CHAPTER 9

HYDROCARBONS

Classification of Hydrocarbons

- Hydrocarbons are carbon and hydrogen compounds derived mainly from coal and petroleum. They are classified into three categories:

1. **Saturated hydrocarbon** – C – C single bonds; eg. $CH_3 – CH_3$ ethane
2. **Unsaturated hydrocarbon** – C = C, and C ≡ C or both e.g $CH_2 = CH_2$, ethene, or $CH \equiv CH$, ethyne.
3. **Aromatic hydrocarbon**-One aromatic ring atleast; e.g C_6H_6, benzene.

Alkanes

- Alkanes are the simplest organic compounds made of carbon and hydrogen only. They have the general formula C_nH_{2n+2} (where n = 1, 2, 3, etc.) Alkanes contain strong C—C and C—H bonds. Therefore, this class of hydrocarbons is relatively chemically inert. Hence, they are sometimes referred to as paraffins (Latin: parum affinis = little affinity).
- Methane (CH_4) is the first member of this family. In methane, carbon forms single bonds with four hydrogen atoms. All H—C—H bond angles are of 109.5°. Methane has a tetrahedral structure. C—C and C—H bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1s orbitals of hydrogen atoms.
- Alkanes exhibit chain isomerism, position isomerism and conformational isomerism.
- Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°).
- Groups or substituents derived from alkanes by removal of one hydrogen atom is known as alkyl groups. Their general formula is C_nH_{2n+1}.
- **Steps to write correct structure from the given IUPAC name:**

(i) Write the longest chain of carbon atoms corresponding to the parent alkane.

(ii) Give number to carbon atoms.

(iii) The substituents are attached to the correct carbon atoms after their numbering.

(iv) Satisfy the valency of each carbon atom by putting the correct number of hydrogen atoms.

- **Preparation of Alkanes:**

(i) Alkanes can be prepared by hydrogenation of unsaturated hydrocarbons in the presence of catalyst (Ni, Pd or Pt).

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{\text{Ni/Pd/Pt}} \underset{\text{Ethane}}{CH_3—CH_3}$$

$$\underset{\text{Ethyne}}{HC \equiv CH} + 2H_2 \xrightarrow{\text{Ni/Pd/Pt}} \underset{\text{Ethane}}{H_3C—CH_3}$$

(ii) **By reduction of alkyl halides:** Alkanes can be prepared by the reduction of alkyl halides (except fluorides) with zinc and dilute hydrochloric acid.

$$\underset{\text{Chloromethane}}{CH_3—Cl + H_2} \xrightarrow{\text{Zn, H}^+} \underset{\text{Methane}}{CH_4} + HCl$$

(iii) **Wurtz Reaction:** This reaction is used to increase the length of the carbon chain.

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} CH_3—CH_3 + 2NaBr$$

Note: From wurtz reaction only these alkane can be formed which have even number of C atom.

(iv) **Decarboxylation:** Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid.

$$\underset{\text{Sodium ethanoate}}{CH_3COO^-Na^+} + NaOH \xrightarrow[\Delta]{\text{CaO}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(v) **Kolbe's Electrolytic Method:**

$$\underset{\text{Sodium acetate}}{2CH_3COO^- Na^+} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3—CH_3} + 2CO_2 + H_2 + 2NaOH$$

- **Physical properties:** Alkanes are almost non-polar molecule. They possess weak van der Waals forces. Due to the weak forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. With the increase of branching, the boiling points of alkanes decrease as on increasing the branching, the molecule attains the shapes of a sphere, decreasing surface area, thereby decreasing van der Waals forces. Alkanes with even number of carbon atoms have higher melting points as compared to next higher or lower alkanes with odd number of carbon atoms.

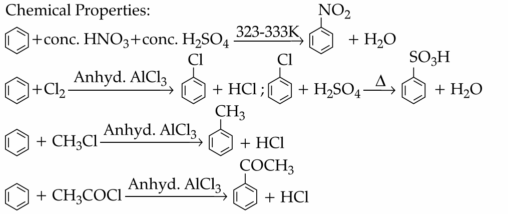
Hydrocarbons

Compounds of Carbon and Hydrogen

Physical Properties:

- Non-polar, usually colourless liquids or solids with characteristic aroma.
- Immiscible with water but miscible with organic solvents.
- Burns with sooty flame.

Chemical Properties:

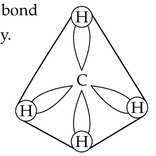


Classification

- **Saturated:** Contain C-C and C-H single bonds. (alkanes)
- **Unsaturated:** Contain C-C multiple bonds (alkenes, alkynes)
- **Aromatic**: Contain cyclic compounds

Alkane (C_2H_{2n+2})

- H-C-H bond angles – 190.5°, C-C and C-H bond lengths are 154 pm and 112 pm respectively.
- Shows structural and chain isomerism.



Preparation :

$CH_2 = CH_2 + H_2 \xrightarrow{pt/pd} CH_3 - CH_3$

$CH_3Cl + H_2 \xrightarrow{Zn,H^+} CH_4 + HCl$

Wurtz reaction :

$CH_3Br + 2Na + BrCH_3 \xrightarrow{Dryether} CH_3 - CH_3 + 2NaBr$

$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

$2CH_3COONa + 2H_2O \longrightarrow C_2H_6 + 2CO_2 + H_2 + 2NaOH$

- Physical Properties:

Non-polar, weak van der Waals forces, colourless, odourless.

B.P. increases with increases in molecular size.

Chemical Properties:

$CH_4 \xrightarrow[hv/-HCl]{+Cl_2} CH_3Cl + \xrightarrow[hv/-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[hv/-HCl]{+Cl_2} CHCl_3 \xrightarrow[hv/-HCl]{+Cl_2}$

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

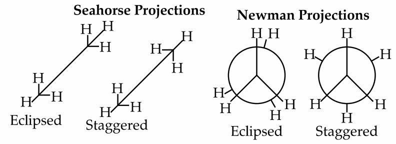
$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$

$CH_4 + O_2 \xrightarrow[\Delta]{Mn_2O_3} HCHO + H_2O$

$CH_4(CH_2)CH_3 \xrightarrow{Anhyd.AlCl_3/HCl} CH_3\text{–}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{–}(CH_2)_2\text{–}CH_3 + CH_3\text{–}CH_2\text{–}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{–}CH_2\text{–}CH_3$

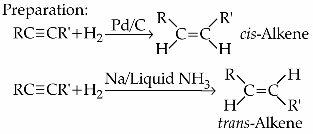
$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$

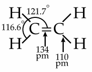
$C_6H_{14} \xrightarrow{733\ K} C_6H_{12} + H_2$; $C_4H_8 + C_2H_6$; $C_3H_6 + C_2H_4 + CH_4$



Alkenes (C_2H_{2n})

- Shows structural and geometrical isomerism
- Preparation:





$H_3C - CH_2X \xrightarrow[\Delta]{Alc.KOH} H_2C = CH_2$

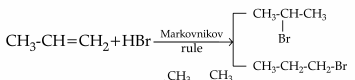
$CH_2Br - CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$

$H_3CCH_2OH \xrightarrow[\Delta]{conc.H_2SO_4} CH_2 = CH_2 + H_2O$

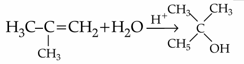
- Physical Properties :
  - Ethene is a colourless gas with faint sweet smell.
  - All other are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents.
  - Increase in b.p. with increase in molecular size.
- Chemical Properties:

$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2 - CH_2Br$

$CH_2 = CH_2 + HBr \longrightarrow CH_3CH_2Br$



$CH_3\text{-}CH{=}CH_2 + HBr \xrightarrow[rule]{Markovnikov} CH_3\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}CH_3,\ CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$



$H_3C\text{–}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + H_2O \xrightarrow{H^+} (CH_3)_2\,C(CH_3)\,OH$

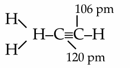
$CH_3 - CH = CH - CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$

$n(CH_2 = CH_2) \xrightarrow[Catalyst]{HighTemp/Pressure} \text{-}(CH_2 - CH_2)\text{-}_n$

$n(CH_3\text{–}CH = CH_2) \xrightarrow[Catalyst]{HighTemp/Pressure} \text{-}(CH_3\text{–}CH_2\text{–}CH_2)\text{-}_n$

Alkynes (C_nH_{2n-2})

- IUPAC name: replacing 'ane' by the suffix 'yne'.
- Shows position and chain isomerism



Preparation:

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CaO + 3C \longrightarrow CaC_2 + CO$

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$CH_2Br - CH_2Br + KOH \xrightarrow[-KBr,\ -H_2O]{alcohol} H_2C = CHBr \xrightarrow[-NaBr,\ -NH_3]{NaNH_2} CH \equiv CH$

Physical Properties:

- First three members are gases, next eight are liquids and higher ones are solids.
- Colourless, ethyne has characteristic odour and other are odourless.
- Lighter than water, immiscible with water but soluble in organic solvents.
- M.p, b.p. and density increase with increase in molar mass.

Chemical Properties:

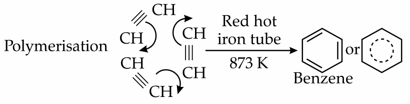
$HC \equiv CH + Na \longrightarrow HC \equiv CNa + 1/2\,H_2$

$HC \equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} [H_2C = CH_2] \xrightarrow{H_2} CH_3 - CH_3$

$CH_3 - C \equiv CH + Br_2 \longrightarrow [CH_3CBr = CHBr] \xrightarrow{Br_2} CH_3\text{–}\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}\text{–}\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}H$

$HC \equiv C - H + HBr \longrightarrow [CH_2C = CH - Br] \longrightarrow \underset{\displaystyle CH_2}{\underset{|}{CHBr_2}}$

$HC \equiv CH + H_2O \xrightarrow[333\ K]{Hg^{2+}/H^+} [CH_2 = \underset{\displaystyle OH}{\underset{|}{C}} - H] \xrightarrow{Isomersation} CH_3 - \underset{\displaystyle O}{\underset{\|}{C}} - H$

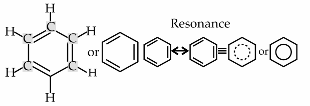


Mechanism of Electrophilic substitution reactions

(i) Generation of Electrophile
(ii) Formation of carbocation intermediate
(iii) Removal of proton

Aromatic Hydrocarbon

- Types: Benzenoids – contain benzene ring, Non-benzenoids – does not contain benzene ring.
- Isomerism: Ortho (o-), Meta (m-), Para (p-)
- Structure:



- Aromaticity: Planarity, complete delocalisation of the π–electros in the ring, presence of (4n + 2) π electrons in the ring where n is an integer (n = 0,1,2,......) (Huckel rule)

Preparation:

- Cyclic polymerisation of ethyne

$C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$

$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$

Trace the Mind Map

▸ First Level ▸ Second Level ▸ Third Level

- **Chemical Properties:**

(i) Substitution Reactions: One or more atom of alkanes is replaced by halogens, nitro group and sulphonic acid group, e.g., halogenation.

$$CH_4 + Cl_2 \xrightarrow{hv} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{hv} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{hv} \underset{\text{Trichloromethane (chloroform)}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{hv} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

Mechanism:

(i) Initiation: Homolysis of chlorine molecule in the presence of light or heat.

$$Cl_2 \xrightarrow{hv} 2Cl^{\bullet}$$

(ii) Propagation: Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C–H bond to generate methyl free radical with the formation of H–Cl.

$$Cl^{\bullet} + CH_4 \longrightarrow HCl + CH_3^{\bullet}$$

The methyl radical obtained attacks the second molecule of chlorine to form CH_3–Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

(iii) Termination:

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3 - CH_3$$

$$Cl^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3Cl$$

(ii) Combustion: Due to the evolution of a large amount of heat during combustion, alkanes are used as fuels.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

$$\text{e.g., } C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l);$$

$$\Delta H^{\circ} = -2875.84 \text{ kJ mol}^{-1}$$

(iii) Controlled Oxidation:

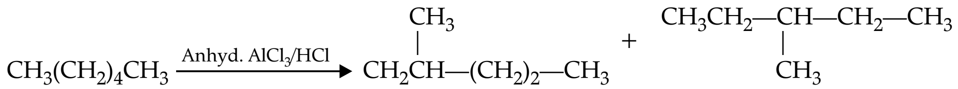
(i) $2CH_4 + O_2 \xrightarrow{Cu/523K/100\ atm} 2CH_3OH$
Methanol

(ii) $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$
Methanal

(iii) $2CH_3CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2 Mn} 2CH_3COOH + 2H_2O$
Ethanoic acid

(iv) $(CH_3)_3CH \xrightarrow[{[O]}]{KMnO_4} (CH_3)_3COH$
2-Methylpropane (3°-alkane) 2-Methylpropan-2-ol

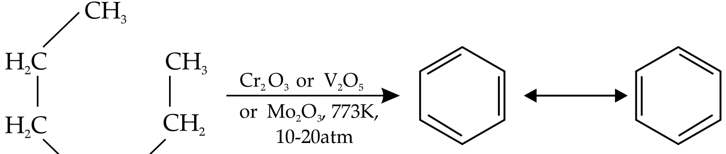
(iv) Isomerisation: *n*-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhyd. } AlCl_3/HCl} CH_2\overset{\overset{CH_3}{|}}{C}H—(CH_2)_2—CH_3 + CH_3CH_2—\underset{\underset{CH_3}{|}}{C}H—CH_2—CH_3$$

n-hexane 2-methylpentane 3-methylpentane

(v) Aromatization or Reforming: Dehydrogenation and cyclization to benzene and its homologues.



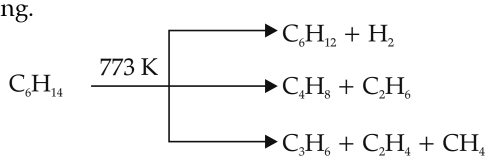
Benzene

n–Hexane

(vi) Reaction with steam: (Industrial preparation of dihydrogen gas)

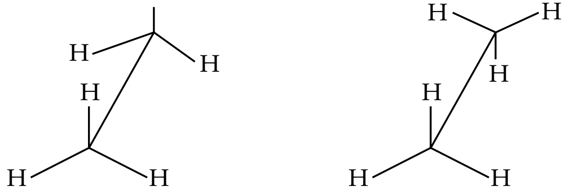
$$CH_4 + H_2O \xrightarrow[\Delta]{Ni(1273\ K)} CO + 3H_2$$

(vii) Pyrolysis: Decomposition of higher alkanes to lower alkanes by the application of heat is called pyrolysis or cracking.



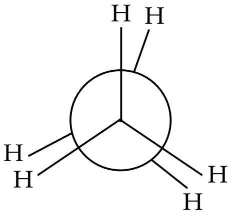
- **Conformations of Alkanes:** Alkanes have C—C sigma (σ) bonds and rotation about C—C single bond is allowed. This rotation results in different spatial arrangements of atoms in space which can change into one another, such spatial arrangements are called conformations or conformers or rotamers. Alkanes can have infinite number of conformations. Ethane shows eclipsed, staggered and skew conformations. Eclipsed form is least stable but staggered form is most stable due to greater distance between the bond pairs or lesser torsional strain. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}.

(i) Sawhorse projections: In this projection, the molecule is viewed along the molecular axis.

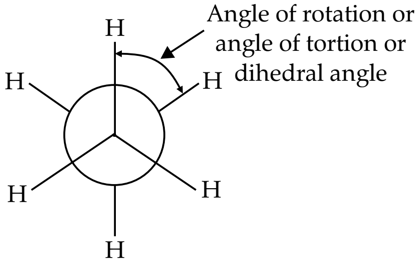


(i) Eclipsed (ii) Staggered

(ii) Newman projections: In this projection, the molecule is viewed at the C–C bond head on.



(i) Eclipsed



(ii) Staggered

Newman's Projections of ethane

Alkenes

- These are unsaturated non-cyclic hydrocarbons containing at least one double bond and have sp^2 -hybridisation with 120° bond angle. Alkenes are also called olefins [oil forming] which indicates their high reactive nature. Alkenes have general formula C_nH_{2n}, where $n = 2,3,4 \ldots$

  Example- C_2H_4 (ethene), C_3H_6 (propene), etc.
- **Structure of Double Bond:** Carbon-carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol^{-1}) due to head-on overlapping of sp^2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about 284 kJ mol^{-1}) obtained by lateral or sideways overlapping of the two $2p$ orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm).
- **Nomenclature:**

(i) The longest chain of carbon atoms containing the double bond is selected.

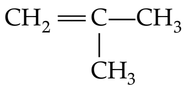
(ii) Numbering of the chain is done from the end which is nearer to the double bond.

(iii) The suffix 'ene' replaces 'ane' of alkanes.

- **Isomerism:** Alkenes show chain, position and geometrical isomerism.

  Chain isomers have different chains of carbon atoms, e.g.,

$CH_2 = CH—CH_2—CH_3$ and



$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}—CH_3$$

But-1-ene

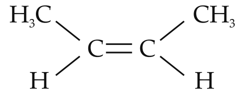
2-Methyprop-1-ene

Position isomers differ in the position of double bonds.

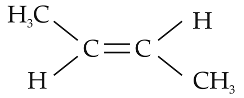
$CH_2 = CH—CH_2—CH_3$ and $CH_3—CH = CH—CH_3$

But-1-ene But-2-ene

The stereoisomerism is exhibited by alkenes due to difference in the spatial arrangement of groups around double bonded carbon atoms. The simplest alkene that can exhibit geometrical isomerism is but-2-ene. Cis form of alkene is more polar than the trans form.



cis-But-2-ene



trans-But-2-ene

The boiling point of *cis*-form is more than the *trans*-form due to high polarity of *cis*-form. However, melting point of trans-form is more than that the *cis*-form.

Mnemonics

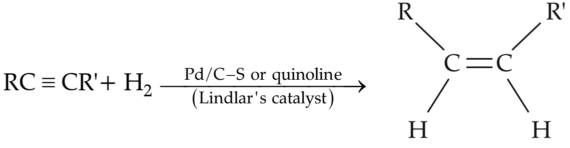
Concept: To Learn Bond Length

Mnemonics: See Duet Trial

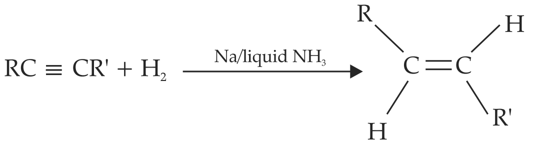
Interpretation:-C-C Single bond>Double bond > Triple bond

- **Preparation of Alkenes:**

(i) From alkynes: Alkynes on partial reduction with calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst.

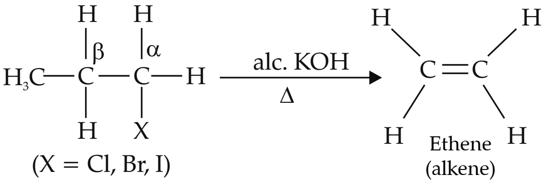


cis-Alkene



trans-Alkene

(ii) From alkyl halides: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation, i.e., removal of halogen acid. This is example of β-elimination reaction, since hydrogen atom is eliminated from the β carbon atom.



(X = Cl, Br, I)

The rate of the reaction:

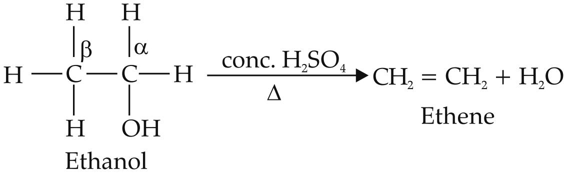
For halogens: Iodine > Bromine > Chlorine

For alkyl group: Tertiary > Secondary > Primary

(iii) From vicinal dihalides: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. The reaction is known as dehalogenation.

$$CH_3CHBr—CH_2Br + Zn \rightarrow CH_3CH = CH_2 + ZnBr_2$$

(iv) From Alcohols: Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. This reaction is known as acidic dehydration of alcohols.



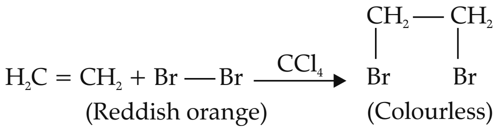
$$\underset{\text{Ethanol}}{H—\overset{H}{\underset{H}{C_{\beta}}}—\overset{H}{\underset{OH}{C_{\alpha}}}—H} \xrightarrow[\Delta]{\text{conc. } H_2SO_4} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2O$$

- **Physical Properties:** Alkenes as a class resembles alkanes in physical properties, except in types of isomerism and difference in polar nature. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in nonpolar solvents like benzene, petroleum, ether. Alkenes show a regular increase in boiling point with increase in size.
- **Chemical Properties:** Alkenes undergo electrophilic addition reaction because of loosely held π-electrons.

(i) Addition of dihydrogen:

$$\underset{\text{Ethene}}{H_2C = CH_2} \xrightarrow[Ni/Pt/Pd]{H_2} \underset{\text{Ethane}}{H_3C—CH_3}$$

(ii) Addition of halogen: This reaction is used for the test of unsaturation.

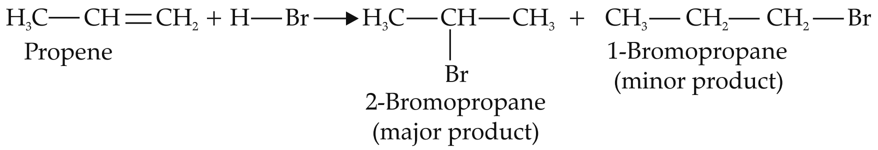


$$H_2C = CH_2 + \underset{\text{(Reddish orange)}}{Br—Br} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{\underset{Br}{CH_2}—\underset{Br}{CH_2}}$$

(iii) Addition of hydrogen halides: The order of reactivity of the hydrogen halide is HI > HBr > HCl.

(a) $\underset{\text{(symmetrical alkene)}}{CH_2 = CH_2} + HBr \rightarrow CH_3—CH_2—Br$

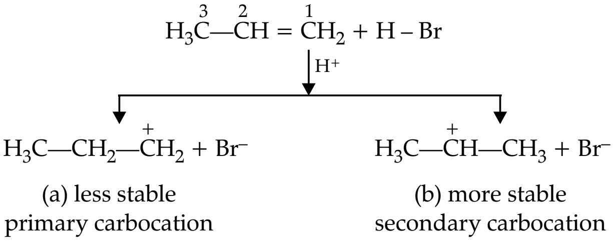
(b) However, addition of hydrogen halide to an unsymmetrical alkene takes place according to Markovnikov's rule. This rule states that, "the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms". e.g.,



$$\underset{\text{Propene}}{H_3C—CH=CH_2} + H—Br \longrightarrow \underset{\text{(major product)}}{\underset{\text{2-Bromopropane}}{H_3C—\underset{Br}{CH}—CH_3}} + \underset{\text{(minor product)}}{\underset{\text{1-Bromopropane}}{CH_3—CH_2—CH_2—Br}}$$

Mechanism:

Hydrogen bromide provides an electrophile, H^+, which attacks the double bond to form carbocation as:



$$H_3\overset{3}{C}—\overset{2}{C}H = \overset{1}{C}H_2 + H – Br \xrightarrow{H^+} H_3C—CH_2—\overset{+}{C}H_2 + Br^- \quad \text{or} \quad H_3C—\overset{+}{C}H—CH_3 + Br^-$$

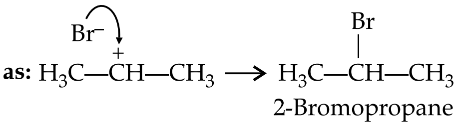
(a) less stable primary carbocation

(b) more stable secondary carbocation

(i) The secondary carbocation is more stable than the primary carbocation, therefore, the former predominates because it is formed at a faster rate.

(ii) The secondary carbocation is attacked by Br^- ion to form the product.

as:

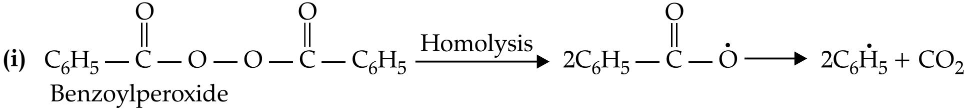


$$Br^- \quad H_3C—\overset{+}{C}H—CH_3 \longrightarrow \underset{\text{2-Bromopropane}}{H_3C—\overset{Br}{CH}—CH_3}$$

Peroxide effect or Kharash effect or Anti-Markovnikov addition: In the presence of peroxide, addition of HBr to unsymmetrical alkene takes place contrary to Markovnikov rule. This reaction is known as peroxide or Kharash effect or anti-Markovnikov addition. e.g.,

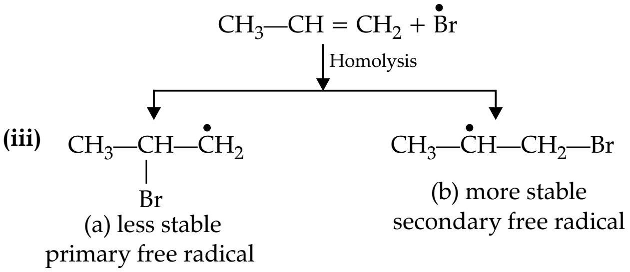
$$H_3C—CH=CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} \underset{\text{1-Bromopropane}}{CH_3—CH_2—CH_2Br}$$

This reaction proceeds by free radical mechanism. Peroxide effect is observed only in case of HBr and not in case of H—Cl and H—I.



(i) $\underset{\text{Benzoylperoxide}}{C_6H_5—\overset{O}{\overset{\|}{C}}—O—O—\overset{O}{\overset{\|}{C}}—C_6H_5} \xrightarrow{\text{Homolysis}} 2C_6H_5—\overset{O}{\overset{\|}{C}}—\dot{O} \longrightarrow 2C_6\dot{H}_5 + CO_2$

(ii) $\dot{C}_6H_5 + H—Br \xrightarrow{\text{Homolysis}} C_6H_6 + \dot{B}r$



$$CH_3—CH = CH_2 + \dot{B}r \xrightarrow{\text{Homolysis}}$$

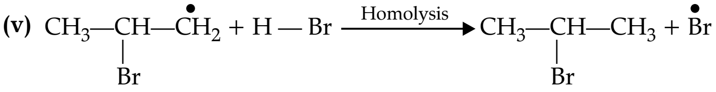
(iii) $CH_3—\underset{Br}{CH}—\dot{C}H_2$ $CH_3—\dot{C}H—CH_2—Br$

(a) less stable primary free radical

(b) more stable secondary free radical

(iv) $CH_3—CH—\overset{\bullet}{C}H_2Br + H — Br \xrightarrow{\text{Homolysis}} CH_3—CH_2—CH_2Br + \overset{\bullet}{Br}$

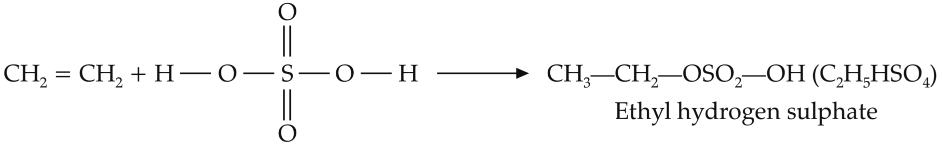
(major product)



(v) $CH_3—\underset{\displaystyle Br}{\underset{|}{C}H}—\overset{\bullet}{C}H_2 + H — Br \xrightarrow{\text{Homolysis}} CH_3—\underset{\displaystyle Br}{\underset{|}{C}H}—CH_3 + \overset{\bullet}{Br}$

(minor product)

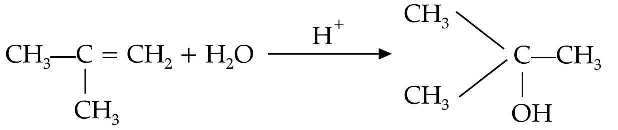
(iv) Addition of sulphuric acid:



$$CH_2 = CH_2 + H — O — \underset{\displaystyle O}{\underset{\|}{\overset{\displaystyle O}{\overset{\|}{S}}}} — O — H \longrightarrow CH_3—CH_2—OSO_2—OH\ (C_2H_5HSO_4)$$

Ethyl hydrogen sulphate

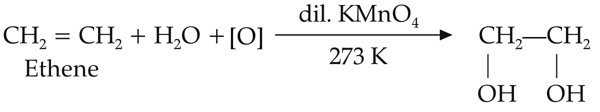
(v) Addition of water: In presence of few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.



2-Methylpropene 2-Methylpropan-2-ol

(vi) Oxidation:

(a) Oxidation with cold dilute, aqueous solution of potassium permanganate (Baeyer's reagent). This reaction is used as a test for unsaturation as it decolourises $KMnO_4$ solution.



$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2O + [O] \xrightarrow[\text{273 K}]{\text{dil. } KMnO_4} \underset{\displaystyle OH}{\underset{|}{CH_2}}—\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

Ethane-1, 2-diol

(Glycol)

(b) Oxidation with acidic potassium permanganate or acidic potassium dichromate to ketones and/or acids.

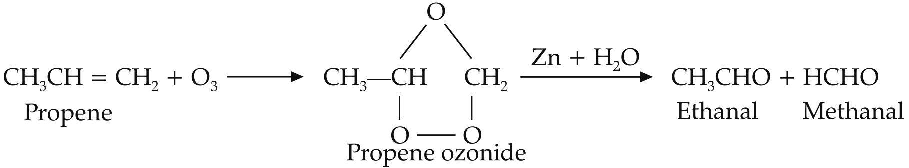
$(CH_3)_2C = CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C = O + CO_2 + H_2O$

2-Methylpropene Propan-2-one

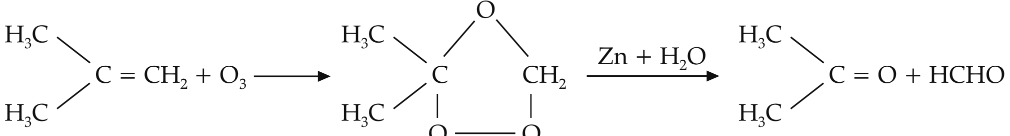
$CH_3—CH = CH—CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$

But-2-ene Ethanoic acid

(vii) Ozonolysis:



Propene ozonide



2-methylpropene Ozonide Propan-2-one

(viii) Polymerisation: Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as polymerisation. The simple compounds from which polymers are made are called monomers.

$$n(CH_2CH = CH_2) \xrightarrow[\text{Catalyst}]{\text{High Temp. (Pressure)}} —\!\!(—CH_2—CH_2—)_n—$$

Polythene

Alkynes

- Alkynes are unsaturated hydrocarbons that contain at least one carbon-carbon triple bond. General formula of alkyne is C_nH_{2n-2} e.g., C_2H_2 (ethyne), C_2H_4 (propyne). The first and the most important member of this series of hydrocarbons is ethyne, C_2H_2 and hence they are also called the acetylene.

- **Structure:** In ethyne, the carbon atoms are *sp* hybridised. Carbon-carbon sigma (σ) bond is obtained by the head on overlapping of the two *sp* hybridised orbitals of the two carbon atoms. The remaining *sp* hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with 1*s* orbital of each of the two hydrogen atoms forming two C–H sigma bonds. H–C–C bond angle is of 180°. Ethyne H—C ≡ C—H is a linear molecule.

- **Preparation of alkynes:**

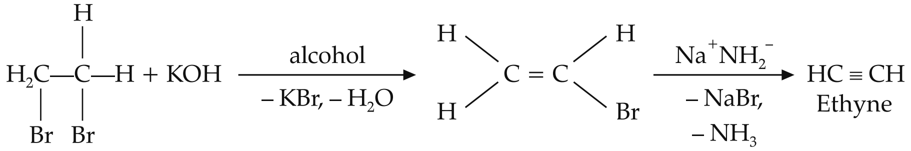
(i) From calcium carbide: Ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared as follows:

$$\underset{\text{Limestone}}{CaCO_3} \xrightarrow{\Delta} \underset{\text{Quicklime}}{CaO} + CO_2$$

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

(ii) From vicinal dihalides: When vicinal dihalides react with alcoholic potassium hydroxide then they undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



- **Physical Properties:** Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. They are weakly polar in nature. Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Melting point, boiling point and density increase with increase in molar mass.
- **Chemical Properties:** Alkynes show electrophilic as well as nucleophilic addition reactions.

(i) Acidic character of alkyne:

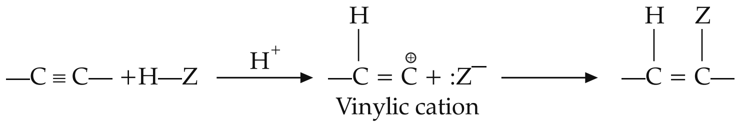
$$HC \equiv CH + Na \rightarrow \underset{\text{Monosodium ethynide}}{HC \equiv C^{-}Na^{+}} + \tfrac{1}{2}H_2$$

$$HC \equiv C^{-}Na^{+} + Na \rightarrow \underset{\text{Disodium ethynide}}{Na^{+}C^{-} \equiv C^{-}Na^{+}} + \tfrac{1}{2}H_2$$

$$CH_3—C \equiv C—H + Na^{+}NH_2^{-} \rightarrow \underset{\text{Sodium propynide}}{CH_3C \equiv C^{-}Na^{+}} + NH_3$$

This reaction can be used for the distinction among alkynes, alkenes and alkanes and even for distinguishing terminal alkynes from non-terminal alkynes as only terminal alkynes undergo this reaction.

(ii) Addition reactions:



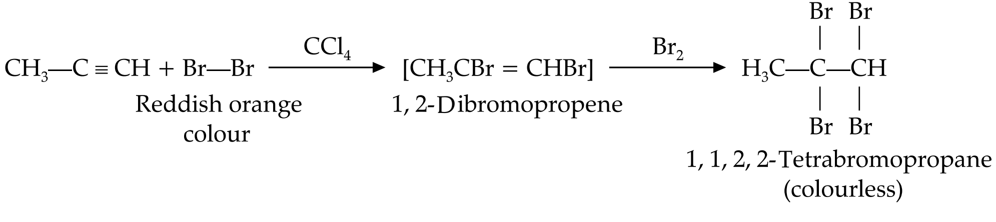
$$—C \equiv C— + H—Z \xrightarrow{H^{+}} \underset{\text{Vinylic cation}}{—\overset{\overset{H}{|}}{C} = \overset{\oplus}{C}} + :Z^{-} \longrightarrow —\overset{\overset{H}{|}}{C} = \overset{\overset{Z}{|}}{C}—$$

Alkynes undergo electrophilic addition reaction and addition to unsymmetrical alkynes takes place according to Markovnikov's rule. The addition product formed depends upon the stability of vinylic cation.

(a) Addition of dihydrogen:

$$\underset{\text{Propyne}}{CH_3—C \equiv CH + H_2} \xrightarrow{Ni/Pd/Pt} \underset{\text{Propene}}{[CH_3—CH = CH_2]} \xrightarrow{H_2} \underset{\text{Propane}}{CH_3—CH_2—CH_3}$$

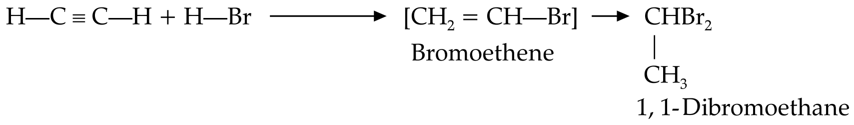
(b) Addition of halogens:



$$CH_3—C \equiv CH + \underset{\substack{\text{Reddish orange}\\ \text{colour}}}{Br—Br} \xrightarrow{CCl_4} \underset{\text{1, 2-Dibromopropene}}{[CH_3CBr = CHBr]} \xrightarrow{Br_2} \underset{\substack{\text{1, 1, 2, 2-Tetrabromopropane}\\ \text{(colourless)}}}{H_3C—\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}—\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}H}$$

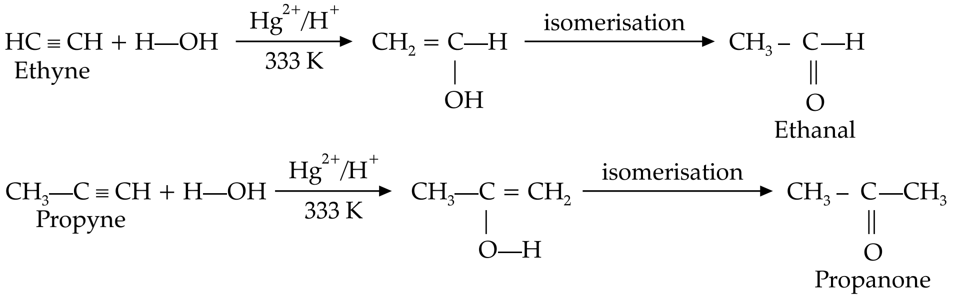
This reaction is used as a test of unsaturation as reddish orange colour of solution of bromine in CCl_4 is decolourised.

(c) Addition of hydrogen halides:



$$H-C\equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2=CH-Br]} \longrightarrow \underset{\text{1, 1-Dibromoethane}}{\underset{CH_3}{\underset{|}{CHBr_2}}}$$

(d) Addition of water:



$$\underset{\text{Ethyne}}{HC\equiv CH} + H-OH \xrightarrow[333\,K]{Hg^{2+}/H^{+}} CH_2=\underset{OH}{\underset{|}{C}}-H \xrightarrow{\text{isomerisation}} \underset{\text{Ethanal}}{CH_3-\underset{O}{\underset{||}{C}}-H}$$

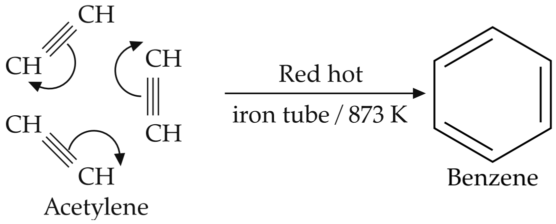
$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H-OH \xrightarrow[333\,K]{Hg^{2+}/H^{+}} CH_3-\underset{O-H}{\underset{|}{C}}=CH_2 \xrightarrow{\text{isomerisation}} \underset{\text{Propanone}}{CH_3-\underset{O}{\underset{||}{C}}-CH_3}$$

(e) Polymerization:

(1) Linear polymerization: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH – CH = CH) and can be represented as $-(CH=CH-CH=CH)_n-$

Acetylene → Polyacetylene

(2) Cyclic polymerization: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization.



Mnemonics

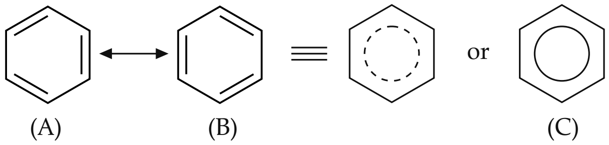
Concept: Order of Reactivity of Addition Halogens to Alkenes

Mnemonics: Flaming Clear Bright Identity

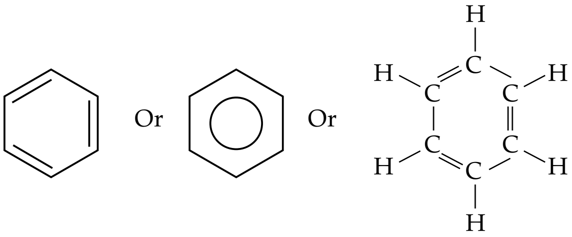
Interpretation: Fluorine >Chlorine >Bromine >Iodine

Aromatic Hydrocarbon

- These hydrocarbons are also known as 'arenes'. Most of the aromatic hydrocarbons were found to contain benzene ring. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids.
- Benzene molecule is a planar or flat molecule in which all the carbon atoms are sp^2 hybridised. It has hexagonal ring of six carbon atoms with three double bonds at alternate positions. It is resonance stabilised and the structure may be represented as given below.



- **Isomerism:** When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the *ortho* (*o*–), the 1, 3 or 1, 5 as *meta* (*m*–) and the 1, 4 as *para* (*p*–) disubstituted compounds.
- **Structure of Benzene:** August Kekule in 1865 proposed benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.



- **Aromaticity:** It is a property of the sp^2 hybridised planar rings in which the *p* orbitals allow cyclic delocalization of π electrons. Aromatic compounds have specific electronic structure in accordance with Huckel rule. The rule states that all planar cyclic conjugated polyenes containing (4n + 2)π electrons where $n = 0, 1, 2, \ldots$ are aromatic in nature.

(i) Aromatic: They are cyclic, planar molecule where complete delocalisation of π electron takes place.

Huckle's rule $(4n + 2)$ π electrons

(ii) Anti aromatic: They are cyclic planar molecule which follows $4n\pi$ electrons.

(iii) Non aromatic: These are cyclic, non planar where no delocalisation of π electron takes place.

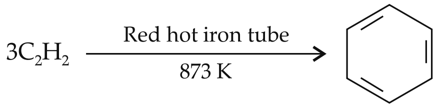
They may or may not follow Huckel's rule.

Mnemonics

Concept: Aromaticity
Mnemonics: A Police Car Drove near High Court
Interpretation: Polarity, Complete Delocalisation, Huckel Rule

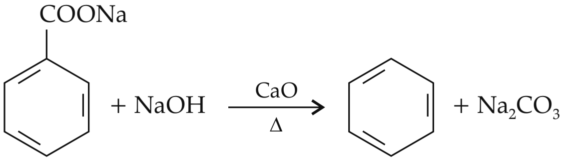
- **Preparation of benzene:**

(i) Cyclic polymerisation of ethyne: Ethyne on passing through red hot iron tube at 873 K undergoes cyclic polymerisation. Three molecules polymerise to form benzene.

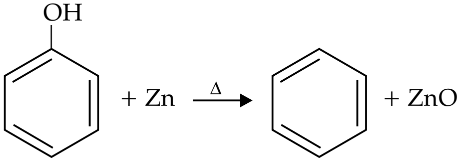


Benzene

(ii) Decarboxylation of Aromatic acids: Sodium salt of benzoic acid on heating with sodalime gives benzene.



(iii) Reduction of Phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust.

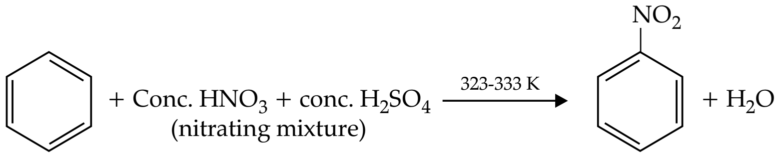


- **Physical Properties:** Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma. Benzene itself is a good solvent for many organic and inorganic substances, e.g., fat, resins, sulphur and iodine. It burns with a luminous, sooty flame in contrast to alkanes and alkenes which usually burn with a bluish flame.

- **Chemical Properties:** Benzene undergoes following types of chemical reactions:
  - **(a)** Electrophilic Substitution Reaction
  - **(b)** Addition Reaction

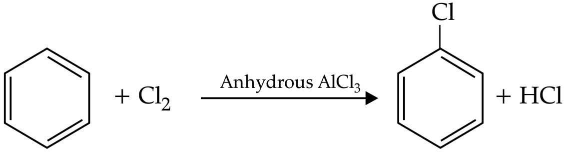
Electrophilic Substitution Reactions: Aromatic hydrocarbons undergo electrophilic substitution reactions, e.g., nitration, halogenation, sulphonation and Friedel-Craft alkylation/acylation.

(i) Nitration:



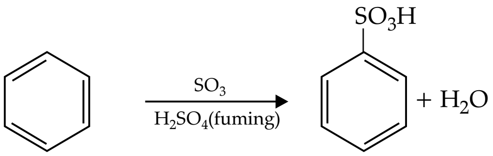
Nitrobenzene

(ii) Halogenation:



Chlorobenzene

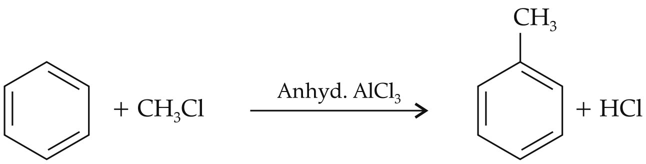
(iii) Sulphonation:



Benzene

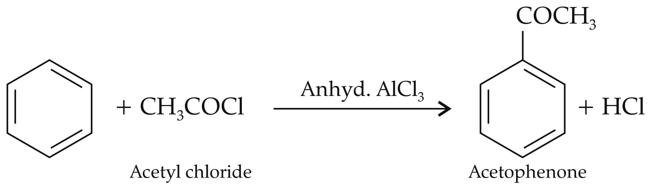
Benzene sulphonic acid

(iv) Friedel-Crafts alkylation reaction:

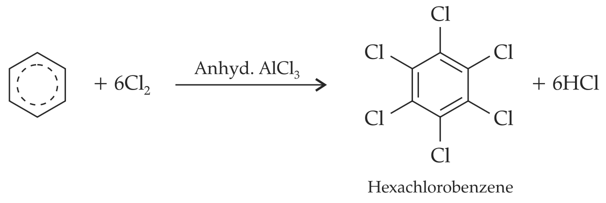


Toluene

(v) Friedel-Craft's acylation reaction:



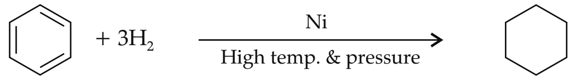
Benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ can be chlorinated to hexachlorobenzene (C_6Cl_6)



Hexachlorobenzene
$(C_6Cl)_6$

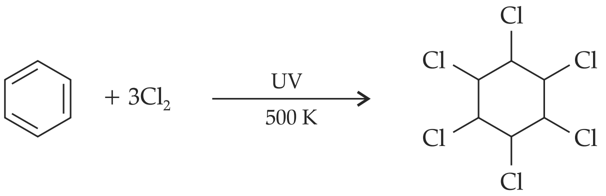
Addition reactions:

(a) Under vigorous conditions i.e. at high temperature and/or pressure in presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.



Cyclohexane

(b) Under UV light, three chlorine molecules add to benzene to produce benzene hexachloride, $C_6H_6Cl_6$.



Benzene hexachloride
(BHC or gammaxane)

Combustion—When heated in air, benzene burns with sooty flame:

$$C_6H_6 + \frac{15}{2} O_2 \rightarrow 6CO_2 + 3H_2O$$

- The presence of substituent groups in aromatic ring activates/deactivates electrophilic substitution and also directs the orientation of incoming groups. Electron donating substituents facilitate further substitution with incoming groups at *o*- and *p*-positions while electron attracting groups deactivate the ring with substitution at *m*-position.

  $–CH_3$, $–OH$, $–OR$, $–NH_2$, $–NHR$, $–NR_2$ are electron donating (or activating groups) while $–NO_2$, $–CN$, $–CHO$, $–COOH$, $–SO_3H$ are electron withdrawing (or deactivating groups). Halogens (– Cl, – Br, – I) are *o*-, *p*-directing but moderately deactivating (due to strong – I effect).

Carcinogenicity and Toxicity

- Polynuclear aromatic hydrocarbons (PAHs) have a number of condensed benzene rings and are suspected carcinogens (toxic and they are having cancer producing property). They are actually formed due to incomplete combustion of some organic materials like tobacco, coal, petroleum, etc. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer.

  For example : 1, 2-Benzanthracene, 1, 2-Benzpyrene, etc.

Mnemonics

Concept: Newmann Projection for Staggered and Eclipsed Conformations of *n*-Butane After Every 60 Degree Rotation.
Mnemonics: Fish-Giraffe-Elephant-Ant-EagleGoat
Interpretation: Fully eclipsed-Gauche-Eclipsed-Anti-EclipsedGauche
Concept: Conformations of Cyclohexane As Per Stability And Energy
Mnemonics: Cat Twigs But Horse-Clubs
Interpretation: Chair>Twist-boat>Boat>Half- Chair
Concept: Order of Reactivity of Addition Halogens to Alkenes
Mnemonics: Flaming Clear Bright Identity
Interpretation: Fluorine >Chlorine >Bromine >Iodine
Concept: PHMTOM
Mnemonics: Please Help Me,TOM
Interpretation: Para have High M.p. Than Ortho and Meta
1. Concept: m-directing Group
Mnemonics: Queen Elizabeth Second's Navy Commands, Controls
Interpretation: Quarternary amino ($–NR^{3+}$) Ester ($–COOR$)
Sulphonic acid ($–SO_3H$)
Nitro ($–NO_2$)
Carbonyl ($–CHO$)
Carboxyl ($–COOH$)
Cyano ($–CN$)
2. Concept: o, p–directing
Mnemonics: AHA AHA P
Interpretation:
Alkyl (–R)
Halogen (–X)
Halogen (–X)
Alkoxyl (–OR)
Amino ($–NH_2$, NHR, NR_2)
Hydroxyl (–OH)
Amide ($–CONH_2$)
Phenyl (C_6H_5)

Key Words

Cis-isomer: The geometrical isomer in which two identical atoms or groups lie on the same side of the double bond is called cis-isomer.

Trans-isomer: The geometrical isomer in which two identical atoms or groups lie on the opposite sides of the double bond is called trans-isomer.

Acidic Dehydration of Alcohols: The reaction in which a water molecule is eliminated from the alcohol molecule in the presence of an acid is called acidic dehydration of alcohols.

Polymerization: The process by which a long chain like molecule is obtained by the intermolecular combination of small molecules (monomers) is called polymerization.

Key Terms

- **Cycloalkanes:** Cyclic hydrocarbons having molecular formula C_nH_{2n}. These are isomeric with alkenes.
- **Cracking:** The process of breaking down less volatile higher molecular mass hydrocarbons from petroleum into different types of more volatile lower molecular mass hydrocarbons by heating in the presence of catalyst.
- **Reforming:** Cyclization followed by aromatization (or dehydrogenation of 6-8 C alkanes on heating to 773 K in the presence of Pt catalyst (e.g., *n*-heptane → methyl cyclohexane → toluene).
- **Knocking:** A sharp metallic rattling sound produced in an internal combustion engine.
- **Octane Number:** A scale for determining knocking quality in petrol. *n*-Heptane with very high knocking has octane number 0 while iso-octane has maximum value 100.
- **Cetane Number:** A scale for determining knocking quality of a diesel fuel. Cetane number of *n*-hexadecane (cetane) is 100 and that of α-methylnapthalene is zero.
- **Conformation isomerism:** the different arrangements of atoms in space that results from free rotation of groups about the carbon- carbon bond axes is known as conformation for rotational isomers and the phenomena is known as conformational or rotational isomerism

- **Aromaticity:** It is a property of conjugated cycloalkenes in which the stabilization of the molecule is enhanced due to the ability of the electrons in the π orbitals to delocalize. This acts as a framework to create a planar molecule.

Key Facts

- Iodination is a reversible reaction. So it is carried out by heating alkane in the presence of oxidising agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidises HI formed during the reaction.

$$\mathbf{CH_4 + I_2 \rightleftharpoons CH_3I + HI}$$

$$\mathbf{HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O}$$

- Fluorination of alkane takes place explosively resulting even in the rupture of C—C bond in higher alkanes.
- Petroleum is an important source of aliphatic hydrocarbons. It is refined in to several useful fractions and is a source of several petrochemicals. Coal tar is a rich source of aromatic hydrocarbons.
- LPG and CNG are petroleum products used as energy source in automobile industry and domestic fuel. Natural gas contains about 90% CH_4.
- The alkaline potassium permanganate solution is known as Baeyer's reagent. It has bright pink colour. It oxidises alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer test.
- Bromine water test and Baeyer's test are used to detect the presence of double bond while ozonolysis is used to detect the position of double bond.
- Originally fragrant substances were called aromatic compounds.
- In the laboratory, benzene was first prepared by heating benzoic acid or phthalic acid with calcium oxide.
- Most of the benzene is produced from petroleum.
- Compounds having atoms other than carbon in a ring system, which satisfies the conditions of aromaticity are called heteroaromatics.
- Those who follow neither Huckle's rule, i.e., $(4n + 2)$ π nor $4n\pi$ electrons are non aromatic.

NCERT CORNER

Q. 1. How do you account for the formation of ethane during chlorination of methane?

[NCERT Ex. Q. 9.1, Page 326]

Ans. Chlorination of methane proceeds through a free radical chain mechanism. The whole reaction takes place in the given three steps.

Step 1: Initiation: The reaction begins with the homolytic cleavage of Cl – Cl bond as:

$$Cl - Cl_2 \xrightarrow{hv} \dot{C}l + \dot{C}l$$

Chlorine free radicals

Step 2: Propagation: In the second step, chlorine free radicals attack methane molecules and break down the C–H bond to generate methyl radicals as:

$$\underset{\text{Methane}}{CH_4} + \dot{C}l \xrightarrow{h\nu} \dot{C}H_3 + H-Cl$$

These methyl radicals react with other chlorine free radicals to form methyl chloride along with the liberation of a chlorine free radical.

$$\dot{C}H_3 + Cl{-}Cl \longrightarrow \underset{\text{Methyl chloride}}{CH_3{-}Cl} + \dot{C}l$$

Hence, methyl free radicals and chlorine free radicals set up a chain reaction. While HCl and CH_3Cl are the major products formed, other higher halogenated compounds are also formed as:

$$CH_3Cl + \dot{C}l \longrightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl-Cl \longrightarrow CH_2Cl_2 + \dot{C}l$$

Step 3: Termination: Formation of ethane is a result of the termination of chain reactions taking place as a result of the consumption of reactants as:

$$\dot{C}l + \dot{C}l \longrightarrow Cl-Cl$$

$$H_3\dot{C} + \dot{C}H_3 \longrightarrow \underset{\text{(Ethane)}}{H_3C-CH_3}$$

Hence, by this process, ethane is obtained as a by-product of chlorination of methane.

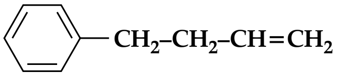
Q. 2. Write IUPAC names of the following compounds:

(a) $CH_3CH{=}C(CH_3)_2$

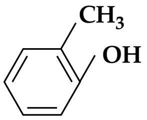
(b) $CH_2 = CH{-}C \equiv C{-}CH_3$

(c)

(d)



(e)



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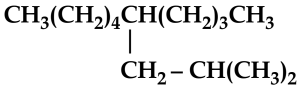


$$CH_3(CH_2)_4\underset{\substack{|\\ CH_2-CH(CH_3)_2}}{CH}(CH_2)_3CH_3$$

(g)

$$CH_3CH{=}CH{-}CH_2{-}CH{=}CH{-}\underset{\substack{|\\ C_2H_5}}{CH}{-}CH_2{-}CH{=}CH_2$$

[NCERT Ex. Q. 9.2, Page 326]

Ans. **(a)** 2-Methylbut-2-ene

(b) Pent-1-ene-3-yne

(c) 1, 3-Butadiene or Buta-1,3 diene

(d) 4-Phenyl but-1-ene

(e) 2-Methyl phenol

(f) 5-(2-Methylpropyl)-decane

(g) 4-Ethyldeca-1, 5, 8-triene

Q. 3. For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated:

(a) C_4H_8 **(one double bond)**

(b) C_5H_8 **(one triple bond)** **[NCERT Ex. Q. 9.3, Page 326]**

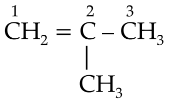
Ans. **(a)** The following structural isomers are possible for C_4H_8 with one double bond:

$$\overset{1}{H_2C} = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_3$$

(I)

$$\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$$

(II)



$$\overset{1}{C}H_2 = \underset{\substack{|\\ CH_3}}{\overset{2}{C}} - \overset{3}{C}H_3$$

(III)

The IUPAC name of
Compound (I) is But-1-ene,
Compound (II) is But-2-ene, and
Compound (III) is 2-Methylprop-1-ene.

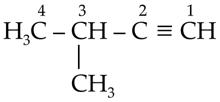
(b) The following structural isomers are possible for C_5H_8 with one triple bond:

$$\overset{1}{H}C \equiv \overset{2}{C} - \overset{3}{C}H_2 - \overset{4}{C}H_2 - \overset{5}{C}H_3$$

(I)

$$H_3\overset{1}{C} - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{C}H_2 - \overset{5}{C}H_3$$

(II)



$$H_3\overset{4}{C} - \underset{\substack{|\\ CH_3}}{\overset{3}{C}H} - \overset{2}{C} \equiv \overset{1}{C}H$$

(III)

The IUPAC name of
Compound (I) is Pent-1-yne,
Compound (II) is Pent-2-yne, and
Compound (III) is 3-Methylbut-1-yne.

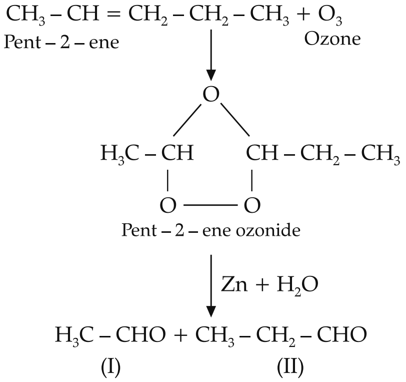
Q. 4. Write IUPAC names of the products obtained by the ozonolysis of the following compounds :

(i) Pent-2-ene (ii) 3,4-Dimethylhept-3-ene

(iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene

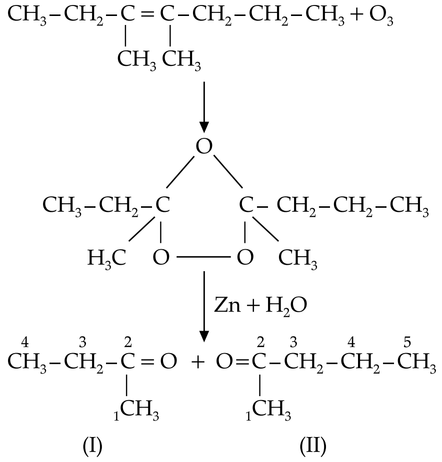
[NCERT Ex. Q. 9.4, Page 326]

Ans. **(i)** Pent-2-ene undergoes ozonolysis as:



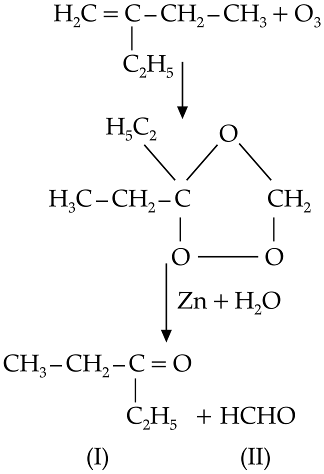
The IUPAC name of product (I) is ethanal and product (II) is propanal.

(ii) 3, 4-Dimethylhept-3-ene undergoes ozonolysis as:



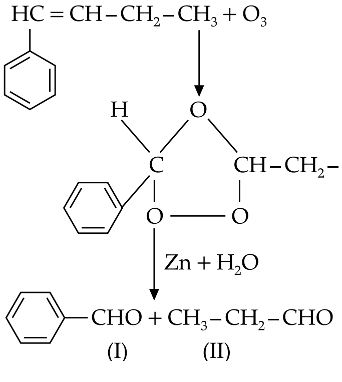
The IUPAC name of product (I) is butan-2-one and product (II) is pentan-2-one.

(iii) 2-Ethylbut-1-ene undergoes ozonolysis as:



The IUPAC name of product (I) is pentan-3-one and product (II) is methanal.

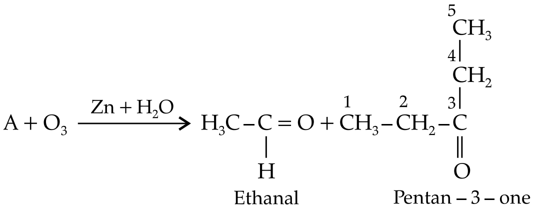
(iv) 1-Phenylbut-1-ene undergoes ozonolysis as:



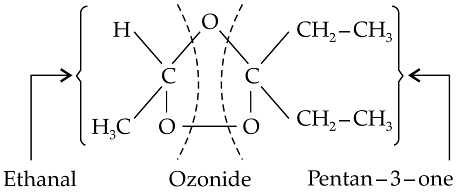
The IUPAC name of product (I) is benzaldehyde and product (II) is propanal.

Q. 5. An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3- one. Write structure and IUPAC name of 'A'. [NCERT Ex. Q. 9.5, Page 327]

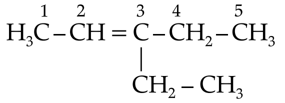
Ans.



During ozonolysis, an ozonide having a cyclic structure is formed as an intermediate which undergoes cleavage to give the final products. Ethanal and pentan-3-one are obtained from the intermediate ozonide. Hence, the expected structure of the ozonide is:



This ozonide is formed as an addition of ozone to 'A'. The desired structure of 'A' can be obtained by the removal of ozone from the ozonide. Hence, the structural formula of 'A' is:



$$\overset{1}{H_3C}-\overset{2}{CH}=\overset{3}{C}(CH_2-CH_3)-\overset{4}{CH_2}-\overset{5}{CH_3}$$

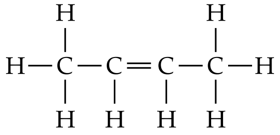
The IUPAC name of 'A' is 3-Ethylpent-2-ene.

Q. 6. An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'. [NCERT Ex. Q. 9.6, Page 327]

Ans. As per the given information, 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms. Hence, the structure of 'A' can be represented as:

$$XC = CX$$

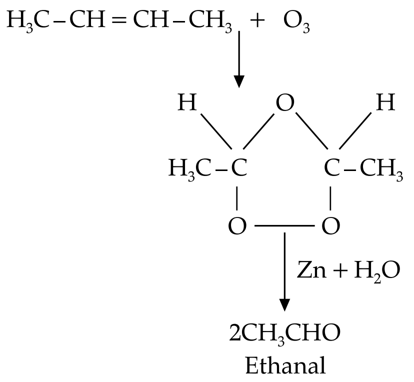
There are eight C–H σ bonds. Hence, there are 8 hydrogen atoms in 'A'. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of 'A'. Combining the inferences, the structure of 'A' can be represented as:



$$CH_3-CH=CH-CH_3$$

(A)

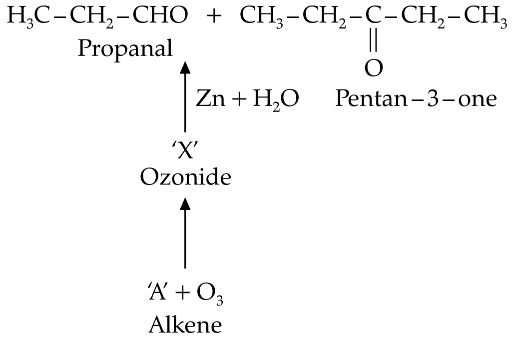
'A' has 3 C–C bonds, 8 C–H π bonds and one C–C π bond. Hence, the IUPAC name of 'A' is But-2-ene. Ozonolysis of 'A' takes place as:



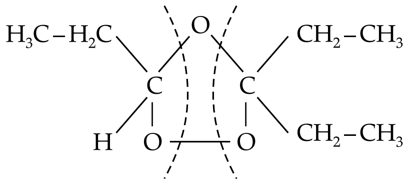
The final product is ethanal with molecular mass= 44u.

Q. 7. Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene? [NCERT Ex. Q. 9.7, Page 327]

Ans. As per the given information, propanal and pentan-3-one are the ozonolysis products of an alkene. Let the given alkene be 'A'. Writing the reverse of the ozonolysis reaction, we get:

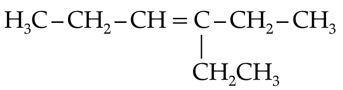


The products are obtained on the cleavage of ozonide 'X'. Hence, 'X' contains both products in the cyclic form. The possible structure of ozonide can be represented as:



X

Now, 'X' is an addition product of alkene 'A' with ozone. Therefore, the possible structure of alkene 'A' is:



$$H_3C-CH_2-CH=\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}-CH_2-CH_3$$

Q. 8. Write chemical equations for combustion reaction of the following hydrocarbons:

(i) Butane **(ii) Pentene**

(iii) Hexyne **(iv) Toluene**

[NCERT Ex. Q. 9.8, Page 327]

Ans. (i) $2C_4H_{10}(g) + 13O_2(g) \rightarrow$

Butane $8CO_2(g) + 10\,H_2O(g)$ + Heat

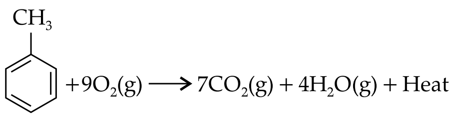
(ii) $2C_5H_{10}(g) + 15O_2(g) \rightarrow$

Pentene $10CO_2(g) + 10\,H_2O(g)$ + Heat

(iii) $2C_6H_{10}(g) + 17O_2(g) \rightarrow$

Hexyne$12CO_2(g) + 10H_2O(g)$ + Heat

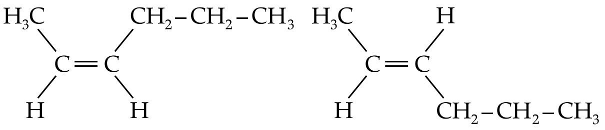
(iv)



Toluene

Q. 9. Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.p. and why? [NCERT Ex. Q. 9.9, Page 327]

Ans. Geometrical isomers of hex-2-ene are :

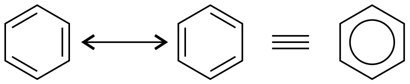


Cis – isomer *Trans* – isomer

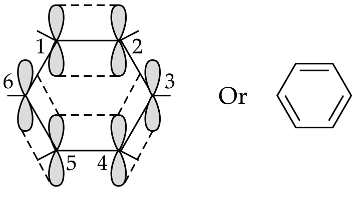
The dipole moment of *cis*-compound is a sum of the dipole moments of C–CH_3 and C– $CH_2\,CH_2CH_3$ bonds acting in the same direction. The dipole moment of trans-compound is the resultant of the dipole moments of C–CH_3 and C–$CH_2CH_2CH_3$ bonds acting in opposite directions. Hence, *cis*-isomer is more polar than trans-isomer. The higher the polarity, the greater is the intermolecular dipole-dipole interaction and the higher will be the boiling point. Hence, *cis*-isomer will have a higher boiling point than trans-isomer.

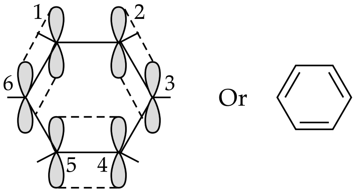
Q. 10. Why is benzene extra ordinarily stable though it contains three double bonds? [NCERT Ex. Q. 9.10, Page 327]

Ans. Benzene is a hybrid of resonating structures given as:



All six carbon atoms in benzene are sp^2 hybridised. The two sp^2 hybrid orbitals of each carbon atom overlap with the sp^2 hybrid orbitals of adjacent carbon atoms to form six sigma bonds in the hexagonal plane. The remaining sp^2 hybrid orbital on each carbon atom overlaps with the *s*-orbital of hydrogen to form six sigma C–H bonds. The remaining unhybridised *p*-orbital of carbon atoms has the possibility of forming three π bonds.





The six π-electrons are delocalized and can move freely about the six carbon nuclei. Even after the presence of three double bonds, these delocalized π-electrons stabilize benzene.

Q. 11. What are the necessary conditions for any system to be aromatic? [NCERT Ex. Q. 9.11, Page 327]

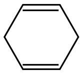
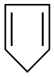
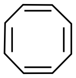
Ans. A compound is said to be aromatic if it satisfies the following three conditions:

(i) It should have a planar structure.

(ii) The π–electrons of the compound are completely delocalized in the ring.

(iii) The total number of π–electrons present in the ring should be equal to $(4n + 2)$, where $n = 0, 1, 2$ ..., etc., This is known as Huckel's rule.

Q. 12. Explain why the following systems are not aromatic?

(i)  $=CH_2$ **(ii)**  **(iii)** 

[NCERT Ex. Q. 9.12, Page 327]

Ans. (i) For the given compound, the number of π-electrons is 6.

By Huckel's rule,

$$4n + 2 = 6$$
$$4n = 4$$
$$n = 1$$

For a compound to be aromatic, the value n must be an integer ($n = 0, 1, 2...$). Since, the value of n is an integer, it should be aromatic However, for a compound to be aromatic p electron cloud should be equally distributed on all the ring, hence, it is non-aromatic in nature **(1)**

(ii) For the given compound, the number of π-electrons is 4.

By Huckel's rule,

$$4n + 2 = 4$$
$$4n = 2$$
$$n = 1/2$$

For a compound to be aromatic, the value of n must be an integer ($n = 0, 1, 2...$), which is not true for the given compound. Hence, it is not aromatic in nature.

(iii) For the given compound, the number of π-electrons is 8.

By Huckel's rule,

$$4n + 2 = 8$$
$$4n = 6$$
$$n = 3/2$$

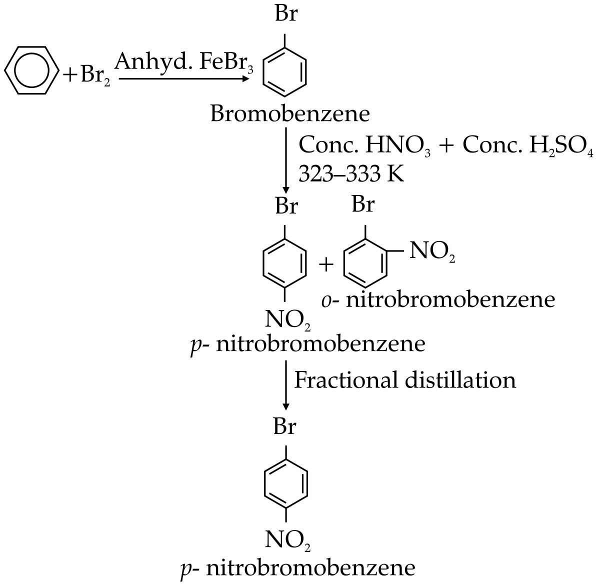
For a compound to be aromatic, the value of n must be an integer ($n = 0, 1, 2...$). Since the value of n is not an integer, the given compound is not aromatic in nature.

Q. 13. How will you convert benzene into:

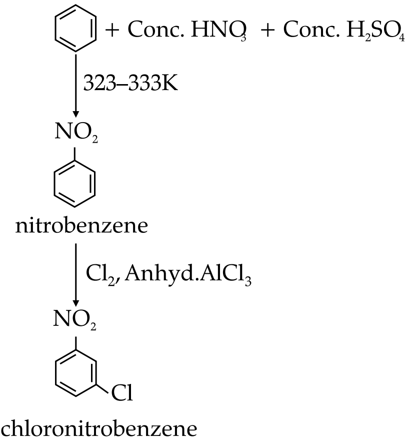
(i) *p*-nitrobromobenzene (ii) *m*- nitrochlorobenzene
(iii) *p* - nitrotoluene (iv) acetophenone?

[NCERT Ex. Q. 9.13, Page 327]

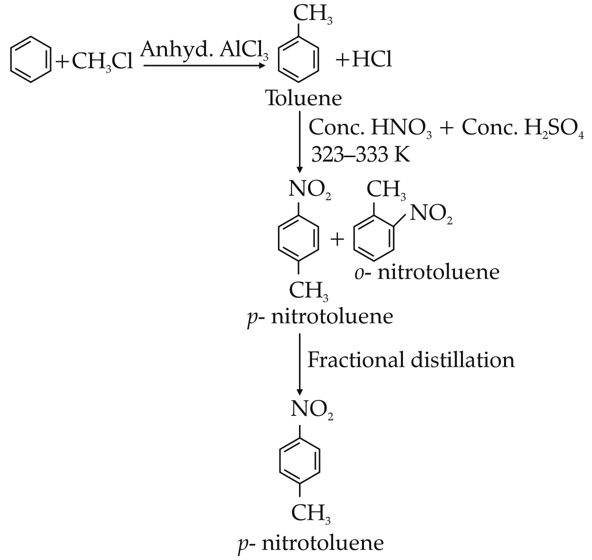
Ans. (i) Benzene can be converted into p-nitrobromobenzene as:



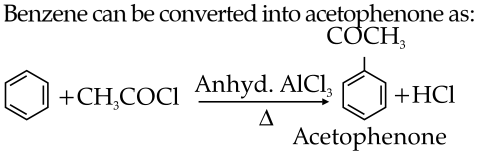
(ii) Benzenecanbeconvertedintom-nitrochlorobenzene as:



(iii) Benzene can be converted into *p*-nitrotoluene as:



(iv) Benzene can be converted into acetophenone as:

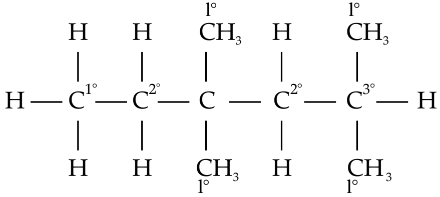


Acetophenone

Q. 14. In the alkane $H_3C - CH_2 - C(CH_3)_2 - CH_2 - CH(CH_3)_2$, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these.

[NCERT Ex. Q. 9.14, Page 327]

Ans.



$$\begin{array}{ccccccccccc} & & H & & H & & \overset{1°}{CH_3} & & H & & \overset{1°}{CH_3} \\ & & | & & | & & | & & | & & | \\ H & — & C^{1°} & — & C^{2°} & — & C & — & C^{2°} & — & C^{3°} & — & H \\ & & | & & | & & | & & | & & | \\ & & H & & H & & \underset{1°}{CH_3} & & H & & \underset{1°}{CH_3} \end{array}$$

1° carbon atoms are those which are bonded to only one carbon atom, i.e., they have only one carbon atom as their neighbour. The given structure has five 1° carbon atoms and fifteen hydrogen atoms attached to it.

2° carbon atoms are those which are bonded to two carbon atoms, i.e., they have two carbon atoms as their neighbours. The given structure has two 2° carbon atoms and four hydrogen atoms attached to it.

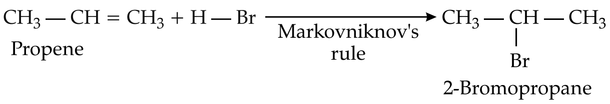
3° carbon atoms are those which are bonded to three carbon atoms, i.e., they have three carbon atoms as their neighbours. The given structure has one 3° carbon atom and only one hydrogen atom is attached to it.

Q. 15. What effect does branching of an alkane chain has on its boiling point? [NCERT Ex. Q. 9.15, Page 327]

Ans. Alkanes experience intermolecular van der Waals forces. The stronger the force, the greater will be the boiling point of the alkane. As branching increases, the surface area of the molecule decreases which results in a small area of contact. As a result, the van der Waals force also decreases which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching. **(2)**

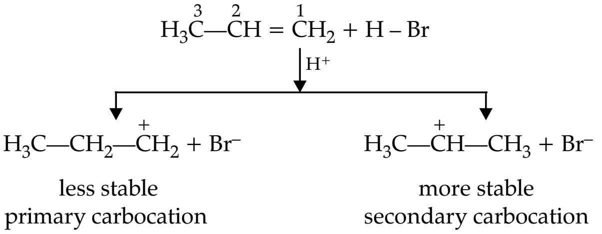
Q. 16. Addition of HBr to propene yields 2-bronopropane, while in the presence of Benzoyl peroxide the same reaction yields 1-bromopropane. Explain and give mechanism. [NCERT Ex. Q. 9.16, Page 327]

Ans. Addition of HBr to propene (unsymmetrical alkene) follows Markovnikov's rule according to which the negative part of the addendum gets attached to that C atom which possesses lesser number of hydrogen atoms.



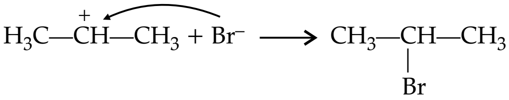
$$\underset{\text{Propene}}{CH_3—CH=CH_3} + H—Br \xrightarrow[\text{Markovniknov's rule}]{} \underset{\text{2-Bromopropane}}{CH_3—\underset{Br}{\underset{|}{CH}}—CH_3}$$

Mechanism: Hydrogen bromide provides an electrophile, H^+, which attacks the double bond to form carbocation as:



$$\overset{3}{H_3C}—\overset{2}{CH}=\overset{1}{CH_2}+H-Br \xrightarrow{H^+} \underset{\text{less stable primary carbocation}}{H_3C—CH_2—\overset{+}{C}H_2+Br^-} \; ; \; \underset{\text{more stable secondary carbocation}}{H_3C—\overset{+}{C}H—CH_3+Br^-}$$

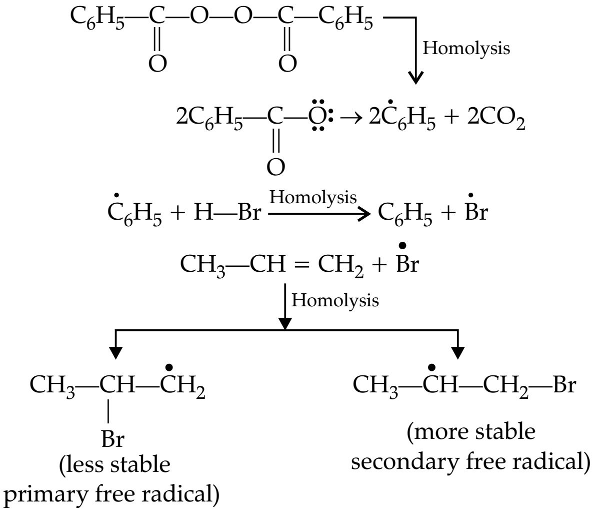
Secondary carbocations are more stable than primary carbocations. Therefore, the former predominates as it will form at a faster rate. Thus, in the next step, Br^- attacks the carbocation to form 2-bromopropane as the major product.



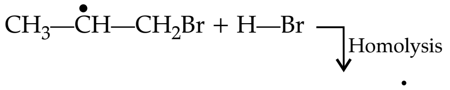
$$H_3C—\overset{+}{C}H—CH_3+Br^- \longrightarrow CH_3—\underset{Br}{\underset{|}{CH}}—CH_3$$

2-Bromopropane

Addition of HBr to unsymmetrical alkenes like propene in the presence of light or peroxide takes place contrary to the Markovnikov's rule. This so happens only with HBr but not with HCl and HI. This addition of HBr to propene in the presence of benzoyl peroxide follows anti-Markovnikov's rule or peroxide effect or Kharash effect.



Secondary free radicals are more stable than primary radicals. Therefore, the former predominates since it forms at a faster rate. Thus, 1-bromopropane is obtained as the major product.



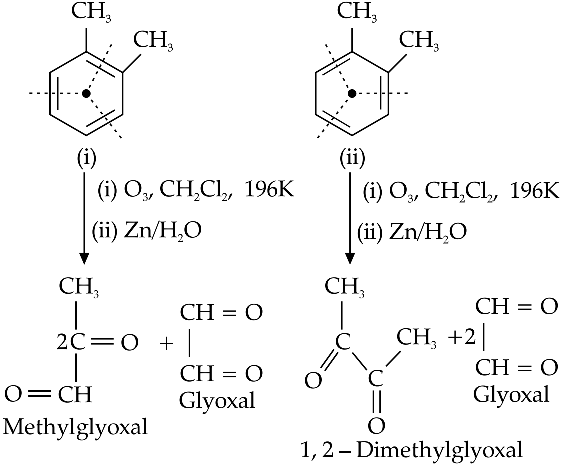
$$CH_3—\dot{C}H—CH_2Br + H—Br \xrightarrow{\text{Homolysis}} CH_3—CH_2—CH_2Br + \dot{Br}$$

1-Bromopropane
major product

Q. 17. Write down the products of ozonolysis of 1,2-dimethylbenzene (*o*-xylene). How does the result support Kekulé structure for benzene?

[NCERT Ex. Q. 9.17, Page 327]

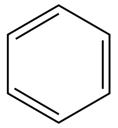
Ans. *o*-xylene has two resonance structures:



All three products, i.e., methyl glyoxal, 1, 2-dimethyl glyoxal and glyoxal are obtained from two Kekule structures. Since all three products cannot be obtained from any one of the two structures, this proves that *o*-xylene is a resonance hybrid of two Kekule structures.

Q. 18. Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour. [NCERT Ex. Q. 9.18, Page 327]

Ans. Acidic character of a species is defined on the basis of ease with which it can lose its H– atoms. The hybridization state of carbon in the given compound is:



Benzene
sp^2

$CH_3—(CH_2)_4—CH_3$
n-hexane
sp^3

$H—C\equiv C—H$
Ethyne
sp

As the *s*–character increases, the electronegativity of carbon increases and the electrons of C–H bond pair lie closer to the carbon atom. As a result, partial positive charge of H– atom increases and H^+ ions are set free. The *s*–character increases in the order:

$$sp^3 < sp^2 < sp$$

Hence, the decreasing order of acidic behaviour is Ethyne > Benzene > *n*-Hexane.

Q. 19. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty? [NCERT Ex. Q. 9.19, Page 327]

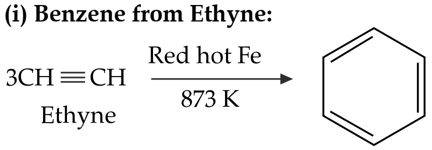
Ans. Benzene is a planar molecule having delocalized electrons above and below the plane of ring. Hence, it is electron-rich. As a result, it is highly attractive to electron deficient species i.e., electrophiles. Therefore, it undergoes electrophilic substitution reactions very easily. Nucleophiles are electron-rich. Hence, they are repelled by benzene. Hence, benzene undergoes nucleophilic substitutions with difficulty.

Q. 20. How would you convert the following compounds into benzene?

(i) Ethyne (ii) Ethene (iii) Hexane

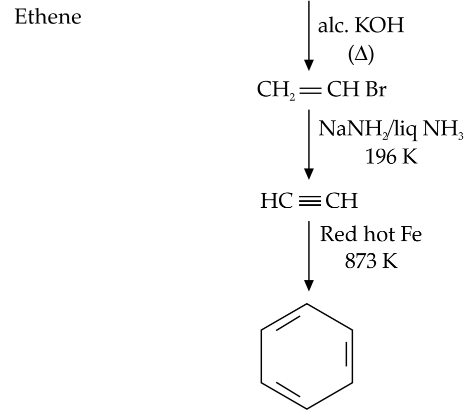
[NCERT Ex. Q. 9.20, Page 327]

Ans. (i) Benzene from Ethyne:



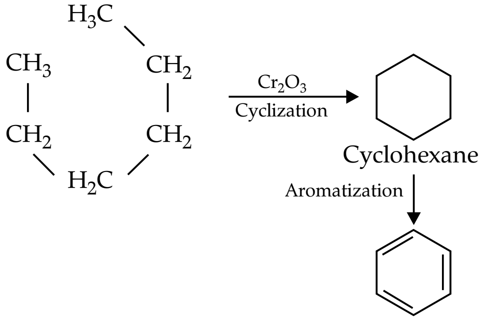
Benzene

(ii) Benzene from Ethene:



Benzene

(iii) Hexane to Benzene:

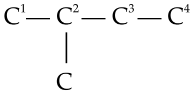


Benzene

Q. 21. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

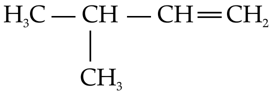
[NCERT Ex. Q. 9.21, Page 327]

Ans. The basic skeleton of 2-methylbutane is shown below:

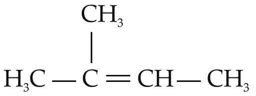


$$C^1—\underset{\displaystyle C}{\underset{|}{C^2}}—C^3—C^4$$

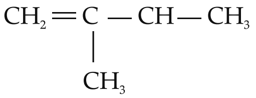
On the basis of this structure, various alkenes that will give 2-methylbutane on hydrogenation are:

(a) 

$$H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH{=}CH_2$$

(b) 

$$H_3C—\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH—CH_3$$

(c) 

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}—CH—CH_3$$

Q. 22. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+

(a) Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene

(b) Toluene, *p*-$H_3C - C_6H_4 - NO_2$, *p*-$O_2N - C_6H_4 - NO_2$.

[NCERT Ex. Q. 9.22, Page 327]

Ans. Electrophiles are reagents that participate in a reaction by accepting an electron pair in order to bond to nucleophiles. The higher the electron density on a benzene ring, the more reactive is the compound towards an electrophile, E^+ (Electrophilic reaction).

(a) The presence of an electron withdrawing group (i.e., $-NO_2$ and $-Cl$) deactivates the aromatic ring by decreasing the electron density. Since $-NO_2$ group is more electron withdrawing (due to resonance effect) than the $-Cl$ group (due to inductive effect), the decreasing order of reactivity is as follows:

Chlorobenzene > *p* – nitrochlorobenzene > 2, 4 – dinitrochlorobenzene.

(b) While $-CH_3$ is an electron donating group, $-NO_2$ group is electron withdrawing. Hence, toluene will have the maximum electron density and is most easily attacked by E^+. $-NO_2$ is an electron withdrawing group. Hence, when the number of $-NO_2$ substituent is greater, the order is as follows:

Toluene > *p*–CH_3–C_6H_4–NO_2, *p* –O_2N–C_6H_4–NO_2

Q. 23. Out of benzene, *m*–dinitrobenzene and toluene which will undergo nitration most easily and why?

[NCERT Ex. Q. 9.23, Page 327]

Ans. The ease of nitration depends on the presence of electron density on the compound to form nitrates. Nitration reactions are examples of electrophilic substitution reactions where an electron-rich species is attacked by a nitronium ion ($-NO_2$). Now, $-CH_3$ group is electron donating and $-NO_2$ is electron withdrawing. Therefore, toluene will have the maximum electron density among the three compounds followed by benzene. On the other hand, m– dinitrobenzene will have the least electron density. Hence, it will undergo nitration with difficulty. Hence, the increasing order of nitration is as follows:

m–dinitrobenzene → benzene → toluene

Q. 24. Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

[NCERT Ex. Q. 9.24, Page 327]

Ans. The ethylation reaction of benzene involves the addition of an ethyl group on the benzene ring. Such a reaction is called a Friedel-Crafts alkylation reaction. This reaction takes place in the presence of a Lewis acid. Any Lewis acid like anhydrous $FeCl_3$, $SnCl_4$, BF_3, etc. can be used during the ethylation of benzene.

Q. 25. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example. [NCERT Ex. Q. 9.25, Page 327]

Ans. Wurtz reaction is limited for the synthesis of symmetrical alkanes (alkanes with an even number of carbon atoms). In the reaction, two similar alkyl halides are taken as reactants and an alkane, containing double the number of carbon atoms, are formed.

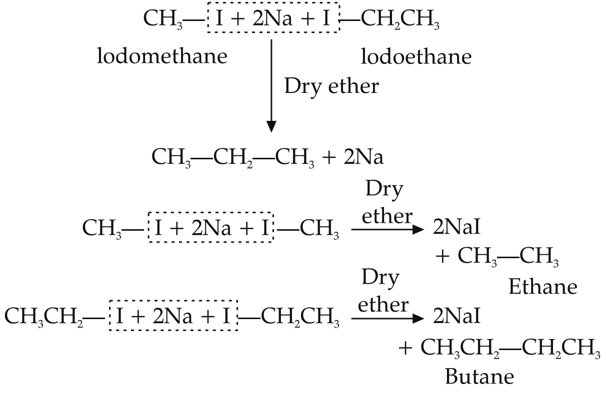
Example:

$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}}$

Bromomethane$CH_3 - CH_3 + 2NaBr$

Ethane

Wurtz reaction cannot be used for the preparation of unsymmetrical alkanes because if two dissimilar alkyl halides are taken as the reactants, then a mixture of alkanes is obtained as the products. Since the reaction involves free radical species, a side reaction also occurs to produce an alkene. For example, the reaction of iodomethane and iodoethane gives a mixture of alkanes.



$$CH_3—\boxed{I + 2Na + I}—CH_2CH_3 \xrightarrow{\text{Dry ether}} CH_3—CH_2—CH_3 + 2Na$$

Iodomethane, Iodoethane

$$CH_3—\boxed{I + 2Na + I}—CH_3 \xrightarrow{\text{Dry ether}} 2NaI + \underset{\text{Ethane}}{CH_3—CH_3}$$

$$CH_3CH_2—\boxed{I + 2Na + I}—CH_2CH_3 \xrightarrow{\text{Dry ether}} 2NaI + \underset{\text{Butane}}{CH_3CH_2—CH_2CH_3}$$

The boiling points of alkanes (obtained in the mixture) are very close. Hence, it becomes difficult to separate them.