4} CH_3.CH_2\,\underset{\underset{\large OH}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3$$

2-Methylbutene-1

2-Methylbutanol-2
(*tert*-Pentyl alcohol)

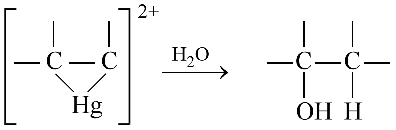


$$CH_3.CH_2.CH_2.CH{=}CH_2 + H_2O + (AcO)_2Hg \xrightarrow{NaBH_4} CH_3CH_2.CH_2.\underset{\displaystyle OH}{CH}.CH_3$$

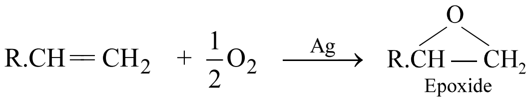
Pentanol-2

NOTES

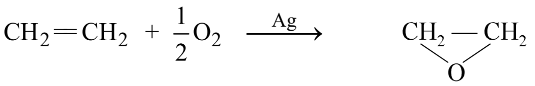
Oxymercuration involves the electrophilic addition to carbon-carbon double bond, mercuric ion acting as an electrophile. Cyclic mercurinium ion formed is attacked by nucleophilic solvent water to yield the addition product. Mercury is recovered in elemental state.



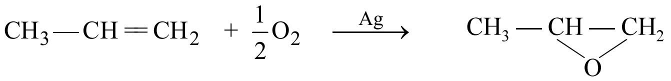
9. Epoxidation (Addition of Oxygen): When mixed with oxygen or air and passed over a silver catalyst at high temperature and pressure, lower alkenes add an atom to oxygen to form epoxides (alkene-oxides)



Epoxide

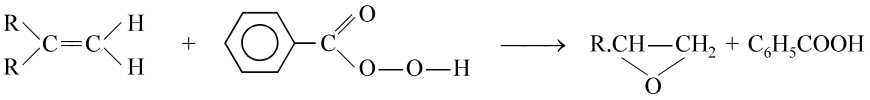


Ethylene oxide or Oxirane



Propylene oxide or Methyl oxirane

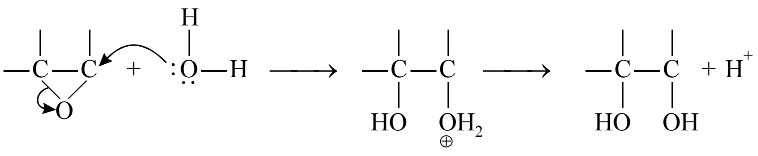
Epoxides are also obtained when alkenes are reacted with peracids like perbenzoic acid.



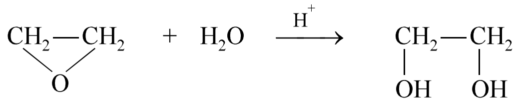
Perbenzoic acid

Epoxide or Oxirane

Peroxybenzoic acid and alkene are allowed to stand in chloroform or ether solution. Reaction takes place resulting in epoxide formation along with benzoic acid. Epoxides are very useful and give glycols and other alcohols under varying conditions. In acid catalysed cleavage protonation of epoxide takes place which can then be attacked by nucleophilic agent like water or ethyl alcohol.

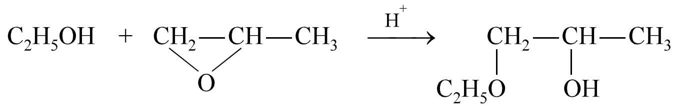


(i)



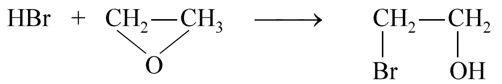
Ethylene glycol

(ii)



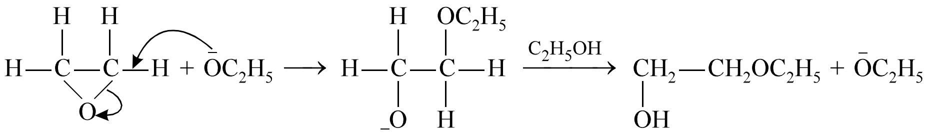
3-Ethoxy propanol-2

(iii)

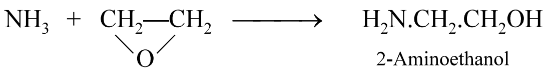


Ethylene bromohydrin

In base catalysed cleavage the epoxide itself undergoes nucleophilic attack. The non-protonated epoxide has lower reactivity hence only strong nucleophilic reagents like alkoxides and ammonia can straight away attack non-protonated epoxide.

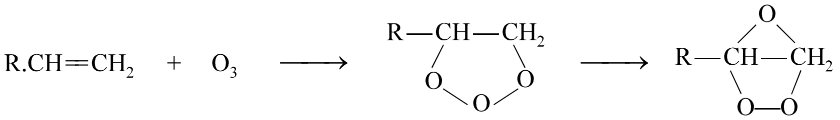


2-Ethoxyethanol

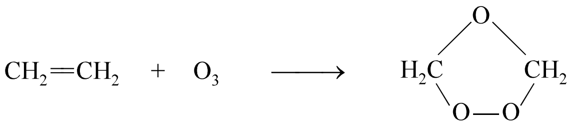


2-Aminoethanol

10. Addition of Ozone and Ozonolysis: When a stream of ozone or ozonised oxygen is passed through a solution of alkene in an inert solvent like ether or carbon tetrachloride it adds a molecule of ozone at the double bond to give an ozonide.

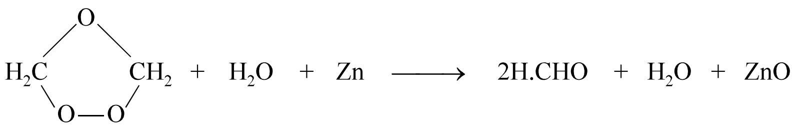


Alkene Ozone Iso-ozonide Ozonide

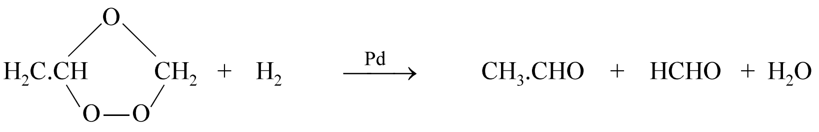


Ethene Ethene ozonide

The ozonides are explosive and on reduction with hydrogen in presence of a catalyst (Pt or Pd) or on boiling with water containing traces of zinc dust, split to give aldehydes and/or ketones. The fission of the molecules takes place at the position occupied by the double bond.



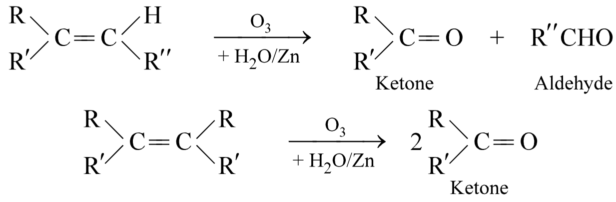
Ethene ozonide Formaldehyde



Propene ozonide Acetaldehyde Formaldehyde

NOTES

An alkene of the type R.R′.C═CHR″ gives a mixture of aldehyde and ketones whereas R.R′.C ═ C.R.R′ type alkene gtives ketones only.



The process of the formation of ozonide and its decomposition to give carbonyl compounds is known as Ozonolysis.

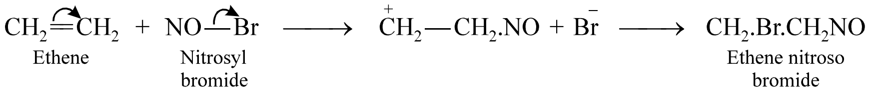
11. Addition of Hydrogen Peroxide: The addition of H_2O_2 to alkenes is catalyzed by acids and gives a mixture of hydroperoxides and peroxides. For example:

$$\underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} + H_2O_2 \xrightarrow{H^+} \underset{\textit{ter}\text{-Butyl-hydroperoxide}}{(CH_3)_3C—O—O—H}$$

$$(CH_3)_2C—O—O—H + CH_2{=}C.(CH_3)_2 \xrightarrow{H^+} \underset{\textit{ter}\text{-Butyl-peroxide}}{(CH_3)_2C—O—O—C(CH_3)_3}$$

12. Addition of Nitrosyl Halide: Alkenes add nitrosyl chloride or bromide at the double bond to give crystalline nitrosohalides.

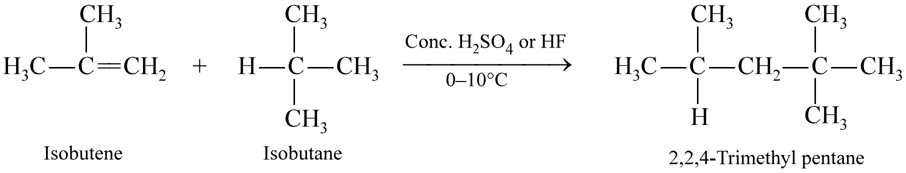
$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Nitrosyl halide}}{NO—X} \longrightarrow \underset{\text{Nitroso halide}}{R.CHX.CH_2NO}$$



$$\underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Nitrosyl bromide}}{NO—Br} \longrightarrow \overset{+}{C}H_2—CH_2.NO + \overset{-}{Br} \longrightarrow \underset{\text{Ethene nitroso bromide}}{CH_2.Br.CH_2NO}$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Nitrosyl chloride}}{NO—Cl} \longrightarrow \underset{\text{Intermediate carbocation}}{CH_3.\overset{+}{C}HCH_2NO} + Cl^- \longrightarrow \underset{\text{Propene nitroso chloride}}{CH_3CHClCH_2NO}$$

13. Addition of Alkanes to Alkenes (Alkylation): When 1 part of isobutane and 1 part of isobutene are allowed to react in presence of acid catalyst like HF, H_2SO_4, $AlCl_3$ etc. then alkylation of isobutene takes place to form 2,2,4-trimethylpentane. Alkane used for alkylation should have a tertiary hydrogen.

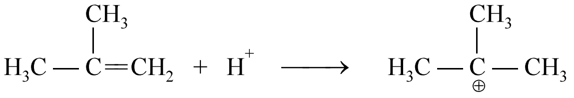


$$\underset{\text{Isobutene}}{H_3C—\overset{\overset{\Large CH_3}{|}}{C}{=}CH_2} + \underset{\text{Isobutane}}{H—\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_3} \xrightarrow[0–10°C]{\text{Conc. } H_2SO_4 \text{ or HF}} H_3C—\underset{\underset{\Large H}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_2—\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_3$$

2,2,4-Trimethyl pentane
(Iso-octane)

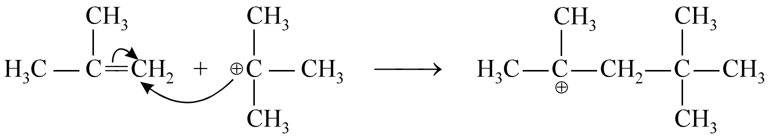
The alkylation is supposed to take place in 3 steps:

(i) Isobutene accepts a proton to provide *tert*-butyl carbocation:



$$H_3C—\overset{\overset{\Large CH_3}{|}}{C}{=}CH_2 + H^+ \longrightarrow H_3C—\underset{\oplus}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_3$$

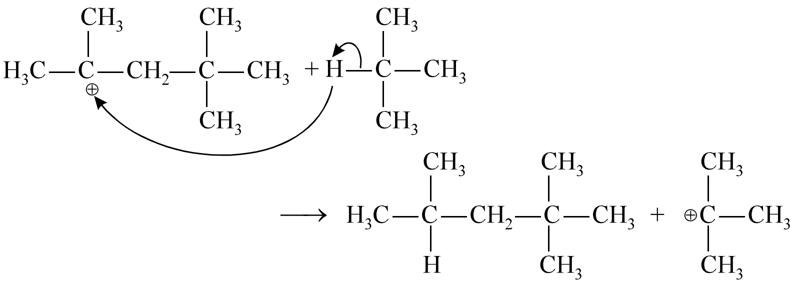
(ii) The carbocation goes to site of π electrons to add up to isobutene.



$$H_3C—\overset{\overset{\Large CH_3}{|}}{C}{=}CH_2 + \oplus\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_3 \longrightarrow H_3C—\underset{\oplus}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_2—\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}—CH_3$$

NOTES

(iii) The carbocation formed in step (*ii*) abstracts a hydride ion from isobutane.



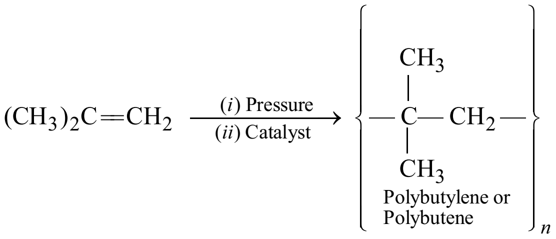
Iso-octane

The conditions of the reactions have to be controlled to avoid other reactions. Iso-octane is formed yielding *tert*-butyl carbocation to continue the chain reaction. 2,2,4-Trimethylpentane is a high grade gasoline and its efficiency as a fuel is used for rating other gasolines.

14. Self-Addition or Polymerization. Alkenes in the presence of acid catalysts and high temperature and pressure undergo self-addition (addition of one molecule to another alkene molecule) to give a new alkene. The product alkene has twice the molecular weight of initial alkene and is called a dimer. Addition of another alkene to this dimeric alkene can give a new trimeric alkene. The process can repeat itself to give a polymeric product (polymer) of high molecular weight. The process by which polymer is formed is known as polymerization.

$$\underset{\text{Ethene}}{CH_2{=}CH{-}H + CH_2{=}CH_2} \xrightarrow[(ii)\text{ Pressure, } (iii)\text{ Catalyst}]{(i)\text{ High temp.}} \underset{\text{Butene}}{CH_2{=}CH{-}CH_2{-}CH_3}$$

$$\xrightarrow{CH_2=CH_2} \underset{\text{Polyethylene or Polythene}}{(-CH_2-CH_2)_n}$$



$$(CH_3)_2C{=}CH_2 \xrightarrow[(ii)\text{ Catalyst}]{(i)\text{ Pressure}} \left\{ \underset{\text{Polybutylene or Polybutene}}{-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-} \right\}_n$$

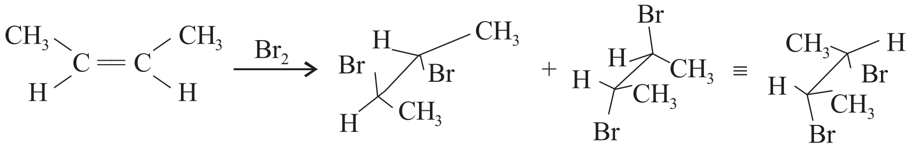
Polythene and polybutene are plastics of industrial importance.

Stereochemistry of Addition Reactions

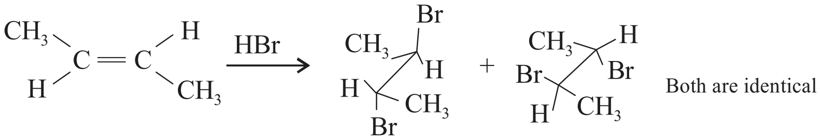
In a carbon-carbon double bond, since the carbon atoms are *sp*^{2} hybridized, all the six atomes (two carbon and four atoms attached to them) lie in one plane. During addition reactions, both the adding groups may come from the same side leading to *syn*- addition or from opposite side leading to *anti*- addition.

Let us take the case of 2-butene which exists as *cis*- and *trans*- isomers. Addition of bromine results in the formation of two asymmetric centres in the molecules. If *syn*- and *anti*- additions both take place randomly then the reaction is non-stereospecific. If the additions are only *syn*- or only *anti*- then we get one set of stereisomers from *cis*-2-butene and a different set of stereoisomers from *trans*-2-butene. Such reactions are called stereospecific.

In actual practice, addition of bromine to *cis*-2-butene gives a *dl*-mixture while addition of bromine to *trans*- 2-butene gives a meso compound suggesting that it is a stereospecific *anti*-addition



cis-2-Butene A mixture of *d*- and *l*-isomer



trans-2-Butene *meso*- isomer

(B) Oxidation Reactions

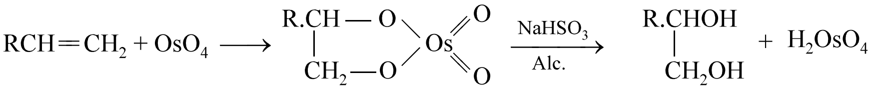
Alkenes undergo oxidation reactions readily with a wide variety of reagents to give different products depending upon the nature of oxidizing agent and the conditons of the reactions.

1. Oxidation with mild oxidizing agents: When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline potassium permanganate solution (Baeyer's reagent) at low temperatures, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of potassium permanganate solution is discharged during the reaction and so this reaction is used as a test for the unsaturation in molecules.

$$\underset{\text{Alkene}}{\text{R.CH}{=}\text{CH}_2} + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{Alk. KMnO}_4} \underset{\text{Glycol}}{\text{R.CHOH.CH}_2\text{OH}}$$

$$\text{CH}_3\text{.CH}{=}\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{Alk. KMnO}_4} \underset{\substack{\text{Propylene glycol or}\\ \text{Propene-1,2-diol}}}{\text{CH}_3\text{.CHOH.CH}_2\text{OH}}$$

Glycols are also formed when osmium tetraoxide is added to the olefin and then refluxed with alcoholic $NaHSO_3$ solution.

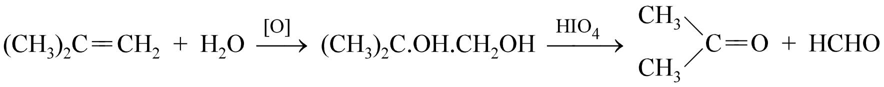


Alkene Osmate ester Glycol Osmic acid

In these addition reactions both the —OH groups are added to the same side of the double bond resulting in a *syn*- addition.

2. Oxidation with periodic acid or lead tetra acetate: These are moderately strong oxidizing agents and the oxidation of alkene first results in the formation of glycol which is subsequently oxidized to aldehydes or ketones.

$$\underset{\text{Alkene}}{\text{R.CH}{=}\text{CH}_2} + \text{H}_2\text{O} \xrightarrow[\text{(CH}_3\text{COO)}_4\text{Pb}]{\text{HIO}_4\text{ or}} \text{RCHOH.CH}_2\text{OH} \xrightarrow{\text{HIO}_4} \underset{\text{Aldehyde}}{\text{R.CHO}} + \underset{\text{Formaldehyde}}{\text{HCHO}}$$



$$\underset{\text{Isobutylene}}{(\text{CH}_3)_2\text{C}{=}\text{CH}_2} + \text{H}_2\text{O} \xrightarrow{[\text{O}]} \underset{\text{Glycol}}{(\text{CH}_3)_2\text{C.OH.CH}_2\text{OH}} \xrightarrow{\text{HIO}_4} \underset{\text{Acetone}}{(\text{CH}_3)_2\text{C}{=}\text{O}} + \text{HCHO}$$

The overall addition of two –OH groups occurs on opposite sides of the double bond leading to overall *anti*-addition.

3. Oxidation with acidic potassium permanganate or potassium dichromate: Alkenes when oxidized with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ first give glycols which are further oxidized to aldehydes, ketones and acids.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + H_2O \xrightarrow{O} \underset{\text{Glycol}}{R.CHOH.CH_2OH} \xrightarrow[KMnO_4]{Acid} \underset{\text{Aldehydes}}{R.CHO + HCHO}$$

$$\xrightarrow{KMnO_4} \underset{\text{Acids}}{HCOOH + RCOOH}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2O + O \xrightarrow[Acid]{KMnO_4} \underset{\text{Glycol}}{CH_3.CHOH.CH_2OH}$$

$$\xrightarrow{KMnO_4} \underset{\text{Acetaldehyde}}{CH_3.CHO} \quad + \quad \underset{\text{Formaldehyde}}{HCHO}$$

$$\Big\downarrow{\scriptstyle KMnO_4\,(acid)} \qquad\qquad \Big\downarrow$$

$$CH_3COOH$$

HCOOH

$$\underset{\text{Butene}}{(CH_3)_2C{=}CH_2} + H_2O + O \xrightarrow[K_2Cr_2O_7]{Acid} \underset{\text{Glycol}}{(CH_3)_2COH.CH_2OH}$$

$$\Big\downarrow{\scriptstyle Acid\ K_2Cr_2O_7}$$

$$CH_3CO.CH_3 + HCHO \xrightarrow{Acid\ K_2Cr_2O_7}$$

$$HCOOH$$

These oxidation reactions are used for locating the presence of the double bond by identifying the reaction products.

4. Combustion: Alkenes when burnt in air, are completely oxidised resulting in the formation of carbon dioxide and water.

$$C_nH_{2n} + \frac{3}{2}nO_2 \longrightarrow nCO_2 + nH_2O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

They form an explosive mixture with air or oxygen and burn with luminous flame.

(C) Isomerisation Reactions

When alkenes are heated in the presence of a catalyst or alone, they undergo isomerisation to form isomeric alkenes. The double bond generally shifts towards centrally located carbon atoms. In some cases hydrogen or alkyl groups migrate to form a branched chain alkene.

$$\underset{\text{1-Pentene}}{CH_3.CH_2.CH_2CH{=}CH_2} \xrightarrow[200\text{–}300°C]{Al_2(SO_4)_3} \underset{\text{2-Pentene}}{CH_3CH_2.CH{=}CH.CH_3}$$

$$\underset{\text{3-Methyl-1-butene}}{(CH_3)_2CH.CH{=}CH_2} \xrightarrow[200\text{–}300°C]{Al_2(SO_4)_3} \underset{\text{2-Methyl-2-butene}}{(CH_3)_2C{=}CH.CH_3}$$

$$\underset{\text{2-Butene}}{CH_3.CH{=}CHCH_3} \xrightarrow{Al_2(SO_4)_3} \underset{\text{2-Methyl-1-propene}}{(CH_3)_2C{=}CH_2}$$

(D) Substitution Reactions

The alkyl group of alkenes undergo substitution reactions at higher temperatures. Thus, when alkenes like ethene and propene are chlorinated at 500°C the double bond does not break up but hydrogen of alkyl group is substituted by chlorine, for example:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{500°C} CH_2{=}CHCl$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + Cl_2 \xrightarrow{500°C} \underset{\text{Allyl chloride}}{CH_2{=}CH{—}CH_2Cl} + HCl$$

The substitution reactions proceed by a free radical mechanism and is similar to substitution of alkanes. If the alkyl group contains more than one carbon atom, even then the substitution occurs at the carbon α- to the double bond or at allylic carbon atom.

$$\underset{\text{1-Butene}}{CH_3.CH_2.CH{=}CH_2} + Cl_2 \xrightarrow{500°C} \underset{\text{3-Chloro-1-butene}}{CH_3.CHCl.CH{=}CH_2}$$

Detection of Carbon to Carbon Double Bond

Most of the tests used for detecting the presence of a $>C{=}C<$ are also shown by compounds having a triple bond. Therefore, these are actually the tests of unsaturation which may be due to a double or triple bond.

- **Baeyer's Test:** To the aqueous solution of the compound, a few drops of 1% $KMnO_4$ solution in water, made alkaline with Na_2CO_3 (Baeyer's reagent), are added. The pink colour of the solution disappears on shaking and a brown precipitate (due to MnO_2) appears, indicating the presence of unsaturation in the molecule.
- **Addition of Bromine:** The compound is dissolved in carbon tetrachloride or chloroform and then a few drops of 5% bromine solution in carbon tetrachloride are added to it; declourisation of bromine indicates that the compound is unsaturated.

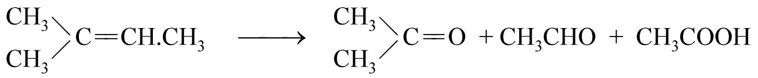
A positive Baeyer's test is also answered by compounds like aldehydes or primary and secondary alcohols which are quickly oxidised. On the other hand, alkenes without any hydrogen atom on the carbon forming the double bond fail to respond to this test, *e.g.*, $(CH_3)_2C{=}C(CH_3)_2$ does not give the above tests.

Location of a Double Bond

It has been seen that alkene molecules on oxidative cleavage and on ozonolysis split up at the site of the double bond. The aldehydes, ketones and acids so obtained are isolated and purified. The identification of these products gives an idea of the position of the double bond in the molecule. Thus if acetaldehyde and formaldehyde are obtained on ozonolysis or oxidation, then the double bond may be considered to be present between two carbon atoms on one side and one carbon on the other as shown below:

$$CH_3CHO \;+\; H.CHO \text{ are obtained from } CH_3CH{=}CH_2$$

Similarly formation of acetone, acetaldehyde and acetic acid might result from the cleavage of the double bond placed between three carbon (isopropyl type) and two carbon atoms. Acids may be considered to be derived from aldehydes by oxidation.



$$(CH_3)_2C{=}CH.CH_3 \longrightarrow (CH_3)_2C{=}O + CH_3CHO + CH_3COOH$$

3.2.2 Alkynes

Besides dienes there is another class of unsaturated hydrocarbons which contain four hydrogen atoms less than corresponding alkanes and are represented by the general formula C_nH_{2n-2}. This class of the compounds is known as Alkynes and has a carbon-carbon triple bond as its characteristic and distinguishing feature. Thus, they contain a functional group different from the alkenes and constitute a homologous series. The first member of the alkyne series has the formula C_2H_2 and is known as acetylene. The alkynes are therefore also known by the general name Acetylenes. The triple bond implies the sharing of three pairs of electrons between two carbon atoms and is often called as the Acetylenic or Alkynic linkage.

The nature of a carbon-carbon triple bond is essentially similar to that of a double bond. However, the difference lies in the hybridization state of carbon, which is *sp* in alkynes, and the availability of two unhybridized *p* orbitals at right angles to each other and to the plane of carbon atoms, giving two π bonds between *sp* hybridized carbon atoms. Thus the linear carbon skeleton of alkynes is enclosed in a cylindrical π electron cloud. The total bond strength of a triple bond is 196 kcal which is more than the bond strength of single or double bonds yet the alkynes are highly reactive because of their tendency to acquire less strained configuration. The length of a carbon-carbon triple bond is still shorter (being only 1.20 Å) than that of a double bond. The free rotation of carbon atoms around triple bond is highly restricted as in the case of alkenes but alkynes do not exhibit geometrical isomerism due to the linearity of the molecule around the triple bond.

Nomenclature

There are three systems for naming alkynes, which are as follows:

1. The Common name System: The common name of the first member of the series (C_2H_2) is acetylene. This name has been adopted even in IUPAC system. The common names of the alkynes do not bear any relationship and are based on the names of related compounds, for example,

Formula	*Common name*
$C_2H_2(CH{\equiv}CH)$	Acetylene
$C_3H_4(CH_3.C{\equiv}CH)$	Allylene
$C_4H_6(CH_3.C{\equiv}C.CH_3)$	Crotonylene.

However, except acetylene other names are no longer used.

2. Acetylene Derivative System: Acetylene is considered to be the parent member of the alkynes series and all other alkynes are named as alkyl derivatives of acetylene. for example;

Formula	*Derived name*
$CH\equiv CH$	Acetylene
$CH_3.C\equiv CH$	Methylacetylene
$CH_3.CH_2.C\equiv CH$	Ethylacetylene
$CH_3.C\equiv C.CH_3$	Dimethylacetylene
$CH_3.C\equiv C.C_2H_5$	Ethylmethyl acetylene

3. The IUPAC system. In this system of nomenclature the ending 'ane' of the corresponding alkane is dropped and 'yne' is added as suffix which also indicates the presence of a triple bond. If the triple bond can take up more than one position in the molecule, the carbon chain is numbered in such a way so as to assign minimum number to carbon atom preceding the triple bond. Some IUPAC names are given For example,

Formula of alkyne	*IUPAC name of corresponding alkane*	*IUPAC name of alkyne*
$CH\equiv CH$	C_2H_6 Ethane	Ethyne
$CH_3.C\equiv CH$	C_3H_8 Propane	Propyne
$\overset{4}{C}H_3.\overset{3}{C}\equiv\overset{2}{C}.\overset{1}{C}H_3$	C_4H_{10} Butane	2-Butyne
$\overset{4}{C}H_3.\overset{3}{C}H_2.\overset{2}{C}\equiv\overset{1}{C}H$	C_4H_{10} Butane	1-Butyne
$\overset{5}{C}H_3.\overset{4}{C}H_2.\overset{3}{C}\equiv\overset{2}{C}.\overset{1}{C}H_3$	C_5H_{12} Pentane	2-Pentyne
$\overset{5}{C}H_3.\overset{4}{C}H_2.\overset{3}{C}H_2.\overset{2}{C}\equiv\overset{1}{C}H$	C_5H_{12} Pentane	1-Pentyne
$\overset{4}{C}H_3.\underset{\overset{\vert}{CH_3}}{\overset{3}{C}H}.\overset{2}{C}\equiv\overset{1}{C}H$	C_5H_{12} 2-Methylbutane	3-Methyl-1-butyne

The monovalent radicals obtained by the removal of one hydrogen of alkynes are known as Alkynyl radicals and their names are obtained by replacing '*e*' of corresponding alkyne by '*yl*'. For example,

$HC\equiv C-$	Ethynyl	$CH\equiv C.CH_2-$	2-Propynyl
$CH_3.C\equiv C-$	Propynyl	$CH\equiv C.\underset{\overset{\vert}{CH_3}}{CH}-$	2-(1-Methyl)-propynyl
$C_2H_5.C\equiv C-$	Butynyl		

If the molecule contains more than one triple bond the suffix '*ane*' of the alkanes is replaced by '*adiyne*', '*atriyne*' etc., depending on the number of triple bonds. Compounds having many triple bonds are known as 'Alkapolyenes'. The positions of triple bonds are indicated by the number of carbon atoms preceding these bonds. For example,

$\overset{4}{H}C\equiv\overset{3}{C}-\overset{2}{C}\equiv\overset{1}{C}H$

1,3-Butadiyne (Diacetylene)

$\overset{6}{C}H\equiv\overset{5}{C}.\overset{4}{C}H_2.\overset{3}{C}H_2.\overset{2}{C}\equiv\overset{1}{C}H$

1,5-Hexadiyne (Dipropargyl)

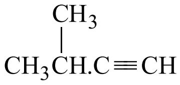
Isomerism

Ethyne, and propyne do not exhibit any type of isomerism. Other alkynes exhibit various types of isomerism.

1. Chain Isomerism: It is due to difference in the type of carbon skeleton or chain. For example C_5H_8 is represented by two formulae which are chain isomers:

$CH_3.CH_2.CH_2.C\equiv CH$

1-Pentyne (Straight chain)



$$\overset{\displaystyle CH_3}{\underset{}{|}}\hspace{-1.5em}\;CH_3\overset{CH_3}{\overset{|}{C}}H.C\equiv CH$$

3-Methyl-1-butyne (Branched chain)

2. Position Isomerism: Butyne, pentyne etc., exhibit isomerism due to the various structures which may be written by changing the position of the triple bond, for example,

$CH_3.CH_2.C\equiv CH$ 1-Butyne

$CH_3.C\equiv C.CH_3$ 2-Butyne

$CH_3.CH_2.CH_2C\equiv CH$ 1-Pentyne

$CH_3.CH_2.C\equiv C.CH_3$ 2-Pentyne

3. Functional Isomerism: Alkynes are isomeric with dienes. Thus C_4H_6 represents butyne and butadiene.

$CH_3.CH_2.C\equiv CH$ 1-Butyne

$CH_2=CH.CH=CH_2$ 1,3-Butadiene

All these isomers are known. However, alkynes do not exhibit geometrical isomerism because of linearity of the molecule around the triple bond.

Butyne exists in two isomeric forms: 1-Butyne and 2-Butyne. Pentyne exists in three isomeric forms: 1-Pentyne, 2-Pentyne and 3-Methyl-1-butyne.

Occurrence of Alkynes

Alkynes or acetylenes do not occur in nature in the free state because of their high reactivity. However, they are produced by combustion of coal and decomposition of organic matter. Traces of acetylene are present in coal gas and in gases produced by the decomposition of compounds like hydrocarbons and alcohols in the absence of air. Large amounts of alkynes, particularly acetylene, are obtained by cracking of various fractions of petroleum.

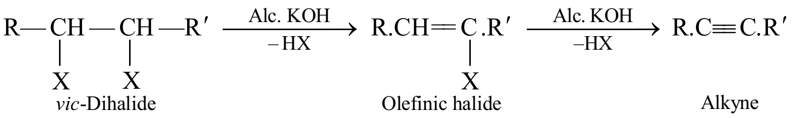
General Methods of Preparation

The general methods of formation of a triple bond in the molecule are essentially similar to those employed for the preparation of alkenes. The simplest alkyne *i.e.*, acetylene or ethyne, is conveniently obtained by the action of water on calcium carbide, and can be used as starting material for the formation of higher alkynes. The important general methods of formation are as follows:

1. Dehydrohalogenation of Dihaloalkanes: When dihaloalkanes are treated with excess of alcoholic potassium hydroxide alkynes are formed by the elimination of two moles of halogen acids. Dihaloalkanes or alkyl dihalides may have two halogens attached at the same carbon (*gem*-dihalides) or at adjacent carbon atoms (*vic*-dihalides). However, both these types of dihaloalkanes yield alkynes on treatment with strong bases. Besides alcoholic potash, sodamide may also be used for dehydrohalogenation.

(i) From vic-Dihalides

The *vic*-dihalides on treatment with alcoholic KOH or sodamide give alkynes. The reaction occurs in two stages: first an olefinic halide is formed which on subsequent elimination of a mole of hydrogen halide yields an alkyne.



$$\underset{vic\text{-Dihalide}}{\mathrm{R{-}\underset{|\atop X}{CH}{-}\underset{|\atop X}{CH}{-}R'}} \xrightarrow[-\mathrm{HX}]{\text{Alc. KOH}} \underset{\text{Olefinic halide}}{\mathrm{R.CH{=}\underset{|\atop X}{C}.R'}} \xrightarrow[-\mathrm{HX}]{\text{Alc. KOH}} \underset{\text{Alkyne}}{\mathrm{R.C{\equiv}C.R'}}$$

$$\underset{\text{Ethylene bromide}}{\mathrm{CH_2Br.CH_2Br}} \xrightarrow[-\mathrm{HBr}]{\text{Alc. KOH}} \underset{\text{Vinyl bromide}}{\mathrm{CH_2{=}CH.Br}} \xrightarrow[-\mathrm{HBr}]{\text{Alc. KOH}} \underset{\text{Acetylene or Ethyne}}{\mathrm{CH{\equiv}CH}}$$

$$\underset{\text{1,2-Dibromopropane}}{\mathrm{CH_3.CHBr.CH_2Br}} \xrightarrow[-\mathrm{HBr}]{\text{Alc. KOH}} \underset{\text{1-Bromo-1-propene}}{\mathrm{CH_3.CH{=}CH.Br}} \xrightarrow[-\mathrm{HBr}]{\mathrm{NaNH_2}} \underset{\text{Propyne}}{\mathrm{CH_3.C{\equiv}CH}}$$

(ii) From gem-Dihalides

The reaction of *gem*-dihalides with strong bases like alcoholic potash, is similar to that of *vic*-dihaloalkanes and gives alkynes.

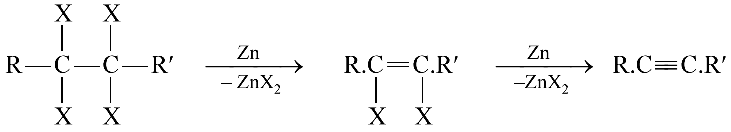
$$\underset{gem\text{-Dihalide}}{\mathrm{R.CH_2.CHX_2}} \xrightarrow[-\mathrm{HX}]{\text{Alc. KOH}} \underset{\text{Haloalkene}}{\mathrm{RCH{=}CH.X}} \xrightarrow[-\mathrm{HX}]{\text{Alc. KOH}} \underset{\text{Alkyne}}{\mathrm{R.C{\equiv}CH}}$$

$$\underset{\text{Ethylidene bromide}}{\mathrm{CH_3.CHBr_2}} \xrightarrow[-\mathrm{HBr}]{\text{Alc. KOH}} \underset{\text{Vinyl bromide}}{\mathrm{CH_2{=}CH.Br}} \xrightarrow[-\mathrm{HBr}]{\text{Alc. KOH}} \underset{\text{Acetylene}}{\mathrm{CH{\equiv}CH}}$$

$$\underset{\text{2,2-Dibromopropane}}{\mathrm{CH_3.CHBr_2.CH_3}} \xrightarrow[-2\mathrm{HBr}]{\text{Alc. KOH}} \underset{\text{Propyne}}{\mathrm{CH_3.C{\equiv}CH}}$$

As both *vic*- and *gem*-dihalides are readily obtained by the treatment of alkenes with halogen and of aldehydes or ketones with phosphorus pentachloride respectively; the dehydrohalogenation constitutes an important method of the formation of alkynes.

2. Dehalogenation of Tetrahalides: Tetrahaloalkanes, in which the four halogens are attached to two adjoining carbon atoms, on treatment with active metals like zinc, magnesium etc., form alkynes.



$$\mathrm{R{-}\overset{X\atop |}{\underset{|\atop X}{C}}{-}\overset{X\atop |}{\underset{|\atop X}{C}}{-}R'} \xrightarrow[-\mathrm{ZnX_2}]{\mathrm{Zn}} \mathrm{R.\underset{|\atop X}{C}{=}\underset{|\atop X}{C}.R'} \xrightarrow[-\mathrm{ZnX_2}]{\mathrm{Zn}} \mathrm{R.C{\equiv}C.R'}$$

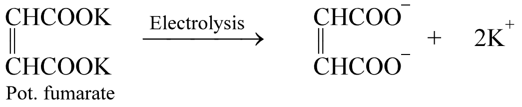
$$\underset{\text{1,1,2,2-Tetrabromoethane}}{\mathrm{CHBr_2.CHBr_2}} + 2\mathrm{Zn} \longrightarrow \mathrm{CH{\equiv}CH} + 2\mathrm{ZnBr_2}$$

$$\mathrm{CH_3.CBr_2.CHBr_2} + 2\mathrm{Zn} \longrightarrow \mathrm{CH_3.C{\equiv}CH} + 2\mathrm{ZnBr_2}$$

The method is used mainly for the purification of alkynes or protection of a triple bond as the tetrahaloalkanes are themselves obtained from alkynes.

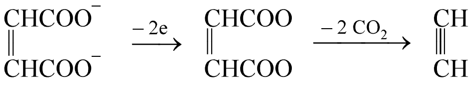
NOTES

3. Electrolysis of Salts of Unsaturated Dicarboxylic Acids: Extension of Kolbe's electrolytic method to suitable unsaturated dicarboxylic acids produces alkynes. Potassium fumarate on electrolysis gives ethyne.



$$\underset{\text{Pot. fumarate}}{\begin{array}{l}\text{CHCOOK}\\ \|\\ \text{CHCOOK}\end{array}} \xrightarrow{\text{Electrolysis}} \begin{array}{l}\text{CHCOO}^-\\ \|\\ \text{CHCOO}^-\end{array} + 2\text{K}^+$$

At anode



$$\begin{array}{l}\text{CHCOO}^-\\ \|\\ \text{CHCOO}^-\end{array} \xrightarrow{-2e} \begin{array}{l}\text{CHCOO}\\ \|\\ \text{CHCOO}\end{array} \xrightarrow{-2\,CO_2} \begin{array}{l}\text{CH}\\ |||\\ \text{CH}\end{array}$$

At cathode

$$2H_2O + 2e^{\ominus} \longrightarrow 2OH^- + H_2$$

$$K^+ + OH^- \longrightarrow KOH$$

or

$$2K^+ \xrightarrow{2e} 2K \xrightarrow{H_2O} 2KOH + H_2$$

4. Hydrolysis of Alkynides: Metallic derivatives of alkynes are known as alkynides or acetylides. When these are treated with water or dilute acids, alkynes are formed due to the hydrolysis of alkynides. For example,

$$\underset{\substack{\text{Silver ethynide}\\ \text{or}\\ \text{Silver acetylide}}}{CH\equiv C.Ag} + H_2O \xrightarrow{H^+} CH\equiv CH + AgOH$$

$$\underset{\text{Sodium propynide}}{CH_3.C\equiv C.Na} + H_2O \longrightarrow \underset{\text{Propyne}}{CH_3C\equiv CH} + NaOH$$

5. Alkylation of Acetylene: Higher alkynes may be obtained by the alkylation of ethyne or acetylene. The acetylene is first converted to mono or disodium acetylide by treatment with sodium metal or sodamide in liquid ammonia, and acetylide is then treated with primary (1°) alkyl halides to obtain higher alkyne.

$$CH\equiv CH \xrightarrow[\text{or } NaNH_2/NH_3]{Na/NH_3} \underset{\text{Sod. acetylide}}{CH\equiv C^-:Na^+} \xrightarrow[-NaBr]{CH_3Br} CH_3.C\equiv CH$$

$$CH\equiv CH \xrightarrow[NH_3]{2NaNH_2} \underset{\substack{\text{Disodium}\\ \text{acetylide}}}{\overset{+}{Na}:\overset{-}{C}\equiv C^-:Na^+} \xrightarrow[-2NaBr]{2CH_3Br} \underset{\text{2-Butyne}}{CH_3C\equiv C.CH_3}$$

$$CH_3.C\equiv CH \xrightarrow{NaNH_2/NH_3} CH_3C\equiv C.Na \xrightarrow[-NaBr]{C_2H_5Br} \underset{\text{2-Pentyne}}{CH_3C\equiv C.C_2H_5}$$

6. Decarboxylation of Acetylenic acids. Decarboxylation (heating with soda lime) of acids containing a triple bond gives alkynes. For example, tetrolic acid yields propyne.

$$\underset{\text{Tetrolic acid}}{CH_3.C\equiv C.COOH} \xrightarrow{NaOH} CH_3.C\equiv C.COONa \xrightarrow{NaOH(CaO)} \underset{\text{Propyne}}{CH_3.C\equiv CH} + Na_2CO_3$$

General Physical Characteristics

- Alkynes have physical characteristics similar to alkenes and alkanes but are generally less volatile than the corresponding alkenes or alkanes.
- Lower alkynes upto four carbon atoms are gases, those containing five to thirteen carbon atoms are liquids and higher alkynes are solids. Alkynes are colourless compounds and except for acetylene, which has garlic odour, other members are odourless.

- The boiling points, melting points, heats of combustion and specific gravities of alkynes show a regular increase with increasing molecular weight. The physical constants of a few alkynes are listed in Table 3.4.

Table 3.4 *Physical Constants of Alkynes*

Sl. No.	*Name*	*Formula*	*B.P., °C*	*M.P., °C*	*Sp.Gr. at 20°C*	*Heat of combustion ΔH (kcal)*
1.	Acetylene or Ethyne	$CH \equiv CH$	– 84	– 81	—	310.6
2.	Propyne	$CH_3.C \equiv CH$	–23.2	– 103	—	463.1
3.	1-Butyne	$CH_3.CH_2.C \equiv CH$	8.1	– 126	0.650	620.6
4.	2-Butyne	$CH_3.C \equiv C.CH_3$	27.0	– 32	0.691	620.6
5.	1-Pentyne	$CH_3.(CH_2)_2.C \equiv CH$	40.2	– 106	0.690	778.0
6.	2-Pentyne	$CH_3.CH_2C \equiv C.CH_3$	56.0	– 109	0.711	774.3
7.	3-Methyl 1-butyne	$(CH_3)_2.CH.C \equiv CH$	29.0	—	0.665	—
8.	1-Hexyne	$CH_3(CH_2)_3.C \equiv CH$	71.5	–132	0.716	935.5
9.	2-Hexyne	$CH_3(CH_2)_2.C \equiv C.CH_3$	84.0	–88	0.732	935.5
10.	3-Hexyne	$CH_3.CH_2.C \equiv C.CH_2.CH_3$	81.7	–105	0.724	935.5
11.	1-Heptyne	$CH_3.(CH_2)_4.C \equiv CH$	99.7	–81	0.733	1092.9
12.	1-Octyne	$CH_3.(CH_2)_5.C \equiv CH$	126.2	–79	0.746	1250.3
13.	1-Nonyne	$CH_3.(CH_2)_6.C \equiv CH$	150.8	–50	0.757	1407.8
14.	1-Decyne	$CH_3.(CH_2)_7.C \equiv CH$	174.0	–44	0.766	1565.2

They are sparingly soluble in water but readily soluble in organic solvents such as a alcohol, acetone and benzene. Lower alkynes produce general anaesthesia, when inhaled in large amounts.

Spectroscopic Properties

In the UV spectroscopy alkynes absorb strongly below 2000 Å (200 mμ) like alkenes. The absorption between 170 to 196 mμ is generally attributed to the presence of a triple bond or multiple bond. However, if the triple bond is conjugated then the absorption shifts to higher wavelength.

Symmetrical alkynes like acetylene do not absorb in IR region. Mono-substituted alkynes show strong carbon-carbon triple bond stretching absorption in the region 2140 to 2100 cm^{-1} and a carbon-hydrogen stretching for hydrogens attached to a triply bonded carbon near 3300 cm^{-1}.

In the NMR spectra, chemical shift of acetylenic protons appears to have an anomalous value because the absorption peak appears around 2.36 τ, *i.e.,* at much higher magnetic field as compared to ethylenic or vinyl protons. This is because of large polarizability of π electrons resulting in shielding of acetylenic protons.

General Chemical Characteristics

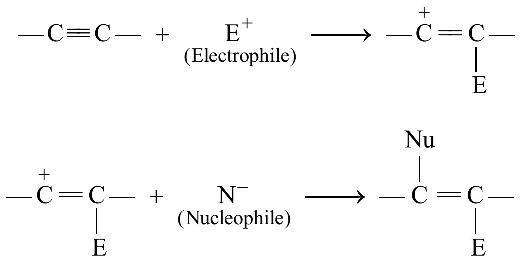
Alkynes behave in a manner similar to typical alkenes. In fact in some reactions they behave as unsaturated compounds with two double bonds. They are also highly reactive like alkenes presumably because of their tendency to release the strain by forming less unsaturated or fully saturated compounds. Because of the presence of two π bonds and thus of π electrons, the most important reactions of alkynes are electrophilic addition reactions. However, they are more readily attacked by nucleophiles than alkenes.

The molecules of alkynes are made up of a triple bond between carbon atoms and hydrogen(s) and/or alkyl group(s) attached to triple bonded carbons. The alkyl group attached to a carbon involved in triple bond formation is generally unreactive or inert. Thus alkynes show the reactions of a triple bond and of the hydrogens attached to triply bonded carbon atoms.

(A) Addition Reactions

Alkynes undergo addition reactions like alkenes but add two molecules of the reagent or addendum instead of one; the addition occurring in two stages.

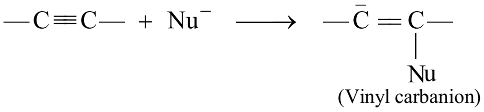
Electrophilic addition reactions in alkynes involve attack by the electrophile in the same way as in alkenes but they involve the change of the two π bonds one after the other to σ bonds



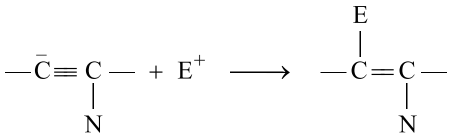
$$\text{(i)}\quad —C\equiv C— + \underset{\text{(Electrophile)}}{E^{+}} \longrightarrow —\overset{+}{C}=\underset{\underset{E}{|}}{C}—$$

$$\text{(ii)}\quad —\overset{+}{C}=\underset{\underset{E}{|}}{C}— + \underset{\text{(Nucleophile)}}{N^{-}} \longrightarrow —\overset{\overset{Nu}{|}}{C}=\underset{\underset{E}{|}}{C}—$$

The above steps then repeat themselves to remove another π bond. The two π bonds in alkynes are thus converted to s bonds during addition. Addition of hydrogen, halogens, halogen acids, water, hypohalous acids etc., are example of electrophilic addition reactions. Nucleophilic additions are also observed in case of alkynes because alkynes are more susceptible to nucleophilic attack than double bonds. Hence, certain reactions of alkynes are nucleophilic addition reactions. This is so because of the greater stability of vinyl carbanion.



$$—C\equiv C— + Nu^{-} \longrightarrow —\bar{C}=\underset{\underset{\substack{Nu\\ \text{(Vinyl carbanion)}}}{|}}{C}—$$



$$—\bar{C}\equiv \underset{\underset{N}{|}}{C}— + E^{+} \longrightarrow —\overset{\overset{E}{|}}{C}=\underset{\underset{N}{|}}{C}—$$

Many vinyl derivatives are obtained by nucleophilic addition reaction. However, further reaction is again possible for removal of the second π bond. Addition of acids, alcohol, thioalcohols, hydrogen cyanide, ammonia etc., take place by nucleophilic addition mechanism.

NOTES

1. Addition of Hydrogen: Alkynes combine with hydrogen gas in presence of suitable catalysts like finely divided Ni, Pt or Pd. Initially alkenes are formed which then take up another molecule of hydrogen to form alkanes.

$$\underset{\text{Alkyne}}{R.C\equiv CH} \xrightarrow[\Delta]{H_2/Ni} \underset{\text{Alkene}}{R.CH=CH_2} \xrightarrow{H_2/Ni} \underset{\text{Alkane}}{R.CH_2.CH_3}$$

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{H_2\,/\,Ni} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[\Delta]{H_2/Ni} \underset{\text{Ethane}}{CH_3.CH_3}$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow[\Delta]{2H_2/Pt} \underset{\text{Propane}}{CH_3.CH_2CH_2}$$

If the Lindlar's catalyst (Palladium partially inactivated with traces of heavy metals salts or quinoline) is used, the hydrogenation does not proceed beyond the alkene stage. Thus:

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow{H_2/\text{Lindlar's catalyst}} \underset{\text{Propene}}{CH_3.CH=CH_2}$$

Catalytic hydrogenation in presence of Lindlar's catalyst of disubstituted acetylenes gives *cis*-alkenes.

2. Addition of Halogens: One or two molecules of gaseous halogens can be added to alkynes giving dihalides and tetrahalides respectively chlorine and bromine add readily to the triple bond, while iodine reacts rather slowly. The reaction is catalysed by light or metallic halides.

$$\underset{\text{Alkyne}}{R.C\equiv CH} + X_2 \longrightarrow \underset{\text{Dihaloalkene}}{R.CX=CHX} \xrightarrow{X_2} \underset{\text{Tetrahaloalkane}}{R.CX_2CHX_2}$$

$$\underset{\text{Acetylene}}{CH\equiv CH} + Cl_2 \longrightarrow \underset{\text{1,2-Dichloroethene}}{CHCl=CHCl} \xrightarrow{Cl_2} \underset{\substack{\text{1,1,2,2-Tetrachloroethane}\\ \text{or Acetylene tetrachloride}}}{CHCl_2CHCl_2}$$

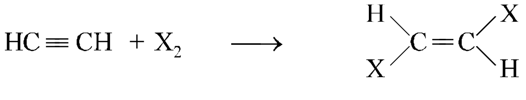
Acetylene reacts with dilute bromine water to form dibromide but with liquid bromine and in absence of solvent tetrabromide is formed. With propyne reaction is similar.

$$\underset{\text{Propyne}}{CH_3.C\equiv CH} + Br_2 \longrightarrow \underset{\text{1,2-Dibromo-propene-1}}{CH_3Br.C=CH\,Br} \xrightarrow{Br_2} \underset{\text{1,1,2,2-Tetrabromo-propane}}{CH_3.CBr_2.CHBr_2}$$

Acetylene adds on iodine with difficulty but if reaction is carried out in ethanolic solution acetylene di-iodide is obtained.

$$\underset{\text{Acetylene}}{CH\equiv CH} + I_2 \xrightarrow{C_2H_5OH} \underset{\text{1,2-Di-iodethene}}{CHI=CHI}$$

The alkenes formed by the addition of halogen to alkynes are, generally *trans*-isomers because the addition is stereoselective.



3. Addition of Halogen acids: The addition of halogen acids and other unsymmetrical reagents to alkynes occur in accordance with Markovnikov's rule. Addition of one molecule of halogen acid gives an unsaturated halide, which then adds another molecule of hydrogen halide to form dihaloalkane. The addition of the halogen acids can take place in the dark but is catalysed by light or metallic halides.

$$\underset{\text{Alkyne}}{\mathrm{R.C{\equiv}CH}} + \mathrm{HX} \longrightarrow \underset{\text{Haloalkene}}{\mathrm{R.CX{=}CH_2}} \xrightarrow{\mathrm{HX}} \underset{\text{Dihaloalkanes}}{\mathrm{R.CX_2CH_3}}$$

$$\underset{\text{Ethyne}}{\mathrm{CH{\equiv}CH}} + \mathrm{HCl} \longrightarrow \underset{\substack{\text{1-Chloroethene}\\ \text{or Vinyl chloride}}}{\mathrm{CH_2{=}CH.Cl}} \xrightarrow{\mathrm{HCl}} \underset{\substack{\text{1,1-Dichloroethane}\\ \text{or Ethylidene chloride}}}{\mathrm{CH_3.CHCl_2}}$$

When acetylene is passed in dilute hydrochloric acid at 65°C in presence of Hg^{2+} as catalyst vinyl chloride is formed.

$$\mathrm{CH{\equiv}CH + HCl} \xrightarrow{\mathrm{Hg^{2+}}} \mathrm{CH_2{=}CHCl}$$

$$\underset{\text{Propyne}}{\mathrm{CH_3.C{\equiv}CH}} + \mathrm{HBr} \longrightarrow \underset{\text{2-Bromopropene}}{\mathrm{CH_3.CBr{=}CH_2}} \xrightarrow{\mathrm{HBr}} \underset{\text{2,2-Dibromopropane}}{\mathrm{CH_3.CBr_2CH_3}}$$

In presence of peroxides *anti*-Markownikov product is obtained.

$$\underset{\text{Propyne}}{\mathrm{CH_3.C{\equiv}CH}} + \mathrm{HBr} \xrightarrow{\text{Peroxide}} \underset{\text{1-Bromopropene}}{\mathrm{CH_3.CH{=}CHBr}} \xrightarrow{\mathrm{HBr}} \underset{\text{1,2-Dibromopropane}}{\mathrm{CH_3.CHBr.CH_2Br}}$$

The order of reactivity of the halogen acids is HI > HBr > HCl > HF.

4. Addition of Hypohalous Acids. Alkynes when passed in hypochlorous or hypobromous acids yield, haloaldehyde or haloketones. With acetylene dichloroacetaldehyde formed is partially oxidised to dichloroacetic acid by hypochlorous acid.

$$\mathrm{R.C{\equiv}CH} \xrightarrow{\mathrm{HOX}} \mathrm{R(OH)C{=}CHX} \xrightarrow{\mathrm{HOX}} \mathrm{R.(OH)_2C.CHX_2} \xrightarrow{-\mathrm{H_2O}} \underset{\alpha\text{-Dihaloketone}}{\mathrm{R.CO.CHX_2}}$$

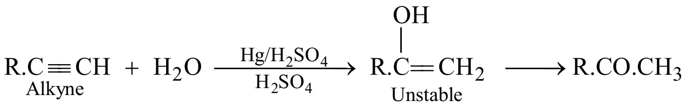
$$\begin{aligned} \mathrm{CH{\equiv}CH + HOCl} &\longrightarrow \mathrm{HO{-}CH{=}CH.Cl} \xrightarrow{\mathrm{HO.Cl}} \mathrm{(HO)_2CH.CHCl_2} \\ &\xrightarrow{-\mathrm{H_2O}} \underset{\text{Dichloroacetaldehyde}}{\mathrm{CHCl_2.CHO}} \end{aligned}$$

$$\begin{aligned} \mathrm{CH_3.C{\equiv}CH + HOBr} &\longrightarrow \mathrm{CH_3.(OH)C{=}CHBr} \xrightarrow{\mathrm{HO.Br}} \mathrm{CH_3.(HO)_2C.CHBr_2} \\ &\xrightarrow{-\mathrm{H_2O}} \underset{\text{1,1-Dibromoacetone}}{\mathrm{CH_3CO.CHBr_2}} \end{aligned}$$

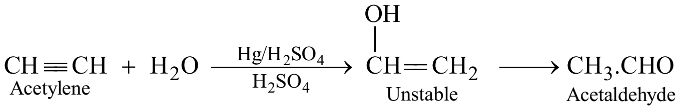
The addition occurs according to Markownikov's rule and gives a dihydroxy-dihaloalkane, which is unstable because of the two hydroxyl groups attached to same carbon atom and hence elimination of a molecule of water takes place. Addition of halogen, halogen acids and hypohalous acid are electrophilic addition reaction.

5. Addition of Water: Alkyne molecule adds one molecule of water in presence of sulphuric acid and mercurous sulphate (or mercury-mercuric sulphate mixture) to yield carbonyl compounds unlike alkenes. The addition of water to alkyne initially yields a hydroxy alkene in which hydroxyl group is on doubly bonded carbon atom (structure known as *Enolic* form or *Enol*). These simple enols immediately rearrange to form a more stable carbonyl or *Keto* form.

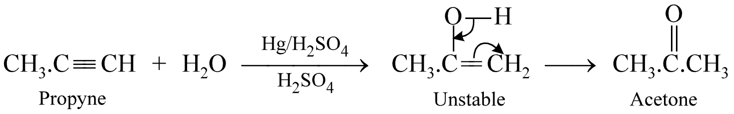
NOTES



$$\underset{\text{Alkyne}}{R.C{\equiv}CH} + H_2O \xrightarrow[H_2SO_4]{Hg/H_2SO_4} \underset{\text{Unstable}}{R.\overset{\overset{\large OH}{|}}{C}{=}CH_2} \longrightarrow R.CO.CH_3$$



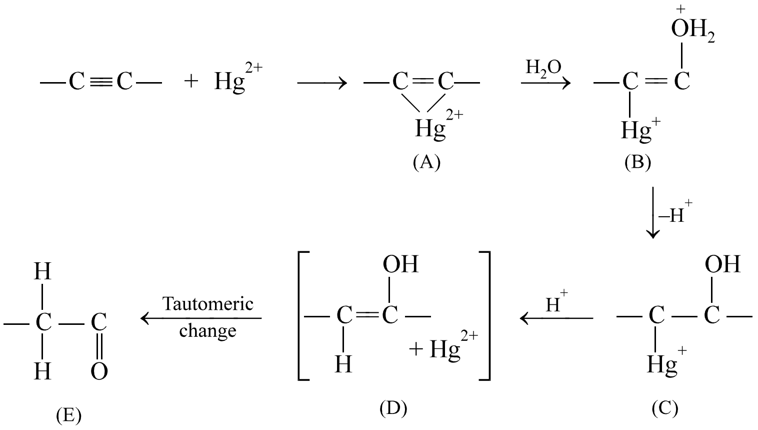
$$\underset{\text{Acetylene}}{CH{\equiv}CH} + H_2O \xrightarrow[H_2SO_4]{Hg/H_2SO_4} \underset{\text{Unstable}}{\overset{\overset{\large OH}{|}}{CH}{=}CH_2} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO}$$



$$\underset{\text{Propyne}}{CH_3.C{\equiv}CH} + H_2O \xrightarrow[H_2SO_4]{Hg/H_2SO_4} \underset{\text{Unstable}}{CH_3.\overset{\overset{\large O-H}{|}}{C}{=}CH_2} \longrightarrow \underset{\text{Acetone}}{CH_3.\overset{\overset{\large O}{\|}}{C}.CH_3}$$

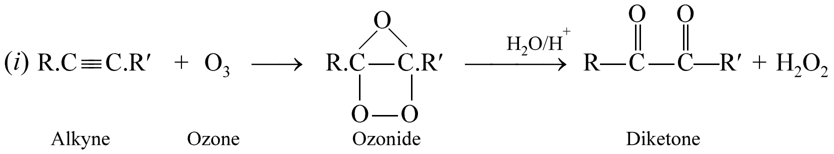
The reaction is used industrially for the preparation of aldehydes and ketones.

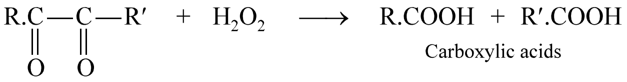
The first step in the mechanism is the formation of the complex (A) involving Hg^{2+}. Water then attacks the complex (A) in S_N2 type process to give the intermediate (B) which forms (C) losing a proton. Hydrolysis of (C) gives (D) which after a tautomeric change forms (E) the carbonyl compound.



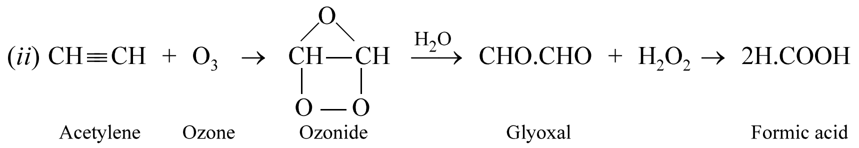
Since the addition follows Markovnikov's rule only acetylene will give an aldehyde, all other homologues will give ketone. With alkynes of the type of RC≡CH methyl ketones are obtained but with alkynes of the type RC≡CR′ both possible products are obtained.

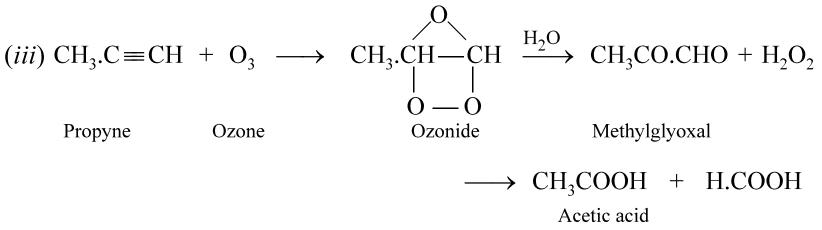
6. Addition of Ozone and Ozonolysis: With ozone, alkynes form ozonides, which are decomposed by water to form diketones and hydrogen peroxide. Diketones are oxidised by hydrogen peroxide to carboxylic acids by the cleavage of carbon-carbon bonds.





$$R.\underset{\underset{\large O}{\|}}{C}-\underset{\underset{\large O}{\|}}{C}-R' + H_2O_2 \longrightarrow \underset{\text{Carboxylic acids}}{R.COOH + R'.COOH}$$





Acetylene is exceptional as it gives glyoxal as well as formic acid. Since oxidation (ozonide formation) is very much slower with alkynes as compared to alkenes, a triple bond is left intact in enynes by choosing a suitable oxidising agent.

$$R'C \equiv C(CH_2)_nCH{=}CHR'' \xrightarrow[\text{Acetic acid}]{CrO_3} R'C \equiv C.(CH_2)_nCOOH + R''COOH$$

Ozonolysis of triple bonds is less common and the reaction proceeds less easily since ozone is an electrophilic reagent and prefers double to triple bonds. Ozone behaves like a electrophile in ozonide formation.

7. Addition of Carboxylic Acids and their Derivatives: Unlike alkenes carboxylic acids and their derivatives add to alkynes in presence of catalysts like mercuric oxide or boron trifluoride etc., to give vinyl esters.

$$\underset{\text{Alkyne}}{R.C{\equiv}CH} + \underset{\text{Carboxylic acid}}{R'.COOH} \xrightarrow{BF_3} RC(OOC.R'){=}CH_2 \text{ or } \underset{\text{Vinyl ester}}{CH_2{=}C.R.O.OC.R'}$$

When acetylene is passed into warm acetic acid in presence of mercuric ion as catalyst, vinyl acetate and ethylidene diacetate are formed.

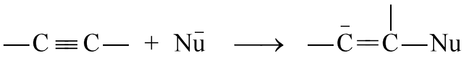
$$CH{\equiv}CH + CH_3COOH \xrightarrow{Hg^{2+}} \underset{\text{Vinyl acetate}}{CH_2{=}CH.OOC.CH_3}$$

$$CH_2{=}CH.OOC.CH_3 + CH_3COOH \xrightarrow{Hg^{2+}} \underset{\text{Ethylidene diacetate}}{CH_3.CH(OOC.CH_3)_2}$$

$$\underset{\text{Propyne}}{CH_3.C{\equiv}CH} + \underset{\text{Acetic acid}}{CH_3.COOH} \xrightarrow[200°C]{BF_3} \underset{\alpha\text{-Methylvinyl acetate}}{CH_2{=}C(CH_3).O.OC.CH_3}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + \underset{\text{Acetyl chloride}}{CH_3.COCl} \xrightarrow[\Delta]{BF_3} \underset{\beta\text{–Chlorovinyl methyl ketone}}{CHCl{=}CH.OC.CH_3}$$

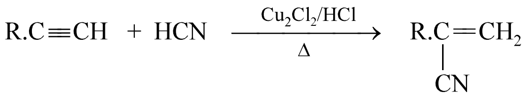
Addition of carboxylic acid to alkynes is an example of nucleophilic addition reaction which is initiated by a carboxylate anion. Other nucleophilic addition reactions of alkynes are additions of alcohol, hydrogen cyanide and ammonia. These result in formation of vinyl derivatives and the reaction is therefore termed as vinylation (W. Reppe, 1940). Nucleophilic additions are observed in alkynes and not in alkene because of greater stability of vinyl carbanion formed from alkynes.



$$—C{\equiv}C— + N\bar{u} \longrightarrow —\bar{C}{=}\overset{|}{C}—Nu$$

8. Addition of Hydrogen Cyanide and Ammonia: Hydrogen cyanide reacts with acetylene in presence of cuprous chloride in hydrochloric acid to form vinyl cyanide or acrylonitrile.

$$HC\equiv CH + HCN \xrightarrow[\Delta]{Cu_2Cl_2/HCl} \underset{\text{Vinyl cyanide}}{H_2C=CHCN}$$



$$R.C\equiv CH + HCN \xrightarrow[\Delta]{Cu_2Cl_2/HCl} R.\underset{\displaystyle CN}{\underset{|}{C}}=CH_2$$

(Substituted acrylonitrile)

Ammonia adds in presence of Al_2O_3 at a temperature of 300–350°C to give nitriles.

$$HC\equiv CH + NH_3 \xrightarrow[\Delta]{Al_2O_3} CH_3C\equiv N + H_2$$

$$R.C\equiv CH + NH_3 \xrightarrow[\Delta]{Al_2O_3} R.CH_2.C\equiv N + H_2$$

9. Addition of Alcohols: Alkynes add to alcohol when passed in them. If passed in methanol at 160–200°C in presence of small amount of CH_3OH under pressure just enough to prevent boiling, methyl vinyl ether is formed.

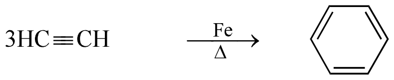
$$HC\equiv CH + CH_3\bar{O} \longrightarrow \bar{C}H=CHOCH_3 \xrightarrow{CH_3OH} CH_2=CH.OCH_3 + CH_3\bar{O}$$

$$HC\equiv CH + C_2H_5OH \xrightarrow{NaOH} \underset{\text{Ethyl vinyl ether}}{CH_2=CHO.C_2H_5}$$

Mechanism is believed to involve nucleophilic attack. The process in which acetylene adds on to compounds containing an active hydrogen atom to form vinyl compounds is known as *Vinylation.*

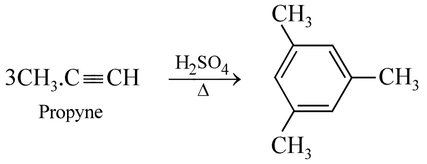
10. Self-Addition or Polymerisation: Alkynes polymerise to give cyclic or linear polymers depending upon the temperature and catalyst used. However these polymers are different from those of alkenes as these are low molecular weight polymers.

(i) When passed through heated tube it polymerises to give a low yield of benzene.

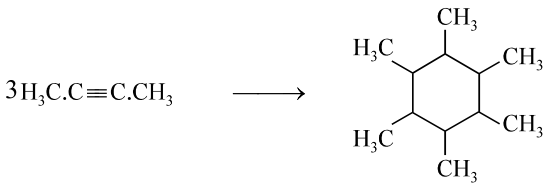


(Benzene)

(ii) Homologues of acetylene behave in a similar manner.

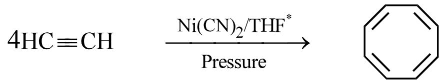


(Trimethyl benzene or Mesitylene)



(Hexamethyl benzene)

(iii) Under pressure and in presence of catalyst acetylene polymerises to cyclo-octatetraene.



NOTES

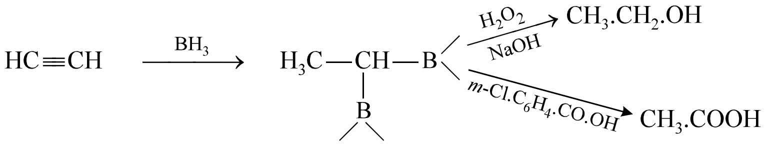
(iv) Acetylene undergoes linear polymerisation when passed in a solution of cuprous chloride in ammonium chloride.

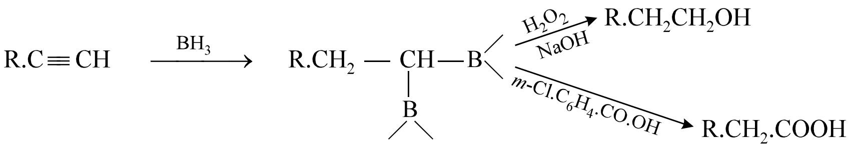
$$2\,HC{\equiv}CH \xrightarrow{Cu_2Cl_2\,/\,NH_4Cl} \underset{\substack{\text{Vinyl acetylene}\\ \text{(1-Buten-3-yne)}}}{CH_2{=}CH{-}C{\equiv}CH} \xrightarrow[C_2H_2]{Cu_2Cl_2\,/\,NH_4Cl}$$

$$\underset{\substack{\text{Divinyl acetylene}\\ \text{(1,5-Hexadien-3-yne)}}}{CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2}$$

(B) Oxidation Reactions

1. Hydroboration-Oxidation: The reaction between terminal alkynes and BH_3 produces 1,1-diboro compounds which on oxidation with ($NaOH—H_2O_2$) give primary alcohols and when oxidised with *m*-chloroperbenzoic acid give carboxylic acids.





The triple bond of alkynes is less susceptible to oxidation than the double bond of alkenes. Different oxidation products are obtained with different reagents.

2. Oxidation with Strong Alkaline Potassium Permanganate: Alkynes on oxidation with strong alkaline potassium permanganate give carboxylic acids containing, generally, lesser number of carbon atoms.

$$R.C{\equiv}C.R\ +2H_2O+2O \xrightarrow{KMnO_4} \underset{\text{Unstable}}{R.C(OH)_2\,C(OH)_2.R}$$

$$\xrightarrow{-2H_2O} \underset{\text{Diketone}}{R.CO.CO.R} \xrightarrow[KMnO_4]{H_2O+O} 2R.COOH \quad \text{(Carboxylic acids)}$$

$$CH_3.C{\equiv}CH + 2H_2O + 2O \xrightarrow[-2H_2O]{KMnO_4} \underset{\text{Methyl glyoxal}}{CH_3CO.CHO}$$

$$\xrightarrow[KMnO_4]{H_2O+O} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Formic acid}}{HCOOH}$$

$$CH{\equiv}CH + 2H_2O + 2O \xrightarrow[-2H_2O]{KMnO_4} \underset{\text{Glyoxal}}{CHO.CHO} \xrightarrow[KMnO_4]{2O} \underset{\text{Oxalic acid}}{HOOC.COOH}$$

3. Oxidation with Acidic Potassium Dichromate: On treatment with acidic dichromate alkynes give carboxylic acids.

$$R.C{\equiv}CH\ +H_2O+O \xrightarrow[H^+]{K_2Cr_2O_7} \underset{\text{Unstable}}{R.C(OH){=}CH.OH} \longrightarrow \underset{\text{Acid}}{R.CH_2.COOH}$$

$$CH\equiv CH + H_2O + O \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$$

4. Oxidation with Selenium Dioxide: Selenium dioxide oxidises alkynes to give diketones or dicarbonyl compounds.

$$\underset{\text{Alkyne}}{R.C\equiv C.R} \xrightarrow[SeO_2]{2O} \underset{\text{Diketone}}{R.CO\,CO.R}$$

$$CH\equiv CH \xrightarrow[SeO_2]{2O} CHO.CHO$$

$$\underset{\text{2-Butyne}}{CH_3.C\equiv C.CH_3} \xrightarrow[SeO_2]{2O} \underset{\text{Butadinone}}{CH_3CO.CO.CH_3}$$

5. Combustion: Alkynes when burnt in air or oxygen produce heat and evolve carbon dioxide and water. The reaction is used industrially for welding when acetylene is burnt with oxygen (oxy-acetylene flame).

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + (n-1)H_2O$$

$$2CH\equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312\text{ kcal}$$

The combustion is an exothermic reaction.

(C) Reduction (Metal-Ammonia Reduction) Reactions

Alkynes can be reduced by hydrogen in presence of catalysts in convenient manner. Metal (Lithium, sodium or potassium) and liquid ammonia can also be used for reducing alkynes but in a restricted manner. Usually metal-ammonia reduction (Birch reduction) is carried out for reducing aromatic rings where 1,4 addition of hydrogen takes place. The mechanism involves solvated electrons, which are transferred from metal to solvent and then to the ring.

Terminal alkynes cannot be reduced by Na—NH_3 combination because they are converted to acetylide ions under these conditions. However, internal alkynes can be reduced by Na—NH_3 procedure.

(D) Isomerization Reactions

In presence of the traces of alkali, alkynes undergo isomerization. Thus 1-alkyne changes to 2-alkyne in presence of alcoholic potash and the reverse isomerization is affected by traces of sodamide.

$$\underset{\text{1-Butyne}}{CH_3.CH_2.C\equiv CH} \underset{NaNH_2}{\overset{\text{Alc. KOH}}{\rightleftarrows}} \underset{\text{2-Butyne}}{CH_3.C\equiv C.CH_3}$$

Formation of Metallic Derivatives or Alkynide

Alkynes differ from alkenes and alkanes in that they exhibit acidic character and the hydrogen attached to a triple bonded atom can be replaced by metals forming alkynides or acetylides. The weak acidic behaviour of alkynes is explained on the basis of M.O. concept. In *sp* hybridized carbon atoms, the hybrid orbitals have greater *s* character (50%) and therefore the electrons of carbon hydrogen bond are held much nearer to the carbon atom making it electronegative and the hydrogen easily ionizable as a proton. Alternatively six electrons forming a triple bond may be considered to be localized between two carbon atoms. As a result of this the bonding electrons of carbon-hydrogen bond suffer less repulsion from these six electrons and shift slightly towards the carbon atom. The hydrogen thus acquires positive character and can be easily removed as a proton. Following is the order of acidity of hydrogen in the hydrocarbons.

$$\text{Alkyne } (sp) > \text{Alkene } (sp^2) > \text{Alkane } (sp^3)$$

The 1-alkynes have one acidic hydrogen atom, acetylene has two such hydrogens while other alkynes have none. Therefore, for formation of alkynides is observed with only acetylene and other 1-alkynes. When 1-alkynes are treated with sodamide in ammonia or passed over molten sodium, alkynides are formed. Treatment with organic compounds of metals gives alkali and alkaline earth alkynides. These are valuable reagents for chemical synthesis and are essentially ionic in nature.

$$\underset{\text{1-Alkyene}}{2R.C{\equiv}CH} + 2Na \longrightarrow \underset{\text{Sodium alkynide}}{2R.C{\equiv}C.Na} + H_2$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + \underset{t\text{-Butyl lithium}}{2(CH_3)_3CLi} \longrightarrow \underset{\text{Dilithium acetylide}}{Li.C{\equiv}C.Li} + 2(CH_3)_3CH$$

$$CH{\equiv}CH + K.NH_2 \xrightarrow[-NH_3]{\text{Xylene}} \underset{\text{Potassium acetylide}}{CH{\equiv}C.K} \xrightarrow[-NH_3]{KNH_2} \underset{\text{Dipotassium acetylide}}{KC{\equiv}C.K}$$

$$CH{\equiv}CH + \underset{\text{Grignard reagent}}{R.Mg.X} \longrightarrow \underset{\text{Acetylenic Grignard reagent}}{CH{\equiv}C.MgX} + R.H$$

$$CH{\equiv}CH + Na \xrightarrow{110^\circ} \underset{\text{Monosodium acetylide}}{CH{\equiv}C.Na} \xrightarrow{Na/110^\circ} \underset{\text{Disodium acetylide}}{Na.C{\equiv}C.Na}$$

$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} + NaNH_2 \longrightarrow \underset{\text{Sodium propynide}}{CH_3.C{\equiv}\overset{-}{C}.\overset{+}{Na}} + NH_3$$

$$CH_3C{\equiv}CH + \underset{\text{Grignard reagent}}{RMg.Br} \longrightarrow \underset{\text{Propynyl magnesium bromide}}{CH_3C{\equiv}C.MgBr} + R.H.$$

In contrast to these the acetylide of copper and silver have greater covalent character. They are obtained by passing alkynes in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

$$R.C{\equiv}CH + Cu(NH_3)_2Cl \longrightarrow R.C{\equiv}\overset{-}{C}.\overset{+}{Cu} + NH_4Cl + NH_3$$

$$R.C{\equiv}CH + Ag(NH_3)_2NO_3 \longrightarrow R.C{\equiv}\overset{-}{C}.\overset{+}{Ag} + NH_4NO_3 + NH_3$$

$$CH{\equiv}CH \xrightarrow{Cu(NH_3)_2Cl} \underset{\substack{\text{Copper}\\ \text{acetylide}}}{CH{\equiv}\overset{-}{C}.\overset{+}{Cu}} \xrightarrow{Cu(NH_3)_2Cl} \underset{\substack{\text{Dicopper acetylide}\\ \text{(Reddish brown)}}}{\overset{+}{Cu}\overset{-}{C}{\equiv}\overset{-}{C}.\overset{+}{Cu}}$$

$$CH{\equiv}CH \xrightarrow{Ag(NH_3)_2NO_3} \underset{\text{Silver acetylide}}{CH{\equiv}\overset{-}{C}.\overset{+}{Ag}} \xrightarrow{Ag(NH_3)_2NO_3} \underset{\text{Disilver acetylide (White)}}{\overset{+}{Ag}.\overset{-}{C}{\equiv}\overset{-}{C}.\overset{+}{Ag}}$$

These heavy metal acetylides are solids and highly explosive when dry. Alkynides are used for the preparation, purification, separation and identification of alkynes.

Detection of Carbon to Carbon Triple Bond

Some of the tests are as follow:

- Alkynes respond to Baeyer's test for unsaturation and discharge the colour of alkaline potassium permanganate. They also decolorise bromine water (*cf.* Alkenes).
- Alkynes give a white precipitate when passed through ammoniacal silver nitrate solution (only 1-alkynes give this test).
- The triple bond is located in the molecule by the identification of the products of ozonolysis in a manner similar to that used for alkenes.

Let us study some alkynes in detail.

Propyne or Allyene or Methyl Acetylene, $CH_3.C{\equiv}CH$

Propyne is the second member of the alkyne homologous series. It does not occur in nature. It can be prepared by the general methods of formation described earlier.

Propyne is conveniently prepared by any one of the following methods:

1. By the Action of Alcoholic Potash on 1,2-Dibromopropane: Dehydrohalogenation of 1,2-dibromopropane with alcoholic potassium hydroxide gives propyne.

$$\underset{\text{1,2-Dibromopropane}}{CH_3.CHBr.CH_2Br} \xrightarrow{\text{Alc. KOH}} \underset{\text{Propyne}}{CH_3.C{\equiv}CH} + 2HBr$$

2. From Acetylene

(i) Action of Grignard reagent on acetylene gives ethenyl magnesium halide, which when reacted with methyl halide gives propyne.

$$CH{\equiv}CH + \underset{\text{Ethyl magnesium bromide}}{C_2H_5MgBr} \longrightarrow \underset{\text{Ethenyl magnesium bromide}}{CH{\equiv}C.MgBr} + C_2H_6$$

$$CH{\equiv}C.MgBr + CH_3Br \longrightarrow CH_3.C{\equiv}CH + MgBr_2$$

(ii) On treatment of acetylene with equimolar amount of sodamide in ammonia, monosodium acetylide is obtained. This on reaction with methyl halide gives propyne.

$$CH{\equiv}CH + NaNH_2 \xrightarrow{NH_3} CH{\equiv}C.Na + NH_3$$

$$\underset{\text{Sodium acetylide}}{CH{\equiv}C.Na} + \underset{\text{Methyl Bromide}}{CH_3Br} \longrightarrow \underset{\text{Propyne}}{CH_3.C{\equiv}CH} + NaBr$$

Physical Properties

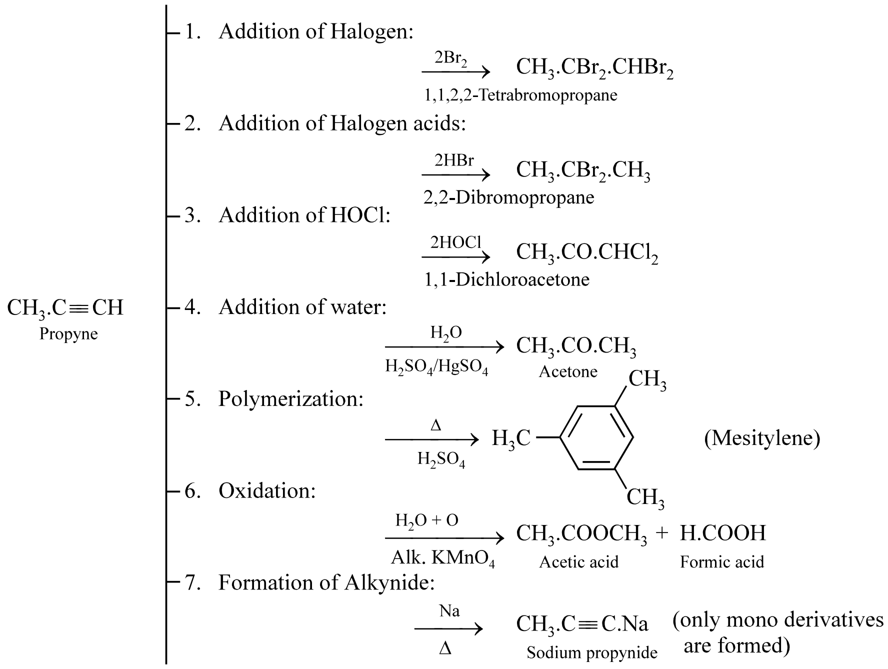
It is a colourless gas, boiling point –23.2°C and melting point –103°C. Like acetylene it is sparingly soluble in water and fairly soluble in alcohol and acetone.

Chemical Properties

Propyne exhibits all the general reactions of alkynes and all the chemical reactions shown by acetylene. It is different from acetylene in being an unsymmetrical alkyne. The additions to propyne with unsymmetrical reagents will therefore be in accordance with Markovnikov's rule.

NOTES

Some chemical reactions of propyne



Uses

It is used for the preparation of polymers, substituted vinyl derivatives and higher alkynes.

Structure

(i) The molecular formula of propyne is C_3H_4 which is obtained by combustion and gas analysis.

(ii) Considering the tetracovalency of carbon and monovalency of hydrogen following formulae may be written for C_3H_4

$$\underset{\text{(I)}}{CH_2{=}C{=}CH_2} \quad \text{and} \quad \underset{\text{(II)}}{CH_3{-}C{\equiv}CH}$$

(iii) Propyne has triple bond in the molecule as shown by its synthesis from acetylene derivatives such as sodium acetylide, and also from its reaction with metals to form propynides.

$$CH{\equiv}CH \xrightarrow[\Delta]{Na} CH{\equiv}C.Na \xrightarrow[-NaX]{CH_3X} \underset{\text{Propyne}}{CH_3.C{\equiv}CH}$$

$$CH_3.C{\equiv}CH \xrightarrow[-NH_3]{NaNH_2} CH_3.C{\equiv}C.Na \quad \text{(Sodium propynide)}$$

Furthermore, formula (I) is known as the structure of allene. Thus, formula (II) represents propyne.

(iv) The formula is supported by spectroscopic properties and measurement of bond angles and bond lengths. The M.O. representation of propyne shows the two carbons, involved in triple bond formation, in *sp* hybridized state. The third carbon is in sp^3 hybridized state. Propyne thus has six σ bonds and two π bonds.

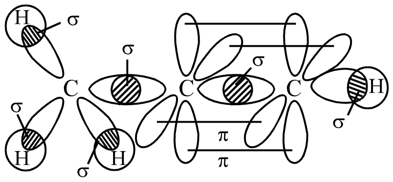


Fig. 3.2. *Structure of Propyne.*

Butynes, C_4H_6

Butynes exits in two isomeric forms 1-butyne and 2-butyne. These do not occur in nature and may be obtained by any of the general methods of formation described earlier.

Physical Properties

Butynes are colourless and odourless gases. Chemical properties. Their chemical characteristics are similar to the general reactions of alkynes. However, they differ from acetylene and propyne in following reactions:

(i) **Isomerization:** 2-Butyne when heated with sodamide in inert solvent isomerizes to 1-butyne. On the other hand 1-butyne, when heated with alcoholic potash changes to 2-butyne.

$$\underset{\text{1-Butyne}}{CH_3.CH_2.C \equiv CH} \underset{NaNH_2}{\overset{\text{Alc. KOH}}{\rightleftharpoons}} \underset{\text{2-Butyne}}{CH_3.C \equiv C.CH_3}$$

(ii) **Formation of Butynides**: Only 1-Butyne reacts with metals or their salts to form monobutynides. 2-Butyne does not form butynide but on heating it with certain substances such as sodamide it isomerizes to 1-butyne which readily forms butynide.

$$CH_3.CH_2.C \equiv CH \xrightarrow[\Delta]{Na} \underset{\text{Sodium butynide}}{CH_3.CH_2.C \equiv C.Na}$$

$$CH_3.C \equiv C.CH_3 \xrightarrow[\Delta]{Na} \text{No reaction}$$

$$\underset{\text{2-Butyne}}{CH_3.C \equiv C.CH_3} \xrightarrow{NaNH_2} \underset{\text{1-Butyne}}{CH_3.CH_2.C \equiv CH} \xrightarrow{NaNH_2} \underset{\text{Sod. butynide}}{CH_3.CH_2C \equiv C.Na}$$

Uses

Butynes do not find much use. However, they may be used for the preparation of ketones and certain substituted vinyl derivatives.

(iii) Alkadiynes or Diacetylenes

Compounds having two triple bonds in the molecule are known as alkadiynes or diacetylenes. As in the case of dienes, these can also be divided into (*i*) conjugated alkadiynes and (*ii*) isolated alkadiynes. The example of the former is diacetylene or 1,3-butadiyne and of latter is dipropargyl or 1,5-hexadiyne.

$$\underset{\text{Diacetylene (1,3-Butadiyne)}}{CH \equiv C — C \equiv CH} \qquad \underset{\text{Dipropargyl (1,5-Hexadiyne)}}{CH \equiv C.CH_2.CH_2.C \equiv CH}$$

Dipropargyl is isomeric to benzene. Alkadiynes readily form addition products and give all the general reactions of alkynes twice over. They also form metal alkynides.

Interconversion, Ascent and Descent of Series in Alkanes, Alkenes and Alkynes

Let us understand the concept of ascent and descent of speries.

Ascent of Series2: Conversion of an organic compound into its next higher homologue is termed as ascent of series or ascending the series.

Descent of Series: Conversion of an organic compound into its next lower homologue is known as descent of series or descending the series.

Alkanes

$$\underset{\text{Ethane}}{CH_3.CH_3} \xrightarrow{Cl_2} \underset{\text{Ethyl chloride}}{CH_3.CH_2.Cl} \xrightarrow[\text{Ether}]{CH_3Cl/Na} \underset{\text{Propane}}{CH_3.CH_2.CH_3}$$

$$\underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow{Cl_2} \underset{\text{Propyl chloride}}{CH_3.CH_2.CH_2Cl} \xrightarrow{\text{Aq. KOH}} \underset{\text{Propyl alcohol}}{CH_3.CH_2.CH_2.OH}$$

$$\xrightarrow{O} \underset{\text{Propionaldehyde}}{CH_3.CH_2.CHO} \xrightarrow{O} \underset{\text{Propionic acid}}{CH_3.CH_2.COOH} \xrightarrow{\text{Soda lime}} \underset{\text{Ethane}}{CH_3.CH_3}$$

Alkenes

$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{HI} \underset{\text{Ethyl iodide}}{CH_3.CH_2I} \xrightarrow[\text{Ether}]{CH_3I/Na} \underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow{Cl_2} \underset{\text{Propyl chloride}}{CH_3.CH_2.CH_2.Cl}$$

$$\underset{\text{Propene}}{CH_3.CH=CH_2} \xleftarrow{\text{Alc. KOH}}$$

$$\underset{\text{Propene}}{CH_3.CH=CH_2} \xrightarrow{O_3/H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[LiAlH_4]{[H]} CH_3CH_2OH \xrightarrow[170°]{H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

Alkynes

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[\Delta]{Na} \underset{\text{Sodium acetylide}}{CH\equiv CNa} \xrightarrow{CH_3Br} \underset{\text{Propyne}}{CH\equiv C.CH_3}$$

$$\underset{\text{Propyne}}{CH_3.C\equiv CH} \xrightarrow{H_2/\text{Lindlar's catalyst}} \underset{\text{Propene}}{CH_3.CH=CH_2}$$

$$\xrightarrow{O_3/H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{PCl_5} \underset{\text{1, 1-Dichloroethane}}{CH_3.CHCl_2} \xrightarrow{\text{Alc. KOH}} CH\equiv CH$$

Let us study the inter conconversion of the hydrocarbon.

Alkane to Alkene

$$\underset{\text{Ethane}}{CH_3.CH_2} \xrightarrow{Cl_2} \underset{\text{Ethyl chloride}}{CH_3.CH_2.Cl} \xrightarrow{\text{Alc. KOH}} \underset{\text{Ethene}}{CH_2=CH_2}$$

Alkene to Alkyne

$$\underset{\text{Ethene}}{CH_2{=}CH_2} \xrightarrow{Br_2} \underset{\text{1,2-Dibromoethane}}{CH_2Br.CH_2.Br} \xrightarrow{\text{Alc. KOH}} \underset{\text{Acetylene}}{CH{\equiv}CH}$$

Alkyne to Alkene and then to Alkane

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow[\text{Lindlar's catalyst}]{H_2} \underset{\text{Ethene}}{CH_2{=}CH_2} \xrightarrow{H_2/Ni} \underset{\text{Ethane}}{CH_3.CH_3}$$

3.2.3 Dienes

Dienes or Diolefins are bifunctional compounds having two carbon-carbon double bonds in the molecule. The general formula of such hydrocarbons is C_nH_{2n-2} which is same as that of alkynes. They are known as Alkadienes in IUPAC system of nomenclature. The properties of compounds containing two double bonds may be similar or different from alkenes depending upon the positions of these double bonds in the molecule. Thus dienes are divided into three main classes:

- **Dienes with Cumulated Double Bonds or Allenes:** In cumulated dienes the double bonds are attached to same carbon atom. Thus:

  $$>C{=}C{=}C< \quad \text{or} \quad \underset{\text{Allene}}{H_2C{=}C{=}CH_2}$$

  Allene is the parent compound of the series and hence these are also known as allenes.

- **Dienes with Isolated Double Bonds:** In these dienes the double bonds are separated from each other by at least two single bonds. Thus:

  $$>C{=}CH{-}CH_2{-}CH{=}C< \quad \text{or} \quad \underset{\text{1,4-Pentadiene}}{CH_2{=}CH{-}CH_2{-}CH{=}CH_2}$$

  The isolated double bonds in dienes behave like independent double bonds. The only difference between the alkenes and dienes is that in dienes the reactions of alkenes or double bonds are given twice because of the presence of two such linkages. Hence they will not be treated separately in this text.

- **Dienes with Conjugated Double Bonds:** When the double and single bonds are present alternately in the molecule, the compound is said to have conjugated double bonds. Thus:

  $$>C{=}CH{-}CH{=}C<; \quad \underset{\text{1,3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2}; \quad \underset{\text{1,3-Pentadiene}}{CH_3{-}CH{=}CH{-}CH{=}CH_2}$$

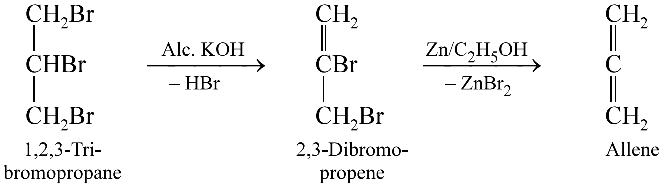
The properties of conjugated dienes are different from those of cumulated or isolated dienes. They may exhibit strikingly different properties and are the most important of all the three classes of dienes. The compounds containing three, four or many double bonds are termed as trienes, tetraenes, polyenes, respectively and the above classification may be extended to them as well. In IUPAC system they are named by replacing the ‘ane’ of the corresponding alkane by ‘diene’, ‘triene’, ‘tetraene’ and ‘polyene’ depending upon the number of double bonds in the molecule and locants are used to indicate the position of the double bonds.

The chemistry of dienes is similar to that of alkenes. They may be prepared by suitable modification of the general methods of formation used for alkenes and their main chemical characteristic is the addition at the double bonds.

General Methods of Preparation

Allene or propadiene is the parent compound of series of dienes with cumulated double bonds. It may be prepared by the following methods :

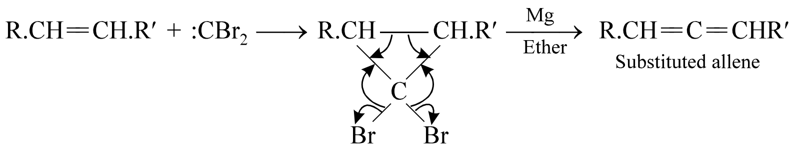
1. From Trihalopropane: Trichloro or tribromopropane on treatment with alcoholic potassium hydroxide and then with zinc and alcohol results in the formation of allene.



1,2,3-Tribromopropane   2,3-Dibromopropene   Allene

2. From Olefins: A more general method for preparing allenes is to treat an alkene with bromoform and potassium-*t*-butoxide, followed by the reaction with magnesium in ether.

$$CHBr_3 + (CH_3)_3C.OK \longrightarrow \underset{\substack{\text{Dibromocarbene}\\\text{(Transitory intermediate)}}}{:CBr_2} + (CH_3)_3C.OH + KBr$$



Allenes are highly reactive and readily undergo rearrangement to form acetylene derivatives. For example, allene on reaction with sodium gives sodium methyl acetylide.

$$\underset{\text{Allene}}{CH_2{=}C{=}CH_2} \xrightarrow[\text{Ether}]{\text{Na}} \underset{\text{Sodium methyl acetylide}}{CH_3.C{\equiv}C.Na}$$

The formula of allene suggests that the central carbon atom is in *sp* hybridized state and therefore the two double bonds and the terminal methylene groups must lie at right angles to each other in different planes. The other two carbon atoms involved in double bonds are in sp^2 hybridized state. Allene may, therefore, be represented by the given molecular orbital (MO) formula.

If the allene is suitably substituted (as in a.b.C═C═C.a.b.), because of its peculiar structure, it will exist in two enantiomorphic forms and exhibit optical activity. Allenes absorb in IR region at 1960 (5.1 μ) and 1060 (9.4 μ) cm^{-1} due to the presence of two double bonds at the same carbon.

Conjugated Dienes

The simplest conjugated diene is butadiene (or 1,3-butadiene). It has been observed that butadiene and other conjugated dienes show remarkable differences in the physical and chemical properties when compared with isolated dienes. In general, they are more reactive and more stable than corresponding isolated dienes. Another important member of the series is isoprene or 2-methyl butadiene.

The butadiene and isoprene may be prepared by the following methods:

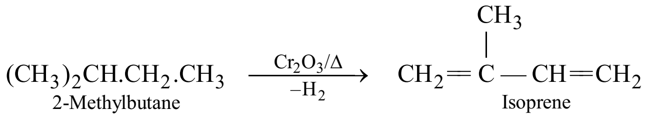
1. Dehydration of 1,2; 1,3 and 1,4 diols: Butanediols when passed over heated acid catalyst eliminate two molecules of water to give butadiene.

$$\underset{\text{Butane-1,4-diol}}{CH_2OH.CH_2.CH_2.CH_2OH} \xrightarrow[-2H_2O]{H_3PO_4/270°C} \underset{\text{1,3-Butadiene}}{CH_2{=}CH-CH{=}CH_2}$$

2. Dehydrogenation of Alkanes or Alkenes: *n*-Butane or butene when passed over heated chromic oxide gives butadiene.

$$\underset{n\text{-Butane}}{CH_3.CH_2.CH_2.CH_3} \xrightarrow[-H_2]{Cr_2O_3/\Delta} \underset{\text{2-Butene}}{CH_3-CH{=}CH-CH_3}$$
$$\xrightarrow[-H_2]{Cr_2O_3/\Delta} \underset{\text{Butadiene}}{CH_2{=}CH-CH{=}CH_2}$$

Iso-pentane (2-Methylbutane) or Iso-pentylene (3-Methyl-1-pentene) similarly give isoprene.



$$\underset{\text{2-Methylbutane}}{(CH_3)_2CH.CH_2.CH_3} \xrightarrow[-H_2]{Cr_2O_3/\Delta} \underset{\text{Isoprene}}{CH_2{=}\overset{\overset{CH_3}{|}}{C}-CH{=}CH_2}$$

3. By Passing Ethyl Alcohol and Acetaldehyde Over Heated Catalyst: The catalyst is silica gel and tantalum oxide.

$$\underset{\text{Ethyl alcohol}}{C_2H_5-OH} + \underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow{\Delta} \underset{\text{Butadiene}}{CH_2{=}CH-CH{=}CH_2}$$

4. By Decomposition of Cyclohexene: Cyclohexene when passed over heated nickel, chromium catalyst gives butadiene.

$$\underset{\text{Cyclohexene}}{C_6H_{10}} \xrightarrow{Ni/Cr} \underset{\text{Butadiene}}{CH_2{=}CH-CH{=}CH_2} + \underset{\text{Ethene}}{CH_2{=}CH_2}$$

Physical Properties

- Butadiene is a gas at room temperature (b.p. –2.6°C) whereas, isoprene is a liquid (b.p. 30°C). The heats of combustion and hydrogenation of butadiene and isoprene are lower than the expected value.
- The bond distances of carbon atoms in butadiene are neither those of pure single nor of pure double bond and they have intermediate value. Thus C_1 to C_2 or C_3 to C_4 bond length is 1.35 Å and C_2 and C_3 bond length is 1.47 Å.
- Butadiene absorbs at 217 mm and isoprene at 222 mμ in UV spectrum; while in IR region they absorb at 1650 and 1600 cm^{-1} due to the presence of conjugated double bonds.

Chemical Properteies

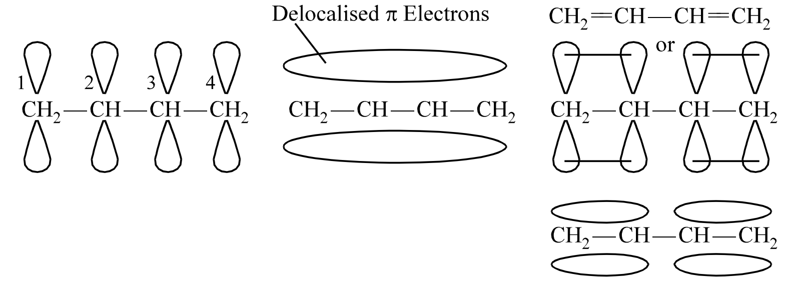
Butadiene, isoprene and other conjugated dienes show the usual reactions of alkenes such as hydrogenation, ionic and free radical additions but they do so more readily. However, they also undergo abnormal additions and polymerize readily.

In 1899, Thiele observed that when butadiene and other conjugated dienes are reacted with one molecule of addendum usually a mixture of 1,4- and 1,2-addition products result; 1,4-addition product predominating. To account for such anomalous behaviour he gave Theory of Partial Valency which assumes that valencies of carbon atoms involved in double bonds are not fully satisfied and each carbon is left with some residual or partial valency and the addition to double bond occurs through these residual valencies. He also pointed that in case of conjugated dienes the partial valencies of carbon atoms 1 and 4 are free, while those of carbon 2 and 3 get mutually satisfied and hence the addition to 1,3-butadiene is preferentially 1,4-addition.

$$\underset{\substack{\text{3,4-Dichlorobutene-1}\\\text{(1,2-addition product)}}}{CH_2Cl.CHCl.CH{=}CH_2} \xleftarrow{Cl_2} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{Cl_2} \underset{\substack{\text{1,4-Dichloro-2-butene}\\\text{(1,4-addition product)}}}{Cl.CH_2.CH{=}CH.CH_2Cl}$$

However, the theory is of only historical interest now. These reactions, greater reactivity and greater stability of butadiene and other conjugated dienes are now better explained in terms of resonance or molecular orbital concept. It is believed that butadiene and other conjugated dienes are resonance hybrids of many structures. The dipolar structures account for 1,4 additions in butadiene.

$$CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2$$



p-Orbitals before delocalisation

Delocalised p-orbitals

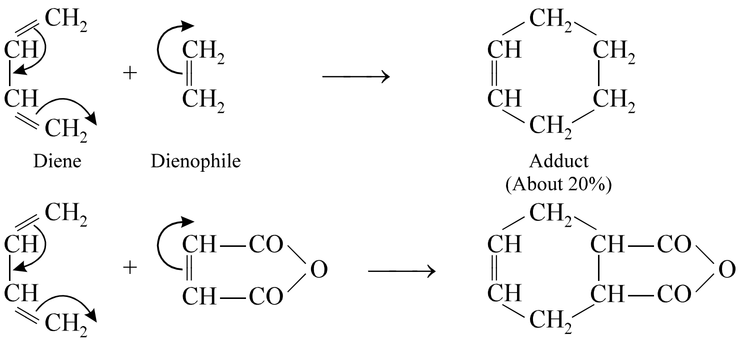
Localised p-orbitals

Fig. 3.3 *Butadiene MO Representation*

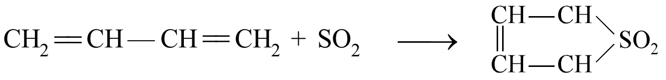
In the MO concept each carbon atom of butadiene is considered to be in sp^2 hybridized state so that each carbon has an unhybridized *p*-orbital. The localized bonds are formed by sidewise overlap of these *p*-orbitals. Thus, the *p*-orbital at carbon-2, can overlap with either *p*-orbital of carbon-1 or that of carbon-3. Similarly the orbital at carbon-3 can overlap with that of carbon-2 or carbon-4 to form p bonds. The net effect is the formation of polycentric uniform orbital overlap giving delocalized bond orbitals over all the four carbon atoms. The delocalization of electrons imparts greater stability. It is supported by bond length measurements, and study of heat of combustion and hydrogenation:

Some of the reactions of conjugated dienes different from isolated dienes are given as follows:

1. Diels-Alder Reaction: Conjugated dienes add to alkenes by 1,4-addition to form cyclic compounds. The reaction is known as Diels-Alder reaction after the names of its discoverers. The alkene is usually referred to as dienophile and is generally having electron attracting group like —COOH; —CN; —COR etc.



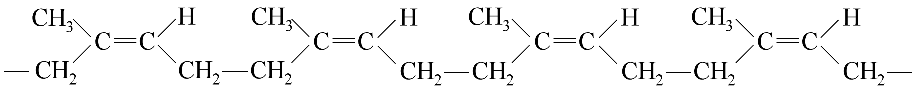
2. Combination with Sulphur Dioxide: Butadiene and isoprene react with SO_2 to give cyclic sulphones. Thus:



$$CH_2{=}CH{-}CH{=}CH_2 + SO_2 \longrightarrow \begin{array}{l} CH{-}CH \\ \| \quad\quad\quad\; SO_2 \\ CH{-}CH \end{array}$$

3. Polymerization: Polymerization is a common feature of all alkenes. However, in case of conjugated dienes the polymer chain may grow either by 1,4- or 1,2-addition depending upon whether it is acid or peroxide catalyzed.

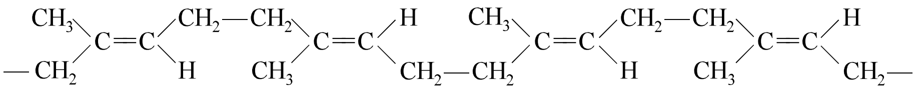
When 1,4-addition occurs to give polymers in acidic conditions it may be either *cis* or *trans*. The two types have widely differing properties. Thus natural rubber[1] is *cis*-1,4-polyisoprene and gutta percha is *trans*-1,4-polyisoprene and the two compounds have different properties.



cis-1,4-Polyisoprene (Natural rubber)

Uses

Butadiene and isoprene readily polymerise in presence of sodium and give products resembling natural rubber and leather substitutes. These are used in Diels-Alder reaction for the synthesis of cyclic compounds. These are also used to prepare emulsion paints.

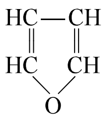


trans-1,4-Polyisoprene (Gutta-percha)

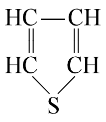
3.2.4 Arenes

Amongst the cyclic compounds aromatic compounds have an important place. The term aromatic is derived from the Greek word aroma meaning pleasant smell. Formerly, the term was applied to compounds which differed chemically from aliphatic and alicyclic compounds. Such substances either themselves possessed pleasant odour or were derived from odourous compounds viz., vanilla, oil of cinnamon, oil of bitter almonds etc. The term, however, is a misnomer, as now it is known that all aromatic compounds do not necessarily possess pleasant smell. Not only that, many of the aliphatic compounds also, such as amyl acetate, possess fine fragrance. On closer examination it was found that these cylic compounds had higher percentage of carbon than the corresponding aliphatic compounds. They also contained at least six carbon atoms connected by a conjugated system of three double bonds forming a hexagonal ring known as benzene nucleus. For this reason such compounds are sometimes also referred to as benzenoid aromatic compounds.

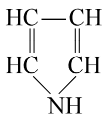
It should, however, be noted that while majority of the aromatic compounds known today contain at least one benzene ring, there are some, which do not contain such a ring, but resemble benzene in their chemical behaviour. Such aromatic compounds, to distinguish them from the above benzenoid compounds, are called as no*n-benzenoid* aromatic compounds. Important ones of this class are mentioned below:



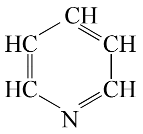
Furan



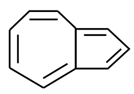
Thiophene



Pyrrole



Pyridine



Azulene

Sources of Aromatic Compounds

Coal and petroleum are two important commercial sources of aromatic compounds. Now let us consider as to how these sources are being exploited to obtain aromatic compounds.

(i) **Coal**: Coal deposits are the remains of vegetable matter buried underneath the surface of earth some 500 million years ago. High pressure and temperature inside changed these deposits to coal by the loss of moisture and elimination of gases like hydrogen and oxygen. Thus, the plant material, originally mainly consisting of cellulose $(C_6H_{10}O_5)_x$, became richer in carbon content. Besides chiefly containing carbon, hydrogen and oxygen; coal contains minor amount of nitrogen and sulphur with varying amount of moisture and mineral impurities.

In India large quantities of coal are being mined at Raniganj, Jharia, Bokaro, Giridih, Karanpura and some places in Assam. From Jharia about 42.43% and Raniganj about 32% of Indian coal is obtained.

Carbonization of Coal

Coal is a complex mixture of aromatic compounds with varying amount of free carbon. When it is heated at high temperature (400°C–1300°C) in absence of air, a large number of products—gaseous, liquid and solid—are obtained along with the nonvolatile residue known as coke. This process, known as carbonization or destructive distillation, is of two types depending on the temperature employed for the purpose:

- **High Temperature Carbonization (H.T.C.):** In this process the coking temperature exceeds 1050°C. It leads to high yield of coal gas, heavier coal tar and hard coke with low volatile contents. This process is more commonly used.
- **Low Temperature Carbonization (L.T.C.):** Here the coking temperature is less than 650°C. It leads to lower yield of gas, though with high calorific

value and smokeless soft solid residue with high content of combustible volatile matter. The solid fuel is known as coalite.

Bituminous coal is taken in iron or fire-clay retorts and heated in absence of air to a temperature of 1000°C–1400°C, when it undergoes destructive distillation producing ammoniacal liquors and coal tar.

Coal Tar

It is black and viscous oily liquid with unpleasant smell. Actual composition of coal tar varies with the nature of coal and carbonizing temperature. Besides suspended carbon particles, which make it appear black, other common substances present in it are of three types:

- ***Neutral*, (*Hydrocarbons*):** Benzene, Toluene, Naphthalene, Anthracene, etc.
- ***Acidic*, (*Phenols*):** Cresols etc.
- ***Basic*, *(Pyridine)*:** Quinoline etc.

Formerly, it was considered to be a waste product, but nowadays, it is considered to be a valuable treasure from which substances finding great applications in dye, explosive, drug, perfumery and other industries are obtained. About 200 important compounds have so far been obtained from it. In our country more than one lac ton of coal tar is being produced every year.

The crude coal tar contains 50% or even more of water, which must be removed to avoid bumping during subsequent distillations. The tar is allowed to stand in large tanks for several days or even weeks. The aqueous layer floats to the surface, while solid particles such as coal dust sink to the bottom. The middle layer of tar is drawn off from an opening some two to three feet from the bottom of the tank and is fed to the stills. The tar thus obtained still contains about 4% of water, but is safe for distillation. This coal tar is then subjected to distillation in specially designed stills and following main fractions are collected.

Table 3.5 Main fractions of Coal Tar

Sl. No.	*Main fraction*	*Temperature range*	*Sp. gr.*	*% Proportion*	*Chief constituents*
1.	Light oil or Crude naphtha	Upto 170°C	0.92	7–8	Benzene, Toluene, Xylenes etc.
2.	Middle oil or Carbolic oil	170°C–230°C	1.01	8–10	Phenol, Naphthalene
3.	Heavy oil or Creosote oil	230°C–270°C	1.04	8–10	Cresols, Naphthalene, Quinolines etc.
4.	Green oil or Anthracene oil	270°C–360°C	1.10	16–20	Anthracene, Phenanthrene etc.
5.	Pitch	Residue	—	50–60	90–95% of Carbon

Each fraction is then worked up and its constituents are separated.

1. Light Oil or Crude Naphtha: The portion distilling upto 170°C is known as light oil, because it is lighter than water. It contains 60–65% of benzene and methyl benzenes with 12–15% of naphthalene, 8–10% of phenol and 1–3% basic substances such as pyridine and a very small amount of thiophene. It is, therefore,

NOTES

first treated with cold concentrated sulphuric acid to remove basic substances, then with water and finally with sodium hydroxide to remove phenol and excess of sulphuric acid. It is then washed with water and subjected to fractional distillation. The following fractions are obtained:

(i) **90 per cent Benzol (80°C–110°C):** This portion contains 70–80 per cent benzene, 4–14 per cent of toluene and the rest xylenes. It is known as 90 per cent benzol, because upto 100°C, 90 per cent of the distillate is obtained.

(ii) **50 per cent Benzol (110°C–140°C):** It contains about 46% of benzene and the rest toluene and xylenes. Upto 100°C about 50 per cent of the distillate is obtained, while between 110°C–140°C, 90 per cent of the distillate is obtained. Hence this fraction is known as 50 per cent benzol or 90% toluol.

(iii) **Solvent Naphtha or Benzene (140°C–170°C).** It consists mainly of xylenes, mesitylene, cummene (isopropyl-benzene) etc.

All these fractions under these commercial names are used as solvents, motor fuels and dry cleaning solvents.

2. Middle Oil or Carbolic Oil (170°C–230°C): This portion chiefly contains naphthalene and carbolic acid (phenol). On cooling crystals of naphthalene separate out leaving behind crude carbolic acid. The crude crystalline naphthalene is pressed and purified by distillation followed by washing successively with concentrated sulphuric acid, water and sodium hydroxide solution. Final purification is done by redistillation followed by sublimation. The oil, free from naphthalene, is treated with sodium hydroxide when phenols dissolve. The alkaline solution is boiled and aerated to remove any naphthalene which might have escaped isolation. It is then cooled and saturated with carbon dioxide gas. The free phenols precipitate out. The crude product thus obtained is fractionally distilled to get pure phenol (b.p. 182°C), cresols (b.p. 190°C–205°C) and xylenols (b.p. 210°C–225°C).

Naphthalene is used for making dyes, drugs and explosives while phenols are used for making dyes, disinfectants, explosives, bakelite etc. The oil remaining after the removal of phenols is washed with dilute sulphuric acid. The tar bases like pyridine go into solution and are regenerated on basification with sodium hydroxide. Careful distillation gives pyridine (b.p. 115°C).

3. Heavy Oil or Creosote Oil (230°C–270°C): It is heavier than water (hence the name) and is greenish-yellow in colour. It contains chiefly naphthalene, cresols and quinoline. It can be worked up in the same way as middle oil, but because the individual compounds can be easily synthesized, it is used as such under the name creosote oil for the preservation of timber and for the preparation of some disinfectants.

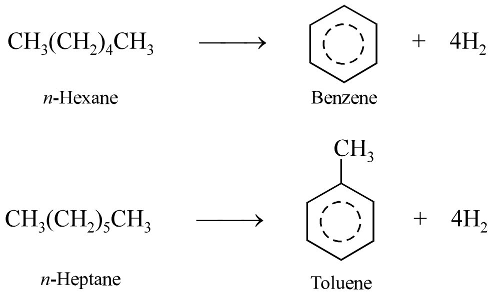
4. Anthracene Oil or Green Oil (270°C–360°C). This portion shows green fluorescence and hence the name green oil. It contains anthracene, phenanthrene and carbazole, which deposit as solids on cooling. The solid is pressed under high pressure, ground and shaken successively with solvent naphtha to remove phenanthrene and pyridine to remove carbazole. The residual solid on sublimation gives pure anthracene. Anthracene is also prepared by synthetic methods and is used for the manufacture of alizarine dyes.

5. **Pitch.** This is the undistilled black residue left in the stills. It contains 92–94% of carbon and may be soft, medium and hard depending upon its softening range. For soft medium and hard pitches the softening ranges are 40°C–65°C, 65°C–85°C and 85°C–105°C respectively. It is used for preparation of varnishes, for making asphalt for road paving and as preservative for wood and metal. It is also used as a binder in waterproofing of flat roofs and in making coal-briquettes used as fuel.

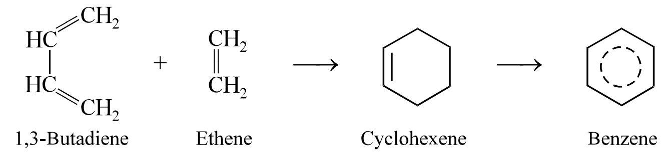
Petroleum

Till recently, petroleum was regarded as an important commercial source for aliphatic compounds alone, but now new techniques such as catalytic reforming or high temperature cracking have been developed to obtain some of the aromatic compounds also.

1. **Catalytic Reforming or Hydroforming.** This process involves cyclization, isomerisation and dehydrogenation of an aliphatic hydrocarbon obtained from petroleum. Catalysts commonly used are oxides of chromium, vanadium and molybdenum deposited on alumina. The reaction is carried out at 450°C–550°C under 10–20 atmospheric pressure. Conversion of *n*-hexane and *n*-heptane to benzene and toluene are given below to illustrate the point.

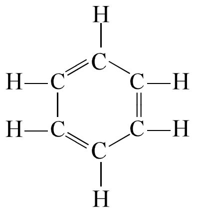


2. **High Temperature Cracking**. This process consists of cracking of petroleum hydrocarbons at 600°C–700°C in presence of catalysts similar to those used in hydroforming. Thus butadiene and ethene obtained from petroleum may be converted to benzene.

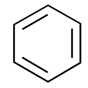


Structural Representation of Benzene and other Benzenoid Compounds

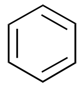
Benzene is the parent aromatic hydrocarbon. It can be represented in the following different manners:



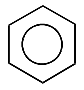
I



II



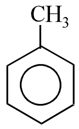
III



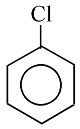
IV

Formula I shows six carbon atoms connected by alternate single and double bonds forming a hexagon. This is the structural formula of benzene, which for the sake of convenience is represented by formulae II, III or IV also. In benzene, as we will see later, each carbon-carbon single bond has somewhat double bond character, so formula IV is a better representation of the molecule, which represents the equivalence of the six carbon-carbon bonds in benzene. However, it is seen that Kekule's formulae is a very convenient in explaining many reactions, hence we shall be using both forms, as and when needed.

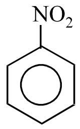
The benzene derivatives are represented, as shown below:



Methylbenzene



Chlorobenzene



Nitrobenzene

Benzene Nucleus and Side Chain

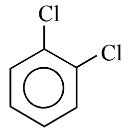
The six carbon atoms of the benzene ring constitute what is known as *benzene nucleus.* The characteristic properties of aromatic compounds are, truly speaking, the properties of this nucleus. In the nucleus all the six carbon atoms are equivalent.

A carbon chain connected to one of the carbon atoms of the nucleus through a carbon atom, other than of the simple functional groups like —CHO, —COOH, >CO, *is called a side chain.* Thus $—CH_3$, $—CH_2.CH_3$, $—CH{=\!=}CH_2$, $—CH_2Cl$, $—CH_2NH_2$ etc., when attached to carbon atom of the benzene nucleus constitute a side chain. The groups like $—NO_2.NH_2$, —Cl (and also —CHO, —COOH, >C==O etc.) when attached to carbon of the benzene nucleus do not constitute a side chain. The side chain shows reactions characteristics of aliphatic compounds and irrespective of its nature, i.e., whether saturated or unsaturated, substituted or otherwise; on oxidation changes to —COOH group ultimately.

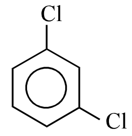
Position Isomerism of Benzene Derivatives

In benzene all the six hydrogen atoms are equivalent, hence the replacement of any one of them by a monovalent atom or group always results in a single monosubstitution product, *e.g.*, there can be only one monochlorobenzene.

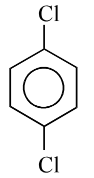
When two hydrogen atoms of benzene are replaced by two similar or dissimilar groups, three isomeric disubstitution products are possible. The position of the substituents are mentioned as *ortho, meta* or *para* depending on the fact, whether substituents are attached to adjacent, alternate or diagonal carbon atoms. Abbreviation *o*, *m* and *p* are used for *ortho*, *meta* and *para* prefixed to the name of the compound, as is shown in the following examples:



o-Dichlorobenzene

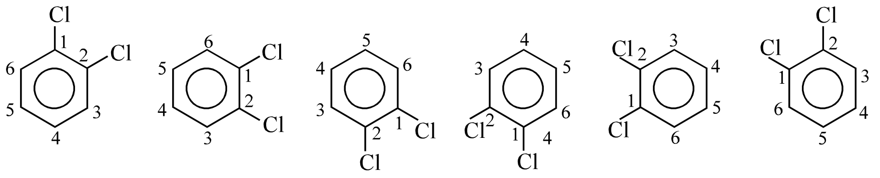


m-Dichlorobenzene



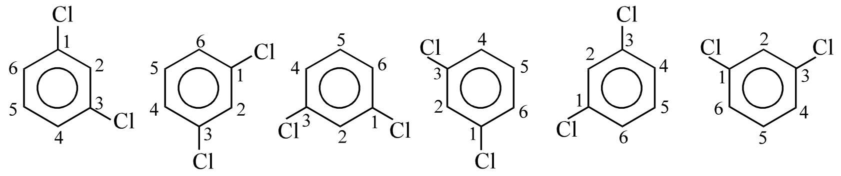
p-Dichlorobenzene

Ortho, *meta* and *para* positions can also be indicated by the using numbers. As the six carbon atoms are equivalent in the benzene ring the numbering of the carbon atoms can start from anyone of the substituent carrying carbon atom and then proceeding in the clockwise direction. However, this has to be kept in mind that the sum of locants indicating the position of the substituent should be least considering all possible combinations. Thus ortho-dichlorobenzene can be represented by any one of the following structures:

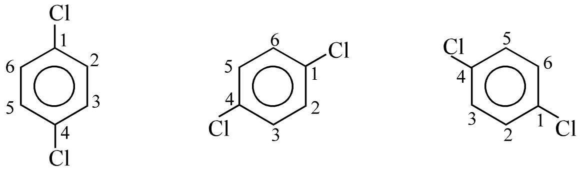


Similarly, the following different structures represent *meta*- and *para*-dichlorobenzenes as shown below:

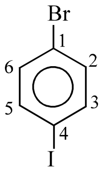
_m_-Dichlorobenzene or 1,3-Dichlorobenzene



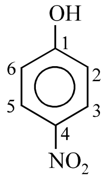
_p_-Dichlorobenzene or 1,4-Dichlorobenzene



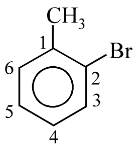
For convenience of fixing the orientation (position of the substituent) the ring should be oriented with position 1 at the top. If the two groups are different and the molecule has no special name, the two groups are successively named in alphabetical order and the name ends with suffix benzene, as for example, bromoiodobenzene, bromonitrobenzene etc. However, if one of the groups is such that it gives a special name to the molecule, then the compound is named as a derivative of that special compound, as for example, *p*-nitrophenol, *o*-bromotoluene etc. The special group or substituent is given number 1 in naming the compound.



p-Bromoiodobenzene
or
1-Bromo-4-iodobenzene

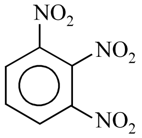


p-Nitrophenol
or
4-Nitrophenol

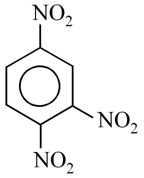


o-Bromotoluene
or
2-Bromotoluene

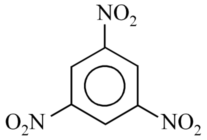
In case of tri or polysubstitution products the number of isomers depend on the fact, whether the substituents are same or different. If three hydrogen atoms of benzene are to be replaced by same monovalent atom or group, the number of isomers will be three but if two substituents are same and the third one different, the number will be six and the number of isomers will be ten when all are different. In such cases the name of the compound can easily be written by numbering the carbon atoms in the above discussed manner.



1,2,3-Trinitrobenzene
or
(*vic*-Trinitrobenzene)



1,2,4-Trinitrobenzene
or
(*asym*-Trinitrobenzene)



1,3,5-Trinitrobenzene
or
(*sym*-Trinitrobenzene)

The trisubstitution products of benzene with three similar groups are termed vicinal or 1,2,3- , asymmetrical or 1,2,4 and symmetrical or 1,3,5 depending upon their relative positions. Abbreviation 'vic' for vicinal, 'as' for asymmetrical and 's' or 'sym' for symmetrical are prefixed to the name of the compound as given above.

Nomenclature

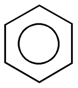
Like aliphatic compounds, aromatic compounds are also classified as hydrocarbons, aryl- halides, hydroxy compounds, aldehydes, ketones etc. The sequence of numbers should be one which gives the lowest sum to the locants of the substituents. If some special group which gives a special name to the compound is present it is given number 1 or number 1 is given to the functional group if present. If more than one functional group is present then the principal functional group is given number 1. In many cases, however, it is found more convenient to name the aromatic compound using trivial or parent hydrocarbon name as suffix and in such cases the root name decides where from the numbering should start.

The names of the following aryl radicals or groups are used in nomenclature and one is expected to be familiar with them.

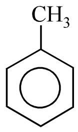
$C_6H_5—$	$C_6H_4<$	$H_3C.C_6H_4—$
Phenyl	(*o*, *m*, *p*) Phenylene	Tolyl
$C_6H_5.CH_2—$	$C_6H_5CH<$	$C_6H_5C\lessdot$
Benzyl	Benzal or Benzylidene	Benzo

Let us study the various classes of aromatic compunds.

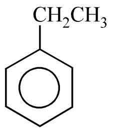
Hydrocarbons



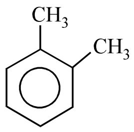
Benzene



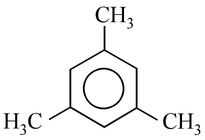
Methylbenzene
(Toluene)



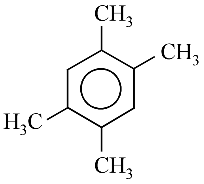
Ethylbenzene



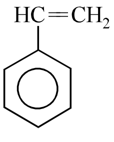
o-Dimethylbenzene
(*o*-Xylene)



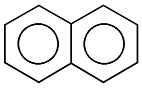
s-Trimethylbenzene
(Mesitylene)
1,3,5-Trimethylbenzene



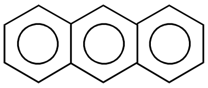
1,2,4,5-Tetramethyl
benzene (Durene)



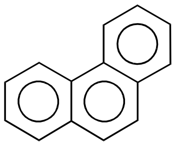
Vinylbenzene
(Styrene)



Naphthalene

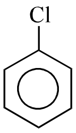


Anthracene

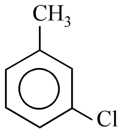


Phenanthrene

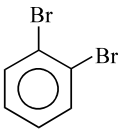
Aryl and Arylalkyl Halides



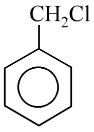
Chlorobenzene
(Phenyl chloride)



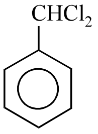
m-Chlorotoluene
(*m*-Tolyl chloride)
or
3-Chlorotoluene



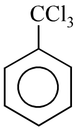
o-Dibromobenzene
o-Phenylenechloride
1,2-Dibromobenzene



Chloromethylbenzene
(Benzyl chloride)

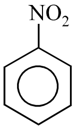


Dichloromethylbenzene
(Benzal chloride)

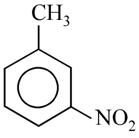


Trichloromethylbenzene
(Benzo trichloride)

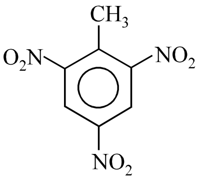
Nitro Compounds



Nitrobenzene



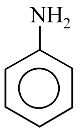
m-Nitrotoluene
or
3-Nitrotoluene



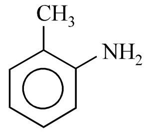
2,4,6-Trinitrotoluene
(TNT)

NOTES

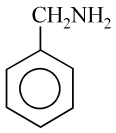
Amino Compounds



Aminobenzene
(Aniline)

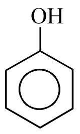


o-Aminotoluene
(*o*-Toluidine)
or
2-Aminotoluene

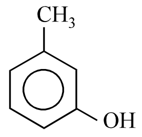


Aminomethylbenzene
(Benzylamine)

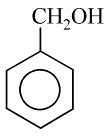
Hydroxy Compounds



Hydroxybenzene
(Phenol)

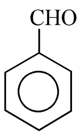


m-Hydroxytoluene
(*m*-Cresol)
or
3-Hydroxytoluene

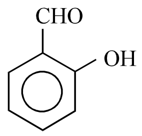


Hydroxymethylbenzene
(Benzyl alcohol)

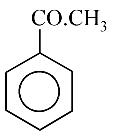
Aldehydes and Ketones



Benzaldehyde

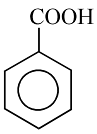


o-Hydroxybenzaldehyde
(Salicylaldehyde)
or
2-Hydroxybenzaldehyde

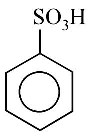


Methylphenyl ketone
(Acetophenone)

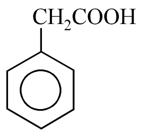
Acids



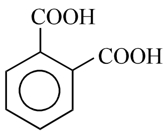
Benzoic acid



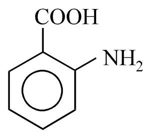
Benzenesulphonic acid



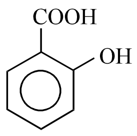
Phenylacetic acid



o-Benzenedicarboxylic acid
(Phthalic acid)

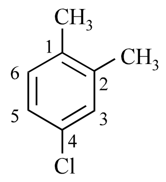


o-Aminobenzoic acid
(Anthranilic acid)

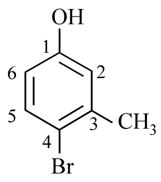


o-Hydroxybenzoic acid
(Salicylic acid)

Some more examples are given to illustrate the method of nomenclature.

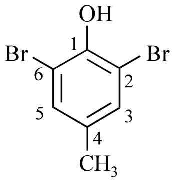


4-Chloro-1,2-dimethylbenzene
or
4-Chloro-*o*-xylene
(I)

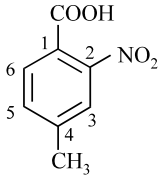


4-Bromo-3-methylphenol
or
p-Bromo-*m*-cresol
(II)

Compound (I) is a derivative of benzene or it can be regarded as a derivative of 1,2-dimethylbenzene (special name *o*-xylene). It can, therefore, be named as a derivative of any of the two hydrocarbons. In compound (II) the numbering will start from the principal function group —OH (phenolic) which should be orientated at the top and given number 1. The compound (II) has a methyl group at *meta*-position with respect to —OH hence its special name is *m*-cresol. The compound (II) can be named as a derivative of phenol or cresol. Since both names end in '*ole*', —OH group is given no. 1.



2,6-Dibromo-4-methylphenol
or
2,6-Dibromo-*p*-cresol
(III)



4-Methyl-2-nitrobenzoic acid
or
2-Nitro-*p*-toluic acid
(IV)

Compound (III) is similar to (II) hence will be named similarly. Compound (IV) can be named as a derivative of benzoic or toluic acid.

With above basic knowledge and more practice the students will become familiar with nomenclature of aromatic compounds.

Structure of Benzene

- **Molecular Formula:** Analysis and molecular weight determination gives the molecular formula of benzene as C_6H_6. Comparing this formula with the corresponding alkane having six carbon atoms, it is eight hydrogen atoms short for saturation. Hence, it is expected to show marked unsaturation.
- **Nature of Unsaturation:** Benzene adds on halogens and can be catalytically hydrogenated. However, it is striking to note that it adds only six atoms of hydrogen or halogens. It also forms a triozonide, pointing to the existence of possibly three double bonds. Hence, the open chain formulae of the following type (4 double bonds or 2 triple bonds or 2 double bonds and one triple bond) were rejected.

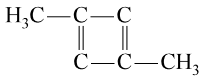
$$CH_2{=}C{=}CH{-}CH{=}C{=}CH_2 \qquad (I)$$

$$CH{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH \qquad (II)$$

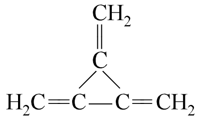
$$CH{\equiv}C{-}CH{=}CH{-}CH{=}CH_2 \qquad (III)$$

The peculiarity of the unsaturation is further demonstrated by the facts that it is resistant to the oxidation by alkaline $KMnO_4$ and contrary to the general nature of unsaturated compounds it gives substitution reactions with halogens in presence of a halogen carrier (in the absence of sunlight). These facts pointed to the existence of unsaturation which was different from the unsaturation hitherto known.

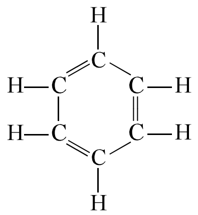
- **Ring Structure and Kekule's Formula:** Benzene formed one and only one monosubstituted derivative. This indicated the identical nature of all the six hydrogen atoms. Keeping this in view the following three ring structures were possible:



(IV)



(V)



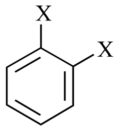
(VI)

However, the formation of 3 disubstituted derivatives by benzene ruled out the existence of structure (IV) and (V) which can give only two disubstituted products. Formula (VI) intuitively suggested by Friedrich August Kekule in 1865, not only explained the possibility of three disubstituted products, but also satisfactorily answered other known facts like, (i) equivalence of all C and H atoms, (ii) addition of six atoms of hydrogen and chlorine and three molecules of ozone, and (iii) its synthesis from acetylene.

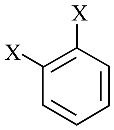
- **Objections to Kekule's formula:** Kekule's formula, however, failed to explain the peculiar stability of benzene despite the presence of double bonds. Other objections to this structural formula were:

  (i) It did not explain the peculiar nature of double bonds because benzene did not respond to characteristic reactions of a hexatriene.

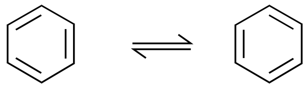
  (ii) This formula predicted the formation of two ortho-disubstituted products, as positions 1,2- and 1,6- are not identical, whereas only one *ortho*-isomer actually existed.



(1,2-)
Substitution



(1,6-)
Substitution



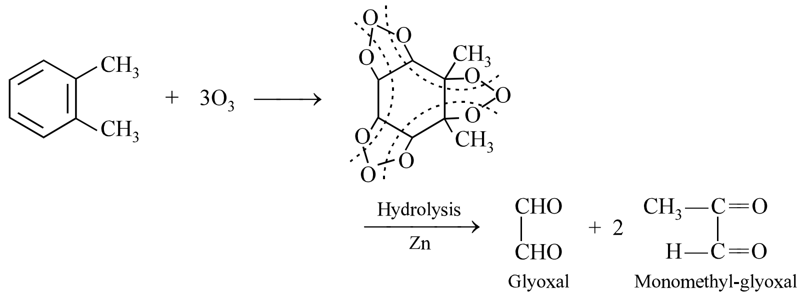
(VI) (VII)

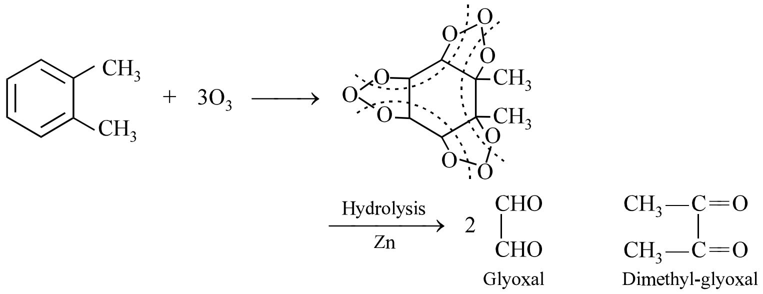
Kekule's dynamic
formula

(*iii*) Benzene behaves as a saturated hydrocarbon and gives substitution reactions more readily than additions reactions. This formula fails to explain this abnormal behaviour of benzene.

To remove the second objection, Kekule later in 1872 suggested that the three double bonds in benzene were in a rapid state of oscillation due to which each C—C pair had a single bond character for half the time and double bond character for rest of the time, *i.e.*, each molecule spending half the time as (VI) and other half as (VII). Hence this left no difference between the two *ortho*-positions. This was referred to as the Kekule's dynamic formula of benzene.

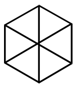
Kekule's dynamic formula got support from the work of Levine and Cole (1932) who obtained glyoxal, methyl-glyoxal and dimethylglyoxal from the ozonolysis of *o*-xylenes.

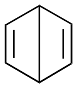


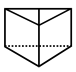


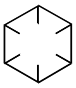
Later, in 1941 Haayman and Wibaut showed that the actual ratio of .88 molecule of dimethyl glyoxal, 2 molecules of methyl-glyoxal and 3.2 molecules of glyoxal obtained was not very much different from the calculated ratio of 1 : 2 : 3.

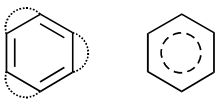
- **Alternatives Structures Suggested:** In order to meet the objections against Kekule's formula, a number of alternative formulae were suggested by different scientists from time to time, each offering some explanation for the unusual stability of benzene.


Claus' diagonal formula (1867) (VIII)


Dewar's parallel formula (1967) (IX)


Ladenburg's prism formula (1869) (X)


Baeyer and Armstrong's centric formula (1887) (XI)


Thiele's partial valency formula (1899) (XII)

(i) Claus introduced his diagonal formula in 1867 which explained the simultaneous formation of *o*- and *p*-isomer. In order to explain the addition reactions Claus later in 1882 said that the *para* bonds had a special character and could be easily ruptured.

(ii) Dewar (1867) suggested formula (IX) for benzene which had its support from the formation of benzoquinone by electrolytic oxidation of benzene but was rejected on the ground that it was not symmetrical. (Later evidence has, however, proved that this was one of the contributing structures of benzene.)

(iii) Ladenburg's (1869) prism formula represented a stable structure but as there was no unsaturation in it, it did not find favour. Further, the three dimensional representation would make some of the trisubstituted derivatives optically active, which, however, was not the case. Besides these shortcomings the formula had no answer for a different angle, other than 109°28′, in between C—C—C linkages.

(iv) Baeyer proved that hexahydrobenzene and cyclohexane were identical and hence supported a six carbon atom ring for benzene. He also showed that the dihydrobenzene behaves like a typical olefin and therefore no *para* link was apparently present. On these grounds he rejected Claus, Dewar and Ladenburg formulae but he did not accept Kekule's formula. Accepting the suggestion of

Armstrong (1887) he proposed Armstrong-Baeyer centric formula (XI). In this formula the fourth valency of each carbon was directed towards the centre of hexagon and the valencies balanced each other thus creating an equilibrium. When benzene was converted to dihydrobenzene this equilibrium was disturbed and the resulting product had typical olefinic bonds. However, this formula had no satisfactory explanation for the behaviour of poly-nuclear hydrocarbons and was therefore rejected.

(v) Thiele applied his theory* of partial valency to the benzene problem in 1899 and gave the formula (XII). Thiele's formula could explain the stability of benzene and also eliminated the difference between 1 : 2 and 1 : 6 positions as there were no real single or double bonds in his structure. However, if Thiele's hypothesis was accepted then cyclooctatetraene should also exhibit aromatic character as it has 4 conjugated double bonds but Willstatter found that this was not so.

Willstatter further proved by experimental methods that the introduction of one or two double bonds in cyclohexane gave the normal unsaturation to the compound but when third double bond was introduced there was a complete change in the properties. This led to the revival of Kekule's dynamic or oscillation formulae again.

- **Present-day position of the structure of benzene:** Since the time of Kekule a large amount of physico-chemical data, from spectroscopic, X-ray and electron diffraction studies, etc., has been gathered about benzene:
  - (i) X-ray studies reveal that benzene is a flat hexagonal ring and the six carbon atoms lie at the corners of a regular hexagon.
  - (ii) Electron diffraction studies show that the bond distance between any two adjacent carbon atoms is 1.397Å and C—C—C bond angles are 120°. This value of bond length lies in-between the values for a C—C single bond (1.54Å in ethane) and $C{=}C$ double bond (1.33Å in ethylene).
  - (iii) The actual heat of hydrogenation of benzene is lower than the theoretically calculated value for Kekule structure by approximately 36 kcal/mole. The same difference of energy is observed in actual and calculated values of heat of combustion.
  - (iv) Infrared and ultraviolet absorption spectra and parachor value of benzene support Kekule's structure.

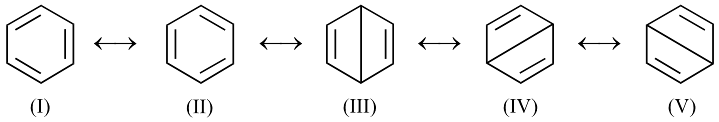
The present-day approach regarding the structure of benzene is to explain its peculiar stability while taking into consideration the above facts. The two important modern methods which are presently in use to explain its structure are: (*a*) Valence-bond or resonance method and (*b*) Molecular orbital method.

Let us study these methods in detail

(a) Resonance Structure of Benzene.

According to the concept of resonance "Any molecule for which two or more classical structural formulae may be written, cannot be represented adequately by any of these formulae (known as contributing or limiting structures or canonical forms) but by the superposition of the entire set." The structure of such molecules is intermediate between the forms represented by the limiting structures or in other words the molecule is a hybrid (known as resonance hybrid) of these resonating limiting structures. Such a molecule cannot be represented diagrammatically in accordance with the usual valency rules of classical structural theory. Therefore to represent such a molecule the limiting structures are written and double headed arrows are placed between them to indicate the resonance. However, these limiting structures or canonical forms do not correspond to any real electronic states of the molecules in unexcited form (i.e., ground state).

Thus five different canonical structures can be written by changing the pairing of six π electrons:



The structures (I) and (II) corresponds to Kekule's structure structures, (III) to (V) are Dewar's structures. However Kekule forms are more stable than either of Dewar's forms and contribute to the extent of 80% to the total structure of benzene. Thus as an approximation for writing most of the reactions and properties of benzene Kekule's structures may be used.

This predominance of Kekule's forms having three alternate single and double bonds explains the addition reactions of benzene and also the equivalence of all the six hydrogens. Due to the resonance among these limiting structures it is to be expected that all carbon to carbon bond lengths must be equal and therefore must be between that of a pure single or double bond. This explains the observed carbon to carbon bond length of 1.397Å in benzene. This equivalence of carbon to carbon bond length also explains the presence of only one *ortho*-isomer.

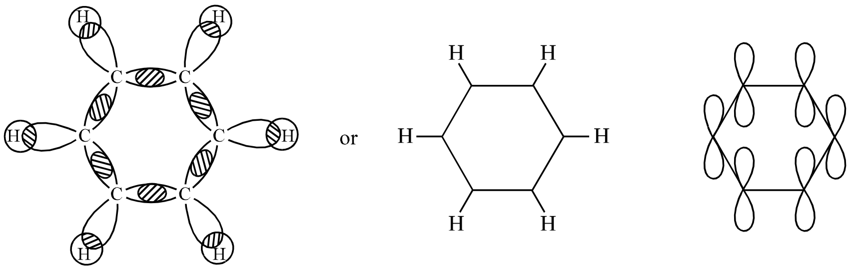
Resonance can occur in a molecule if it is planar. Thus, all the C and H are expected to be planar. Finally a resonance hybrid is always more stable than any of the limiting structures. Thus benzene which is a resonance hybrid is expected to be more stable than the contributing Kekule structures. The difference of energy between the resonance hybrid and its limiting structures is known as 'resonance energy' and is a measure of stabilization of the molecule.

The greater stability of benzene molecule is proved by the observed and theoreticcal values of heat of hydrogenation and combustion of benzene. The heat of hydrogenation of carbon-carbon double bond is 28.6 kcal/mole. Hence the calculated value for benzene, assuming it to be cyclohexatriene, will be 85.8 kcal ($28.6 \times 3 = 85.8$), which is greater than the observed value of 49.8 kcal/mole. Thus benzene should be more stable than the cyclohexatriene.

Similarly, the observed heat of combustion of benzene is less by about 36 kcal/mole than the calculated value which again points to the fact that the molecule has less energy than the cyclohexatriene and hence more stable. This stability and absence of real double bonds in benzene molecule also explains its tendency to undergo substitution reaction rather than addition reactions because the latter will tend to make the molecule non-planar and thus inhibit the resonance.

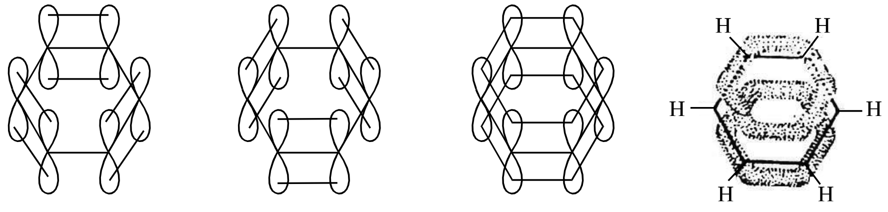
(b) Molecular Orbital Structure of Benzene

Modern approach to the benzene structure is on the basis of M.O. theory. Usually a carbon involved in the double bond formation is in sp^2 hybridized state. Thus if we try to write Kekule structure on the basis of M.O. theory then each of the carbon atom in benzene must be in sp^2 hybridized state. The three hybrid orbitals of each of such a carbon atom are in the same plane and form two σ bonds with two other such carbon atoms on either side by coaxial overlap of hybrid orbitals and one σ bond with *s*-orbital of hydrogen. The usual valency angle among the sp^2 hybrid orbitals is 120° which is also the observed bond angle is benzene. This gives rise to a total of 12σ bonds and carbon skeleton acquires a hexagonal shape with all the C and H in the same plane. At each of the sp^2 hybridised carbon atom there is still an unhybridised *p*-orbital that lies perpendicular to the plane of the hybrid orbitals. The sidewise or parallel overlap of these *p*-orbitals with those on adjacent carbon atoms results in the formation of π bonds as shown in two Kekule's structures above. However since *p*-orbital at any carbon atom can overlap with either of the *p*-orbitals on the carbon at its left or right, and the probability of both types of overlapping being equal, this results in the continuous overlapping as shown in structure (III). This leads to the formation of two continuous or delocalised π electron clouds, one above and the other below the plane of the hexagon of 6 carbon atoms—sandwiching the hexagon between them (IV). The six π electrons are delocalised over all the six carbon atoms and the molecular orbital is polycentric. The energy of these six delocalised π electrons is less than that of three pairs of localised or isolated π electrons and therefore the molecule is stabilised. This difference of energy due to which the molecule is stabilised is known as delocalisation energy.



σ-Framework of benzene

Unpaired *p*-orbital at each carbon



(I) (II) (III) (IV)

The two Kekule structures

Delocalised π electrons cloud of benzene

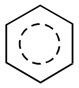
***Fig. 3.4** MO Structure of Benzene*

The MO picture explains all the known facts about the benzene viz., planarity of the molecule, bond angles of 120°, equal C—C bond lengths and stabilisation of molecule as compared to Kekule structure.

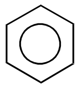
Since the π electrons are delocalised and form electron clouds on either side of the plane of carbon atoms, benzene will act as a source of electrons.

Electrophilic reagents will therefore attack the molecule much more readily, particularly as the π electrons are loosely held (as compared to σ electrons) and easily polarizable. However to preserve the delocalisation and the corresponding stability (or aromatic character) the molecule will tend to undergo substitution rather than addition reactions with these electrophilic reagents. This explains the tendency of benzene to under electrophilic substitution reaction.

To show the delocalisation of 6 π electrons benzene is represented by drawing a dotted line or continuous inscribed circle as shown below:



or



Benzene

Benzene was first isolated by Michael Faraday in 1825 from oil condensed in cylinders of compressed illuminating gas. In 1833 Mitscherlich obtained it by distilling benzoic acid with lime and named it *Benzin*. Later on Liebig suggested the name Benzol for it. In 1845 Hofmann obtained it from coal tar, which is still commercial source of benzene. Large quantities of benzene and alkyl benzenes are prepared in U.S.A. by cracking of petroleum.

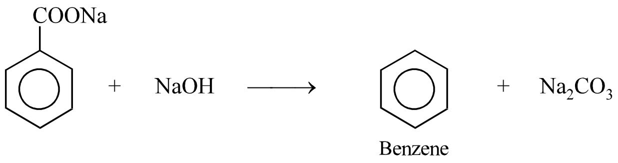
General Methods of Preparation

Let us study some general methods of preparation of Benzene in detail.

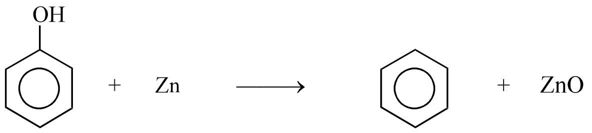
1. Replacement of the Group Already Present in the Nucleus by Hydrogen

The replacement of the following groups in done to prepare benzane:

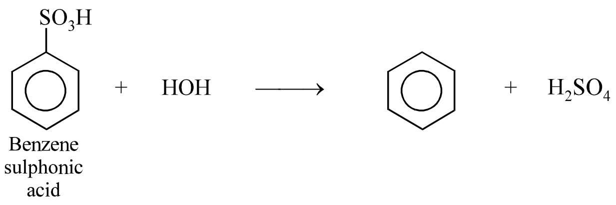
(i) **Replacement of —COOH group:** The salt of benzoic acid or the acid itself is heated with soda lime.



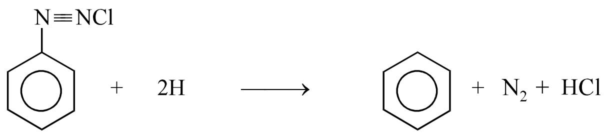
(ii) **Replacement of Phenolic —OH group:** Benzene can be obtained by passing vapours of phenol over heated zinc dust.



(iii) **Replacement of —SO$_3$H group:** Benzene can be obtained by boiling benzene sulphonic acid with dilute hydrochloric acid at 150°C–200°C or by hydrolysing the acid with super heated steam.



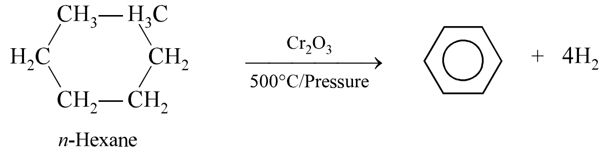
(*iv*) **Replacement of —N_2Cl Group:** Benzene diazonium salt when reduced with alcohol, alkaline sodium stannite or hypochlorous acid gives benzene.



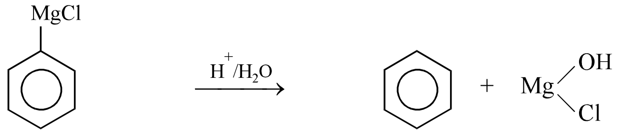
Other Methods

Some of the other methods are as follows:

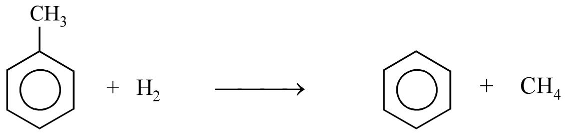
(i) **Hydroforming (Catalytic Reforming):** The method is based on dehydrogenation, cyclisation and isomerisation reactions. The cyclic aromatic hydrocarbon contains same number of carbon atom as the starting acyclic hydrocarbon. Catalyst used is chromium oxide supported on alumina.



(ii) **Treatment of Phenyl Magnesium Chloride with Dilute HCl:** It gives benzene.



(iii) **Hydrodealkylation:** Toluene and xylenes when heated with hydrogen under pressure in presence of metal-oxide catalyst yield benzene.



(iv) **Laboratory Method:** Benzene can be prepared by any one of the general methods described earlier. However, it can be conveniently prepared in the laboratory by heating a mixture of sodium benzoate (20 g) and soda lime (30 g) in a distillation flask connected to a Liebig condenser and receiver. Benzene distils over which is dried over anhydrous calcium chloride and redistilled.

$$C_6H_5COONa + NaOH \longrightarrow C_6H_6 + Na_2CO_3$$

(*v*) **From Coal Gas:** Coal gas contains large amount of benzene and some toluene in vapour state. The gas is passed through towers, in which high-boiling creosote oil is sprayed from the top. Both benzene and toluene dissolve in the oil, from which they are recovered by steam-distillation. The mixture of benzene and toluene is subjected to fractional distillation, when pure benzene (b.p. 80.4°) is obtained.

(vi) **From Light Oil:** Benzene is obtained from light oil, which contains 60–65 per cent of benzene and methyl benzenes, 12–15 per cent of naphthalene, 8–10 per cent of phenol and 1–3 per cent of basic substances such as pyridine with a very small amount of thiophene. The oil is treated with cold dilute sulphuric acid, which removes the bases and also most of the thiophene. It is then washed with sodium hydroxide to remove acidic substances like phenol and excess of sulphuric acid. The oil is washed with water and subjected to fractional distillation, the vapours being passed through a dephlegmator (same as in Coffey's still). The issuing vapours, when condensed from three fractions:

(i) 90 per cent Benzol (80–110°C): It contains 70–80 per cent of benzene and 14–24 per cent of toluene. It is called 90 per cent benzol because 100 ml of the fraction, when distilled, yield 90 ml of distillate upto 100°C.

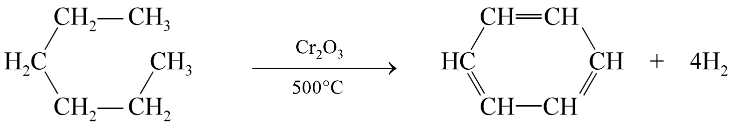
(ii) 50 per cent Benzol (110–140°C): It contains 46 per cent of benzene with toluene and some xylenes. This is also known as 90 per cent toluol.

(iii) Solvent naphtha or benzene (140–170°C): It consists of mainly xylenes, mesitylene, cumene (isopropyl benzene) etc. It is used as a solvent for paints, resins, rubber etc.

Benzol fractions (90 and 50%) are fractionally distilled and the fractions passing between 80–82°C are collected. This is then cooled in freezing mixture and the crystals of benzene (m.p. 5.4°C) are separated. The process of distillation and freezing is repeated until it boils at 80–81°C. It is pure benzene containing some thiophene, which has almost same m.p. and b.p. as that of benzene.

In order to remove thiophene it is repeatedly washed with cold and concentrated sulphuric acid, until it gives no colour with a trace of isatin in concentrated sulphuric acid. This shows the absence of thiopene and the test is known as indophenin test. The product is finally washed, dried and redistilled.

(vii) **From Petroleum:** Benzene is also manufactured by cyclisation of hexane obtained from petroleum. Vapours of hexane are passed under pressure over heated (500°C) chromium catalyst (Cr_2O_3 deposited over alumina).



(viii) **Synthesis:** In 1870 benzene was synthesized by Berthelot by passing acetylene through red-hot tube.

$$3C_2H_2 \longrightarrow C_6H_6$$

Physical properties

- Benzene is a colourless mobile liquid with characteristic odour. It boils at 80.1°C. It is insoluble in water and lighter than it (sp. gr. 0.884 at 15°C). It is miscible with alcohol and ether in all proportions. It is a good solvent for fats, resins, sulphur, phosphorous, iodine, etc.
- It is extremely poisonous substance. The inhalation of vapours or absorption through skin has a toxic effect. Even the presence of 1 part of benzene vapours in ten thousand parts of air produces symptoms of poisoning indicated by giddiness and nausea. A concentration of about two hundred parts per thousand of air causes death in a very short time which is due to respiratory failure or heart failure.

NOTES

Spectroscopic Properties

- It shows absorption maxima at 198 mμ ($\pi \rightarrow \pi^*$) and at 225 mμ (benzenoid band).
- The aromatic ring shows C—H streching between 3000–3100 cm^{-1} and four C—C streching bands at 1450, 1500, 1580 and 1600 cm^{-1}.

Chemical Properties

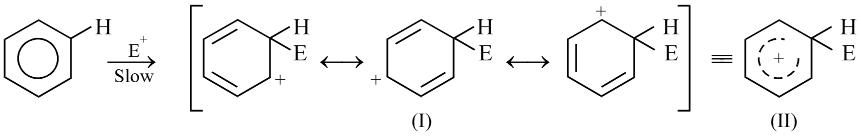
Benzene nucleus shows unusual stability, but the hydrogen atoms attached to it are readily replaced by other atoms are groups shows that there is a cloud of π electrons above and below the plane of the benzene ring of six carbon atoms. Hence, most common reactions of benzene are electrophilic substitution reactions.

(A) Electrophilic Substitution Reactions

The π electrons of benzene ring are losely held and are available to an electrophilic reagent seeking electrons hence typical reactions of benzene are electrophilic substitution reactions. In the reactions the attacking electrophile may be produced in different ways but what happens to the aromatic ring is basically same in all the cases.

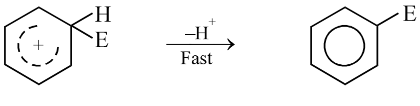
The attacking electrophile may be a positive ion or a dipole. If it is a positive ion it attacks the ring removing a pair of electron from the sextet to give a carbocation which gets resonance stabilized as shown in (I) and is represented as shown in (II).

Step 1

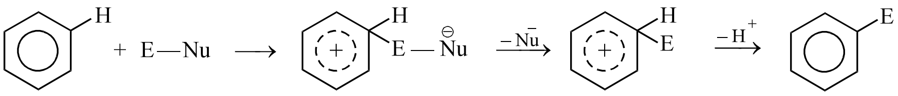


Ions of the type (II) are called carbocation, Wheland intermediates, s-complex or arenium ions. In case of benzenoid system, they are called cyclohexadienyl cations. The arenium ion has been isolated and is quite stable but it stabilizes itself by the loss of either E^+ or H^+. The aromatic sextet is then restored. This is the second step of the mechanism in which the proton is accepted by a proton acceptor (base) to revert the system to stable benzenoid structure. The second step is faster than the first step. Lars Melander (1949, 1950) while studying the nitration of a variety of aromatic compounds established that first step is slower.

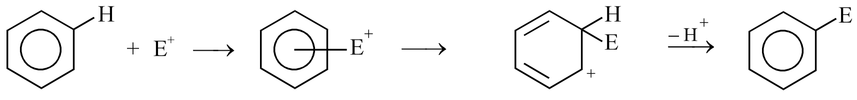
Step 2



If the attacking species is not an ion but a dipole, the product must have a negative charge, unless part of the dipole with its electron pair, is broken off at some stage in the process.

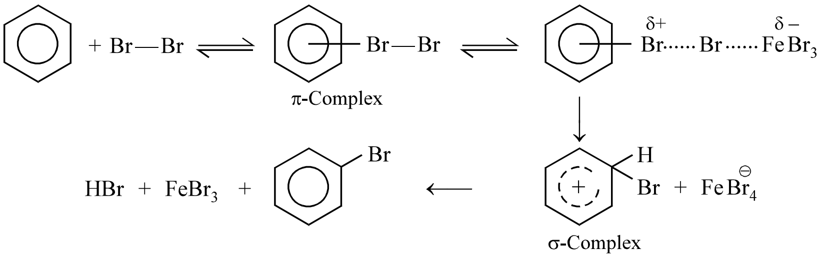


The arenium ion formed and isolated is commonly called s-*complex*. However, it was found that the relative reactivity and the percentage of *o*, *m* and *p* products formed depended not only a particular reaction but also on the nature of the reagent employed. This led some chemists to believe that a π-complex is formed during the electrophilic substitution between the substrate and the electrophile before the formation of arenium ion (s-complex) and that influences the reaction rate.



π-Complex σ-Complex

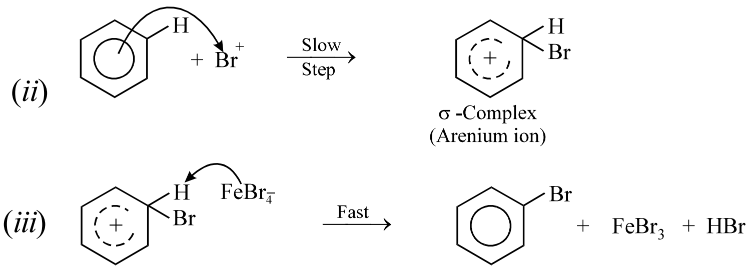
In the electrophilic substitution of bromine, kinetic data has shown that the rate of bromination depends on the concentration of catalyst $FeBr_3$ also besides halogen and benzene. The positive end of the dipole attacks the aromatic ring forming π-complex and the negative end is complexed with the catalyst. The formation of σ-complex (arenium ion) between Br^+ and carbon of the benzene ring is the slow step of the reaction. The reaction may be represented as given below:



However, since s-complex is formed, substitution can also be represented by the steps given below:

(*i*) $Br{-}Br + FeBr_3 \rightleftharpoons Br^+ + FeBr_4^-$

Lewis base Lewis acid Electrophile



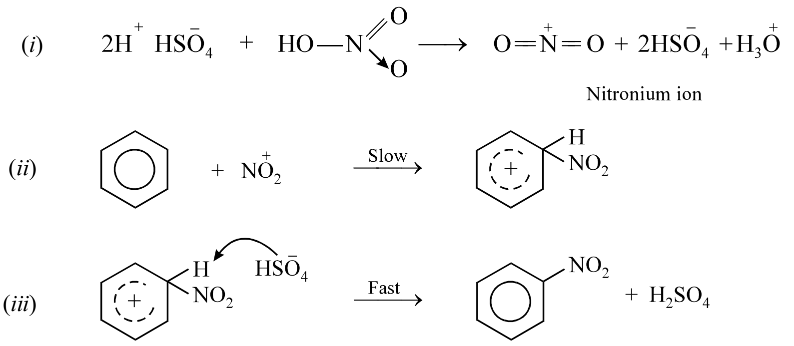
In the substitution reactions given below there are three steps in the reactions. First step is the production of electrophile, the second step is the formation of arenium ion or σ complex and the third step is the removal of the proton to form the substitution product.

1. **Nitration:** Nitration of benzene is carried out with a mixture of conc. nitric and conc. sulphuric acid.

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Mechanism

In the first step of the reaction $\overset{+}{NO}_2$ is produced (strong sulphuric acid causes nitric acid to ionise as $O\bar{H} + \overset{+}{NO}_2$) which reacts with benzene in the second step to give the arenium ion. The arenium ion transfers a proton to some base in the mixture *e.g.*, $HS\bar{O}_4$ to give nitrobenzene.



The energy changes taking place have been shown in the energy profile Figure. 3.5.

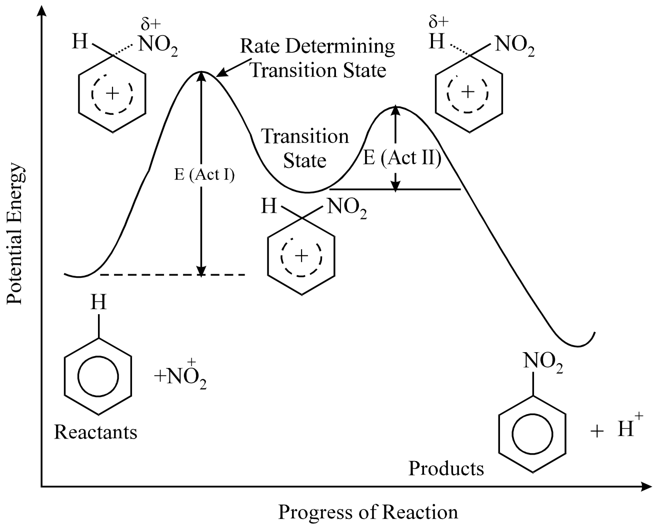
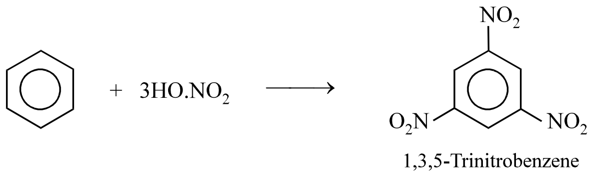


Fig. 3.5 *Energy Changes*

If fuming nitric acid is used for the reaction it is possible to introduce two or three nitro groups.



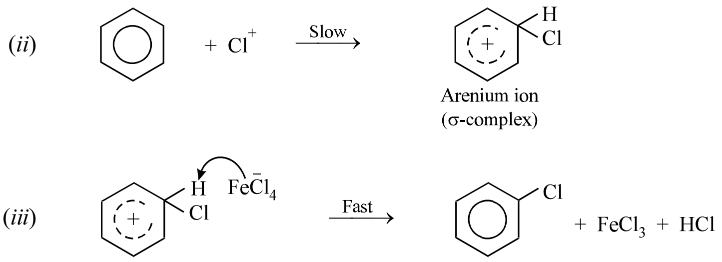
2. **Halogenation:** Benzene undergoes chlorination and bromination forming monochloro or monobromobenzene. The reaction takes place in presence of $FeCl_3$ or $AlCl_3$ at room temperature.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

Mechanism

In the first step the electrophile is formed which in the second step attacks the π electrons to form arenium ion (s-complex). The arenium ion loses the proton to the base in the last step to give monohalo substituted benzene.

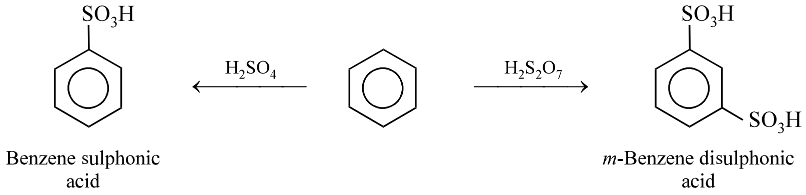
(*i*) $\mathrm{Cl{-}Cl} + \mathrm{FeCl_3} \longrightarrow \mathrm{Cl^+} + \mathrm{Fe\bar{C}l_4}$



The reaction with bromine is given just above. Reaction with iodine presents some difficulty since iodine is the least active among the halogens but if carried out in presence of some oxidising agent *e.g.*, nitric acid or mercuric oxide, the reaction takes place with good yield of iodo-compound.

$$2C_6H_6 + I_2 \xrightarrow[{[O]}]{HNO_3} 2C_6H_5I + H_2O$$

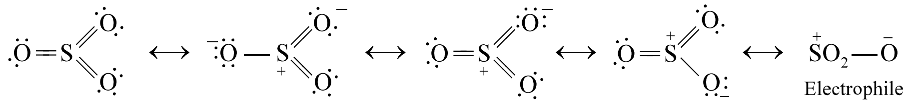
3. **Sulphonation:** With hot and concentrated sulphuric acid benzene forms benzene sulphonic acid. If fuming sulphuric acid is used *m*-benzene disulphonic acid is formed.



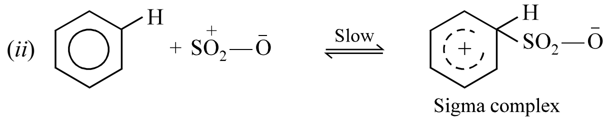
Mechanism

In the first step of reaction H_2SO_4 acts both as an acid and a base to produce the electrophile SO_3 which is a resonance hybrid of many forms in which the following dipolar form predominates.

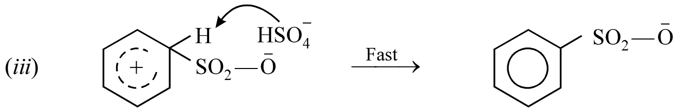
(*i*) $2H_2SO_4 \rightleftharpoons H_3\overset{+}{O} + HS\bar{O}_4 + SO_3$



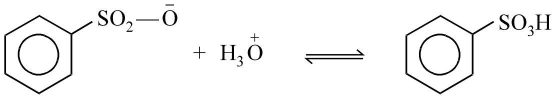
The electrophile SO_3 attacks π electrons of the ring to form arenium ion.



Sigma complex loses a proton to base $HS\bar{O}_4$ to give resonance stabilized substitution product.



The product in step (*iii*) accepts a proton to give the acid which remains dissociated.

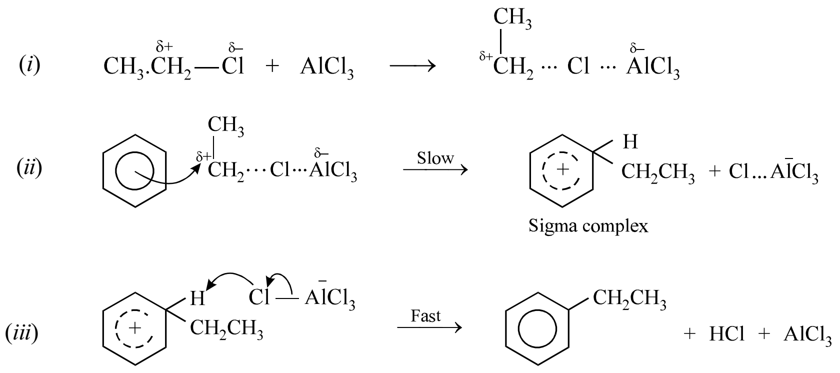


4. **Friedel-Crafts Alkylation of Benzene:** Benzene on being treated with alkyl halide in presence of $AlCl_3$ form alkyl benzenes in which the alkyl group comes from alkyl halide.

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5.CH_3} + HCl$$

Mechanism

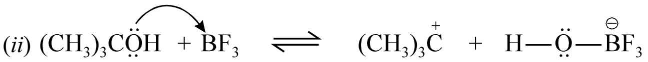
In Friedel-Crafts alkylation, the electrophile is a carbocation which is easily formed if the alkyl halide is secondary or tertiary. The available evidence suggests that the alkyl halide (say on alkyl chloride) reacts with the $AlCl_3$ used to form a ion-pair type complex. This complex attacks the benzene ring in step II to form sigma complex.



In the last step sigma complex loses a proton to base $Cl—\bar{Al}Cl_3$ to give the alkyl benzene.

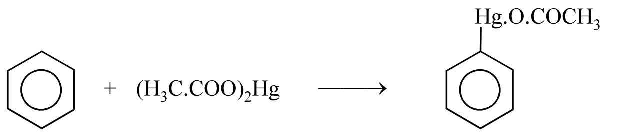
Friedel-Crafts reaction is also used to introduce groups like R.CO— or $(CH_3)_3C$— in benzene nucleus. In each case the electrophile is produced which then reacts in the manner indicated above. Production of electrophile has been indicated in a rather simplified manner here.

(*i*) $R.COCl + AlCl_3 \longrightarrow R.\overset{\delta+}{CO}\cdots Cl\cdots \overset{\delta-}{AlCl_3}$ or $R.C\overset{+}{O}$ $\bar{Al}Cl_4$



(*ii*) $(CH_3)_3C\ddot{O}H + BF_3 \rightleftharpoons (CH_3)_3\overset{+}{C} + H—\ddot{O}—\overset{\ominus}{B}F_3$

5. **Mercuration:** When benzene is heated to (90–160°C) with mercuric acetate for about an hour, one hydrogen atom is replaced by acetoxy-mercuric group. Conditions of the reaction are such that electrophile $H_3C.COOHg^+$ is created for the reaction.



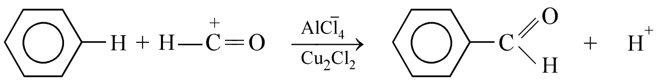
Acetoxymercuribenzene
or
Phenyl mercuric acetate

Mercurated compounds are of great medicinal value.

6. **Formylation:** During some reactions given below an aldehydic group gets introduced into the nucleus. This is called formylation.

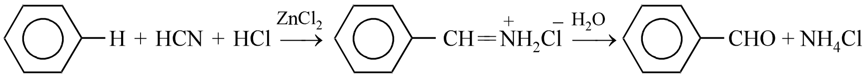
(*i*) **Gattermann Koch Reaction:** When a mixture of carbon monoxide and hydrogen chloride is passed in an ethereal solution of benzene in presence of anhydrous $AlCl_3$ and cuprous chloride, an aldehyde is obtained.

$$CO + HCl \longrightarrow \underset{\text{Formyl chloride}}{Cl.CHO} \ : \ ClCHO + AlCl_3 \longrightarrow \overset{+}{C}HO + Al\overset{-}{Cl}_4$$



$$H^+ + Al\overset{-}{Cl}_4 \longrightarrow AlCl_3 + HCl$$

(*ii*) **Gattermann Aldehyde Synthesis:** When benzene is treated with liquid hydrogen cyanide and dry hydrogen chloride in presence of anhydrous $AlCl_3$ or $ZnCl_2$ then an aldimine is formed which on being hydrolysed give an aldehyde.



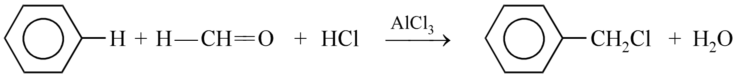
This is also an electrophilic substitution reaction and the attacking electrophile is

$\overset{+}{C}H = NH$.

$$H—C \equiv N + HCl \longrightarrow Cl.CH=NH \xrightarrow[-Al\overset{-}{Cl}_4]{AlCl_3} \overset{+}{C}H = NH$$

The reaction can also be applied to toluene, xylene, etc.

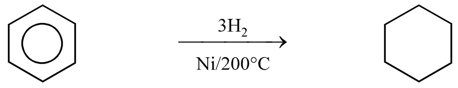
7. **Chloromethylation:** Introduction of the chloromethyl group (— CH_2Cl) in the benzene nucleus is also an electrophilic substitution reaction and is known as chloromethylation. This can be done by heating benzene or its homologues with formaldehyde and HCl in presence of anhydrous $AlCl_3$ or $ZnCl_2$.



Benzyl chloride

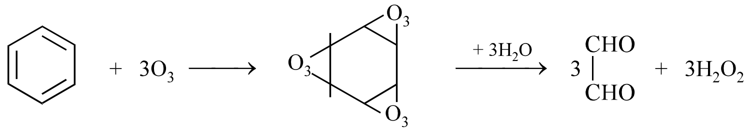
(B) Addition Reactions

1. Hydrogenation. Benzene undergoes hydrogenation in presence of finely divided metal catalyst like nickel, platinum, etc., at about 200°C and form corresponding saturated cyclohexane.



Benzene Cyclohexane

2. Ozonide Formation: Benzene adds up one ozone molecule at each one of the three double bonds to form a triozonide.



Benzene Benzene triozonide

3. Addition of Halogen: In bright sunlight and absence of halogen carrier, benzene react with chlorine and bromine to form hexahalides, *e.g.*,

$$C_6H_6 + 3Cl_2 \longrightarrow \underset{\text{Benzene hexachloride}}{C_6H_6Cl_6}$$

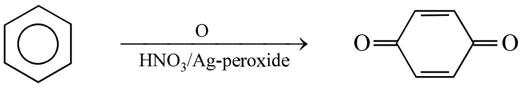
Benzene hexachloride (BHC) exists in several isomeric form. Its g-isomer is a powerful insecticide sold under the name Gammexane (or 666).

(C) Miscellaneous Reactions

1. Combustion: Benzene is highly inflammable liquid and burns with a sooty (smoky) flame forming carbon dioxide and water vapour.

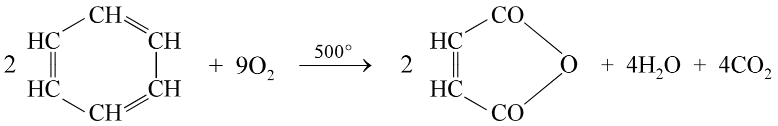
$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

2. Oxidation: Benzene is very stable to oxidising agents like chromic acid, alkaline potassium permanganate or dilute nitric acid. Thus benzene does not decolourise potassium permanganate. However, when oxidised with nitric acid in presence of silver peroxide, it forms *p*-quinone.



p-Benzoquinone

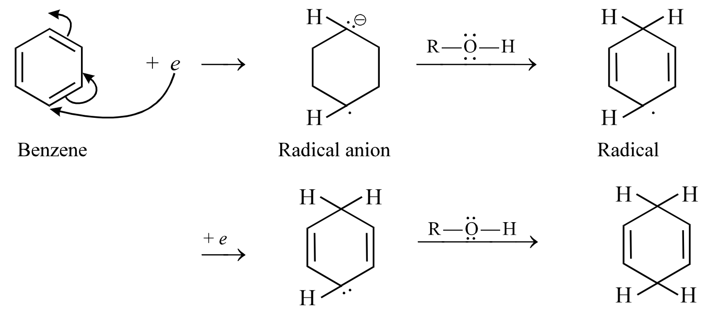
Vapours of benzene mixed with air, when passed over heated vanadium pentoxide form maleic anhydride by oxidation.



3. Birch Reduction: Partial reduction of aromatic ring can be achieved by dissolving lithium, sodium or potassium in liquid ammonia or amine in presence of ethyl, isopropyl or isobutyl alcohol.

$$Na + (x+y)NH_3 \longrightarrow [Na(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The mechanism of Birch reduction involves solvated electron which are transferred from metal to solvent and then to the ring. The reaction begins with addition of an electron to form a radical anion which is resonance stabilized. Protonation of the radical ion gives neutral radical. Addition of electron and protonation repeats itself to yield 1,4-cyclohexadiene.

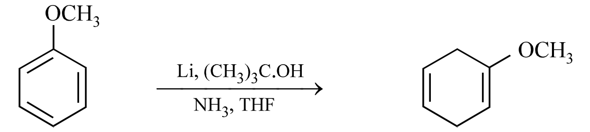


Benzene Radical anion Radical

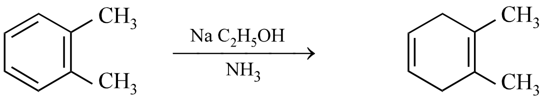
Carbanion 1,4-Cyclohexadiene

The double bonds in 1,4-cyclohexadiene are isolated and are much less reducible, hence the reaction steps. The presence of electron releasing groups like alkyl or alkoxy retard the electron transfer hence retard the reaction whereas the presence of electron withdrawing group like —COONa facilitates reduction.

Electron Releasing Groups Present in Benzene Nucleus and Birch reduction:

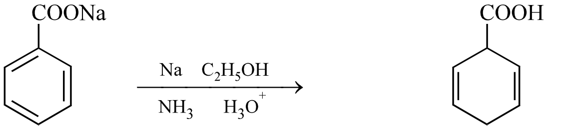


Methoxybenzene (Anisole) 1-Methoxy-1,4-cyclohexadiene



1,2-Dimethylbenzene (*o*-Xylene) 1,2-Dimethyl-1,4-cyclohexadiene

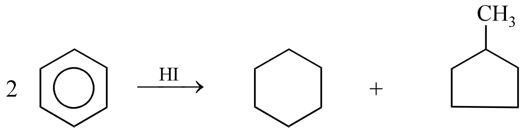
Electron Withdrawing Group Present in Benzene Nucleus and Birch reduction:



2,5-Cyclohexadiene-1-carboxylic acid

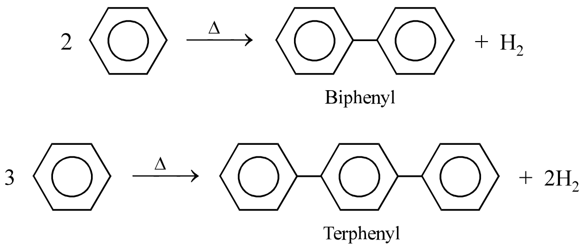
It is to be noted that electron releasing groups remain on the unsaturated carbon atom whereas electron withdrawing groups remain on the saturated carbon atom in the product.

4. Action of HI: Benzene on prolonged heating with HI forms a mixture of cyclohexane and methylcyclopentane.



Cyclohexane Methylcyclopentane

5. **Formation of Polynuclear Hydrocarbons:** Vapour of benzene when passed through a red hot tube form a mixture of polynuclear hydrocarbons, e.g., biphenyl and terphenyl.



Uses

Benzene is used in the following ways:

- As a solvent for extraction of fats and oils
- As a motor fuel along with petrol
- As a starting material for synthesis of various substances to be used for the preparation of dyes, drugs, plastics, perfumes, explosives, etc.
- In the manufacture of maleic acid by catalytic oxidation

3.2.5 Allyls

In Allyl halide the reactivity of halogen is just opposite to that of vinyl halide. A look at the structure will make it clear that *p*-orbital of chlorine is separated from localised molecular orbital of first two carbon atom by a sp^3 hybridised carbon hence no interaction is possible from the *p*-orbitals of first two carbon atoms: On the other hand the release of halogen will give a carbocation which will be resonance stabilized [structures (VI), (VII) and (VIII)].

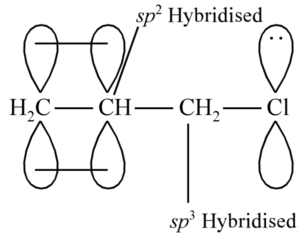
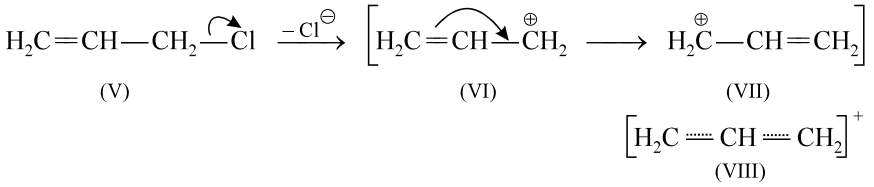


Fig. 3.6 *Allyl Chloride*



$$H_2C{=}CH{-}CH_2{-}Cl \xrightarrow{-Cl^{\ominus}} \left[H_2C{=}CH{-}\overset{\oplus}{C}H_2 \longrightarrow H_2\overset{\oplus}{C}{-}CH{=}CH_2\right]$$

(V) (VI) (VII)

$$\left[H_2C \cdots CH \cdots CH_2\right]^+$$

(VIII)

The greater the stability of the carbocation and faster its formation makes allyl halide give nucleophilic substitutions reactions easily by S_N1 mechanism. In fact the halogen of the allyl halide is more reactive than that of a tertiary alkyl halide. Greater stability of allyl carbocation can also be seen by the formation of delocalised molecular orbital by the *p*-orbitals of three carbon atoms involved.

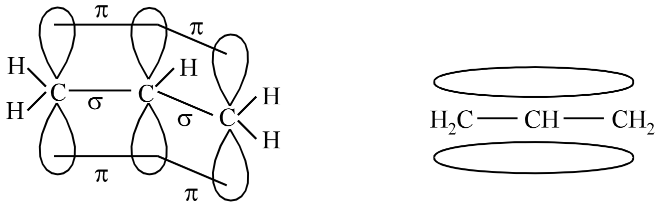


Fig. 3.7 *Allye Carbocation*

3.2.6 Dienyl and Trienyl Complexes

Alkenyl-, dienyl- and trienylidene-chromium and tungsten complexes $(CO)_5M{=}[C(OMe)\{CHCH\text{-}(CHCH)_n\text{-}R\}][n = 0, 1, 2]$ are produced in one step by photolysis of $M(CO)_6[M = Cr, W]$ in the presence of 2-propyn-1-ol derivatives $H–CCC(H)(OH)[(CHCH)_n–R]$ and methanol. The acetylium ion is added by the dienyl complex, however, on hydrolysis, the result decomposes to the metal-free acetylcycloheptadiene. Irradiation of the dienyl complex in the presence of triphenylphosphine results in the replacement of one carbonyl group.

Check Your Progress

1. What are olefins termed as in IUPAC system?
2. Which two members of the alkene series have only one structural formula?
3. What happens when dihaloalkanes are treated with excess of alcoholic potassium hydroxide?
4. What happens during electrophilic addition reactions in alkynes?
5. Write any two methods to prepare allenes.
6. Mention two sources of aromatic compounds.
7. What are the uses of naphthalene?
8. Which catalyst is used when benzene undergoes hydrogenation to form corresponding saturated cyclohexane?

3.3 IMPORTANT REACTIONS RELATED TO NUCLEOPHILIC AND ELECTROPHILIC ATTACH ON LIGANDS AND TO ORGANIC SYNTHESIS

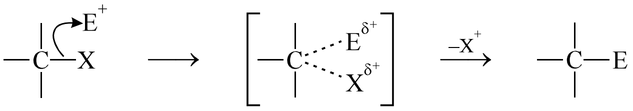
3.3.1 Electrophilic Reaction

Let us study reaction related to electrophilic and nucleophilic attach on ligands and their role in organic synthesis.

Substitution reactions initiated by electrophilic reagents are known as electrophilic substitution reactions. Obviously for such reactions the reactive site in the substrate must be rich in electrons. Two types of such reactions are electrophilic substitutions at saturated or aliphatic carbon atoms and at unsaturated or aromatic carbon atoms. The latter type is important. Electrophilic substitution reactions are designated as S_E reactions. If the reaction is unimolecular it is written as S_E1 and if it is bimolecular it is then written as S_E2 type of reaction. Usually the S_E1 reactions involve two steps—a slow ionization to give a carbanion and then a fast combination of this carbanion with electrophile. Thus:

Step 1. $R{-}X \xrightarrow{\text{Slow}} R^- + X^+$ **Step 2.** $R^- + E^+ \xrightarrow{\text{Fast}} R{-}E$

The S_E2 reactions take place by a concerted mechanism. The incoming group approaches the reactive site from the front side and starts the formation of bond by overlapping with the orbital of carbon on the reactive site. At the same time the departing group is loosening its grip on the bonding pair of electrons. Thus:



This reaction will therefore proceed with the retention of configuration at reactive site whereas S_E1 reactions will result in racemic products because of the probability of attack of E^+ on carbanion from either side.

Reactivity and Structure

Electrophilic substitutions at aliphatic carbon atom are usually observed in organometallic compounds where the metal is less electronegative than carbon. In such reaction the chances for S_E1 type will decrease with the presence of electron donating groups and increase with the presence of electron withdrawing groups. The stability of the resulting carbanion also influences the course of reaction. The greater the polarity of bond C—X, the greater will be the S_E1 reaction rate. Similarly increase in the polarity of solvent favours S_E1 reactions. For S_E2 reactions the electron donating and withdrawing group do not have such rationalized influence. The solvent of greater polarity enhances the S_E2 reaction but lesser than the S_E1 reaction.

The reactivities in substitution at aromatic carbon atoms are strongly influenced by the nature of the substituents present in the ring.

Applications

Some examples of typical electrophilic substitution reactions are given below with their mechanisms.

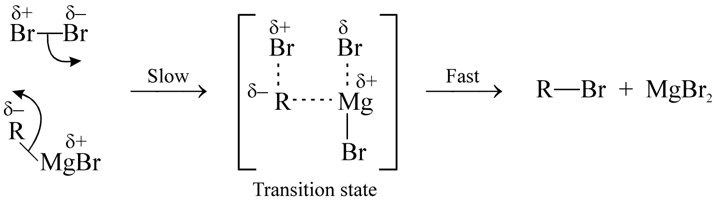
1. Substitution at Aliphatic or Saturated Carbon Atom

Let us see electrophilic substitution reactions and their mechanisms in detail.

(*i*) **Reaction of Grignard reagent with halogen**

$$\underset{\substack{\text{Alkyl magnesium}\\\text{bromide}}}{R{-}Mg{-}Br} + Br_2 \longrightarrow \underset{\substack{\text{Alkyl}\\\text{bromide}}}{R{-}Br} + MgBr_2$$

The reaction proceeds by a S_E2 type mechanism.



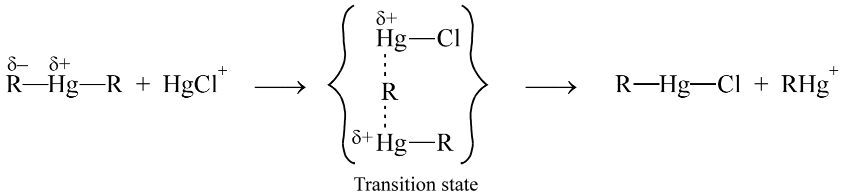
The replacement of—MgBr group by the electrophilic attack of bromonium ion (Br^+) occurs through a transition state resulting in the formation of alkyl bromide.

(*ii*) **Reaction of dialkyl mercury with mercuric chloride**

$$\underset{\text{Dialkyl mercury}}{\text{R—Hg—R}} + HgCl_2 \longrightarrow \underset{\text{Alkyl mercuric chloride}}{\text{2R—Hg—Cl}}$$

This is another example similar to one described above.

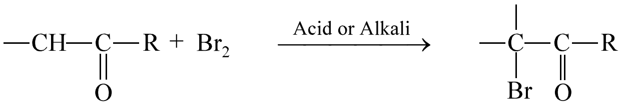
$$HgCl_2 \longrightarrow HgCl^+ + Cl^-$$



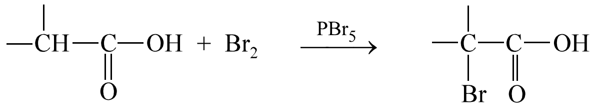
$$\text{R—}Hg^+ + Cl^- \longrightarrow \text{R—Hg—Cl}$$

Here the Hg^+Cl electrophile replaces the Hg^+R group from the molecule by S_E2 mechanism.

(*iii*) **Halogenation of aldehydes, ketones, and acids**



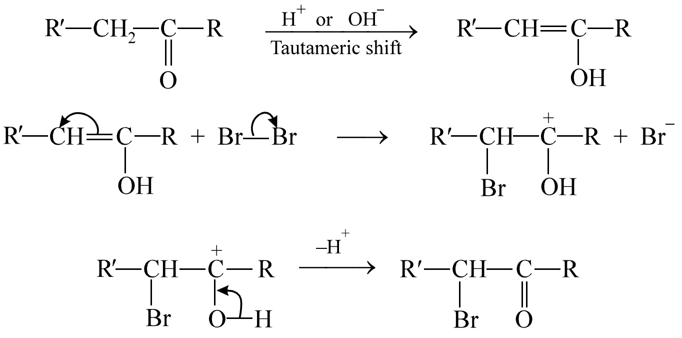
$$\text{—CH—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—R} + Br_2 \xrightarrow{\text{Acid or Alkali}} \text{—}\overset{|}{\underset{\underset{\text{Br}}{|}}{\text{C}}}\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—R}$$



$$\text{—}\overset{|}{\text{CH}}\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—OH} + Br_2 \xrightarrow{PBr_5} \text{—}\overset{|}{\underset{\underset{\text{Br}}{|}}{\text{C}}}\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—OH}$$

(Hell-Volhard-Zelinsky reaction)

The mechanisms for these reactions too is explained by the application of electrophilic substitution.



Thus a bromonium ion has been substituted in place of a hydrogen ion.

2. Mechanism of Haloform Reaction

When methyl carbonyl compounds (CH_3CHO, $CH_3CO.CH_3$ etc.) react with halogens in presence of alkali, haloform (CHX_3) is formed, the reaction is known as haloform reaction. The reaction is given by all compounds containing the acetyl group attached to either carbon or hydrogen, or by compounds which are oxidised under the conditions of the reaction to derivatives containing the acetyl group, *e.g.*, ethyl alcohol, isopropyl alcohol, lactic acid, etc. (Booth and Saunders in 1950 have shown that certain quinones and dihydric phenols also give haloform reaction.) Thus, with ethyl alcohol the following steps are involved in preparation of chloroform.

(*i*) **Oxidation of ethyl alcohol by chlorine to acetaldehyde**

$$CH_3.CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$$

(*ii*) **Chlorination of acetaldehyde to chloral (trichloroacetaldehyde)**

$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3.CHO} + 3HCl$$

(*iii*) **Hydrolysis of chloral by calcium hydroxide yielding chloroform**

$$2CCl_3.CHO + Ca(OH)_2 \longrightarrow \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(H.COO)_2Ca}$$

In case of acetone the following steps are involved:

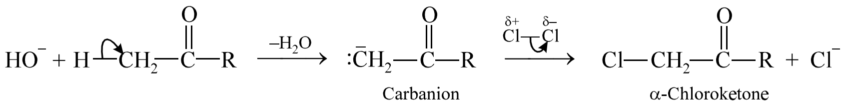
(*i*) **Chlorination of acetone to trichloroacetone**

$$CH_3.CO.CH_3 + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{C.Cl_3.CO.CH_3} + 3HCl$$

(*ii*) **Hydrolysis of trichloroacetone by calcium hydroxide yielding chloroform**

$$2CCl_3.CO.CH_3 + Ca(OH)_2 \longrightarrow \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium acetate}}{(CH_3.COO)_2Ca}$$

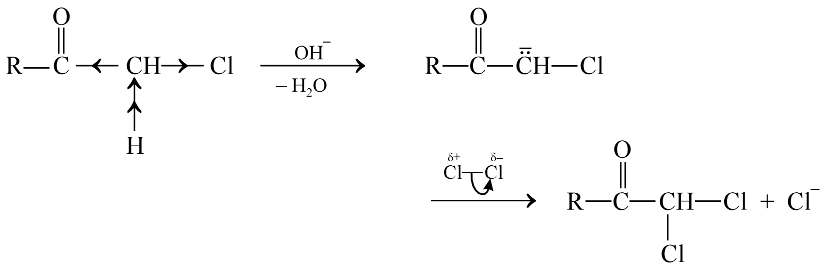
The hydrogen atoms at a-carbon to the carbonyl group are slightly acidic in nature due to the electron withdrawing effect of the carbonyl group. In presence of base $(O\bar{H})$ these hydrogen atoms become still more reactive and are replaced easily by chlorine attacking as chloronium ion.

(*i*) 

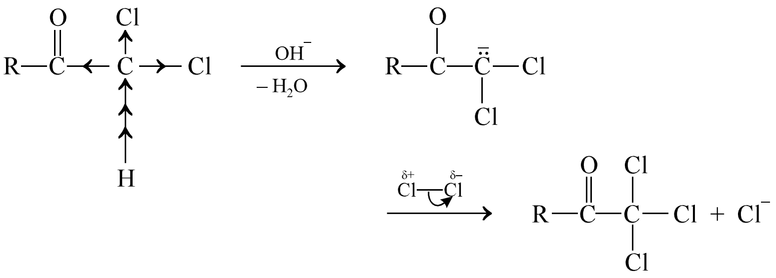
Once a-chloroketone is formed the other H atoms of the carbon having chlorine become more reactive on account of –I effect caused by chlorine and are replaced successively yielding trichloromethyl carbonyl compound.

NOTES

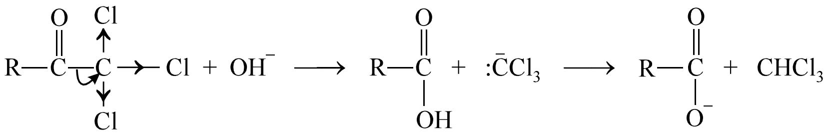
(*ii*)



(*iii*)



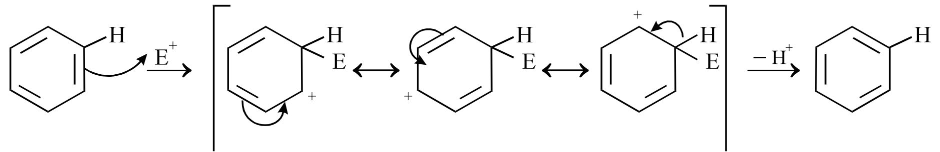
Trihalocarbonyl compound is then cleaved by alkali giving chloroform



(Replacing R with H or CH_3, the reaction with CH_3CHO or CH_3COCH_3 can be written.)

3. **Substitution at Aromatic or Unsaturated Carbon Atoms**

The most important reactions of the aromatic compounds are the electrophilic substitution reactions like nitration, halogenation, sulphonation etc. Nitration is introduction of a nitro group (—NO_2) in place of hydrogen by electrophile $\overset{+}{N}O_2$ (nitronium ion). Sulphonation is the replacement of a hydrogen by —SO_3H group and takes place by electrophilic attack of SO_3 on aromatic carbon. These reactions are dealt at length in the chapter on aromatic hydrocarbons. However, the mechanism of a general electrophilic substitution in benzene by electrophile (E^+) is:



(Carbocation stabilised by resonance)

$\overset{+}{E}$ can be: (*i*) $\overset{+}{N}O_2$ for nitration $(HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3\overset{+}{O} + 2HSO_4^-)$

(*ii*) Cl^+ for chlorination $(Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-)$

(*iii*) Br^+ for bromination $(Br_2 + FeCl_3 \rightarrow Br^+ + \bar{F}eCl_3Br)$

The carbocation formed as intermediate in an aromatic electrophilic substitution is an arenium ion, also known as Wheland intermediate or a sigma (s) complex. The smallest arenium ion is a protonated benzene $C_6H_7^{\text{Å}}$ called *benzenium ion* which can be isolated as a stable compound when benzene is protonated by the carborane super acid.

Electrophilic substitution of a monorsubstituted benzene derivative can give rise to three regioisomeric products in which the new substitutent is placed at C–2 (ortho), C–3 (meta) or C–4 (para) position. There are two ortho- and two meta positions available but a statistical distribution of products is not observed and the actual proportion is dependent upon whether the group present is activating or deactivating.

A vast majority of electrophilic substitution reactions proceed under kinetic control where the rate- and product-determining step is the formation of a Wheland intermediate which is a highly endothemic process. Hammond's postulate states that the factors stabilizing the transition state should also operate in Wheland intermediate. Hence the stabler the intermediate faster is its formation.

When *o*-, *p*-directing and activating groups (e.g., —NH_2, —OH etc.) are attached to benzene then the wheland intermediate resulting from *o*- or *p*-attack is more stabilized by resonance. In case of *o*-, *p*-directing but deactivating group (like —Cl) the Wheland intermediate from *o*- or *p*-attack are stabilized by resonance involving lone pair of chlorine, whereas when *m*-directing and deactivating groups (e.g. —NO_2, —CN etc.) are attached to benzene then Wheland intermediate from *m*-attack is less destabilized as compared to their *o*- or *p*-counterparts.

4. Friedel-Crafts Reaction

The reaction was discovered by C. Friedel and J. Crafts in 1877. It is a better method of introducing an alkyl or acyl group in benzene nucleus by an alkylating or acylating reagent in presence of a suitable catalyst. Recently this reaction has been applied successfully to certain aliphatic and alicyclic compounds. The alkylating agent is usually an alkyl halide, an alcohol or an alkene, while the acylating agent may be an acid chloride or acid anhydride.

The catalyst used for the purpose may be either (*i*) a metal halide (Lewis acid); the order of reactivity being

$$AlCl_3 > BF_3 > SbCl_5 > FeCl_3 > SnCl_4 > ZnCl_2$$

or (*ii*) proton acids, the order of reactivity being

$$HF > H_2SO_4 > H_3PO_4$$

Aluminium chloride is the most frequently used catalyst and its amount depends on the nature of the substrate and/or reagent. For non-oxygenated substrates, (*e.g.*, benzene and toluene) about 0.2 mole is required for alkyl halide and alkene, 0.5–1.0 mole for alchohols and even more than 1.0 mole for acid chloride. However, when the substrate contains oxygen (*e.g.*, ArOH), a large amount of catalyst is needed. Though aluminium chloride may be used with any alkylating agent, it is good to use it with alkyl halides and alkenes; boron trifluoride and hydrogen fluoride are better for alkenes and alcohols; and sulphuric acid is more useful with alkenes and alcohols. Using aluminium chloride as catalyst, the ease of alkylation with alkyl halides depends on the nature of alkyl group and also on halogen atom. Thus, for a given halogen atom, the order is *tri*-alkyl > *sec*-alkyl > *pri*-alkyl, while for a given alkyl group, say R, the order is RF > RCl > RBr > RI. For alcohols also the order of reactivity is the same *i.e.*, *tri*-alkyl > *sec*-alkyl > *pri*-alkyl.

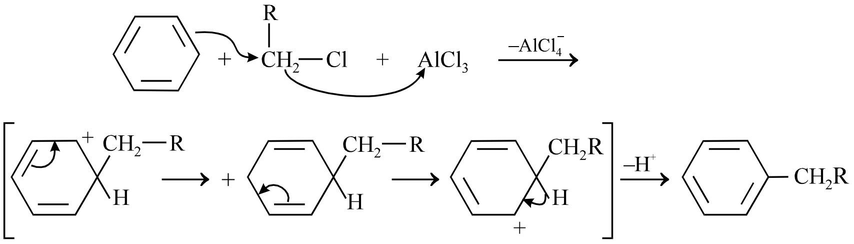
Presence of *o*- and *p*-directing group facilitate Friedel-Crafts reaction, while *m*-directing group inhibits the reaction.

Usually carbon disulphide is used as a solvent in this reaction. Other solvents are ethylene chloride, methylene chloride and nitro-benzene. However, when one of the reactants is liquid, no solvent is needed, but it is rather taken in excess (*e.g.*, in alkylation of benzene).

Mechanism

The reaction involves electrophilic substitution (S_E). Alkylation involving primary or secondary alkyl halides is a bimolecular reaction (S_E2), while that involving tertiary alkyl halide is unimolecular (S_E1).

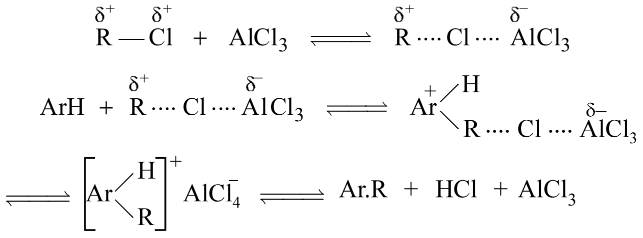
S_E2 mechanism



$$H^+ + \overset{+}{AlCl_4} \longrightarrow AlCl_3 + HCl$$

The attacking electrophile here is slightly electron deficient carbon of the alkyl halide, which results in the formation of resonance stabilized intermediate cation. The latter then expels a proton to form stable alkyl substituted benzene.

Brown *et al.* (1953) have suggested the following mechanism, which has strong evidences for its support.



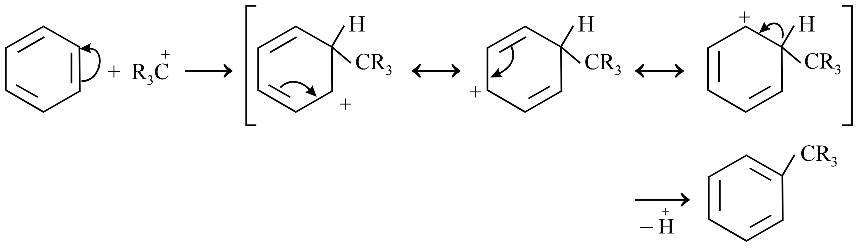
$$\overset{\delta^+}{R}—\overset{\delta^+}{Cl} + AlCl_3 \rightleftharpoons \overset{\delta^+}{R} \cdots\cdot Cl \cdots\cdot \overset{\delta^-}{AlCl_3}$$

$$ArH + \overset{\delta^+}{R} \cdots\cdot Cl \cdots\cdot \overset{\delta^-}{AlCl_3} \rightleftharpoons \overset{+}{Ar}\begin{cases} H \\ R \cdots\cdot Cl \cdots\cdot \overset{\delta-}{AlCl_3} \end{cases}$$

$$\rightleftharpoons \left[Ar\begin{cases} H \\ R \end{cases}\right]^+ \overset{-}{AlCl_4} \rightleftharpoons Ar.R + HCl + AlCl_3$$

S_E1 mechanism

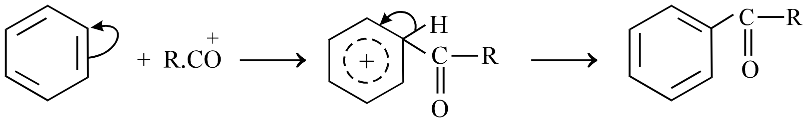
$$R_3C—Cl + AlCl_3 \longrightarrow R_3\overset{+}{C} + \overline{AlCl_4}$$



The first step here is the formation of electrophilic carbocation R_3C^+, which then attacks the benzene ring resulting in the formation of alkyl benzene.

Acylation also proceeds through a similar mechanism. (see also sec. 19.27)

$$R.CO.Cl + AlCl_3 \longrightarrow R.C\overset{+}{O} + Al\overline{Cl}_4$$



Limitations

- It often yields polyalkylated products.
- The intermediate carbocation may rearrange itself to structure of maximum stability, thus giving rise to rearranged alkylated product
- The presence of *m*-directing group hinders or inhibits the reaction, hence in such cases alkyl group cannot be introduced in the ring
- Since an alkyl group gets expelled especially at high temperature, the structure of the product remains uncertain in a number of cases.

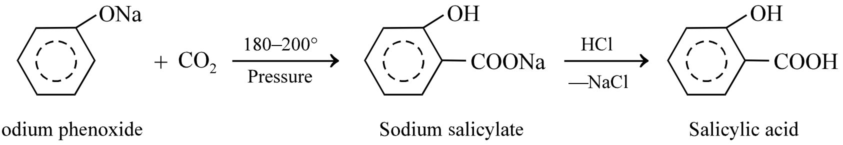
Applications

This reaction is a most useful method for preparing alkyl benzenes and mixed ketones.

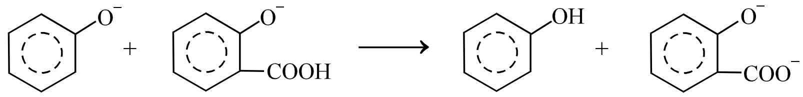
5. Electrophilic Substitutions shown by Activated Aromatic Systems

Some of the reaction are as follow:

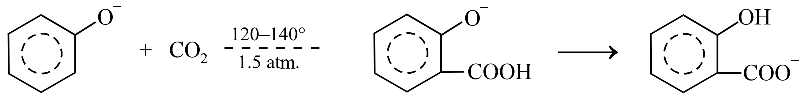
(*i*) **Kolbe Reaction or Kolbe-Schmidt Reaction:** The reaction was discovered in 1859 by Kolbe and later on modified by Schmidt in 1885. Kolbe noticed that when sodium salt of phenols (sodium phenoxides) are heated with carbon dioxide gas under pressure at 180–200°C, a carboxylic group is introduced in the aromatic ring, preferably at ortho-position with respect to phenolic group. The sodium salt of *o*-hydroxybenzoic acid (sodium salicylate) formed, when treated with acid, yields salicylic acid.



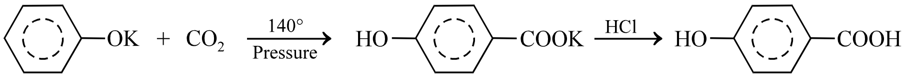
It was, however, found that under these conditions 50 per cent of the phenoxide ion is utilized in converting the carboxyl group into the anion.



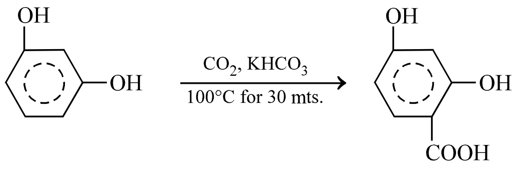
Schmidt found that if the reaction is carried out at 120–140°C for a longer period, the loss of phenoxide ion may be avoided.



A small amount of the *p*-derivative is formed at the same time and if the temperature is above 140°C or potassium phenoxide is used instead of sodium phenoxide the *p*-isomer is the main product.

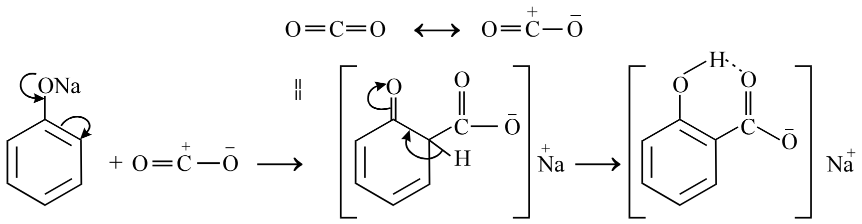


About 3–5 per cent 4-hydroxyisophthalic acid is obtained as by-product in this reaction. This reaction can be applied with great success to di- or trihydroxy phenols also, especially when the phenolic groups are so present in the nucleus as to combine their activating influence on a single position in the nucleus. b-Resorcylic acid is formed in 57–60 per cent yield from resorcinol.



Mechanism

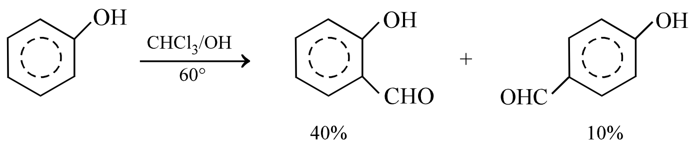
The reaction proceeds through an electrophilic substitution reaction and the slightly electron deficient carbon of carbon dioxide attacks the ring as an electrophile. Since the presence of —OH group increases the electron densities at *o*- and *p*-positions, the electrophile can attack either of these positions. However, the *o*-isomer is formed predominantly, as the intermediate is stabilized due to chelation or intramolecular hydrogen bonding.



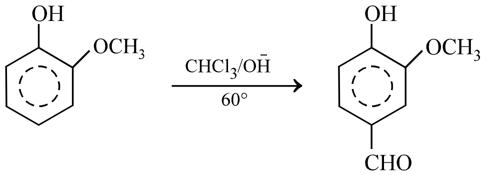
Applications

It is applied industrially for the preparation of aromatic hydroxy acids like salicylic acid. By varying the reaction conditions it may also be used for the preparation of *p*-hydroxybenzoic acid.

(*ii*) **Reimer-Tiemann Reaction:** Reimer and Tiemann in 1876 observed that when phenol is heated with chloroform and alkali at 60°C, the product is a mixture of *o*- and *p*-hydroxybenzaldehydes and usually the *o*-isomer is the main product. The reaction is known as Reimer-Tiemann reaction.



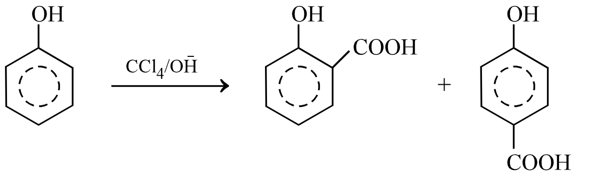
This is a general reaction for phenols that do not contain substituents at *ortho*- or *para*-positions or both and it has been noted that if both the positions are available for reaction, the *ortho*-substitution is favoured. However, if the *ortho*-position is occupied, the —CHO group enters the *para*-position, *e.g.*,



Guaiacol Vanillin

In this reaction the yield of aldehyde is usually below 50 per cent, but the presence of *m*-directing groups *viz.*, —SO_3H, —CN, —CO_2H, —NO_2 etc. further reduce it to below 25 per cent.

If in place of chloroform, carbon tetrachloride is used *o*- and *p*-hydroxy acids are produced.



Salicylic acid *p*-Hydroxybenzoic acid

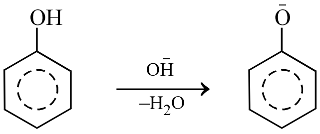
Mechanism

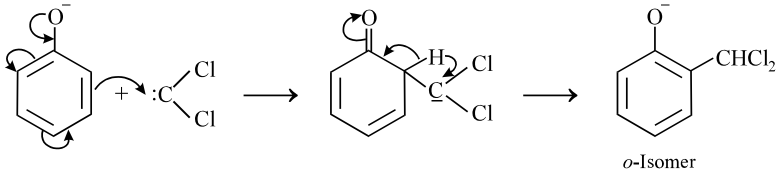
The reaction involves an electrophilic substitution in the ring. The attacking reagent, in this case, is a neutral electrophile CCl_2 (*dichlorocarbene*), a reaction intermediate formed during alkaline hydrolysis (nucleophilic substitution) of chloroform.

$$CHCl_3 + \bar{O}H \xrightleftharpoons{\text{Fast}} H_2O + :\bar{C}Cl_3$$

$$:\bar{C}Cl_3 \xrightleftharpoons{\text{Slow}} \bar{Cl} + :CCl_2$$

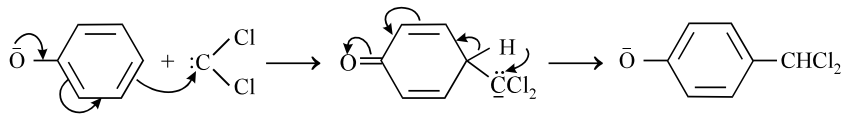
A carbene intermediate is electron deficient species because it contains only six electrons in the outer orbit of carbon and attacks the aromatic ring as an electrophile. The presence of —HO increases the electron density at *ortho*- and the *para*-positions of the ring, so dichlorocarbene attacks at these positions of the ring forming a mixture of *o*- and *p*-isomers. However, the *o*-isomer is formed predominantly, as it is stabilized because of chelation.





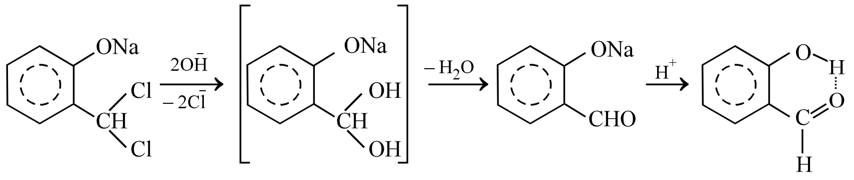
o-Isomer

Similarly



p-Isomer

The *o*- and *p*-hydroxybenzal chlorides, so formed, then undergo hydrolysis in the presence of alkali by nucleophilic substitution reactions to form dihydroxy derivative having two hydroxyl groups attached to the same carbon atom. This readily eliminates a water molecule to form aldehyde.



o-Hydroxybenzaldehyde
(Stabilized by H-bonding)
(Salicylaldehyde)

Applications

This reaction is used for the formylation (introduction of—CHO group) of phenols. It also finds application in the preparation of salicylic acid and other aromatic hydroxy acids. An important industrial application is in the preparation of vanillin from guaiacol.

3.3.2 Nucleophilic Substitution Reactions

Substitution reactions by nucleophilic reagents are known as nucleophilic substitution (S_N) reactions. Nucleophiles generally react at sites that are deficient in electrons. Consequently such reaction will be most important for compounds where a carbon is linked to greater electronegative atom or group (like halogen) and is thus deficient in electrons because of unequal sharing of bonding electrons. Like electrophilic substitution these can also be of two types—nucleophilic substitution at saturated or aliphatic carbon and at unsaturated or aromatic carbon. Unlike electrophilic substitution which predominates in aromatics and unsaturated compounds the nucleophilic substitution is more common in aliphatic compounds and has been extensively studied. Kinetic investigations of conversions of alkyl halides to alcohols by the action of alkali shows that there are two extreme types of reaction. In one type the reaction rate is proportional to the concentration of alkyl halide only and it is designated as S_N1 reaction. Here S stands for substitution, N for nucleophile and 1 for unimolecular. The term unimolecular is used here since the rate determining step involves only one molecule. In general S_N1 reactions follow first order kinetics. In the other type the rate of reaction is proportional to the concentrations of alkyl halide and alkali or hydroxyl ions and is a bimolecular reaction designated as S_N2 reaction. S_N2 reactions follow second order kinetics.

For S_N1: Rate μ [R—X]   Independent of $[\bar{OH}]$.

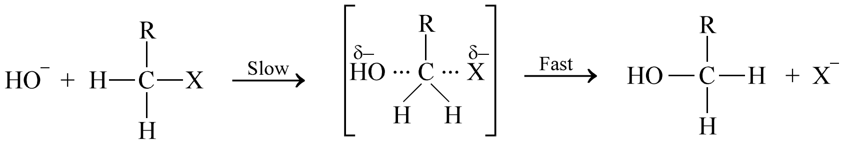
(Stepwise mechanism)

$$(i)\ \mathrm{R{-}X} \xrightarrow{\text{Slow}} \overset{+}{\mathrm{R}} + \overset{-}{\mathrm{X}}$$

$$(ii)\ \overset{+}{\mathrm{R}} + \mathrm{O}\overline{\mathrm{H}} \xrightarrow{\text{Fast}} \mathrm{R{-}OH}$$

For S_N2: Rate $\propto$ [R—X][OH$^-$]

(Concerted mechanism)



Transition state

Some examples of the nucleophilic substitution reaction are hydrolysis of alkyl halides, acyl halides; cleavage of ethers with HI (Ziesel reaction and alkylation with alkyl halides (Williamson's synthesis).

The various factors guiding the reaction to follow S_N1 or S_N2 mechanism have been discussed below.

Structure of the substrate

Alkyl halides have been extensively used as substrate for studying nucleophilic substitution reactions. It has been observed that the hydrolysis of primary and tertiary alkyl halides are fast although the former follows S_N2 and the latter S_N1 mechanism. The rate of hydrolysis of secondary alkyl halides is slow and they follow both S_N1 and S_N2 mechanism of hydrolysis. The rate of reactivity of various alkyl halides is iodide > bromides > chlorides for a particular alkyl group and tertiary > secondary > primary > CH_3 alkyl halides for a particular halogen. Amongst the primary alkyl halide the order of reactivity is $CH_3X > C_2H_5X > n\text{-}C_3H_7X > n\text{-}C_4H_9X$ etc.

The reason from this transformation from S_N2 to S_N1 type mechanism in going from primary to tertiary is the structural difference in their molecules. Tertiary alkyl halides have three alkyl groups attached to the carbon atom joined to halogen. The (+I) effect of the three alkyl groups increases the electron density on the carbon to which they are joined and this increases the repulsion towards halogen thereby increasing the chance of formation of carbocation. Thus in tertiary alkyl halides the tendency to follow the path of S_N1 mechanism increases. Primary alkyl halides follow S_N2 mechanism.

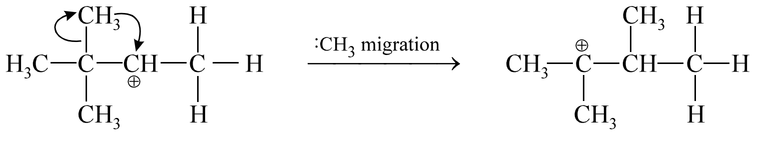
Steric effect

The effects seen in molecules due to the fact that atoms occupy space are known as steric Effects.

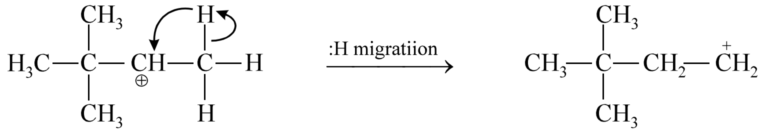
S_N2 mechanism involves the attack by a nucleophile from the side opposite to that of the leaving group. Now if the carbon atom has bulky alkyl group(s) attached to it then it will be difficult for nucleophile to reach the carbon atom hence the reaction will be slowed down. Since S_N2 mechanism operates better in primary alkyl halides therefore with the increase in the size of alkyl group the rate of reaction decreases *i.e.*, $CH_3X > n\text{-}C_4H_9X$. Tertiary alkyl halides are not affected much because they follow S_N1 mechanism.

Rearrangement of Carbocations

Sometimes it is found that the attacking nucleophile joins a carbon atom other than that of the leaving group. This happens due to the rearrangement of the carbocation in S_N1 mechanism to a more stable cation. This is due to 1,2 alkyl or hydrogen shift which results in the formation of stabler cation. The formation of stabler cation decides the shift.



[2° Carbocation] [3° Carbocation]

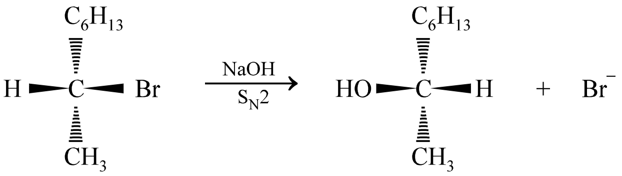


[2° Carbocation] [1° Carbocation]
(This rearrangement not possible forming less stable carbocation)

In the above example of hydrolysis of 3-bromo- 2,2-dimethylbutane the carbocation formed rearranges to stable (3°) cation and therefore the alcohol obtained will be 2,3-dimethyl- butanol-2 and not 3,3-dimethylbutanol-2. It is also clear that in single step S_N2 mechanism such a rearrangement is not possible.

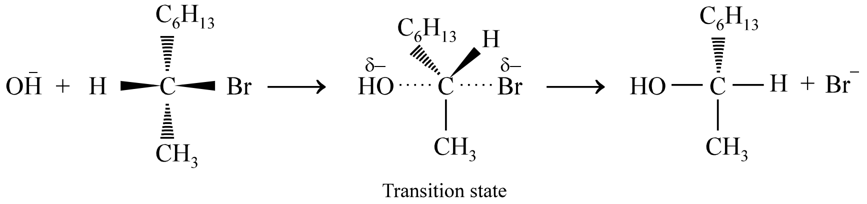
Stereochemistry of S_N2 and S_N1 Reactions

In S_N2 reaction of hydrolysis of 2-bromo-octane, having a chiral centre, it is found that the laevorotatory 2-bromo-octane gives dextro-rotatory 2-octanol. This clearly means that there has been an inversion of rotation. Hence, it shows that S_N2 reaction proceeds with complete inversion of configuration accompanied by inversion in rotation.



(–) 2-Bromo-octane (–) 2-Octanol

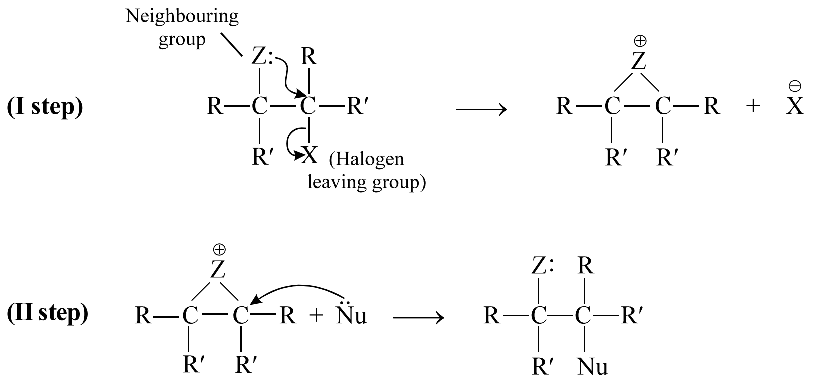
To explain this it is assumed that the nucleophile —OH attacks the carbon from the opposite side of the leaving group so as to avoid over crowding and starts forming a bond by sharing of its pair of electrons. At approximately the same time, the group which is leaving the molecule starts acquiring the bonding electron pair. Thus, a negative charge spreads in the transition state from the nucleophile at one end to the departing group at the other end. The configuration of transition state is perhaps that of a triangular bipyramid with all the other groups in the same plane. Since the nucleophile enter the molecule from the opposite end of the departing group, the configuration of the molecule is turned upside down like an inverted umbrella. This therefore results in the inversion of configuration known as Walden inversion, when bromide ion is expelled and tetrahedral arrangement reverts back with arrangement opposite to that of the original molecule.



Neighbouring Group Participation

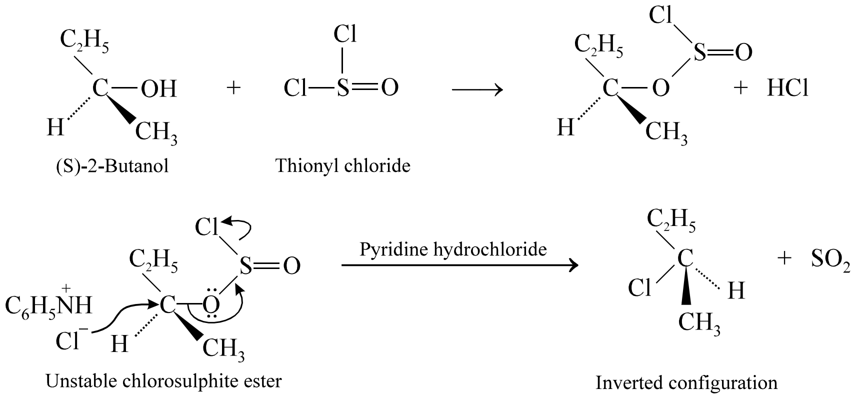
The neighbouring group participation is defined as the interaction of the reaction centre either with a lone pair of electrons as adjacent atom or with electrons present in a sigma or pi-bonds (as in a double bond). It generally leads to increased reaction rates and sometimes results in unexpected stereochemical nature of the product.

If the neighbouring group (the group attached to the carbon which is next to carbon having leaving group) is an electron-rich substituent at a proper place then the configuration is retained. This is a two-step process.



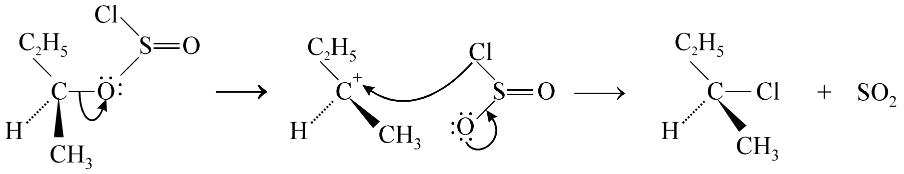
Substitution Nucleophilic Internal (S_Ni)

Substitution nucleophilic internal (S_Ni) are those substitution reactions in which substitution takes place by intramolecular process. In these reactions the configuration of the product may or may not change; depending upon the conditions employed in the reaction. Conversion of an alcohol (S)-2-butanol to corresponding chloride using thionyl chloride, is a reaction where the configuration changes only under a set of conditions and does not change under other conditions.



NOTES

However, in the absence of pyridine the chlorosulphite ester decomposes to give the chloride having the same configuration.



Configuration retained

Solvent Effect

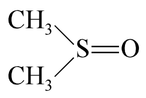
In S_N1 substitution reaction the bond breaking between carbon and halogen requires energy. The ions generated during heterolysis of the bond are surrounded by polar solvent molecules oriented with their negative end towards the carbocation and positive end towards anion. The substrate molecule is then pulled apart as solvated ions. Individually these ion-dipole bonds are weak but altogether they provide a great deal of energy. The transition state has a stretched carbon-halogen bond with well developed charges. The solvent thus stabilizes transition state more than the reactant, thereby lowering the energy of activation and speeding up the reaction. This lowering of energy compensates for the energy required for breaking the bond.

$$\underset{\text{Substrate}}{R{-}X} \longrightarrow \underset{\substack{\text{Transition state}\\ \text{(More polar than reactants}\\ \text{stabilized by solvation)}}}{\left[\overset{\delta+}{R}\ \ldots\ldots\ \overset{\delta-}{X}\right]} \longrightarrow \underset{\text{Products}}{R^{+} + X^{-}}$$

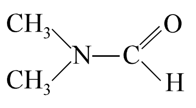
In S_N2 mechanism the solvent stabilizes the reactants specially the nucleophiles, more than it does the transition state and thus raises the energy of activation and slows down the reaction (stabilization deactivates the nucleophile)

$$\underset{\text{Stabilized}}{H\bar{O}} + R{-}X \longrightarrow \underset{\substack{\text{Transition state}\\ \text{(Dispersed charge}\\ \text{stabilized to small-extent)}}}{\left[\overset{\delta-}{HO}{-}R{-}\overset{\delta-}{X}\right]} \longrightarrow HOR + \bar{X}$$

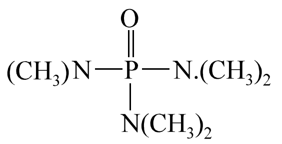
Here we must understand that cations are solvated through unshared pair of electrons but the anions are chiefly solvated through hydrogen bonding. Hence, protic solvents like water and alcohol are good for S_N1 mechanism but they slow down S_N2 reaction. (CF_3CH_2OH, HCOOH and CF_3COOH are other solvents which form strong H-bond with the leaving group and are better solvents for S_N1 mechanism.) In aprotic solvents like DMSO, DMF and HMPT, S_N2 reactions go 10^6 times as fast as in polar solvents like water and alcohol.



Dimethyl sulphoxide
(DMSO)



Dimethyl formamide
(DMF)



Hexamethyl phosphorotriamide
(HMPT)

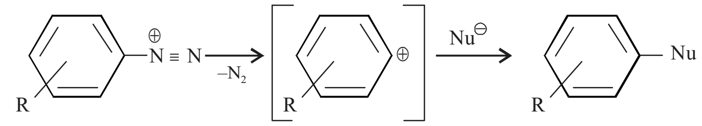
Leaving Group

Most of the leaving groups leave as negative ion and if they stabilize this charge most effectively as they will be considered as good leaving groups. Weak bases which are conjugate bases of strong acids do this best. The anions of strong acids like Cl^-, Br^-, I^- and $HS\bar{O}_4$ are good leaving groups in S_N2 reactions. Amongst the halogens Iodide ion is the best leaving group and fluoride is the poorest of the lot $I^- > Br^- > Cl^- > F^-$.

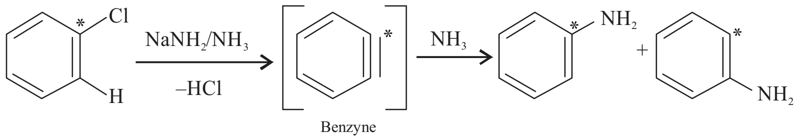
Nucleophilic Aromatic Substitution

This may occur in several ways, including (i) aromatic S_N1 mechanism, (ii) involving benzyne intermediate and (iii) S_NAr mechanism involving addition and elimination.

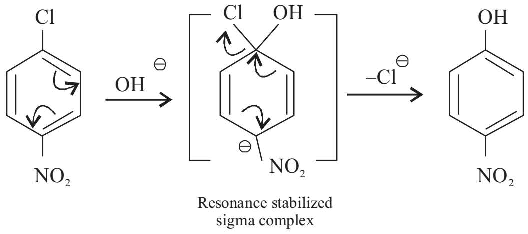
(i) **Aromatic S_N1 mechanism is observed in diazonium salts**



(ii) **Benzyne mechanism is observed in reaction of chlorobenzene with $NaNH_2$.**



(iii) **S_NAR mechanism is observed when an electron withdrawing group like $–NO_2$ activates the ring towards nucleophilic attack.**

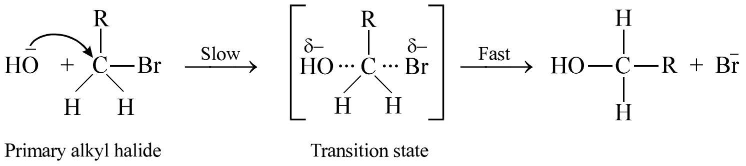


Applications

The mechanisms of the hydrolysis of alkyl halides have been successfully explained by nucleophilic substitution. Some examples are given below:

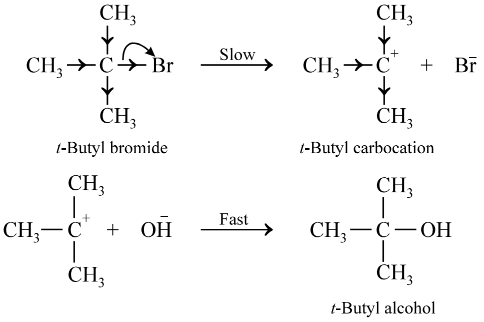
- **Hydrolysis of Alkyl Halide (primary and secondary)**

S_N2 mechanism



Hydrolysis of t-Butyl Bromide

S_N2 mechanism



$$(CH_3)_3C\text{—}Br \xrightarrow{\text{Slow}} (CH_3)_3\overset{+}{C} + Br^-$$

$$(CH_3)_3\overset{+}{C} + OH^- \xrightarrow{\text{Fast}} (CH_3)_3C\text{—}OH$$

In the S_N2 mechanism the nucleophile hydroxide ion approaches the alkyl halide molecule preferably from the side opposite to that occupied by the departing group. As the carbon atom involved in carbon to halogen bond is slightly deficient in electron density because of greater electronegativity of halogen (bromine in above example) the hydroxide ion offers a pair of electrons for the formation of bond with this carbon. Simultaneously bromine starts taking hold of the electron pair through which it is bonded to carbon and a transition state or activated complex is visualized for such reactions in which five groups are linked to carbon. Finally bromine leaves the molecules as a bromide ion and hydroxide ion forms a covalent bond with the carbon giving alcohol as the reaction product.

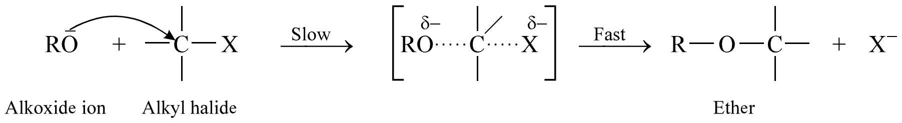
In the hydrolysis of *t*-butyl bromide which occurs by S_N1 mechanism, the first step is the slow dissociation of alkyl halide to give a bromide ion and tertiary butyl carbocation, which is stabilised due to hyperconjugation. The tertiary butyl carbocation then combines with a hydroxide ion to form the tertiary butyl alcohol.

- ***Alkylation with alkyl halides (Williamson synthesis of ethers)***

$$R\text{—}X + R'\text{—}ONa \longrightarrow R\text{—}O\text{—}R' + NaX$$

S_N2 mechanism for the reaction is given below:

$$R'\text{—}ONa \longrightarrow R\text{—}O^- + Na^+$$



$$R\overset{-}{O} + \text{—}\overset{|}{\underset{|}{C}}\text{—}X \xrightarrow{\text{Slow}} \left[\overset{\delta-}{RO}\cdots\overset{|}{\underset{|}{C}}\cdots\overset{\delta-}{X}\right] \xrightarrow{\text{Fast}} R\text{—}O\text{—}\overset{|}{\underset{|}{C}}\text{—} + X^-$$

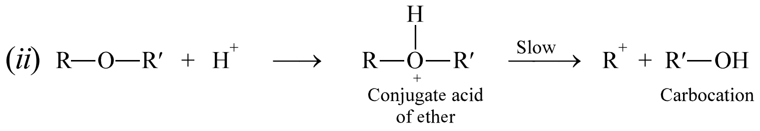
- **Cleavage of ethers (Ziesel's method for determining alkoxy groups)**

$$R\text{—}O\text{—}R' + HI \longrightarrow RI + R'\text{—}OH$$

The mechanism is similar to above reaction and may be S_N1 or S_N2

S_{N1} mechanism

(*i*) $HI \longrightarrow H^+ + I^-$



(*ii*) $R\text{—}O\text{—}R' + H^+ \longrightarrow R\text{—}\overset{H}{\overset{|}{\underset{+}{O}}}\text{—}R' \xrightarrow{\text{Slow}} R^+ + R'\text{—}OH$

(*iii*) $R^+ + I^- \longrightarrow \underset{\text{Alkyl halide}}{R\text{—}I}$

S_N2 mechanism

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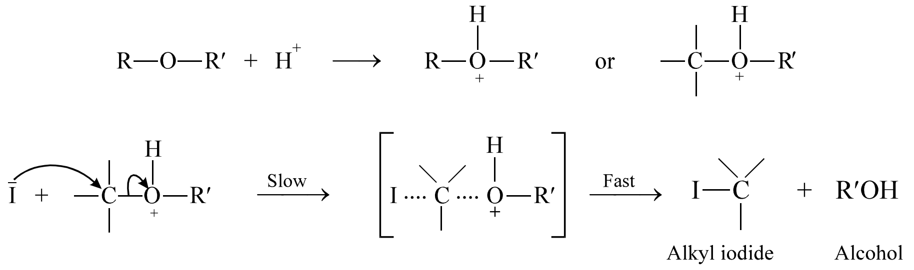

Check Your Progress

9. When are electrophilic substitutions at aliphatic carbon atom observed?
10. What is haloform reaction?
11. Which directing group facilitates Friedel-Crafts reaction?
12. What do you understand by steric effects?
13. Name two compounds that form strong H-bond with the leaving group and are better solvents for S_N1 mechanism.

3.4 ANSWERS TO ‘CHECK YOUR PROGRESS’

1. In IUPAC system, olefins are termed as Alkenes.
2. The two members of the alkene series, ethene and propene, have only one structural formula. Boron has only six electrons in BH_3 hence it acts as an electrophile.
3. When dihaloalkanes are treated with excess of alcoholic potassium hydroxide alkynes are formed by the elimination of two moles of halogen acids.
4. Electrophilic addition reactions in alkynes involve attack by the electrophile in the same way as in alkenes but they involve the change of the two ð bonds one after the other to ó bonds.
5. Allenes can be prepared from trihalopropane and olefins.
6. The two sources of aromatic compounds are coal and petroleum.
7. Naphthalene is used for making dyes, drugs and explosives while phenols are used for making dyes, disinfectants, explosives, bakelite, etc.
8. Benzene undergoes hydrogenation in presence of finely divided metal catalyst like nickel, platinum etc., at about 200°C and form corresponding saturated cyclohexane.
9. Electrophilic substitutions at aliphatic carbon atom are usually observed in organometallic compounds where the metal is less electronegative than carbon.
10. When methyl carbonyl compounds (CH_3CHO, $CH_3CO.CH_3$, etc.) react with halogens in presence of alkali, haloform (CHX_3) is formed. The reaction is known as haloform reaction.

11. Presence of o- and p-directing group facilitates Friedel-Crafts reaction, while m-directing group inhibits the reaction.
12. The effects seen in molecules due to the fact that atoms occupy space are known as steric effects.
13. CH_3CH_2OH, HCOOH and CF_3COOH are the solvents that form strong H-bond with the leaving group and are better solvents for S_N1 mechanism. (Write any two.)

3.5 SUMMARY

- Alkenes have two hydrogen atoms less than the corresponding alkenes (saturated hydrocarbons). The members of this homologous series are represented by the general formula C_nH_{2n} and are also known as olefins.
- Alkenes show chain, position, ring-chain and geometrical isomerism.
- Lower alkenes are obtained on a large scale by cracking of petroleum and higher alkenes are prepared by cracking of petroleum or by using Fischer-Tropsch oils under proper pressure and catalyst.
- The electrons of an alkene double bond are designated as ð electrons. In UV spectroscopy these ð electrons are excited by light of the wavelength 1000- 2000 Å (or 100–200 m ì).
- The alkenes are in general very reactive in contrast to the inert behaviour of alkanes. This high reactivity of alkenes is due to the presence of double bond in the molecule.
- The molecule of an alkene may be considered to be made up of two units—(i) a double bond and (ii) alkyl group(s).
- Markovnikov's rule states that in the addition to an unsymmetrical olefin the negative part of the reagent or addendum goes to that carbon constituting the double bond which is poorer in hydrogen
- In a carbon-carbon double bond, since the carbon atoms are sp^2 hybridized, all the six atomes (two carbon and four atoms attached to them) lie in one plane.
- Alkenes undergo oxidation reactions readily with a wide variety of reagents to give different products depending upon the nature of oxidizing agent and the conditons of the reactions.
- When alkenes are heated in the presence of a catalyst or alone, they undergo isomerisation to form isomeric alkenes.
- The alkyl group of alkenes undergo substitution reactions at higher temperatures.
- It has been seen that alkene molecules on oxidative cleavage and on ozonolysis split up at the site of the double bond.
- Alkynes contain four hydrogen atoms less than corresponding alkanes and are represented by the general formula C_nH_{2n-2}.

- Ethyne, and propyne do not exhibit any type of isomerism. Other alkynes exhibit various types of isomerism, i.e., chain, position and functional isomerism.
- Alkynes or acetylenes do not occur in nature in the free state because of their high reactivity. However, they are produced by combustion of coal and decomposition of organic matter.
- Alkynes can be prepared by dehydrohalogenation of dihaloalkanes, dehalogenation of tetrahalides, electrolysis of salts of unsaturated dicarboxylic acids, hydrolysis of alkynides, alkylation of acetylene and decarboxylation of acetylenic acids.
- Alkynes undergo addition reactions like alkenes but add two molecules of the reagent or addendum instead of one; the addition occurring in two stages.
- Addition of acids, alcohol, thioalcohols, hydrogen cyanide, ammonia, etc., takes place by nucleophilic addition mechanism.
- Terminal alkynes cannot be reduced by Na—NH_3 combination because they are converted to acetylide ions under these conditions.
- Alkynes differ from alkenes and alkanes in that they exhibit acidic character and the hydrogen attached to a triple bonded atom can be replaced by metals forming alkynides or acetylides.
- Butynes are colourless and odourless gases. Their chemical characteristics are similar to the general reactions of alkynes.
- Compounds having two triple bonds in the molecule are known as alkadiynes or diacetylenes.
- Conversion of an organic compound into its next higher homologue is termed as ascent of series or ascending the series.
- Conversion of an organic compound into its next lower homologue is known as descent of series or descending the series.
- Dienes or diolefins are bifunctional compounds having two carbon-carbon double bonds in the molecule. The general formula of such hydrocarbons is C_nH2_{n-2} which is same as that of alkynes.
- Dienes are divided into three main classes, namely dienes with cumulated double bonds or allenes, dienes with isolated double bonds and dienes with conjugated double bonds.
- Coal and petroleum are two important commercial sources of aromatic compounds.
- Benzene was first isolated by Michael Faraday in 1825 from oil condensed in cylinders of compressed illuminating gas. The six carbon atoms of the benzene ring constitute what is known as benzene nucleus.
- In benzene all the six hydrogen atoms are equivalent, hence the replacement of any one of them by a monovalent atom or group always results in a single monosubstitution product, e.g., there can be only one monochlorobenzene.
- The greater the stability of the carbocation and faster its formation makes allyl halide give nucleophilic substitutions reactions easily by S_N1 mechanism.

- Substitution reactions initiated by electrophilic reagents are known as electrophilic substitution reactions. Two types of such reactions are electrophilic substitutions at saturated or aliphatic carbon atoms and at unsaturated or aromatic carbon atoms.
- Substitution reactions by nucleophilic reagents are known as nucleophilic substitution (SN) reactions. Nucleophiles generally react at sites that are deficient in electrons.

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3.6 KEY TERMS

- **Alkenes:** These are the hydrocarbon in which a carbon–carbon is attached by a double bond.
- **Alkynes:** These are the hydrocarbon in which a carbon–carbon is attached by a triple bond.
- **Dienes:** These are covalent compounds that contain two double bonds, usually among carbon atoms.
- **Arenes:** These are known as aromatic compounds. These compounds contain one or more rings with pi electrons delocalized all the way around them.
- **Allyls:** This is a group that has the structural formula, H, C=CH"CH, R, where R is the rest of the molecule. It consists of a methylene bridge attached to a vinyl group.
- **Nucleophilic Reaction:** It is an addition reaction in which a reaction takes place between chemical compound with an electrophilic double or triple bond with a nucleophile, in order to break the double or triple bond.
- **Electrophilic Reactions:** It is a chemical reaction in which a functional group is displaced by an electrophile in a compound, which is usually a hydrogen atom.

3.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Which types of isomerism are shown by alkenes?
2. Compare E2 and E1 elimination.
3. What happens when alkenes are oxidised with periodic acid or lead tetra acetate?
3. Mention the general physical characteristics of alkynes.
4. What do you understand by Markovnikov's rule?
5. Write a brief note on the spectroscopic properties of alkynes.
6. Give equations showing the addition of halogens to alkynes.

7. How is propyne prepared? Also, mention its chemical and physical properties.
8. How does fractional distillation of coal tar take place?
9. How does substitution take place in substitution nucleophilic internal?

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Long-Answer Questions

1. Explain the methods of preparation of alkenes.
2. Discuss the process of detection of carbon to carbon double bond.
3. Describe the nomenclature of alkynes with the help of examples.
4. Analyse the mechanisms of oxidation reactions in alkynes.
5. Explain the three class of dienes in detail.
6. Discuss and illustrate position isomerism of benzene derivatives.
7. Evaluate the molecular orbital representation of allyl halides.
8. Discuss the mechanism of Kolbe reaction and its applications.

3.8 FURTHER READING

Ouellette, R. J., Rawn, J. D. 2014. *Organic Chemistry: Structure, Mechanism, and Synthesis*. United States: Elsevier Science.

Adamson, A. 2012. *A Textbook of Physical Chemistry*. United States: Elsevier Science.

Lumb, N. H., McLintock, S., Lyons, C. G. 2016. *A Concise Text-Book of Organic Chemistry:* The Commonwealth and International Library: Chemistry Division. United Kingdom: Elsevier Science.

Rawn, J. D., Ouellette, R. J. 2015. *Principles of Organic Chemistry*. Netherlands: Elsevier Science.

Anthony Hill. 2002. *Organotransition Metal Chemistry*. Wiley: Great Britain.

John F. Hartwig. 2010. *Organotransition Metal Chemistry: From Bonding to Catalysis*. University Science Books: California.

NOTES

UNIT 4 TRANSITION METAL COMPOUNDS WITH BONDS TO HYDROGEN

Structure

4.0 INTRODUCTION

The elements in groups 4–11 are commonly referred to as transition metals due to their characteristic chemistry, which includes a wide range of complex ions in various oxidation states, colourful complexes, and catalytic characteristics as the element or as ions (or both). The fact that transition metals have two or more oxidation states, usually differing by one, is one of their distinguishing characteristics. The catalytic activity of transition metals and their compounds is known to be both homogeneous and heterogeneous. They have ability to adopt multiple oxidation states and form complexes is credited with this action. This unit will discuss transition metal compounds with bonds to hydrogen. It will also explain the concept of homogenous catalysis. In addition, it will describe various catalytic reactions involving carbon monoxide.

4.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain transition metal compounds with bonds to hydrogen
- Discuss homogenous catalysis
- Describe catalytic reactions involving carbon monoxide

4.2 HYDROGEN BONDING IN TRANSITION METAL COMPLEXES

Transition metal hydrides are chemical compounds containing a transition metal bonded to hydrogen. Most transition metals form hydride complexes and some are significant in various catalytic and synthetic reactions. Chemically, carbon-hydrogen bonds, particularly those with saturated carbon centres, are thought to be chemically inert. The C-H group is not well-liked in general. As a possible ligand, it can play a structural or functional role. In ground states or reaction intermediates, there is an energetically significant portion. Many transition metals produce binary hydrides with hydrogen. They are called binary because there are only two elements in the molecule, and hydride because the hydrogenic ligand is thought to have hydridic (H-like) quality. Because of their polymeric properties, these chemicals are insoluble in all solvents. They frequently have electrical conductivity similar to metal.

4.3 HOMOGENOUS CATALYSIS

A catalyst is a substance which alters the speed of a chemical reaction without undergoing any chemical change and can be recovered at the end of the reaction. The phenomenon of acceleration or retardation of the speed of a chemical reaction by the addition of small amounts of foreign substances to the reactants is referred to as catalysis. Consider, for example, the decomposition of potassium chlorate. This reaction takes place very rapidly and at a low temperature if a pinch of manganese dioxide is added.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

Manganese dioxide does not undergo any chemical change at the end of the reaction and can be recovered and used over again. Thus, manganese dioxide acts as a catalyst. There are numerous examples of catalyzed reactions. Some common examples are:

- Oxidation of sulphur dioxide to sulphur trioxide in the presence of platinum as a catalyst

  $$2SO_2 + O_2 \xrightarrow{Pt} 2SO_3$$

- Combination of hydrogen and oxygen in the presence of platinum

  $$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

- In the manufacture of ammonia by Haber's process, iron acts as a catalyst

  $$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

- Hydrogenation of unsaturated hydrocarbons in the presence of nickel

  $$-CH{=}CH- + H_2 \xrightarrow{Ni} -CH_2-CH_2-$$

There are generally two types of catalysis which are as follows:

(i) Homogeneous Catalysis: In this type, the catalyst is present in the same phase as the reactants. There can be gaseous or liquid phase.

Examples of Homogeneous Catalysis in Gas Phase

Catalyzed homogeneous gas reactions are very rare. A common example of this is the oxidation of sulphur dioxide to sulphur trioxide in the presence of nitric oxide in the lead-chamber process of sulphuric acid.

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

Nitric oxide can also catalyze the combination of carbon monoxide and oxygen and the decomposition of nitrous oxide to nitrogen and oxygen.

$$2CO + O_2 \xrightarrow{NO} 2CO_2$$

$$2N_2O \xrightarrow{NO} 2N_2 + O_2$$

Another example is the decomposition of methyl-ethyl, diethyl and disopropyl ethers in the presence of iodine vapours which acts as a catalyst.

Iodine vapours also act as a catalyst in the decomposition of acetaldehyde.

$$CH_3CHO \xrightarrow{l_2\ \text{vapours}} CH_4 + CO$$

It is found to be of second order and the rate is given by

$$\frac{dx}{dt} = k\, C_{CH_3CHO} . C_{l2}$$

To account for this, it is said that the reaction takes place in two steps:

1. $CH_3CHO + I_2$ ® $CH_3\ I + HI + CO$
2. $CH_3\ I + HI$ ® $CH_4 + I_2$

The first reaction being slower determines the rate of the reaction.

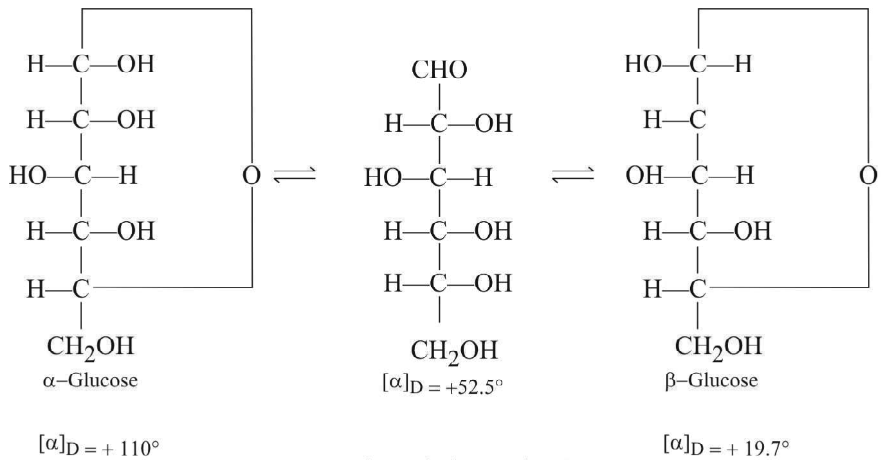
Examples of Homogeneous Catalysis in Liquid Phase

There are many examples of homogeneously catalyzed reactions in solution. The most common are catalyzed by hydrogen or hydroxyl ions and are generally included under the heading of acid-base catalysis. Hydrogen ions are found to catalyze reactions such as the inversion of sucrose and hydrolysis of esters. For such reactions, the rate is proportional to the concentration of hydrogen ions and the concentration of the substrate, i.e., reacting molecule or ion.

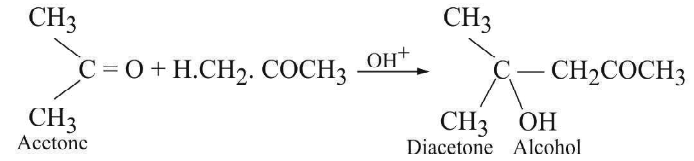
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Ethyle Acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Similarly, hydroxyl ions are found to have catalytic effect for reactions, such as the mutarotation of glucose and the conversion of acetone into diactone alcohol.



Mutarotation of glucose by OH^-



These days, it has been observed that for many reactions which are catalyzed by hydrogen ions, any other substance which is an acid in the Bronsted sense (proton donor) can act as a catalyst for the reaction. This is called general acid catalysis. Similarly general base catalysis refers to reactions which are catalyzed by all bases (proton acceptor).

There are some reactions, e.g., the mutarotation of glucose and the enolization of acetone which are catalyzed by both acids and base and are known as general acid-base catalysis. For such reactions, the general expression for the measured specific rate constant (K) for the overall reaction may be written as:

$$K = K_0 + \sum K_{acid} C_{acid} + \sum K_{base} C_{base}$$

where K_0 is the rate constant for the non-catalyzed reaction, such as occurs in neutral solution and K_{acid} and K_{base} are the catalytic coefficients of each species of acid and base (in accordance with the Lowry's concept of acid and base) of concentrations C_{acid} and C_{base} respectively. The value of K_{acid} can be measured from solutions which are strongly acidic (C_{base} is extremely small) and that of K_{base} from solutions which are strongly basic (C_{acid} is small). By knowing K_{acid} and K_{base}, one can easily compare the catalytic effects of various acids and bases).

In considering the mechanism of acid or base catalyzed reactions, addition or removal of a proton by a catalyst must be taken into consideration.

This can be illustrated by the following examples:

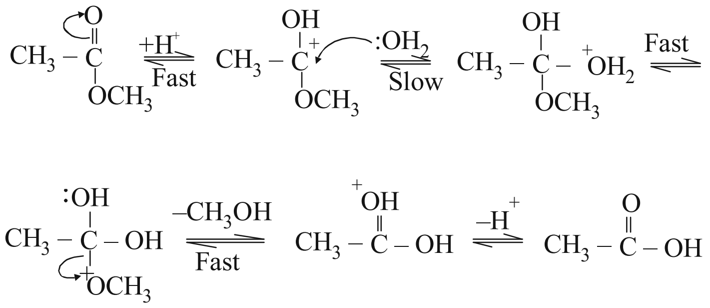
Mutarotation of glucose

$$\underset{\alpha\text{-glucose}}{GH} + H_3O^+ \rightleftharpoons \underset{\text{(Intermediate compound)}}{HGH^+} + H_2O$$

$$HGH^+ + H_2O \rightleftharpoons \underset{\beta\text{-glucose}}{HG} + H_3O^+$$

Here the first step involves addition of proton, supplied by acid, H_3O^+ to a glucose molecule and leads to the formation of an intermediate compound which is unstable. This decomposes to give b-glucose and proton discarded is taken by a water molecule.

Hydrolysis of methyl acetate



It is clear that for such reactions water acts both as an acid and a base as it supplies as well as accepts a proton.

(ii) Heterogeneous Catalysis: Catalysis in which the phase of the catalysts differs from that of the reactants or products is known as heterogeneous catalysis. Solid phase catalysts and gas phase reactants are commonly used in heterogeneous catalysis. At the catalyst surface, a cycle of molecule adsorption, reaction, and desorption takes place. The rate (kinetics) of a process is influenced by thermodynamics, mass transfer, and heat transmission.

4.3.1 Stoichiometric Reactions for Catalysis

The addition or molecular compounds are formed when stoichiometric amounts of two or more stable compounds join together (solutions containing two or more salts in stoichiometric proportions are evaporated or simply mixed), *e.g.*,

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underset{\text{Carnalite}}{KCl \cdot MgCl_2 \cdot 6H_2O}$$

$$K_2SO_4 + Al_2\,(SO_4)_3 + 24\,H_2O \longrightarrow \underset{\text{Potassium alum}}{K_2SO_4 \cdot Al_2\,(SO_4)_3 .\ 24\,H_2O}$$

$$Fe(CN)_2 + 4KCN \longrightarrow \underset{\text{Potassium ferrocyanide}}{Fe(CN)_2 \cdot 4KCN}$$

$$CuSO_4 + 4NH_3 + 2H_2O \longrightarrow \underset{\text{Tetramino copper (II) sulphate monohydrate}}{CuSO_4 \cdot 4NH_3 \cdot 2H_2O}$$

On the basis of behaviour in aqueous medium, the addition compounds are grouped into two categories.

Double Salt

Double salts are those molecular compounds which exist only in crystal lattices and lose their identity when dissolved in aqueous medium. For example, Mohr's salt when dissolved in aqueous medium dissociate to form Fe^{2+}, NH_4^+ and SO_4^{2-} ion and give the positive test of these ions. Thus, the double salts do not retain their identity in solutions.

$$FeSO_4 \cdot (NH_4)_2\,SO_4 \cdot 6H_2O \xrightarrow{H_2O} Fe^{2+}\,(aq) + 2NH_4^+\,(aq) + 2SO_4^{2-}\,(aq) + 6H_2O$$

Complex or Coordination Compounds

Coordination compounds are the molecular or addition compounds which retain their identities in aqueous media or any other solvent and their properties are completely different from those of the constitutes. For example, potassium ferrocyanide is a coordination compound. When this is dissolved it does not form Fe^{2+} and CN^- ions, does not give usual tests of Fe^{2+} and CN^- ions, instead a new complex ion called ferrocyanide ion is formed. This complex ion does not ionise into constituent ions.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

The formation of coordination compounds is one of the remarkable characteristics of transition metals. These compounds are widely present in the minerals, plants and animals and play many important functions. For example, haemoglobin, which is a coordination compound of iron. Chlorophyll is a coordination compound of magnesium.

Compounds containing complex ions are called complex compounds and since the complex ions are formed through coordinate bonds, these are called coordinate ions and the corresponding composed as coordinate compound. A complex ion is an electrically charged (cationic or an ionic) or a neutral speices formed through the combination of simple cations with more than one neutral molecule or negative ion. For example, Argentocyanide ion $[Ag(CN)_2]^+$ is positive charged, nickelocyanide $[Ni(CN)_4]^{2-}$ is negatively charged and iron carbonyl $Fe(CO)_5$. is neutral. The argentocyanide ion is formed by the union of two cyanide ions (anions) with silver ions; nickelocyanide ion is formed by the union of four cyanide ions (anion) with nickel ions and iron carbonyl is formed by the union of five carbonly (neutral) with one iron ion. The anions or neutral molecules attached to the central metal atom are called ligands. The central metal cation is generally a transition metal with positive oxidation state and sometimes in zero oxidation state as in metal carbonyls.

4.3.2 Homogenous Catalytic Hydrogenation

It involves the formation of edible fats from vegetable and animal oils. Raw oils obtained from sources, such as the soyabean have the structure '+' indicates strong chemisorption; '±' weak chemisorption '–' no chemisorption.

Table 4.1 *Chemisorption Abilities*

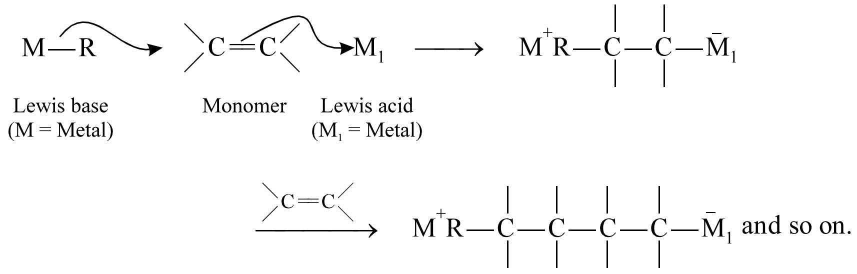
	O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	–
Pd, Pt	+	+	+	+	+	–	–
Mn, Cu	+	+	+	+	±	–	–
Al, Au	+	+	+	+	–	–	–
Li, Na, K	+	+	–	–	–	–	–
Mg, Ag, Zn, Pb	+	–	–	–	–	–	–

$CH_2(O_2CR_1)$. $CH(O_2CR_2)_2$ $C(O_2CR_3)_3$, where R_1, R_2, and R_3 are long chain hydrocarbons with several double bonds. One disadvantage of the presence of many double bonds is that they make the oils susceptible to atmospheric oxidation, which turns the oil rancid. The geometrical configuration of chains containing rigid double bonds is responsible for the liquid nature of the oil, and in many applications (such as on sandwiches) a solid fat is at least much better, and often necessary. Controlled, partial hydrogenation of an oil with a catalyst carefully selected so that hydrogenation is incomplete and so that the chains do not isomerize, is used on a wide scale to produce edible fats. The process, and the industry, is not made any easier by the seasonal variation of the number of double bonds in the oils.

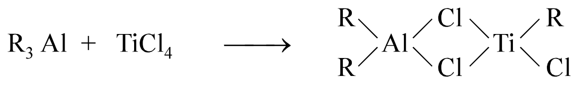
4.3.3 Zeigler-Natta Polymerization of Olefins

Until around 1952 vinyl polymers were obtained by free radical polymerization. This generally required high temperature and pressure and led to random polymerization. To overcome these problems, Ziegler-Natta (1952–1955) introduced novel organometallic initiators (also known as Ziegler-Natta catalysts) for vinyl polymerization. These consist of an organometallic compound (generally an aluminium trialkyl) and a metallic halide containing a metal which is reducible to a lower valence state (generally $TiCl_4$ or $VOCl_3$).

Polymerization reaction using Ziegler-Natta catalysts occurs at room temperature, without high pressure, on a solid surface having characteristic of anionic polymerization and forms a stereoselective polymer which is linear and mechanically stronger. It is believed that during addition polymerization, alkyl aluminium acts as a Lewis acid while titanium chloride acts as a Lewis base to form a coordinated complex. The transition metal compound is reduced by trialkyl aluminium to a lower valency state which coordinates with the π bond of the monomer. The process may be repeated infinitely to produce a highly stereospecific polymer or may be terminated as and when desired.



Alternatively a bimetallic initiator may be obtained by interaction between trialkyl aluminium and titanium chloride which acts as a Lewis base for the above reaction.

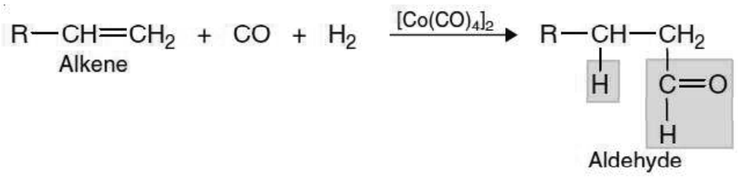


Bimetallic initiator

The Ziegler-Natta polymerization is applicable to polymerization of a-olefins and the product is sterically controlled polymer. Thus it was possible to prepare all *cis*-polyisoprene using these initiators. Also where as metallic initiator $Al(C_2H_5)_3$ + VCl_3 gives *trans*-1,4-polybutadiene the metallic initiator $Al(C_2H_5)_2Cl.H_2O$ + CoX_2 gives *cis*-1,4-polybutadiene. The polystyrene prepared by using Ziegler-Natta initiators is crystalline and has the same configuration on all the asymmetric carbon atoms. For this reason it is also referred to as directed polymerization.

4.3.4 Catalytic Reactions Involving Carbon Monoxide: Hydrocarbonylation of Olefins (Oxo Reaction) and Oxopalladation Reactions

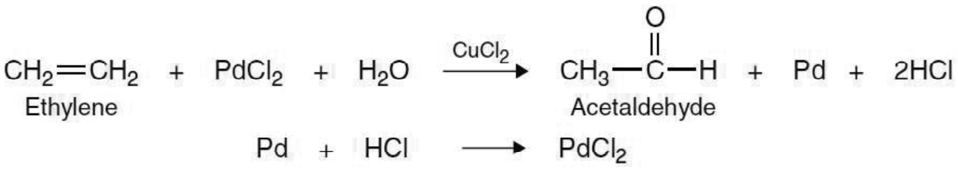
The oxo reaction is an industrially important method for producing aldehydes. It involves the treatment of an alkene with carbon monoxide and hydrogen in the presence of cobalt carbonyl catalyst. High temperatures and pressures are used.



$$\underset{\text{Alkene}}{R-CH=CH_2} + CO + H_2 \xrightarrow{[Co(CO)_4]_2} \underset{\text{Aldehyde}}{R-\underset{H}{\underset{|}{CH}}-\underset{\underset{H}{|}}{\underset{C=O}{\underset{|}{CH_2}}}}$$

The net reaction appears to be an *anti*-Markovnikov addition of formaldehyde to the alkene. Ketones cannot be prepared by this method.

There is another method used to prepare both aldehydes and ketones which is known as 'wacker process'. It is an oxopalladation reaction as an alkene is oxidised in the presence of palladium (II) chloride as a catalyst. This process involves the treatment of an alkene with an acidified aqueous solution of palladium chloride and cupric chloride. For example,



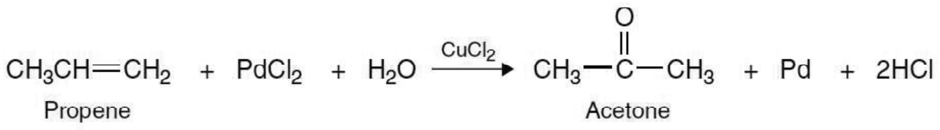
$$\underset{\text{Ethylene}}{CH_2=CH_2} + PdCl_2 + H_2O \xrightarrow{CuCl_2} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + Pd + 2HCl$$

$$Pd + HCl \longrightarrow PdCl_2$$

The cupric chloride promotes the second reaction, enhancing the reconversion of the palladium back into palladium chloride.

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

Acetone is prepared similarly from propene.



$$\underset{\text{Propene}}{CH_3CH=CH_2} + PdCl_2 + H_2O \xrightarrow{CuCl_2} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + Pd + 2HCl$$

4.3.5 Activation of C-H Bond

Stable carbon-hydrogen bonds in organic molecules are cleaved by a series of mechanistic processes known as C-H bond activation. The goal is to allow these molecules to be functionalized, leading to the production of more complicated intermediate or product chemicals with C-0, C-C and C-N bonds. The capacity to break the C-H bond allows for the transformation of low-cost feedstock molecules into commercially useful compounds. Selectivity and specificity in the synthesis of more complex compounds are important in pharmaceutical and fine chemical applications, and directed C-H activation allows for this. C-H bonds are activated through a variety of methods, including oxidative addition, -bond metathesis, electrophilic substitution, and so on. C-H activation, by definition, occurs through catalytic processes. When transition metals, such as Pt, Rh, Ir, and others are utilised in catalytic oxidative addition processes, C-H activation occurs. An intermediate organometallic species is formed when a proton linked to a carbon atom on the substrate hydrocarbon molecule coordinates with the transition metal. The functionalized carbon bond can be formed by reacting this intermediate with additional species. C-H cleavage and functionalization can be done in a stoichiometric manner, such as with Friedel-Craft chemistry and electrophilic aromatic substitution. Transition metal-mediated C-H activation/borylation of substrate molecules is particularly useful for forming C-B bonds. Organoboron compounds are significant in the creation of C-C bonds because they are used in cross-coupling processes.

When it comes to C-H functionalization in general, Friedel-Crafts processes, as well as various alkylation and arylation reactions, result in C-H bond functionalization. In the production of C-M bonds, metalation processes frequently require C-H activation. Numerous cross-coupling reactions functionalize C-H bonds, and the activation/metalation of the C-H to generate a C-B bond is exploited in the creation of the necessary organoboron reactants in Suzuki-Miyaura coupling. C-Li bond formation in lithiation processes is another major C-H activation/ metalation event.

Check Your Progress

1. Why are transition metals called binary hydrides?
2. Mention the types of catalysis.
3. What do you understand by general acid-base catalysis?
4. What happens to double salts when they are dissolved in aqueous medium?
5. Why was Ziegler-Natta catalyst introduced?

4.4 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Many transition metals produce binary hydrides with hydrogen. They are called binary because there are only two elements in the molecule.

2. There are generally two types of catalysis: (i) Homogeneous catalysis, and (ii) Heterogeneous catalysis.
3. There are some reactions, e.g., the mutarotation of glucose and the enolization of acetone which are catalyzed by both acids and base and are known as general acid-base catalysis.
4. Double salts are those molecular compounds which exist only in crystal lattices and lose their identity when dissolved in aqueous medium.
5. Until around 1952 vinyl polymers were obtained by free radical polymerization. This generally required high temperature and pressure and lead to random polymerization. To overcome these problems Ziegler-Natta (1952–1955) introduced novel organometallic initiators (also known as Ziegler-Natta catalysts) for vinyl polymerization.

4.5 SUMMARY

- A catalyst is a substance which alters the speed of a chemical reaction without undergoing any chemical change and can be recovered at the end of the reaction.
- In homogeneous catalysis, the catalyst is present in the same phase as the reactants. There can be gaseous or liquid phase.
- Catalysis in which the phase of the catalysts differs from that of the reactants or products is known as heterogeneous catalysis.
- The addition or molecular compounds are formed when stoichiometric amounts of two or more stable compounds join together.
- Coordination compounds are the molecular or addition compounds which retain their identities in aqueous media or any other solvent and their properties are completely different from those of the constitutes.
- A complex ion is an electrically charged (cationic or an ionic) or a neutral speices formed through the combination of simple cations with more than one neutral molecule or negative ion.
- One disadvantage of the presence of many double bonds is that they make the oils susceptible to atmospheric oxidation, which turns the oil rancid.
- Polymerization reaction using Ziegler-Natta catalysts occurs at room temperature, without high pressure, on a solid surface having characteristic of anionic polymerization and forms a stereoselective polymer which is linear and mechanically stronger.
- The Ziegler-Natta polymerization is applicable to polymerization of a-olefins and the product is sterically controlled polymer.
- The oxo process is an industrially important method for producing aldehydes.
- Wacker process involves the treatment of an alkene with an acidified aqueous solution of palladium chloride and cupric chloride.

4.6 KEY TERMS

NOTES

- **Homogenous Catalysis:** It refers to reactions in which the catalyst is in the same phase as the reactants, usually in solution.
- **Heterogeneous Catalysis:** It refers to reactions in which the phase of catalysts differs from that of the reactants or products.
- **Hydrogenation:** It refers to a chemical reaction that takes place between molecular hydrogen (H_2) and another compound or element to reduce or saturate organic compounds.
- **Zeigler-Natta Catalyst**: It is a catalyst used in the synthesis of polymers of 1-alkenes.
- **Oxo Reactions:** These reactions, also known as hydroformylation, are involved in an industrial process to produce aldehydes from alkenes.

4.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Give a few examples of catalysed reaction.
2. Differentiate between homogenous catalysis and heterogeneous catalysis.
3. How is argentocyanide ion formed?

Long-Answer Questions

1. Discuss homogeneous catalysis in gas phase and in liquid phase with the help of examples.
2. Describe how ionisation of complex compounds takes place in detail.
3. Give a detailed account on Zeigler-Natta polymerization of olefins.
4. Explain how aldehydes and ketones are prepared by the Wacker process.

4.8 FURTHER READING

Ouellette, R. J., Rawn, J. D. 2014. *Organic Chemistry: Structure, Mechanism, and Synthesis*. United States: Elsevier Science.

Adamson, A. 2012. *A Textbook of Physical Chemistry*. United States: Elsevier Science.

Lumb, N. H., McLintock, S., Lyons, C. G. 2016. *A Concise Text-Book of Organic Chemistry:* The Commonwealth and International Library: Chemistry Division. United Kingdom: Elsevier Science.

Rawn, J. D., Ouellette, R. J. 2015. *Principles of Organic Chemistry*. Netherlands: Elsevier Science.

Anthony Hill. 2002. *Organotransition Metal Chemistry*. Wiley: Great Britain.

John F. Hartwig. 2010. *Organotransition Metal Chemistry: From Bonding to Catalysis*. University Science Books: California.

UNIT 5 FLUXIONAL ORGANOMETALLIC COMPOUNDS

NOTES

Structure

5.0 INTRODUCTION

The compounds formed between metals and organic compounds containing metal - carbon bond(s) are called organometallic compounds. The metal in such a compound is bonded to carbon of an organic molecule, radical or ion. Several metals, such as Na, Ca, Zn Al, etc. form organometallic compounds. However, several transition metals or their compounds react with organic molecules forming organometallic compounds, which are actually coordination compounds. The term 'fluxional' has different meanings depending on the context and the method employed to evaluate the dynamics. Chemical exchange causes line-broadening in a molecule's spectroscopic signature, which is sometimes referred to as fluxional. This unit will discuss fluxionality and dynamic equilibria in various compounds.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the concept of fluxionality
- Discuss fluxionality and dynamic equilibria in various compounds

5.2 FLUXIONALITY

When a molecule's spectroscopic signature exhibits line-broadening (beyond that predicted by the Heisenberg uncertainty principle) due to chemical exchange, it is commonly referred to as fluxional. Fluctuation is sometimes identified via isotopic labelling rather than spectroscopy when the rates are slow.

Fluxional (or non-rigid) molecules are those in which some or all of their atoms switch between symmetry-equivalent locations due to dynamics. Because almost every molecule is fluxional in some way, such example bond rotations in most organic compounds, the term fluxional is defined by the context and the method used to measure the dynamics.

The phenomenon of fluxionality is exhibited by several organometallic compounds. The compound Fe (η^5-C_5H_5) (η^1- C_5H_5)$(CO)_2$ exhibits the phenomenon of ring whizzing. At 30 °C, two peaks are shown by the ^{1}H NMR spectrum —typical (δ5.6) of the η5-C5H5 and assigned η^1-C_5H_5. Due to the slow hopping of the Fe center from carbon to carbon in the η^1-C_5H_5 ligand, split of the singlet assigned to the η^1-C_5H_5 ligand takes place at low temperatures. There are two mechanisms proposed with the consensus favouring the 1, 2 shift pathway.

Uses of Organometallic Compounds

The organometallic componds are used in several industrial and laboratory reactions. The following are some of such uses:

- Ferrocene, when added to fuel oils promotes smokeless combustion of the oil.
- $Pb(C_2H_5)_4$ is used as an antiknock agent in petrol.
- Cyclopentadienylmanganese tricarbonyl is an effective antiknock agent for petrol; it is more effective than $Pb(C_2H_5)_4$.
- A mixture of $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_2Cl$ is used as a catalyst for the polymerisation of ethylene.
- $Co_2(CO)_8$ is used as the catalyst in the manufacture of aldehydes and alcohols from olefins (oxo process).
- $Fe(CO)_5$ acts as the catalyst in reactions of the type

$$CO + ROH + C_2H_2 \longrightarrow H_2C = HC\text{-}COOR$$

- In the heterogeneous polymerisation of olefins with Ziegler- Natta catalyst, organometallic intermediates are involved.
- In the hydrogenation of olefins, Wilkinson's catalyst, $[RhCl(PPh_3)_3]$ is used.

5.3 FLUXIONALITY AND DYNAMIC EQUILIBRIA IN VARIOUS COMPOUNDS

Let us study various organometallic compounds showing fluxionality and dynamic equilibria.

5.3.1 The 18-electron Rule and the Organometallic Compounds

The 18-electron rule implies that in a metal complex, 18 electrons are made available to the metal through bonding and then the metal assumes the electron structure of the next noble gas. The 18 electrons are accommodated in the five (n-1)*d* orbitals (10 electrons), the three *np* orbitals (6 electrons) and the one *ns* orbital (2 electrons). These 18 electrons comprise the electrons of the metal together with the electrons contributed by the ligands. The attainment of the 18-electron configuration leads to stability of the complex. For example, in $Fe(CO)_5$, iron $(4s^2\ 3d^6)$ provides 8 electrons and the five CO ligands 10 electrons, so that the 18-electron rule is satisfied. The 18-electron rule applies to several organometallic complexes also. Some examples of such complexes are indicated below:

$[Cr(\eta^6 - C_6H_6)_2]$ $\quad$ Cr $4s^1\ 3d^5$: 6 electrons

C_6H_6 : 6 electrons

Total : $6 + (2 \times 6) = 18$ electrons

$[Ni(cyclo\text{-}octadiene)_2]$ Ni $4s^2\ 3d^8$: 10 electrons

cyclo-octadiene : 2×4 electrons

Total : $10 + (2 \times 4) = 18$ electrons

$[Fe\,(\eta^5 - C_5H_5)_2]$ $\quad$ $6 + (2 \times 6) = 18$ electrons

$[\eta^6 - (C_7H_8)Mo(CO)_3]$ $\quad$ $6 + 6 + (3 \times 2) = 18$ electrons

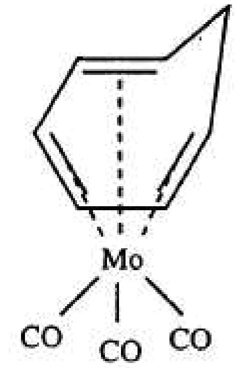
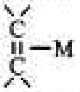
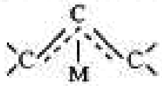
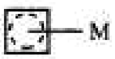
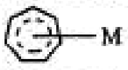
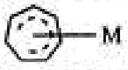
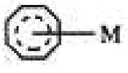


Fig. 5.1 *Structure of Tricarbonylheptatrienemolybdenum*

Some of the common organic ligands which form organometallics are given in Table 5.1.

NOTES

Table 5.1 Some organic Ligands which form Organometallics

Ligand	Available electrons	Metal-ligand structure	Hapticity
Methyl, alkyl, CH_3, CH_2R	1	$M-CH_2R$	η^1
Alkylidene (carbene)	2	$M=CR_2$	η^1
Alkene $H_2C=CH_2$	2		η^2
π-Allyl C_3H_6	3		η^3
Alkylidyne (carbyne) C—R	3	$M\equiv CR$	η^1
1,4-Butadiene C_4H_8	4		η^4
Cyclobutadiene C_4H_4	4		η^4
Cyclopentadiene C_5H_5 (Cp)	5 (3) (1)		η^5 η^3 η^1
Benzene C_6H_6	6		η^6
Tropylium ion $C_7H_7^+$	6		η^7
Cycloheptatriene C_7H_8	6		η^6
Cyclooctatetraene C_8H_8 (cot)	8 (6) (4)		η^8 η^6 η^4

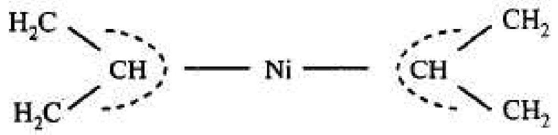
5.3.2 Metal-Allyl Complexes

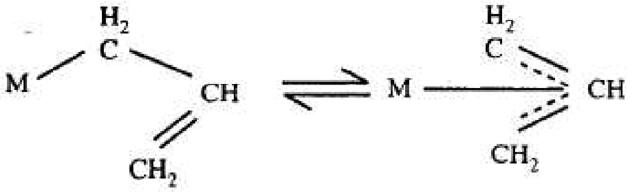
The allyl group, $CH_2=CH-CH_2-$ can function as a sigma ligand (*monohapto*) or as a sigma plus pi ligand (*trihapto*). For example, nickel chloride reacts with allyl magnesium bromide forming a π-allyl complex.

$$NiCl_2 + 2\,CH_2=CH-CH_2-MgBr \longrightarrow (\pi\text{-}CH_2CHCH_2)_2Ni + MgBr_2 + MgCl_2$$

Such a π-allyl complex has a three-carbon delocalised allylic system $CH_2 \underline{\cdots} CH \underline{\cdots} CH_2$ which acts as "half sandwich".

NOTES



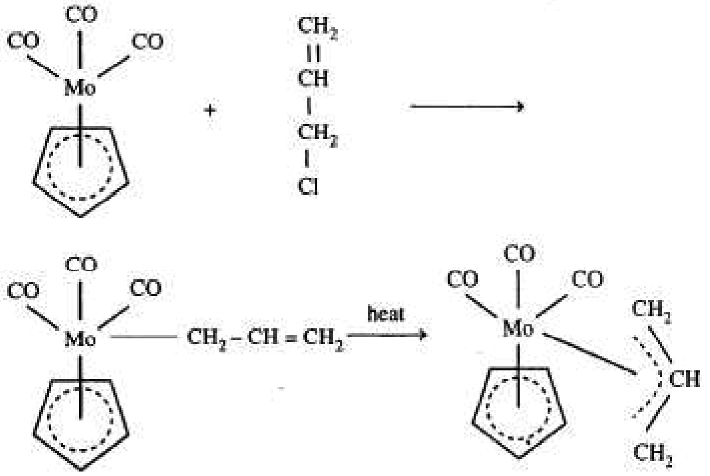


π-allyl (η¹)
(monohaptoallyl)

π-allyl (η³)
(trihaptoallyl)

The π-allyl complex is believed to be formed via the σ-bonded allyl derivative of the metal $[(\mathrm{CH_2 = CH - CH_2 -})_2\mathrm{M}]$. The σ-compound is transformed to the π-compound (η^3-allyl complex) by thermal or photochemical energy. Such a complex is called a *fluxional complex*; it isomerises with a little energy.

π-(Cyclopentadienyl)-molybdenum tricarbonyl reacts with allyl chloride to form first the σ-compound which on warming isomerises to the π-complex.

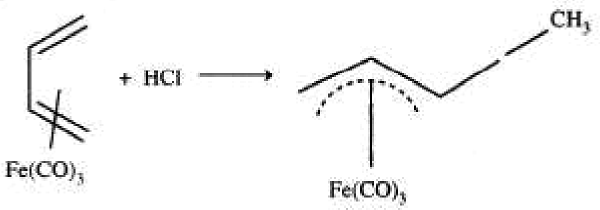


σ-compound, yellow oil

π-complex, yellow solid

Fig. 5.2 *Fluxional Complexes*

Some allyl complexes are obtained by protonation of butadiene complexes; the following is an example for such transformations:



5.3.3 η^3 – Allylpalladium Chloride Dimer

Its structure is denoted as in fig. 5.3.

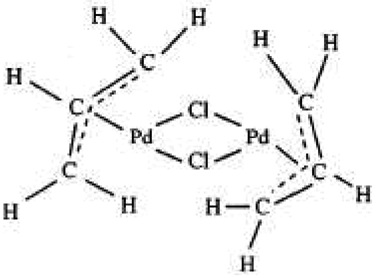


Fig. 5.3 *Structure of* η^3*- Allylpalladium chloride Dimer*

The η^3 – allyl systems in it are related by a centre of symmetry in the molecule. The C-C-C plane makes an angle of 111° with the plane. All the C-C distances are 1.38 Å; the C-C-C angle is 120°. Each Pd atom is equidistant (2.11 Å) from all three carbon atoms of its respective allyl group.

5.3.4 Metal-Acetylene Complexes

The metal-acetylene complexes are similar to the metal-olefin complexes in their formation and formulae. The alkynes also have π system that could be involved in bonding similar to that in metal-alkene complexes; however, the bonding in them is more complicated than that in olefin complexes, because there are more types of bonding possible with triple bonds. An example for an acetylene complex is the Pt-diphenylacetylene, $[\mathrm{Pt}(C_6H_5C\equiv CC_6H_5)(\mathrm{PPh}_3)_2]$. Its structure is denoted in Fig. 5.4.

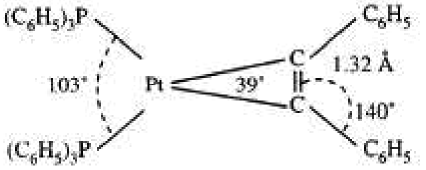
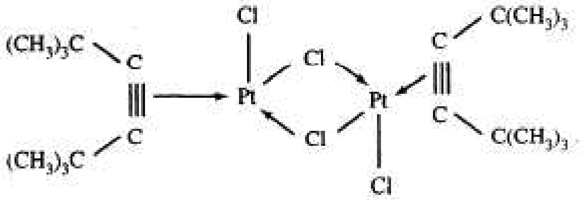


Fig. 5.4 *Structure of Bis(triphenylphosphine)-diphenylacetyleneplatinum(0)*

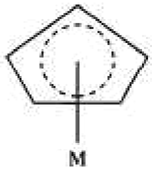
The olefin unit lies almost in the plane of $\mathrm{Pt(PPh_3)_2}$. The structure is approximately square-planar. Another example for an alkyne complex is $[\{\mathrm{PtCl_2}(t\text{-BuC}\equiv\mathrm{C}t\text{-Bu})\}_2]$. It is a bisalkyne, binuclear complex. Its structure is denoted as:



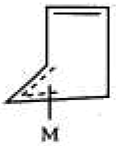
5.4 NOTATION IN THE NOMENCLATURE OF METAL-OLEFIN COMPLEXES-η^2-OLEFIN

An olefin containing more than one π bond can bond with a metal in different ways; more than one carbon atom may be attached to the metal. Therefore, a systematic notation is used to designate the number of carbon atoms that are bound to the metal. This notation uses the Greek term *hapto*, which means *to fasten*. If only one carbon of the olefin is bonded to the metal, then the prefix *monohapto* (symbol η^1) is used for the name of the complex.The prefixes *bihapto* (η^2), *trihapto* (η^3), *tetrahapto* (η^4), *pentahapto* (η^5), etc. designate the other types of binding. In a η^5 complex, five carbon atoms are linked to the metal, [e.g. $(\eta^5\text{-}(\pi\text{-}C_5H_5)_2\,Fe)$].

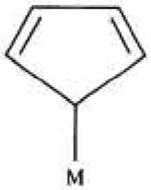
Allyl, for example, may attach itself to a metal through one of its carbon atoms (behaving like an alkyl ligand) or through all three carbon atoms via its π electron system. Ligands with a more extended π systems show a greater number of binding modes. For example, the cyclopentadienyl ligand may function as a penta, tri, or monohapto ligand.



$\eta^5\text{-}C_5H_5$



$\eta^3\text{-}C_5H_5$



$\eta^1\text{-}C_5H_5$

5.5 DIENYL COMPLEXES

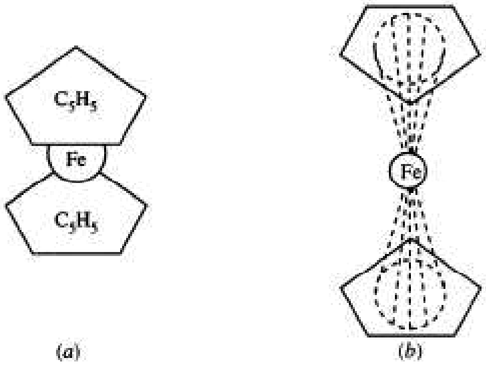
Let us study some of the common dienyl complexes in detail.

5.5.1 Ferrocene

The important structural features of ferrocene are the following:

- The structure of ferrocene, has been determined by X-ray diffraction.
- It has a sandwich structure, in which the two cyclopentadienyl groups are nearly eclipsed with respect to each other (the two planar rings are aligned in space in the same manner, parallel to each other).
- The hydrogen atoms are slightly tilted towards the iron atom.
- All the carbon atoms in it are equidistant from Fe; therefore the ring is assumed to have a hapticity η of 5, i.e., $\eta^5 - C_5H_5$.
- All the C-C distances are same (1.389 Å), a value close to 1.395 Å of benzene. The bond order is similar to that in benzene.
- The two rings are separated by a distance of 3.25 Å.

- The Fe-C distances are all equal (2.04 Å).
- The energy barrier for rotation of the rings about the metal to ring axis is very small (4 kJ mol^{-1}).



(*a*) (*b*)

Fig. 5.5 *Structure of Ferrocene*

Bonding in Ferrocene

The bonding in ferrocene can be understood by considering the molecule to be a combination of a ferrous ion with two $C_5H_5^-$ anions. Each $C_5H_5^-$ is planar with a symmetrical pentagonal shape. The entire ring is bonded uniformly to the metal atom. The bonding in it occurs by overlap of the sextet of π electrons of the ring with the 3*d* orbitals of the metal, thereby producing a delocalised covalent bond between the metal atom and the cyclopentadienyl ring as a whole. One such overlap is shown in Figure 5.6.

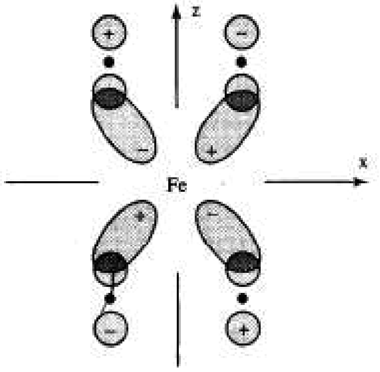


Fig. 5.6 *Overlap of a* d_{xz} *Metal Orbital with a Ring* π *Orbital to Produce a Metal-Ring Bond*

Properties of Ferrocene

- Ferrocene is a crystalline orange solid, with a m.p. of 174°C.
- It is insoluble in water but soluble in organic solvents.
- It is thermally stable up to 500°C in the absence of air.
- It is diamagnetic and non-polar.
- Alkalis and acids do not attack this complex.

- It gets oxidised to blue paramagnetic ferricinium ion $[\pi\text{-}(C_5H_5)_2Fe]^+$ by Ag^+. This ion can form salts with X^- ions. This oxidation is reversible.

  $$[(\pi\text{-}C_5H_5)_2\overset{(III)}{Fe}]^+ + e^- = [(\pi\text{-}(C_5H_5)_2)\overset{(II)}{Fe}] \quad E^\circ = 0.5\text{ V}$$

- Ferrocene undergoes electrophilic substitution reactions such as halogenation, acetylation and alkylation like an aromatic compound; Woodward named it ferrocene because of its aromatic character. This aromatic character is in accord with the Huckel rule which requires $(4n+2)$ π electrons for aromatic character.
- It cannot be catalytically hydrogenated, and it does not add on maleic anhydride. Thus, it does not show the unsaturated character of the parent reactant cyclopentadiene. This is justifiable as the π electrons of the rings are involved in the bonding with the Fe atom.

5.5.2 Bis(cyclopentadienyl) Beryllium

$Be(C_5H_5)_2$ is prepared by metathesis of $BeCl_2$ with $Na[C_5H_5]$:

$$BeCl_2 + 2\ Na[C_5H_5] \rightarrow Be\ (C_5H_5)_2 + 2\ NaCl$$

In the gas phase, it has an antisymmetrical sandwich structure. It has pentahapto bonding (η^5), as all the C atoms of each C_5H_5 group are within bonding distance of the Be atom. In the solid phase, the structure corresponds to $\eta^5-C_5H_5.\eta^1-C_5H_5$; the hapticity for one of the C_5H_5 groups is reduced from 5 to 1.

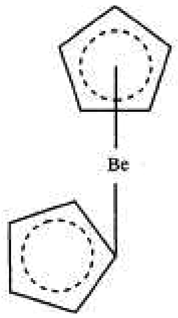


Fig. 5.7 *Structure of Solid Bis(cyclopentadienyl) Beryllium*

5.5.3 Metallocenes

Several other 3*d* metals also form sandwich compounds similar to iron. Elements which form carbonyls generally also form π-cyclopentadienyls. These compounds and also ferrocene are commonly called *metallocenes*. The metallocenes are isostructural. Some of the metallocenes and their properties are summarised in Table 5.2. Ferrocene is the most stable of the metallocenes.

Table 5.2 *Some Bis-π-(cyclopentadienyl) Metal Complexes*

Formula	Name	Colour	m.p.(°C)	Magnetic Property(BM)
$(\pi\text{-}C_5H_5)_2Ti$	titanocene	green	200	diamagnetic
$(\pi\text{-}C_5H_5)_2V$	vanadocene	violet	168	3.78
$(\pi\text{-}C_5H_5)_2Cr$	chromocene	scarlet	173	3.02
$(\pi\text{-}C_5H_5)_2Mn$	manganocene	brown	173	2.50 at 195°C
$(\pi\text{-}C_5H_5)_2Fe$	ferrocene	orange	174	diamagnetic
$(\pi\text{-}C_5H_5)_2Co$	cobaltocene	purple	174	1.76
$(\pi\text{-}C_5H_5)_2Ni$	nickelocene	green	173	2.86
$(\pi\text{-}C_5H_5)_2WH_2$	dihydridotungstocene	yellow	163	diamagnetic

Not all these metallocenes obey the 18-electron rule. Among these, only ferrocene is thermally stable (upto 500°C) and unaffected by air. The 19-electron cobaltocene understandably gets easily oxidized to the 18-electron cobaltocenium ion, $[Co(\eta^5 - C_5H_5)_2]^+$; this ion is remarkably stable.

Several cyclopentadienyl complexes containing other ligands such as carbonyl, nitrosyl and hydride are known. Some of these are isoelectronic. Assuming that each cyclopentadiene ring contributed all its π electrons to the molecular orbitals, an 18-electron valence shell is conferred on the central atom of most of these complexes (Table 5.3).

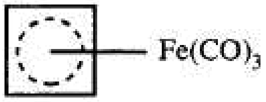
Table 5.3 *Valence Electron Numbers in Cyclopentadienyl Complexes*

Complex	Valence Electron Number
$[Ti(C_5H_5)_2]^{2+}$	$(2 \times 5) + 2 = 12$
$[V(C_5H_5)(CO)_4]$	$5 + 5 + (4 \times 2) = 18$
$[V(C_5H_5)_2]$	$(2 \times 5) + 5 = 15$
$[Cr(C_5H_5)_2]$	$(2 \times 5) + 6 = 16$
$[Cr(C_5H_5)(NO)_2]^+$	$5 + 5 + (2 \times 3) = 16$
$[Cr(C_5H_5)(CO)_2NO]$	$5 + 6 + (2 \times 2) + 3 = 18$
$[Cr(C_5H_5)(CO)_3H]$	$5 + 6 + (3 \times 2) + 1 = 18$
$[Mn(C_5H_5)(CO)_3]$	$7 + 5 + (3 \times 2) = 18$
$[Fe(C_5H_5)_2]$	$8 + (2 \times 5) = 18$
$[Fe(C_5H_5)(CO)_2]_2$	$8 + 5 + 1 + (2 \times 2) = 18$
$[Co(C_5H_5)_2]$	$9 + (2 \times 5) = 19$
$[Co(C_5H_5)_2]^+$	$8 + (2 \times 5) = 18$
$[Co(C_5H_5)(CO)_2]$	$9 + 5 + (2 \times 2) = 18$
$[Ni(C_5H_5)_2]$	$10 + (2 \times 5) = 20$
$[Mo(C_5H_5)(CO)_3]_2$	$6 + 5 + 1 + (3 \times 2) = 18$

5.5.4 Half-Sandwich Compounds

In a half-sandwich compound, only one ring is coordinated to the metal along with other ligands. These can be prepared from the respective metal carbonyls. Cyclobutadieneiron tricarbonyl is such a complex. This complex is stable though cyclobutadiene itself is not. This is an example for stabilisation of a labile ring species by complexation.

The molecular orbital calculations indicate that there are effectively six pi electrons in the cyclobutadiene-metal system; it is said to be metalloaromatic.

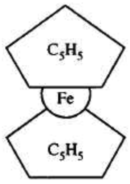


Check Your Progress

1. Define fluxional (or non-rigid) molecules.
2. What happens when ð (Cyclopentadienyl)-molybdenum tricarbonyl reacts with allyl chloride?
3. Why is the bonding in metal-acetylene complexes more complicated than that in olefin complexes?
4. Give the symbol used when three carbons of the olefin is bonded to the metal.
5. Give the structure of ferrocene.
6. What is the structure of bis (cyclopentadienyl)beryllium in the gas phase?

5.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Fluxional (or non-rigid) molecules are those in which some or all of their atoms switch between symmetry-equivalent locations due to dynamics.
2. **π**-(Cyclopentadienyl)-molybdenum tricarbonyl reacts with allyl chloride to form first the c-compound which on warming isomerises to the **π**-complex.
3. The bonding in them is more complicated than that in olefin complexes, because there are more types of bonding possible with triple bonds.
4. If only one carbon of the olefin is bonded to the metal, then the prefix monohapto (symbol η^1) is used for the name of the complex. The prefixes bihapto (η^2), trihapto (η^3), tetrahapto (η^4), pentahapto (η^5), etc.
5. The structure of ferrocene is as follows:



6. In the gas phase, it has an antisymmetrical sandwich structure.

5.7 SUMMARY

- When a molecule's spectroscopic signature exhibits line-broadening (beyond that predicted by the Heisenberg uncertainty principle) due to chemical exchange, it is commonly referred to as fluxional.

NOTES

- The 18-electron rule implies that in a metal complex, 18 electrons are made available to the metal through bonding and then the metal assumes the electron structure of the next noble gas.
- The attainment of the 18-electron configuration leads to stability of the complex.
- The allyl group, $CH_2 = CH - CH_2$ - can function as a sigma ligand (monohapto) or as a sigma plus pi ligand (trihapto).
- The metal-acetylene complexes are similar to the metal-olefin complexes in their formation and formulae. The alkynes also have $\boldsymbol{\pi}$ system that could be involved in bonding similar to that in metal-alkene complexes.
- An olefin containing more than one $\boldsymbol{\pi}$ bond can bond with a metal in different ways; more than one carbon atom may be attached to the metal.
- The structure of ferrocene has been determined by X-ray diffraction.
- The bonding in ferrocene can be understood by considering the molecule to be a combination of a ferrous ion with two $C_5H_5^-$ anions.
- In a half-sandwich compound, only one ring is coordinated to the metal along with other ligands. These can be prepared from the respective metal carbonyls.

5.8 KEY TERMS

- **Fluxionality:** It is a phenomenon in which a molecule goes through a dynamic molecular process in which two or more chemically and/or magnetically distinct groups of the molecule are interchanged.
- **Organometallic Compounds:** These compounds that have at least one bond between a metallic element and a carbon atom in an organic molecule exists in chemical compounds.
- **Allyl Group:** It has a structural formula, H 2 C=CHCH 2 R, where R represents the rest of the molecule.

5.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Mention some uses of organometallic compounds.
2. Give a structure of a fluxional (or non-rigid) molecule.
3. What are the major uses of organometallic compounds?
4. What do you understand by half-sandwich compounds?

Long-Answer Questions

1. Discuss the structure of η^3 - allylpalladium chloride dimer.
2. Explain the notation in the nomenclature of metal-olefin complexes.

3. Describe the properties of ferrocene in detail.
4. Anaylse the types of bonding exist in ferrocene and bis (cyclopentadienyl) beryllium.

5.10 FURTHER READING

Ouellette, R. J., Rawn, J. D. 2014. *Organic Chemistry: Structure, Mechanism, and Synthesis*. United States: Elsevier Science.

Adamson, A. 2012. *A Textbook of Physical Chemistry*. United States: Elsevier Science.

Lumb, N. H., McLintock, S., Lyons, C. G. 2016. *A Concise Text-Book of Organic Chemistry:* The Commonwealth and International Library: Chemistry Division. United Kingdom: Elsevier Science.

Rawn, J. D., Ouellette, R. J. 2015. *Principles of Organic Chemistry*. Netherlands: Elsevier Science.

Anthony Hill. 2002. *Organotransition Metal Chemistry*. Wiley: Great Britain.

John F. Hartwig. 2010. *Organotransition Metal Chemistry: From Bonding to Catalysis*. University Science Books: California.