DAY TWENTY EIGHT

Hydrocarbons

Learning & Revision for the Day

- Alkanes
- Alkenes
- Alkynes
- Aromatic Hydrocarbons
- Directive Influence of Functional Group in Monosubstituted Benzene

Hydrocarbons means compounds containing carbon and hydrogen only. These may contain only single bonds (saturated hydrocarbons) or double/triple bonds (unsaturated hydrocarbons) alongwith single bond. Hydrocarbons are mainly obtained from petroleum which is the major source of commercial energy.

Hydrocarbons are of different types and classified into three main categories (i) saturated hydrocarbons (alkanes) (ii) unsaturated hydrocarbons (alkenes and alkynes) (iii) aromatic hydrocarbons.

Alkanes

Alkanes are the simplest organic compounds made up of carbon and hydrogen only. Chemically, these are almost inert that's why also called **Paraffins** (Latin, *Parum affinis*=Little affinity). The general formula for this series is C_nH_{2n+2}.

- **Nomenclature** The names of such compounds are based on their chain structure and end with suffix-'ane' and carry a prefix indicating the number of carbon atoms present in the chain.
- **Isomerism** Alkanes shows structural isomerism. Structural isomers which differ in chain of carbon atoms are known as chain isomers. e.g. pentane, 2-methyl butane and 2, 2-dimethyl propane.

General Methods of Preparation

General methods of preparation of alkanes are as follows:

1. **Hydrogenation** Hydrogenation of alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes.

$$CH_2{=\!=}CH_2 + H_2 \xrightarrow{\text{Pt/Pd/Ni}} CH_3{-\!-}CH_3$$

$$CH_3{-\!-}C{\equiv}C{-\!-}H + 2H_2 \xrightarrow{\text{Pt/Pd/Ni}} CH_3{-\!-}CH_2{-\!-}CH_3$$

This reaction is known as **Sabatier-Senderens reduction**.

2. **From Alkyl Halides** Alkyl halides on reduction with zinc and dil. HCl produces alkanes.

$$\underset{\text{Chloromethane}}{CH_3Cl} + H_2 \xrightarrow[\text{Reduction}]{\text{Zn, H}^+} \underset{\text{Methane}}{CH_4} + HCl$$

3. **Wurtz Reaction** Alkyl halides when treated with sodium metal in the presence of dry ether produces higher alkanes. This reaction is known as **Wurtz reaction**.

$$\underset{\text{Ethyl bromide}}{2C_2H_5Br} + 2Na \xrightarrow{\text{Dry ether}} \underset{n\text{-butane}}{C_2H_5{-\!-}C_2H_5} + 2NaBr$$

4. **Decarboxylation** Sodium salt of carboxylic acid ($RCO\overset{-}{O}\overset{+}{Na}$) when heated with hot sodalime ($CaO + NaOH$) gives alkane.

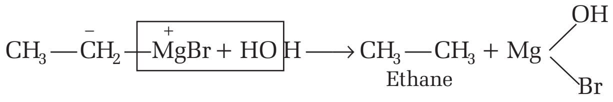
$$CH_3CO\overset{-}{O}\overset{+}{Na} + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

This process of elimination of carbon dioxide from a carboxylic acid is known as **decarboxylation**.

5. **Kolbe's Electrolytic Method** Sodium or potassium salt of carboxylic acid on electrolysis gives alkane (R—R) containing even number of carbon atoms at anode.

$$2CH_3CO\overset{-}{O}\overset{+}{Na} + 2H_2O \xrightarrow{\text{Electrolysis}} \underbrace{C_2H_6 + 2CO_2\uparrow}_{\text{Anode}} + \underbrace{H_2 + 2NaOH}_{\text{Cathode}}$$

6. **From Grignard's Reagent** Grignard reagent ($RMgX$) when reacts with H_2O or ROH, gives alkane.



$$CH_3-\overset{-}{C}H_2-\boxed{\overset{+}{Mg}Br + HO}\,H \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + Mg\begin{matrix}OH\\Br\end{matrix}$$

7. **Other Methods of Preparation** Action of water on aluminium carbide or beryllium carbide gives methane.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$
$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

These reactions produce methane, hence called methanides.

Physical Properties

Alkanes show following physical properties:

1. **Boiling point** increases with increase in molecular mass. If molecular mass is same and the contact surface area increases, boiling point increases. More branched chain has lesser boiling point.
2. **Melting point** increases with increase in molecular mass. But symmetric molecules have higher melting point than asymmetric ones.

   Therefore, alkanes with even number of carbon atoms have higher melting point than the successive alkanes with odd number of carbon atoms.
3. Alkanes are non-polar, therefore soluble in non-polar solvents such as petroleum, benzene etc.
4. The **densities** of alkanes increase with increase in the molecular masses till the limiting value of about 0.8 g/cm^3 is reached.

Chemical Properties

Various chemical properties of alkanes are as follow:

1. **Halogenation of Alkanes** It is a free radical substitution reaction which occurs in the presence of UV light.
   - Rate of replacement of H of alkanes $3° > 2° > 1°$.

   The steps involved in chlorination of methane is

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow{Cl_2/h\nu} CH_2Cl_2 \xrightarrow{Cl_2/h\nu} CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4$$

   - Bromination is same as chlorination but occurs at a slightly slower rate. Iodination is reversible but fluorination of alkanes is too vigorous.

The **mechanism of halogenation** can be discussed in the following three steps:

(i) **Initiation** The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat.

$$Cl—Cl \xrightarrow[\text{Homolysis}]{h\nu} \underset{\text{Chlorine free radicals}}{\dot{Cl} + \dot{Cl}}$$

(ii) **Propagation** Chlorine free radical reacts with methane molecule and generates methyl free radical.

$$CH_4 + \dot{Cl} \xrightarrow{h\nu} \dot{C}H_3 + H—Cl$$
$$\dot{C}H_3 + Cl—Cl \xrightarrow{h\nu} CH_3—Cl + \dot{Cl}$$
$$CH_3Cl + \dot{Cl} \longrightarrow \dot{C}H_2Cl + HCl$$
$$\dot{C}H_2Cl + Cl—Cl \longrightarrow CH_2Cl_2 + \dot{Cl}$$

(iii) **Termination** The possible chain terminating steps are

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl—Cl$$
$$H_3\dot{C} + \dot{C}H_3 \longrightarrow CH_3—CH_3$$
$$H_3\dot{C} + \dot{Cl} \longrightarrow CH_3—Cl$$

Due to consumption of free radicals, chain is terminated.

2. **Combustion** Combustion of alkanes give CO_2 and H_2O.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

   During incomplete combustion alkanes give carbon black which is used in the manufacture of ink, printer ink, black pigments and as filters.

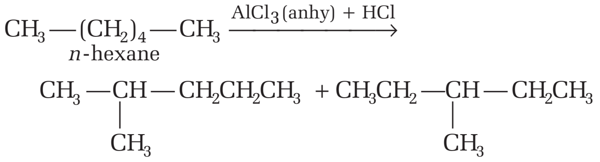
3. **Controlled Oxidation** On controlled oxidation (at high pressure and in presence of suitable catalyst) alkanes give different products as

$$2CH_4 + O_2 \xrightarrow{Cu/523K/100\text{ atm}} 2CH_3OH$$
$$CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$$
$$2CH_3—CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

   Ordinarily alkanes resist oxidation but *iso*-alkanes (3°H) on oxidation with $KMnO_4$ gives tertiary alcohol.

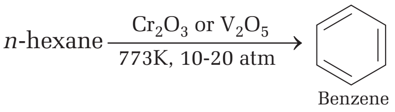
$$(CH_3)_3CH \xrightarrow[\text{Oxidation}]{KMnO_4} \underset{3°\text{ alcohol}}{(CH_3)_3C—OH}$$

4. **Isomerisation** On heating in presence of $AlCl_3$ (anhydrous) and $HCl(g)$ n-alkane isomerises to give branched chain alkanes.



$$CH_3-(CH_2)_4-CH_3 \xrightarrow{AlCl_3(\text{anhy}) + HCl} \underset{\textstyle CH_3}{CH_3-\underset{|}{CH}}-CH_2CH_2CH_3 + CH_3CH_2-\underset{\textstyle CH_3}{\underset{|}{CH}}-CH_2CH_3$$

5. **Aromatisation** *n*-alkanes having six or more carbon atoms on heating to 773 K at 10-20 atmospheric pressure in the presence of oxides of vanadium, Mo or Cr supported over alumina get dehydrogenated and cyclised to benzene. This reaction is known as **aromatisation**.



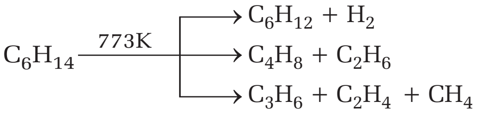
$$n\text{-hexane} \xrightarrow[773\text{K}, \ 10\text{-}20 \text{ atm}]{Cr_2O_3 \text{ or } V_2O_5}$$

6. **Reaction With steam** Alkane (such as methane) react with steam at 1273 K in presence of Ni catalyst to form CO and H_2.

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

This method is used for industrial preparation of H_2 gas.

7. **Pyrolysis or Cracking** Higher alkanes on heating to higher temperature decompose into lower alkanes. This reaction is called **pyrolysis** or **cracking.**



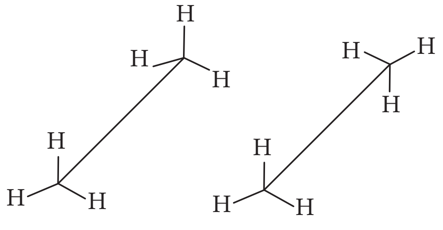
$$C_6H_{14} \xrightarrow{773\text{K}} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$

Conformations

Spatial arrangements of atoms which can be converted into one another by rotation around a C—C single bond are called conformations or conformers or rotamers. Ethane has three stable conformations. These are follows :

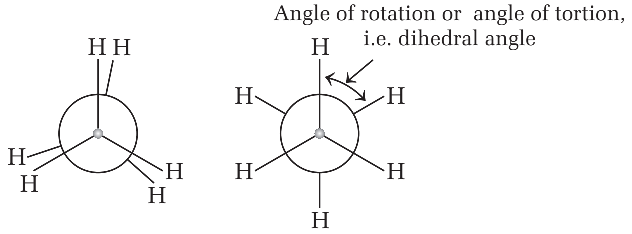
1. **Eclipsed conformation** in which the hydrogen atoms attached to two carbons are as closed together as possible. This conformation is highly unstable and has maximum energy.
2. **Staggered conformation** in which hydrogens are as far apart as possible. It is highly stable and has minimum energy.
3. **Skew conformation** is intermediate conformation of the above two conformations.

   Eclipsed and staggered conformations are represented by Sawhorse and Newman projections.



Eclipsed Staggered

Sawhorse projections of ethane



Eclipsed Staggered

Newman projections of ethane

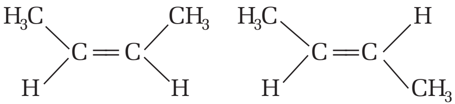
The energy difference between two extreme forms is of the order of 12.5 kJ/mol which is very small, therefore eclipsed and staggered form cannot be isolated.

Alkenes

Alkenes are unsaturated hydrocarbons containing at least one double bond. Double bonded carbon has sp^2 hybridisation.

General formula for alkenes is C_nH_{2n}.

- **Nomenclature** In IUPAC system of alkenes, numbering of the chain is done from the end which is nearer to the double bond. The suffix 'ene' replaces 'ane' of alkanes.
- **Isomerism** Alkenes show **structural** as well as **geometrical isomerism**. For exhibiting geometrical isomerism two different atoms or groups should be attached to double bonded carbon atoms. If same atoms or groups lie on the same side of the double bond, it is known as ***cis* form** and if same atoms or groups lie on the opposite sides of the double bond, it is known as **trans form**. e.g.



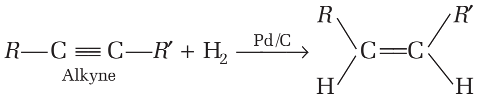
cis but-2-ene *trans* but-2-ene

- *cis*-form of alkene is found to be more polar (i.e. has more dipole moment) than the *trans*.
- *cis*-form has higher boiling point than *trans*-form and *trans*-isomer has higher melting point than that of *cis* form.

General Methods of Preparation

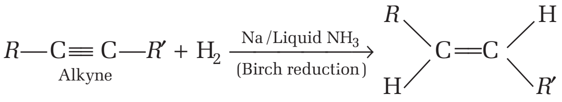
General methods of preparation of alkenes are as follows:

1. **Controlled Hydrogenation** Alkynes when treated with Lindlar's catalyst [Pd/C/$H_2(g)$] give *cis*-alkenes while on reduction with Na/liquid NH_3 give *trans*-alkenes **(Birch reduction).**

e.g. 

$$R-C\equiv C-R' + H_2 \xrightarrow{Pd/C}$$

cis-alkene



$$R-C\equiv C-R' + H_2 \xrightarrow[\text{(Birch reduction)}]{Na/\text{Liquid } NH_3}$$

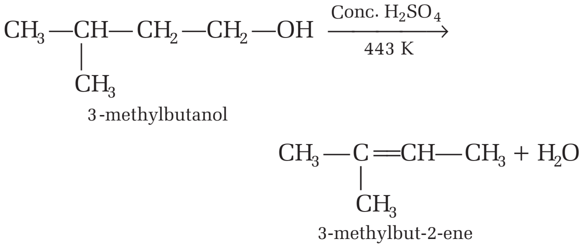
trans-alkene

2. **Dehydrohalogenation** Alkyl halides on heating with alcoholic potash undergoes dehydrohalogenation **(β-elimination reaction)** to form alkenes.

$$CH_3—\overset{\beta}{C}H_2—\overset{\alpha}{C}H_2Br \xrightarrow[\text{KOH} + C_2H_5OH]{\text{KOH(alc)}/\Delta \text{ or}} CH_3CH{=}CH_2$$

Nature of halogen atom and the alkyl group determine rate of reaction. For halogen, the rate is iodine > bromine > chlorine while for alkyl group, rate is 3° > 2° > 1°.

3. **Dehydration of Alcohols** Alcohols on acidic dehydration give alkenes. This reaction is an example of β-elimination.

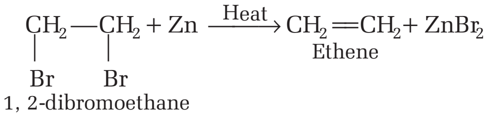


$$\underset{\text{3-methylbutanol}}{CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_2—CH_2—OH} \xrightarrow[443\text{ K}]{\text{Conc. } H_2SO_4} \underset{\text{3-methylbut-2-ene}}{CH_3—\underset{\substack{|\\CH_3}}{C}{=}CH—CH_3} + H_2O$$

In this reaction, intermediate carbocation is formed and rearrange, therefore double bond is formed at maximum degree of carbon.

NOTE Dehydration and dehydrohalogenation both are governed by **Saytzeff's rule**, i.e. the greater is the number of alkyl groups attached to double bonded 'C' atoms, the more stable is the alkene. If dehydrohalogenation of alkyl halide takes place in the presence of potassium *t*-butoxide, less substituted alkene is obtained due to steric hindrance.

4. **Dehalogenation** *Vicinal dihalides* when treated with zinc metal lose a molecule of ZnX_2 to lose a molecule of ZnX_2 to give alkenes. This reaction is known as **dehalogenation**.



$$\underset{\text{1, 2-dibromoethane}}{\underset{\substack{|\\Br}}{CH_2}—\underset{\substack{|\\Br}}{CH_2}} + Zn \xrightarrow{\text{Heat}} \underset{\text{Ethene}}{CH_2{=}CH_2} + ZnBr_2$$

Physical Properties

Various physical properties alkenes are as follows:

- The melting point of alkenes do not show regular trend. Alkenes have higher melting point than corresponding alkanes.
- The boiling point of alkenes vary in the same manner as in alkanes. Their boiling points are higher than that of the corresponding alkanes.
- Alkenes are quite soluble in non-polar solvents such as benzene, CCl_4 etc.

Chemical Properties

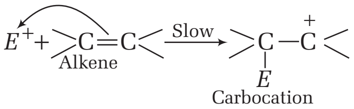
Alkenes generally undergo **electrophilic addition reactions** because of the presence of a double bond (a strong σ and a weaker π-bond), π electrons of which being loosely held are easily polarisable.

The mechanism involved in electrophilic addition reaction are as follows:

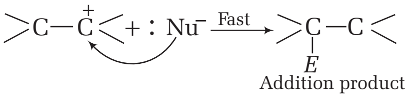
***Step* I** Ionisation of reagent to generate electrophile and nucleophile

$$E—Nu \longrightarrow E^+ + :Nu^-$$

***Step* II** Attack of electrophile on alkene.



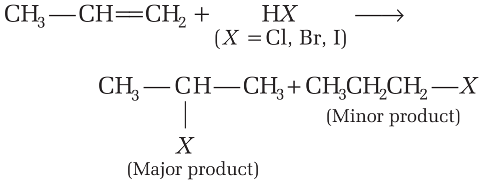
***Step* III** Attack of nucleophile to give addition product.



A brief description of different reactions of alkenes is as follows :

1. **Addition of hydrogen** on alkenes occur in the presence of finely divided nickel, palladium or platinum to form alkanes (discussed earlier).
2. **Addition of halogens** like bromine or chlorine when reacted wiith alkene results in the formation of *vicinal* dihalides. However, iodine does not show addition reaction under normal conditions.
3. **Addition of hydrogen halide when** alkenes reacts with hydrogen halides (HCl, HBr, HI) alkyl halides are obtained. According to **Markownikoff's rule** which states that negative part of the adding molecule gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

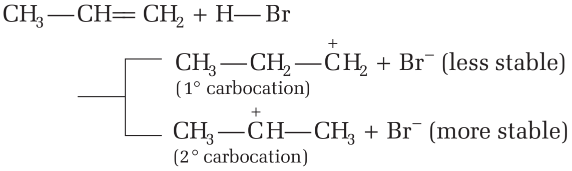
e.g.



$$CH_3—CH{=}CH_2 + \underset{(X\,=\text{Cl, Br, I})}{HX} \longrightarrow \underset{\text{(Major product)}}{CH_3—\underset{\substack{|\\X}}{CH}—CH_3} + \underset{\text{(Minor product)}}{CH_3CH_2CH_2—X}$$

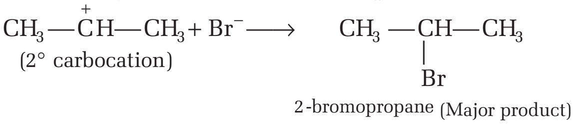
- Steps involved in the **mechanism** are as follows :

(i) HBr provides an electrophile, H^+ which attacks the double bond to form carbocation.



$$CH_3—CH{=}CH_2 + H—Br \longrightarrow \begin{cases} \underset{(1^\circ \text{ carbocation})}{CH_3—CH_2—\overset{+}{C}H_2} + Br^- \text{ (less stable)} \\ \underset{(2^\circ \text{ carbocation})}{CH_3—\overset{+}{C}H—CH_3} + Br^- \text{ (more stable)} \end{cases}$$

(ii) 2° carbocation is formed at a faster rate and it is attacked by Br^- ion to form major product.

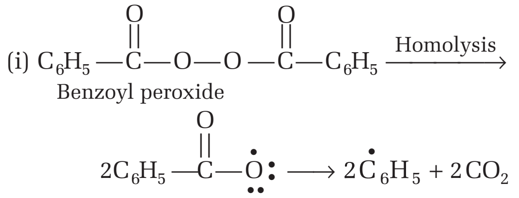


$$\underset{(2^\circ\text{ carbocation})}{CH_3—\overset{+}{C}H—CH_3} + Br^- \longrightarrow \underset{\text{2-bromopropane (Major product)}}{CH_3—\underset{\substack{|\\Br}}{CH}—CH_3}$$

- Alkenes with HBr only in presence of peroxide shows **free radical addition reaction** contrary to the Markownikoff's rule. This is also known as **Kharasch effect**.

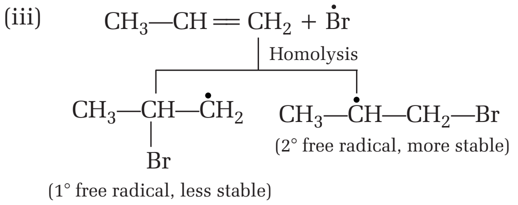
$$CH_3—CH=CH_2 + HBr \xrightarrow{\text{Benzoyl peroxide}} \underset{\text{1-bromopropane}}{CH_3—CH_2—CH_2—Br}$$

- Peroxide effect proceeds *via* free radical chain mechanism. The steps involved in the process are as follows :



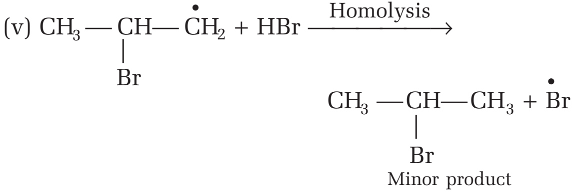
$$\text{(i)}\ \underset{\text{Benzoyl peroxide}}{C_6H_5—\overset{O}{\overset{\|}{C}}—O—O—\overset{O}{\overset{\|}{C}}—C_6H_5} \xrightarrow{\text{Homolysis}} 2C_6H_5—\overset{O}{\overset{\|}{C}}—\dot{\ddot{O}}: \longrightarrow 2\dot{C}_6H_5 + 2CO_2$$

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



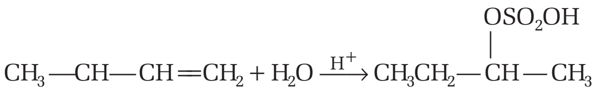
$$\text{(iii)}\ CH_3—CH=CH_2 + \dot{Br} \xrightarrow{\text{Homolysis}} \underset{\text{(1° free radical, less stable)}}{CH_3—\underset{Br}{\underset{|}{CH}}—\dot{C}H_2} \quad \underset{\text{(2° free radical, more stable)}}{CH_3—\dot{C}H—CH_2—Br}$$

$$\text{(iv)}\ CH_3—\dot{C}H—CH_2Br + HBr \xrightarrow{\text{Homolysis}} \underset{\text{Major product}}{CH_3CH_2CH_2Br} + \dot{Br}$$



$$\text{(v)}\ CH_3—\underset{Br}{\underset{|}{CH}}—\dot{C}H_2 + HBr \xrightarrow{\text{Homolysis}} \underset{\text{Minor product}}{CH_3—\underset{Br}{\underset{|}{CH}}—CH_3} + \dot{Br}$$

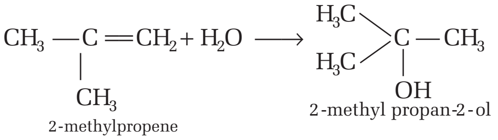
4. **Addition of Sulphuric Acid** Alkene when treated with cold conc. H_2SO_4 gives alkyl hydrogen sulphate by electrophilic addition reaction.



$$CH_3—CH—CH=CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2—\overset{OSO_2OH}{\overset{|}{CH}}—CH_3$$

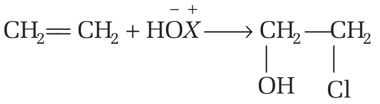
In this reaction intermediate carbocation is formed, which rearranges to form an alcohol.

5. **Addition of Water** Alkenes react with water in the presence of few drops of conc. H_2SO_4 in accordance with Markownikoff's rule.



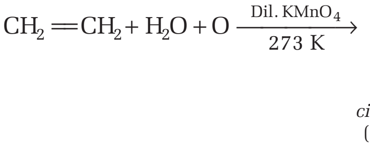
$$\underset{\text{2-methylpropene}}{CH_3—\underset{CH_3}{\underset{|}{C}}=CH_2} + H_2O \longrightarrow \underset{\text{2-methyl propan-2-ol}}{(H_3C)_2\underset{OH}{\underset{|}{C}}—CH_3}$$

6. **Addition of Hypohalous acid** Alkenes react with hypohalous acid to form halohydrins. These compounds contain —OH and —X groups at successive C-atoms.



$$CH_2=CH_2 + \overset{-}{HO}\overset{+}{X} \longrightarrow \underset{OH}{\underset{|}{CH_2}}—\underset{Cl}{\underset{|}{CH_2}}$$

7. **Oxidation** Cold dilute $KMnO_4$ **(Baeyer's reagent)** when treated with alkene undergoes oxidation to give glycol (*vicinal* dihydric alcohol).



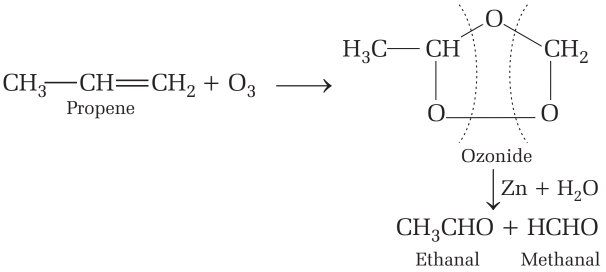
$$CH_2=CH_2 + H_2O + O \xrightarrow[273\ K]{\text{Dil. }KMnO_4} \underset{\text{(Ethylene glycol)}}{\underset{\textit{cis}\text{-ethane-1, 2-diol}}{\underset{OH}{\underset{|}{CH_2}}—\underset{OH}{\underset{|}{CH_2}}}}$$

This reaction is used as a test unsaturation as purple colour of $KMnO_4$ disappears during the reaction and a brown precipitate of MnO_2 is obtained.

Acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ oxidises alkenes to ketones and /or acids depending upon the nature of the alkene.

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

8. **Ozonolysis of Alkenes** It involves the addition of ozone molecule to alkene to form ozonide and then cleavage of the oxonide by Zn-H_2O to smaller molecules. This reaction is used to locate the position of double bond in an alkene.



$$\underset{\text{Propene}}{CH_3—CH=CH_2} + O_3 \longrightarrow \text{Ozonide} \xrightarrow{Zn + H_2O} \underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{Methanal}}{HCHO}$$

9. **Polymerisation** Alkenes undergo polymerisation and form polymers. Polymers are used for manufacture of plastic bags, radio, T.V. cabinets, buckets etc.

$$\underset{\text{Ethene}}{n(CH_2=CH_2)} \xrightarrow[\text{catalyst}]{\text{High temperature and pressure}} \underset{\text{Polythene}}{\text{—}(CH_2—CH_2)_n\text{—}}$$

10. **Combustion of Alkene** It involves the formation of carbon dioxide and water. The generalised combustion reaction can be seen as :

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O + \text{Heat}$$

Alkynes

Alkynes are also unsaturated hydrocarbons. They contain atleast one triple bond between two carbon atoms. Their general formula is C_nH_{2n-2}.

- **Nomenclature** In IUPAC system of alkynes, the suffix 'yne' replaces the 'ane' of alkanes.
- **Isomerism** Alkynes show positional and chain isomerism. The two compounds differ in their structures due to the position of triple bond. e.g. pent-1-yne, pent-2-yne, 3-methylbut-1-yne.

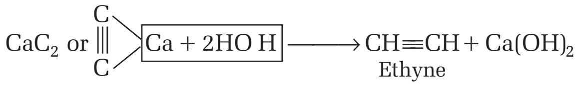
General Methods of Preparation

The various methods of preparation of alkynes are as follows:

1. **By Hydrolysis of Metal Carbides** On industrial scale, ethyne is prepared by treating calcium carbide with water. The steps involved in the process are as follows :

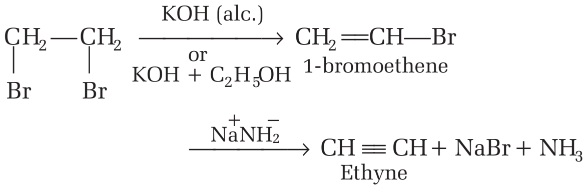
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

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



$$CaC_2 \text{ or } \overset{C}{\underset{C}{|||}} \boxed{Ca + 2HO\,H} \longrightarrow \underset{\text{Ethyne}}{CH\equiv CH} + Ca(OH)_2$$

2. **From Vicinal Dihalides** *Vicinal* dihalides on treatment with alc. KOH undergoes dehydrohalogenation.



$$\underset{\underset{Br}{|}}{C}H_2-\underset{\underset{Br}{|}}{C}H_2 \xrightarrow[\text{or KOH} + C_2H_5OH]{\text{KOH (alc.)}} \underset{\text{1-bromoethene}}{CH_2=CH-Br}$$

$$\xrightarrow{\overset{+}{Na}\overset{-}{N}H_2} \underset{\text{Ethyne}}{CH\equiv CH} + NaBr + NH_3$$

3. **From Sodium Acetylide** Higher alkynes can be prepared from lower alkynes by reaction of sodium acetylide with alkyl halide.

$$R-C\equiv CH \xrightarrow{NaNH_2,\ liq.\ NH_3} R-C\equiv \overset{-}{C}-\overset{+}{Na}$$

$$\xrightarrow{R'X} R-C\equiv C-R'$$

Physical Properties

Various physical properties of alkynes are as follows:

1. All alkynes are odourless, however acetylene has garlic smell due to the impurity of phosphine.
2. The melting and boiling points of alkynes are slightly higher than those of the corresponding alkenes and alkanes.

Chemical Properties

The various chemical properties of alkynes are as follows:

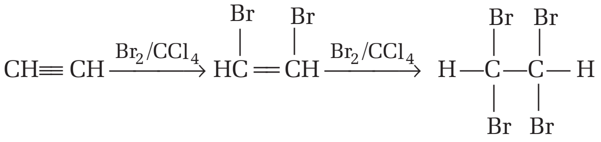
1. Electrophilic Addition Reaction

Alkynes contain a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides etc. A few addition reactions are as follows :

(i) **Addition of Dihydrogen**

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

(ii) **Addition of Halogen**



$$CH\equiv CH \xrightarrow{Br_2/CCl_4} \overset{\overset{Br}{|}}{HC}=\overset{\overset{Br}{|}}{CH} \xrightarrow{Br_2/CCl_4} H-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-H$$

(iii) **Addition of Hydrogen Halides**

$$\underset{(X = Cl,\ Br,\ I)}{CH\equiv CH + HX} \longrightarrow [CH_2=CH-X] \xrightarrow{HX} CH_3CHX_2$$

(iv) **Addition of Water**

$$CH\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4}$$

$$[CH_2=CH-OH] \xrightarrow{\text{Tautomerises}} \underset{\text{Ethanal}}{CH_3CHO}$$

The reaction, called **hydration of alkynes** and is used commercially for the preparation of aldehydes and ketones.

2. Reactions Showing Acidic Character of Alkynes

Due to the presence of acidic H-atom, alkynes (terminal) exhibit following reactions:

(i) **Reaction with Na in liq. NH_3** Terminal alkynes have acidic H because C—H bond has ionic character due to resonance.

$$2CH\equiv CH + 2Na \xrightarrow{475K} 2CH\equiv\overset{-}{C}\overset{+}{Na} + H_2$$

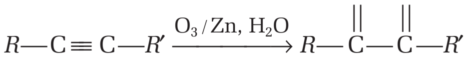
$$CH\equiv CH + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\underset{\text{(white ppt.)}}{\text{Silver acetylide}}}{AgC\equiv CAg\downarrow}$$

$$+ 2H_2O + 4NH_3$$

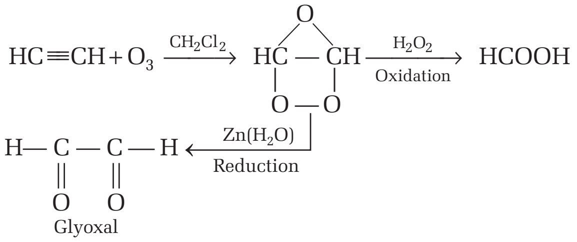
(ii) **Oxidation** Alkyne on oxidation with hot $KMnO_4$ produces carboxylic acids.

$$R-C\equiv C-R' \xrightarrow[\text{Heat}]{KMnO_4/H^+} RCOOH + R'COOH$$

(iii) **Ozonolysis** Alkynes on ozonolysis gives diketones while oxidative ozonolysis of acetylene gives a mixture of glyoxal and formic acid while reductive ozonolysis of acetylene gives glyoxal.



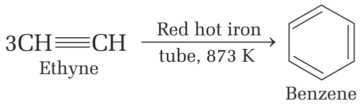
$$R-C\equiv C-R' \xrightarrow{O_3/Zn,\ H_2O} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R'$$



(iv) **Polymerisation** Ethyne undergoes linear polymerisation under suitable conditions to produce polyacetylene or polyethyne,

$$-\!\!\left(CH=CH-CH=CH\right)\!\!-_{n}$$

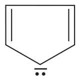
while ethyne on passing through red hot iron tube at 873 K undergoes cyclic polymerisation.



Aromatic Hydrocarbons

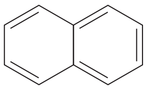
Aromatic hydrocarbons are specialised cyclic compounds which are also known as arenes and since, most of them possess pleasant odour [Aroma = fragrance] these are known as **aromatic compounds**.

- **Nomenclature** For IUPAC nomenclature of substituted benzene compounds, the substituents is placed as prefix to the word benzene.
- **Aromaticity** Ring systems whether having benzene ring or not with the following characteristics are said to be **aromatic**.
  - (i) Planarity.
  - (ii) Complete delocalisation of the π-electrons in the ring.
  - (iii) Presence of $(4n+2)$ π-electrons in the ring, where n is an integer $(n = 0, 1, 2 \ldots)$. This is known as **Huckel's rule.**



$n = 1$

$(4n + 2) = 6\pi$-electrons



Naphthalene

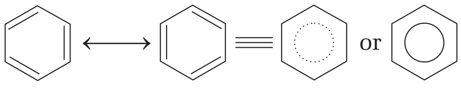
$n = 2$

$(4n + 2) = 10\pi$-electrons

- Certain compounds such as pyrrole, furan etc., although do not contain benzene ring, but behaves like benzene. These compounds are called **non-benzenoid aromatic compounds**.

Structure of Benzene

- According to Kekule, benzene is said to be resonance hybrid of the following forms.



Kekule structure

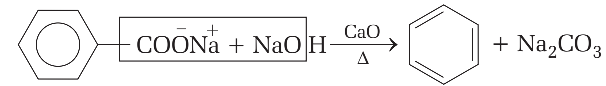
Delocalised π-bond

- It is aromatic, $(4n+2)\pi = 6\pi$. Here, n = number of π-electrons delocalised (Huckel's rule is followed).
- Benzene yields only one substitution product and three isomeric substitution product.
- All C—C bond distance in benzene are equal (139 pm).
- A compound with delocalised electrons is more stable and benzene has six delocalised π-electrons.

General Methods of Preparation

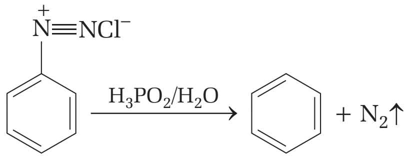
Various methods of preparation of benzene are as follows:

1. **Polymerisation** Polymerisation of ethyne to produce benzene in presence of red hot iron tube (discussed earlier).
2. **Decarboxylation** Sodium salt of benzoic acid on heating with sodalime gives benzene.

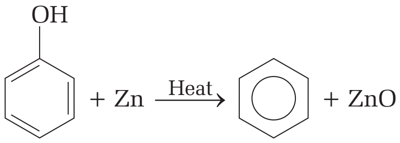


Sodium benzoate

3. **Reduction of benzene diazonium chloride** Diazonium salts are reduced to benzene by passing H_3PO_2/H_2O.



4. **Dehydroxylation** Phenol is reduced to benzene by passing its vapours over heated zinc dust.



Phenol

Benzene

Physical Properties

Various physical properties of benzene are as follows:

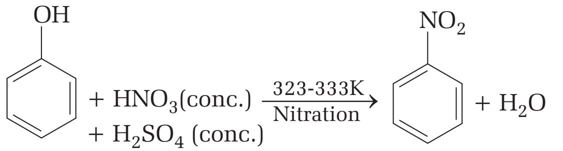
- Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.
- They are immiscible with water but are readily miscible with organic solvents.
- They burn with sooty flame.

Chemical Properties

Arenes are characterised by electrophilic substitution reactions but under special conditions they can also undergo addition and oxidation reaction.

1. **Electrophilic Substitution Reactions** Various types of electrophilic substitution reactions are as follows :

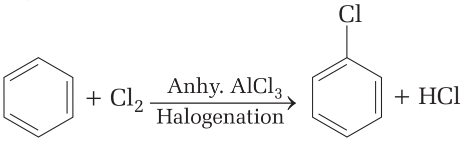
(i) **Nitration**



Nitrobenzene

Attacking reagent (electrophile) is NO_2^+.

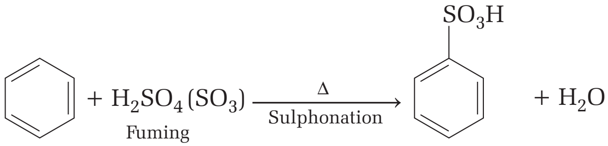
(ii) **Halogenation**



Chlorobenzene

Electrophile is Cl^+.

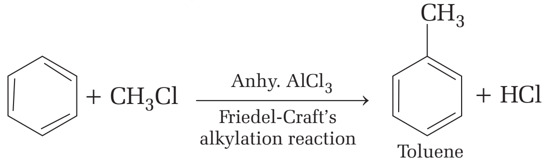
(iii) **Sulphonation**



Benzene sulphonic acid

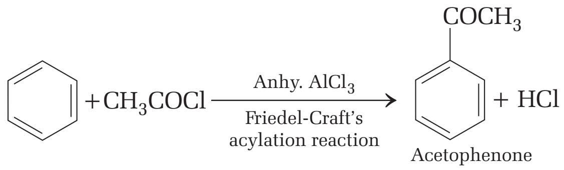
Electrophile is SO_3.

(iv) **Friedel Craft Alkylation**



Electrophile is $\overset{+}{C}H_3$.

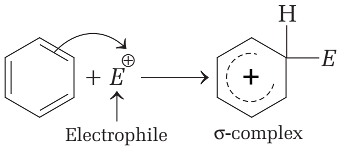
(v) **Friedel-craft Acylation**



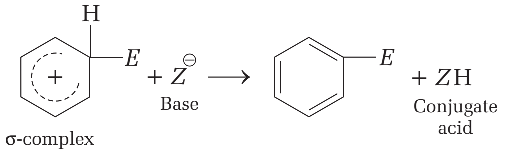
- If excess of electrophilic reagent is used, further substitution reaction may take place in which other hydrogen atoms of benzene ring may also be successively replaced by the electrophile.

Mechanism of electrophilic substitution involves following steps :

Step **I Formation of σ-complex**

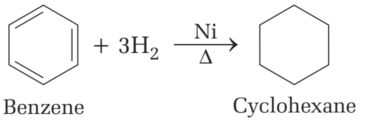


Step **II Elimination of Proton**

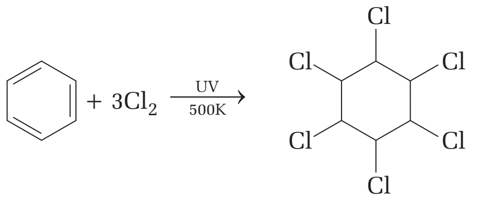


$Z^- = FeX_4^-$ (X = Cl, Br) in halogenation; HSO_4^- in nitration; H_2O in sulphonation, AlX_4^- (X = Cl, Br) in Friedel-Crafts alkylation/ acylation.

2. **Addition Reactions** Under vigorous conditions, i.e. at high temperature or pressure in the presence of Ni catalyst, hydrogenation of benzene gives cyclohexane.



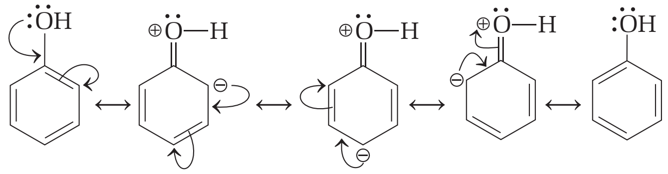
Under UV light, three chlorine molecules add to benzene to produce benzene hexachloride $C_6H_6Cl_3$, also called gammaxane.



Benzene hexachloride (BHC),

Directive Influence of Functional Group in Monosubstituted Benzene

- The substituent already present in the benzene ring directs the incoming group either to *ortho*- and *para*- or to *meta*-position. *o*-, *p*-directing groups increase the electron density on the ring and thus, increase the reaction rate while *m*-directing groups decrease the electron density on the benzene ring and thus, decrease the reaction rate.
- Example for *ortho* and *para* directing groups (activating).

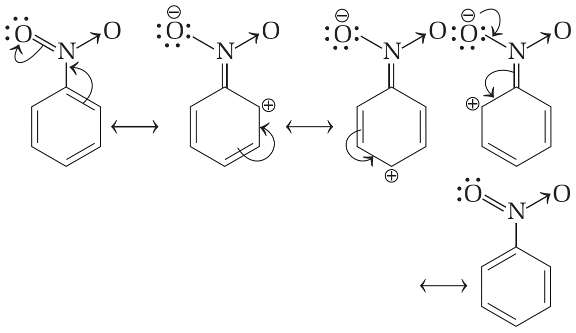


Resonating structures of phenol

In case of phenol, electron density is more concentrated on *o*- and *p*-positions.

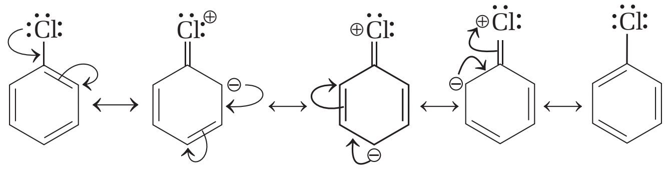
Therefore, substitution is mainly in these positions. Other activating groups are $—OH$, $—NH_2$, $—NHR$, $—NHCOCH_3$, $—OCH_3$, $—CH_3$, $—C_2H_5$ etc.

- Example for *meta* directing group (deactivating) :



Resonating structures of nitrobenzene

- Other deactivating groups are $—NO_2$, $—CN$, $—CHO$, $—COR$, $—COOH$, $—COOR$, $—SO_3H$ are *meta*-directing groups.
- In case of haloarenes, halogens are moderately deactivating because of –*I*- effect overall electron density on benzene ring decreases. Due to resonance, electron density on *o*- and *p*-position increases, hence halogens are *o*-, *p*-directing groups.



Resonating structures of chlorobenzene

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Butene-1 may be converted to butane by reaction with ➞ AIEEE 2003

(a) Zn-HCl (b) Sn-HCl (c) Zn-Hg (d) Pd/H_2

2 The increasing order of reduction of alkyl halides with zinc and dilute HCl is

(a) R—Cl<R—I<R—Br (b) R—Cl<R—Br<R—I
(c) R—I<R—Br<R—Cl (d) R—Br<R—I<R—Cl

3 A mixture of ethyl iodide and *n*-propyl iodide is subjected to Wurtz reaction. The hydrocarbon which will not be formed is

(a) butane (b) propane (c) octane (d) hexane

4 Pure methane can be produced by

(a) Wurtz reaction
(b) Kolbe's electrolytic method
(c) sodalime decarboxylation
(d) reduction with H_2

5 Which one of the following has the minimum boiling point?

(a) *n*-butane (b) 1-butyne (c) 1-butene (d) *Iso*-butene

6 Arrange the following in the decreasing order of their boiling points.

A. *n*-butane B. 2-methylbutane
C. *n*-pentane D. 2, 2-dimethylpropane

(a) $A > B > C > D$ (b) $B > C > D > A$
(c) $D > C > B > A$ (d) $C > B > D > A$

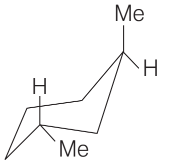
7 The percentage of 1-chloro-2-methylpropane obtained in the chlorination of *iso*-butane is

(a) 38 % (b) 64 % (c) 79 % (d) 36 %

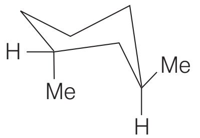
8 On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane would be

(a) propane (b) pentane
(c) *iso*-pentane (d) *neo*-pentane

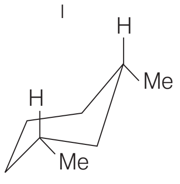
9 Arrange in the correct order of stability (decreasing order) for the following molecules ➞ JEE Main (Online) 2013



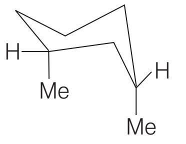
I



II



III

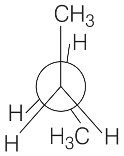


IV

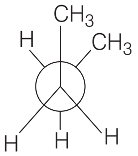
(a) (I) > (II) > (III) > (IV) (b) (IV) > (III) > (II) ≈ (I)
(c) (I) > (II) ≈ (III) > (IV) (d) (III) > (I) ≈ (II) > (IV)

10 Which of the following is the most stable conformation of *n*-butane?

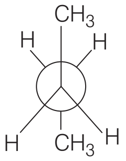
(a)



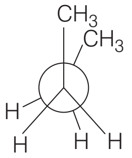
(b)



(c)



(d)



11 The *trans*-alkenes are formed by the reduction of alkynes with ➞ JEE Main 2018

(a) H_2-Pd/C, $BaSO_4$ (b) $NaBH_4$
(c) Na/liq. NH_3 (d) Sn-HCl

12 2-phenylpropene on acidic hydration gives

(a) 2-phenyl propan-2-ol
(b) 2-phenyl propan-1-ol
(c) 3-phenyl propan-1-ol
(d) 1-phenyl propan-2-ol

13 When subjected to acid catalysed hydration, the order of reactivity of the alkenes is

I. $(CH_3)_2C{=}CH_2$ II. $CH_3CH{=}CH_2$
III. $CH_2{=}CH_2$

(a) III > II > I (b) I > III > II
(c) I > II > III (d) II > I > III

14 The intermediate formed during the addition of HCl to propene in the presence of peroxide is

(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

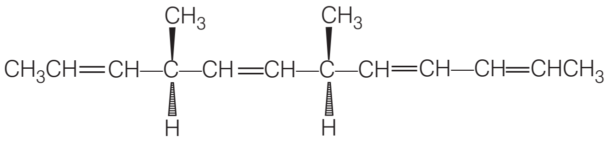
15 Which of the following is the predominant product in the reaction of HOBr with propene? ➞ JEE Main 2016

(a) 2-bromo-1-propanol (b) 3-bromo-1-propanol
(c) 2-bromo-2-propanol (d) 1-bromo-2-propanol

16 The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate

(a) $CH_3—\overset{+}{C}H—CH_2—Cl$ (b) $CH_3—CH(OH)—\overset{+}{C}H_2$
(c) $CH_3—CHCl—\overset{+}{C}H_2$ (d) $CH_3—\overset{+}{C}H—CH_2—OH_2$

17 The number of optically active products obtained from the complete ozonolysis of the given compound is



$CH_3CH{=}CH-\overset{CH_3}{\underset{H}{C}}-CH{=}CH-\overset{CH_3}{\underset{H}{C}}-CH{=}CH-CH{=}CHCH_3$

(a) 0 (b) 1 (c) 2 (d) 4

18 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of ➞ AIEEE 2011

(a) two ethylenic double bonds
(b) a vinyl group
(c) an *iso* propyl group
(d) an acetylenic triple bond

19 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is ➞ AIEEE 2010

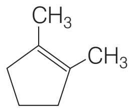
(a) propene (b) 1-butene (c) 2-butene (d) ethene

20 Ozonolysis of 2,3-dimethyl but-1-ene followed by reduction with zinc and water gives

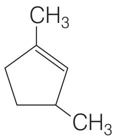
(a) methanoic acid and 3-methyl butan-2-one
(b) methanal and 2-methyl butan-2-one
(c) methanal and 3-methyl butan-2-one
(d) methanoic acid and 2-methyl butan-2-one

21 Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? ➞ JEE Main 2015

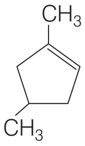
(a)



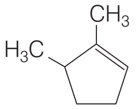
(b)



(c)



(d)



22 6 L of an alkene require 27 L of oxygen at constant temperature and pressure for complete combustion. The alkene is ➞ JEE Main (Online) 2013

(a) ethene (b) propene (c) 1-butene (d) 2-butene

23 Acetylene does not react with ➞ AIEEE 2002

(a) Na (b) ammonical $AgNO_3$
(c) HCl (d) NaOH

24 2-hexyne gives *trans*-2-hexene on treatment with ➞ AIEEE 2012

(a) Pt/H_2 (b) Li/NH_3 (c) $Pd/BaSO_4$ (d) $LiAlH_4$

25 What is the best way to carry out the following transformation?

1-pentyne ⟶ pentanal

(a) $HgSO_4/H_2SO_4$
(b) H_2 /Lindlar's catalyst; O_3;Zn-H_2O
(c) HIO_4/H_2O
(d) BH_3; H_2O_2 /NaOH

26 1-butyne on oxidation with hot alkaline $KMnO_4$ would yield

(a) $CH_3CH_2CH_2COOH$
(b) CH_3CH_2COOH
(c) $CH_3CH_2COOH + CO_2 + H_2O$
(d) $CH_3CH_2COOH + HCOOH$

27 Match the following and choose the correct option.

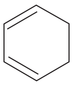
	Reactions	Reaction type
A.	$CH_2=CH_2+H_2O\xrightarrow{H^+}CH_3CH_2OH$	1. Hydrogenation
B.	$CH_2=CH_2+H_2\xrightarrow{Pd}CH_3-CH_3$	2. Halogenation
C.	$CH_2=CH_2+Cl_2\longrightarrow Cl-CH_2-Cl$	3. Polymerisation
D.	$3CH\equiv CH\xrightarrow[\text{Heat}]{\text{Cu tube}}C_6H_6$	4. Hydration

Codes

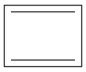
	A	B	C	D		A	B	C	D
(a)	4	2	1	3	(b)	4	1	2	3
(c)	1	3	4	2	(d)	2	1	3	4

28 Which of the following molecules, in pure form, is (are) unstable at room temperature? ➞ IIT JEE 2012

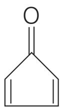
(a)



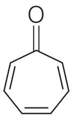
(b)



(c)



(d)

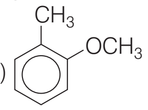


29 Which one of the following is the most reactive towards ring nitration?

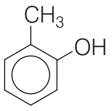
(a) Benzene (b) Mesitylene
(c) Toluene (d) *m*-xylene

30 Which one is the most reactive towards electrophilic reagent?

(a)



(b)



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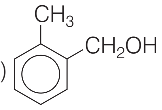

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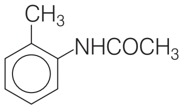
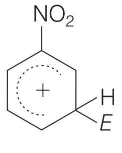


31 The correct sequence of reactions to be performed to convert benzene into *m*-bromoaniline is

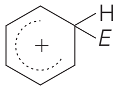
(a) nitration, reduction, bromination
(b) bromination, nitration, reduction
(c) nitration, bromination, reduction
(d) reduction, nitration, bromination

32 The electrophile E^+ attacks the benzene ring to generate the intermediate σ-complex. Of the following, which σ-complex is of lowest energy ?

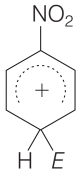
(a)



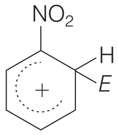
(b)



(c)

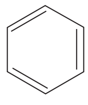


(d)

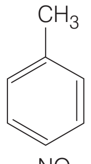


33 Given,

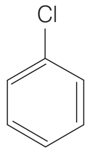
I.



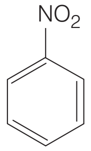
II.



III.



IV.



In the above compounds correct order of reactivity in electrophilic substitution reactions will be

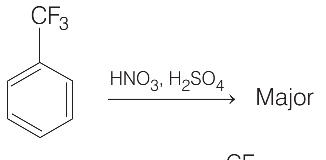
(a) II > I > III > IV ➞ JEE Main (Online) 2013

(b) IV > III > II > I

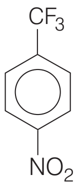
(c) I > II > III > IV

(d) II > III > I > IV

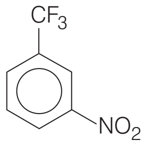
34 Give the major product of the following reaction



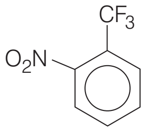
(a)



(b)



(c)



(d) Cannot say

Direction (Q. Nos. 35-36) *In the following questions Assertion (A) followed by a Reason (R) is given. Choose the correct option out of the choices given below.*

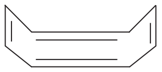
(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion

(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion

(c) Assertion is correct and Reason is incorrect

(d) Both Assertion and Reason are incorrect

35 **Assertion** (A) The compound cyclooctatetraene has the following structural formula.



It is cyclic and has conjugated 8π -electron system but it is not an aromatic compound.

Reason (R) $(4n+2)\pi$-electrons rule does not hold good and ring is not planar.

36 **Assertion** (A) Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

Reason (R) The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+.

Direction (Q. Nos. 37-40) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

37 **Statement I** Addition of Br_2 to 1-butene gives two optical isomers.

Statement II The product contains one asymmetric carbon atom.

38 **Statement I** 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

Statement II It involves the formation of a primary radical.

39 **Statement I** Acetylene on reacting with sodamide gives sodium acetylide and ammonia.

Statement II *sp* hybridised carbon atoms of acetylene are considerably electronegative.

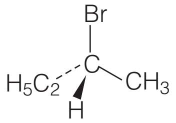
40 **Statement I** Both toluene and *iso*-propyl benzene give the same product on oxidation with $KMnO_4$.

Statement II $KMnO_4$ oxidises side aliphatic chain of arenes to —COOH group.

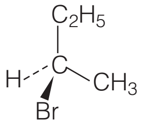
DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The addition of HBr to 1-butene gives a mixture of products *A, B* and *C*



(*A*)



(*B*)

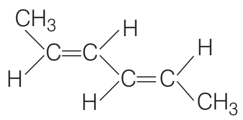
$CH_3CH_2CH_2CH_2Br$
(*C*)

The mixture consists of

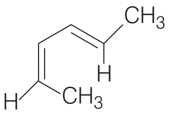
(a) *A* and *B* as major and *C* as minor products
(b) *B* as major, *A* and *C* as minor products
(c) *B* as minor, *A* and *C* as major products
(d) *A* and *B* as minor and *C* as major products

2 The most stable conformer of 2, 4-hexadiene is

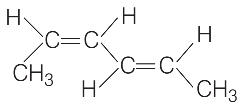
(a)



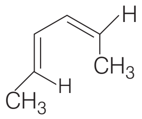
(b)



(c)



(d)



3 When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$, the major product is

(a) propanal
(b) *n*-propyl hydrogen sulphate
(c) acetone
(d) propanol

4 Which of the following reactions will yield 2,2-dibromopropane?

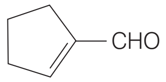
(a) $CH_3C{\equiv}CH + 2HBr \rightarrow$
(b) $CH_3CH{=}CHBr + HBr \rightarrow$
(c) $CH{\equiv}CH + 2HBr \rightarrow$
(d) $CH_3CH{=}CH_2 + HBr \rightarrow$

5 896 mL vapour of a hydrocarbon '*A*' having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of '*A*' gives 2-methylpentane. Also '*A*' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone '*B*' having molecular formula $C_6H_{12}O$. The ketone '*B*' gives a positive iodoform test. Find the structure of '*A*'.

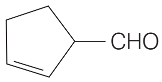
(a) $(CH_3)_3CC{\equiv}C{-}CH_2CH_3$
(b) $(CH_3)_2CHCH_2C{\equiv}CH$
(c) $CH_3CH_2C{\equiv}CCH_2CH_2CH_2CH_3$
(d) $(CH_3)_2CHCH_2CH_2C{\equiv}CH$

6 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound *E*. Compound *E* on further treatment with aqueous KOH yields compound *F*. Compound *F* is

(a)



(b)



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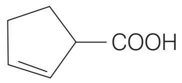
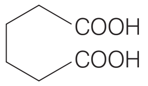
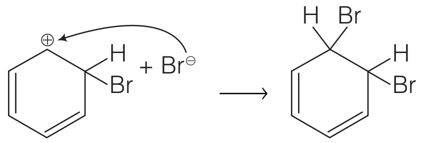


(d)



7 Select the correct statement(s).

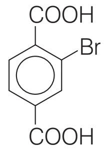
(a) Addition of Br^- in the following leads to the loss of resonance energy that is associated with the aromatic ring.



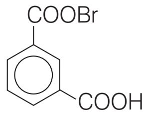
(b) The π-system of the benzene ring is the nucleophile
(c) The sulphur atom in SO_3 is electrophilic by virtue of the formal positive charge in each of the resonance structures
(d) All of the above statements are correct

8 An organic compound, C_9H_{12} *A* can be oxidised with $KMnO_4$ to *B* having molecular formula $C_8H_6O_4$. *B* is a dicarboxylic acid but does not form inner anhydride on heating. *B* on treating with Br in presence of iron gives only one monoderivative *C*, $C_8H_5BrO_4$. What is the structure of compound *C* ?

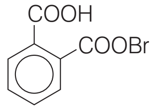
(a)



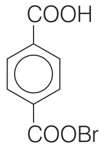
(b)



(c)

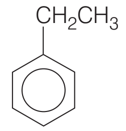


(d)



9 Which of the following compounds is expected to give the highest ratio of *ortho*/*para*-isomer (relatively more *ortho*) when reacted with Cl_2 / $FeCl_3$?

(a)



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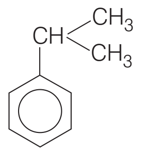

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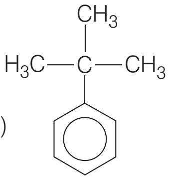
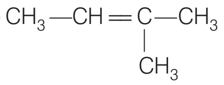


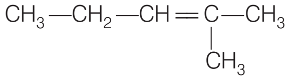
(d) They would all give the *meta*-isomer

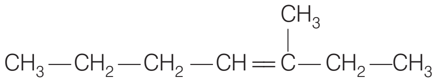
10 When 1, 1-dichloropropane and 2, 2-dichloropropane are reacted separately with *aq*. KOH solution, compounds '*A*' and '*B*' are formed. Both '*A*' and '*B*' gave the same product '*C*' on reduction using amalgamated zinc and HCl. Identify *C*.

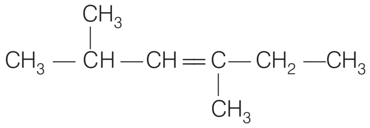
(a) Propyl alcohol (b) Isopropyl alcohol
(c) Propyl chloride (d) Propane

11 A hydrocarbon '*A*' on ozonolysis gives two isomeric forms '*B* ' and '*C* '. *B* on oxidation gives '*D*', silver salt of *D* contains 59.6% Ag. Structure of hydrocarbon is

(a) 
$CH_3—CH{=}\underset{\substack{|\\CH_3}}{C}—CH_3$

(b) 
$CH_3—CH_2—CH{=}\underset{\substack{|\\CH_3}}{C}—CH_3$

(c) 
$CH_3—CH_2—CH_2—CH{=}\overset{\substack{CH_3\\|}}{C}—CH_2—CH_3$

(d) 
$CH_3—\overset{\substack{CH_3\\|}}{CH}—CH{=}\underset{\substack{|\\CH_3}}{C}—CH_2—CH_3$

12 Two gases *P* and *Q* decolourise aqueous bromine but only one of them gives a white precipitate with aqueous ammoniacal silver nitrate solution. *P* and *Q* are likely to be

(a) ethane and ethyne
(b) but-1-yne and but-2-yne
(c) ethane and but-2-yne
(d) ethyne and propyne

ANSWERS

SESSION 1	**1** (d)	**2** (b)	**3** (b)	**4** (c)	**5** (d)	**6** (d)	**7** (b)	**8** (d)	**9** (d)	**10** (c)
	11 (c)	**12** (a)	**13** (c)	**14** (b)	**15** (d)	**16** (a)	**17** (a)	**18** (b)	**19** (b)	**20** (c)
	21 (b)	**22** (b)	**23** (d)	**24** (b)	**25** (d)	**26** (c)	**27** (b)	**28** (b)	**29** (b)	**30** (b)
	31 (c)	**32** (b)	**33** (a)	**34** (b)	**35** (a)	**36** (a)	**37** (a)	**38** (c)	**39** (a)	**40** (a)
SESSION 2	**1** (a)	**2** (a)	**3** (c)	**4** (a)	**5** (b)	**6** (a)	**7** (d)	**8** (a)	**9** (a)	**10** (d)
	11 (b)	**12** (b)								

Hints and Explanations

SESSION 1

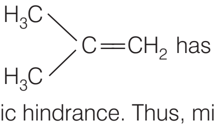
1 Using Pd/H_2, but-1-ene can be converted to butane.

2 The reactivity of reduction of alkyl halides with Zn/HCl increases with the decrease in the strength of C—*X* bond. Therefore, reactivity order will be *R*—Cl < *R*—Br < *R*—I.

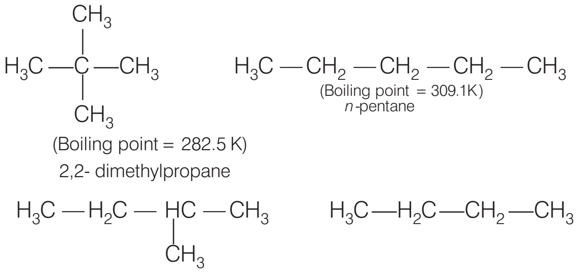
3 Propane will not formed as in Wurtz reaction two molecules of each reacting species combine with the removal of Na*X*.

4 Pure methane can be produced from sodalime decarboxylation.

$$CH_3CO\overset{-}{O}\overset{+}{Na} + NaOH \xrightarrow[\Delta]{\text{Sodalime}} CH_4 + Na_2CO_3$$

5 *Iso*-butene  $\begin{matrix}H_3C\diagdown\\ \quad C{=}CH_2\\ H_3C\diagup\end{matrix}$ has minimum force of attraction due to steric hindrance. Thus, minimum boiling point.

6 As the number of carbon atom increases, boiling point increases. Moreover, boiling point decreases with branching as shown below:



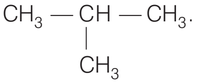
$H_3C—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—CH_3$
(Boiling point = 282.5 K)
2,2- dimethylpropane

$H_3C—CH_2—CH_2—CH_2—CH_3$
(Boiling point = 309.1K)
n-pentane

$H_3C—H_2C—\underset{\substack{|\\CH_3}}{HC}—CH_3$
Boiling point = 301 K
2- methylbutane

$H_3C—H_2C—CH_2—CH_3$
Boiling point = 273K
n-butane
(4 carbon atoms with no branching)

Thus, the correct order of boiling point is *C* > *B* > *D* > *A*.

7 *Iso*-butane is  $CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_3$.

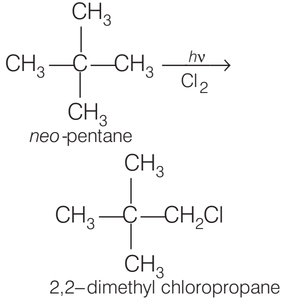
Its chlorination would give two isomers.

$$\frac{1° \text{ isomer}}{3° \text{ isomer}} = \frac{\text{number of } 1° \text{ H}}{\text{number of } 3° \text{ H}} \times \frac{\text{reactivity of } 1° \text{ H}}{\text{reactivity of } 3° \text{ H}} = \frac{9}{1} \times \frac{1}{5} = \frac{9}{5}$$

[∵ The relative reactivities of 3°, 2° and 1° H-atoms are 5.0 : 3.8 : 1] (percentage of 1° isomer)

$$= \frac{9}{9+5} \times 100 = 64.3\% \simeq 64\%$$

8 In *neo*-pentane, all H are equivalent. Thus, it forms only one monochloroalkene



neo-pentane

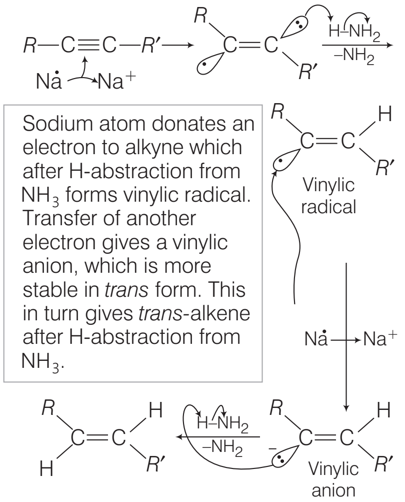
2,2−dimethyl chloropropane

9 The structure in which bulkier groups (which is Me group here) occupy equatorial positions is more stable than the one in which bulkier group are at axial positions. Here, the order of stability is III > I ≈ II > IV.

10 Anti-staggered conformation is most stable. Hence, option (c) is correct.

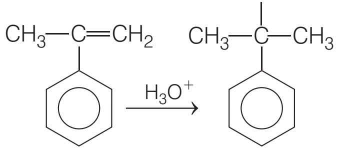
11 Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.

Mechanism



Sodium atom donates an electron to alkyne which after H-abstraction from NH_3 forms vinylic radical. Transfer of another electron gives a vinylic anion, which is more stable in *trans* form. This in turn gives *trans*-alkene after H-abstraction from NH_3.

12 Acidic hydration of 2-phenylpropene follows electrophilic reaction mechanism forming an intermediate 3° carbocation (more stable), thereby forming 2-phenyl propan-2-ol.



2-phenylpropene 2-phenyl propan-2-ol

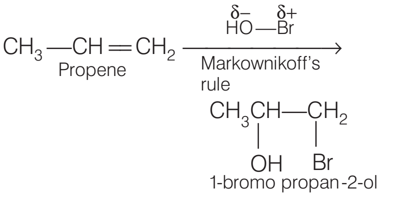
13 Acid catalysed hydration of alkenes involve formation of carbocation intermediate. Higher the stability of carbocation intermediate, more is the reactivity towards acid catalysed hydration. The order of stability of carbocation is

$$(CH_3)_2\overset{+}{C}CH_3 > CH_3\overset{+}{C}HCH_3 > \overset{+}{C}H_2CH_3$$

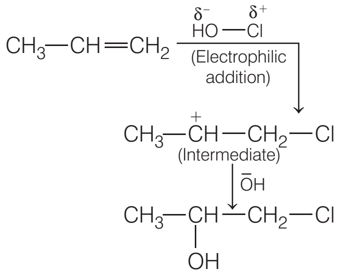
∴ The order of reactivity towards acid catalysed hydration is

$$\underset{I}{(CH_3)_2C=CH_2} > CH_3CH=CH_2 . \cancel{>} \underset{III}{CH_2=CH_2}.$$

14 Peroxide effect (or free radical addition) occurs only in the case of HBr. The addition of HCl in the presence or absence of peroxides occur by an ionic mechanism.

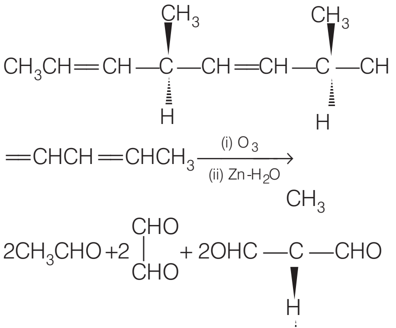
15 

$$\underset{\text{Propene}}{CH_3-CH=CH_2}\xrightarrow[\text{Markownikoff's rule}]{\overset{\delta-}{HO}-\overset{\delta+}{Br}}\underset{\text{1-bromo propan-2-ol}}{CH_3\underset{OH}{CH}-\underset{Br}{CH_2}}$$

16 

$$CH_3-CH=CH_2\xrightarrow[\text{(Electrophilic addition)}]{\overset{\delta^-}{HO}-\overset{\delta^+}{Cl}}\underset{\text{(Intermediate)}}{CH_3-\overset{+}{C}H-CH_2-Cl}\xrightarrow{\bar{O}H}CH_3-\underset{OH}{CH}-CH_2-Cl$$

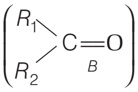
17 Ozonolysis of the given triene occurs as follows :



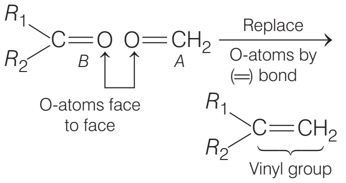
Since, none of the above dial is chiral, no optically active product is obtained.

18 Alkenes give carbonyl compounds on ozonolysis.

$$\text{Alkene}\xrightarrow[\text{Vinyl group}]{O_3/Zn/H_2O}\underset{A}{HCHO}+\text{other}$$
carbonyl compound



To determine alkene, place carbonyl compounds with their O-atom face to face. Replace O-atom by a double bond.



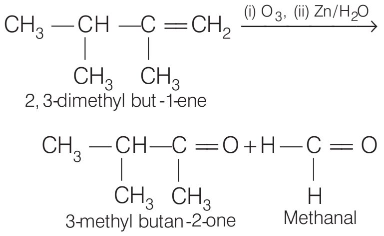
Thus, formation of HCHO confirms the presence of vinyl group.

19 $C_nH_{2n}O = 44$ $C_nH_{2n} = 44 - 16 = 28$

∴ $n = 2$

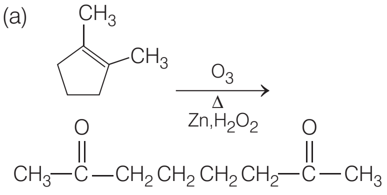
So, $CH_3-CH=CH-CH_3$ is the symmetrical alkene.

$$\text{Thus, }\underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3}\xrightarrow[\text{ii. }Zn/H_2O]{\text{i. }O_3}\underset{\text{Acetaldehyde}}{2CH_3-CH=O}$$

20 

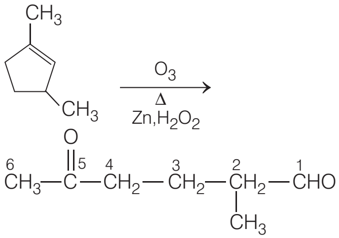
$$\underset{\text{2, 3-dimethyl but-1-ene}}{CH_3-\underset{CH_3}{CH}-\underset{CH_3}{C}=CH_2}\xrightarrow{\text{(i) }O_3,\text{ (ii) }Zn/H_2O}\underset{\text{3-methyl butan-2-one}}{CH_3-\underset{CH_3}{CH}-\underset{CH_3}{C}=O}+\underset{\text{Methanal}}{H-\underset{H}{C}=O}$$

21 (a)



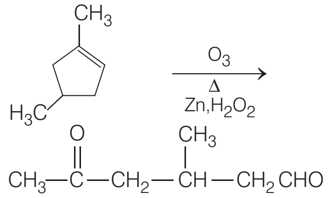
Heptane-2, 6-dione

(b)

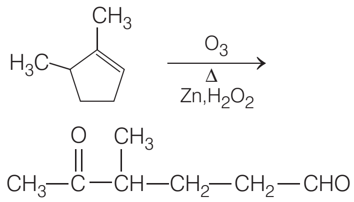


5-keto-2-methylhexanal

(c)



5-keto-3-methylhexanal

(d) 

$\overset{O}{\overset{\|}{CH_3—C}}—\overset{CH_3}{\overset{|}{CH}}—CH_2—CH_2—CHO$

5-keto-4-methyl hexanal

22 General reaction for the combustion of alkene is

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

Given, 6L alkene require $O_2 = 27$ L

$\therefore$ 1 L alkene will require $O_2 = \frac{27}{6}$ L = 4.5 or $\frac{9}{2}$ L

On comparing the amount of O_2,

$$\frac{3n}{2} = \frac{9}{2}$$

$\therefore \quad 3n = 9$

or $\quad n = 3$

On putting the value of n in general formula of alkene, we get $C_3H_{2\times3} = C_3H_6$. Hence, the alkene is propene $(CH_3CH{=}CH_2)$.

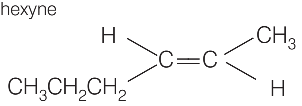
23 Acetylene does not react with NaOH. It reacts with other given reagents as follows:

$$CH\equiv CH + Na \longrightarrow CH\equiv C^{\ominus}Na^{\oplus} + \frac{1}{2}H_2$$

$$CH\equiv CH + \underset{\text{(Ammoniacal)}}{AgNO_3} \longrightarrow \underset{\text{White ppt.}}{CH\equiv C^{\ominus}Ag^{\oplus}}$$

$$CH\equiv CH + HCl \longrightarrow CH_2{=}CH—Cl$$

24 $\underset{\text{2-hexyne}}{CH_3CH_2CH_2—C\equiv C—CH_3} \xrightarrow{Li/NH_3}$

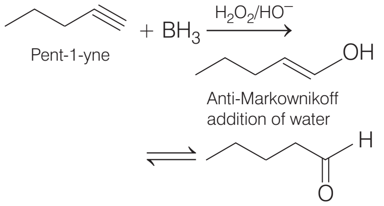


trans-2-hexene

2-hexyne $\xrightarrow{(a)\ Pt/H_2}$ *n*-hexane

$\xrightarrow{(c)\ Pd/BaSO_4}$ *cis*-2-hexene

$\xrightarrow{(d)\ LiAlH_4}$ no reaction

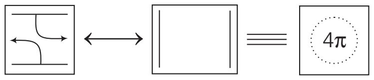
25 

26 $\underset{\text{1-butyne}}{CH_3CH_2C\equiv CH} \xrightarrow{\text{Hot } KMnO_4} CH_3CH_2COOH + HCOOH$

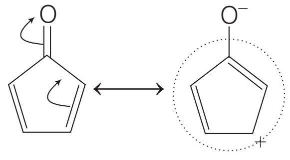
$$HCOOH \longrightarrow CO_2 + H_2O$$

27 A $\longrightarrow$ 4, B $\longrightarrow$ 1, C $\longrightarrow$ 2, D $\longrightarrow$ 3

28 According to Huckel rule, the compounds which have $4n$ (n = 0, 1, 2, 3,) delocalised π-electrons in a close-loop are anti aromatic and characteristically unstable. Compound '*B*' satisfy the criteria of anti-aromaticity as

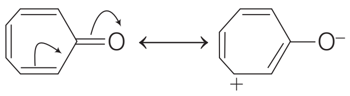


Compound *C* is anti-aromatic in its resonance form



Antiaromatic

Compound '*A*' has 4π-electrons which are also delocalised but do not constitute close loop, hence, non-aromatic. Compound '*D*' is aromatic, characteristically stable.



Tropium ion (Aromatic)

29 Mesitylene (1, 3, 5-trimethylbenzene) has three *m*-xylene (1, 3-dimethylbenzene) has two while toluene has only one electron donating —CH_3 group. Therefore electron density is maximum in mesitylene and hence, it is most reactive towards ring nitration.

30 Due to greater electron releasing effect of methyl group in case of *o*-methylphenol, it is most reactive towards electrophilic reagent.

31 Conversion of benzene into *m*- bromoaniline can be done by successive nitration, bromination and reduction using following reagent.

Nitration $\longrightarrow$ conc.HNO_3 / conc.H_2SO_4

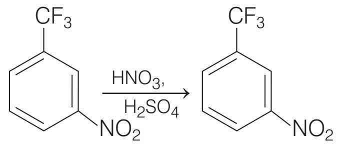
Bromination $\longrightarrow$ Br_2 / H_2O

Reduction $\longrightarrow$ Sn / HCl

32 Since, NO_2 group is a powerful electron withdrawing group therefore, carbocations given in options (a), (c) and (d) are destabilised. However, in carbocation (b), there is no —NO_2 group. Thus, σ-complex (b) is of lowest energy.

33 Presence of electron releasing groups, (like —*R*) increases the electron density over benzene nucleus and makes it more reactive towards electrophile. Electron withdrawing groups (like Cl^-, NO_2^-; NO_2^- is more electron withdrawing than Cl^-) make the benzene nucleus electrons deficient and hence, decrease its reactivity towards electrophile.

Hence, the correct order of reactivity towards electrophilic substitution reaction will be II > I > III > IV.

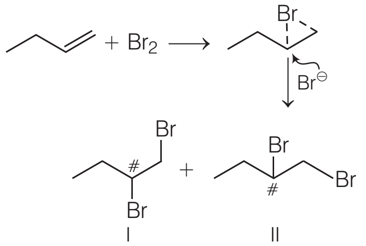
34 

Since, CF_3 is deactivating and *meta*-directing group.

35 Cyclooctatetraene has a tub like structure. It loses planarity. Number of πe^- delocalised = 8. Hence, according to Huckel rule of aromaticity it is a non-aromatic compound.

36 In nitration of benzene with conc. nitric acid, conc. sulphuric acid acts as a calatyst. It helps in the formation of electrophile, i.e. nitronium ion NO_2^+.

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

37 

I and II are optical isomers.
denote chiral carbon.

38 1-butene on reaction with HBr in presence of peroxide produces 1-bromobutane. In this reaction, the intermediate product is secondary free radical.

(i) (a) $(C_6H_5CO)_2O_2 \longrightarrow 2C_6H_5COO^{\bullet}$

(b) $C_6H_5COO^{\bullet} + HBr \longrightarrow C_6H_5COOH + Br^{\bullet}$

(ii) $CH_3CH_2CH{=}CH_2 + Br^{\bullet} \longrightarrow CH_3CH_2\dot{C}HCH_2Br$

(iii) $CH_3CH_2\dot{C}HCH_2Br + HBr \longrightarrow CH_3CH_2CH_2CH_2Br + Br^{\bullet}$

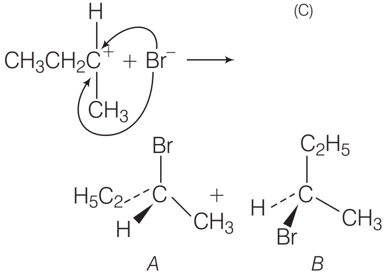
39 Acetylene is acidic due to the presence of *sp* hybridised carbon which makes it more electronegative hence, with strong base it undergo elimination of H^+.

40 Alkyl substituent (having H-atom at α-carbon) at phenyl ring undergo oxidation to produce benzoic acid always.

SESSION 2

1 $CH_3CH_2CH{=}CH_2 + H^+ \longrightarrow \underset{\substack{2^\circ\text{ (planar)}\\\text{(more stable major)}}}{CH_3CH_2\overset{+}{C}H-CH_3} + \underset{\substack{1^\circ\\\text{(less stable)}}}{CH_3CH_2CH_2-\overset{+}{C}H_2}$

$CH_3CH_2CH_2\overset{+}{C}H_2 + Br^- \longrightarrow \underset{(C)}{CH_3CH_2CH_2CH_2Br}$

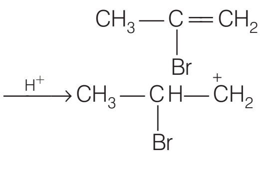


(major products)

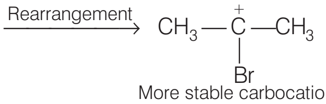
2 *trans-trans* conformer, i.e. (a) is most stable due to minimum steric hindrance.

3 $CH_3C{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} [CH_3C(OH){=}CH_2] \xrightarrow{\text{Tautomerisation}} \underset{\text{Acetone}}{CH_3COCH_3}$

4 $CH_3-C{\equiv}CH + HBr \longrightarrow$



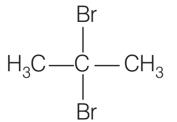
$CH_3-\underset{Br}{\underset{|}{C}}{=}CH_2 \xrightarrow{H^+} CH_3-\underset{Br}{\underset{|}{C}}H-\overset{+}{C}H_2$



$\xrightarrow{\text{Rearrangement}} CH_3-\underset{Br}{\underset{|}{\overset{+}{C}}}-CH_3$

More stable carbocation

$\xrightarrow{Br^-}$



$H_3C-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$

2, 2- dibromopropane

$CH_3-CH{=}CHBr \xrightarrow{HBr} CH_3-CH_2-CHBr_2$

$CH{\equiv}CH \xrightarrow{2HBr} CH_3CHBr_2$

$CH_3-CH{=}CH_2 \xrightarrow{HBr} CH_3-CHBr-CH_3$

7. (i) Determination of empirical formula of hydrocarbon *A*

Element	Percentage	Atomic mass	Relative ratio	Relative number of atoms	Simplest ratio
C	87.8	12	$\frac{87.8}{12} = 7.31$	$\frac{7.31}{7.31} = 1$	$1 \times 3 = 3$
H	12.19	1	$\frac{12.19}{1} = 12.19$	$\frac{12.19}{7.31} = 1.66$	$1.66 \times 3 = 5$

$\therefore$ Empirical formula of hydrocarbon $(A) = C_3H_5$

Empirical formula mass $= 12 \times 3 + 5 \times 1 = 41\,u$

(ii) Determination of molecular mass of hydrocarbon (*A*)

896 mL vapours of hydrocarbon (*A*) weigh at STP = 3.28 g

$\therefore$ 22400 mL vapours of *A* will weigh at STP

$$= \frac{3.28 \times 22400}{896}\ \text{g mol}^{-1} = 82\ \text{g}$$

$\therefore$ Molecular mass of hydrocarbon $(A) = 82\ \text{g mol}^{-1}$

(iii) Determination of molecular formula of hydrocarbon *A*.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{82}{41} = 2$$

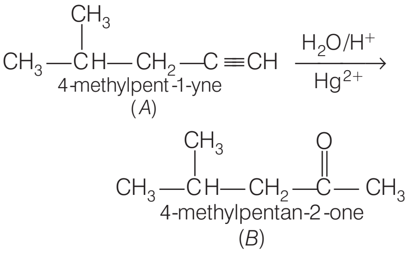
Therefore, molecular formula of hydrocarbon

$(A) = n \times$ Empirical formula

$= 2 \times C_3H_5 = C_6H_{10}$

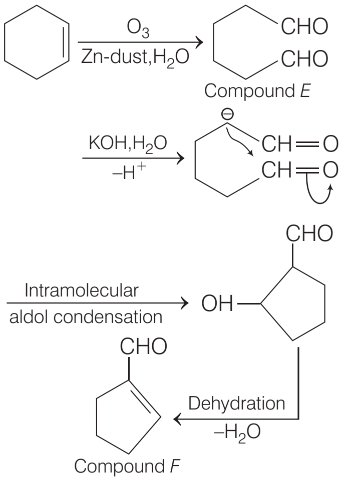
Since, hydrogenation of *A* gives 2-methyl pentane therefore compound '*A*' have 5 carbon atoms in straight chain. It should be an alkyne because compound '*A*' adds a molecule of H_2O in the presence of Hg^{2+} and H^+ to give a ketone '*B*'. Ketone '*B*' gives iodoform test so it should be a methyl ketone.

Therefore, the structures of compound *A* and compound *B* are as follows



$\underset{\substack{\text{4-methylpent-1-yne}\\(A)}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-C{\equiv}CH} \xrightarrow[Hg^{2+}]{H_2O/H^+} \underset{\substack{\text{4-methylpentan-2-one}\\(B)}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$

6



7 (a) Aromatic character in the product is lost due to addition, thus (a) is true.

(b) Sextet of benzene ring is electron rich, thus act as nucleophile. Thus, (b) is true.

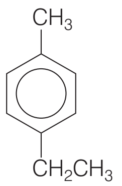
(c) Sulphur carries positive charge due to resonance, thus option (d) is true.

8 (i) *A* on oxidation yields dicarboxylic acid, thus it should have two side chains on benzene ring.

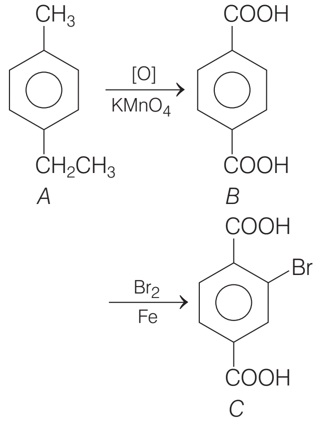
(ii) *B* does not form inner anhydride, thus *B* is not an *ortho* carboxylic acid.

(iii) *B* on bromination gives only one product and thus, '*B*' should be *para*-derivative. Thus, *B* is *p*-benzene dicarboxylic acid.

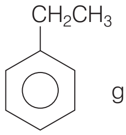
(iv) The above facts and molecular formula of '*A*' suggest that *A* is



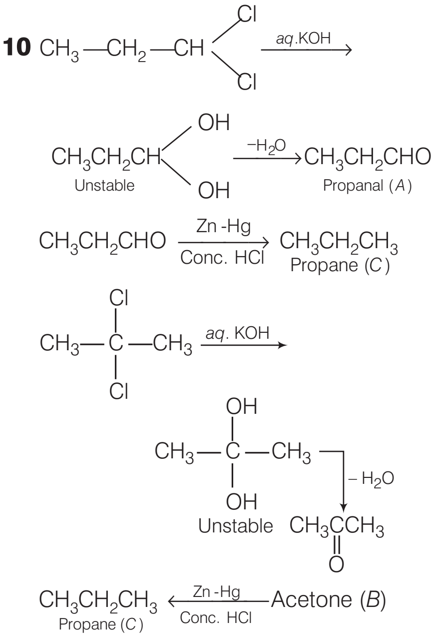
(v) The reactions are



9 Bulky group decreases the proportion of *ortho*-isomer.

Thus,  give the highest ratio of *o*/*p* isomer when reacted with $Cl_2/FeCl_3$.

10



$$CH_3—CH_2—CHCl_2 \xrightarrow{aq.KOH} \underset{\text{Unstable}}{CH_3CH_2CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Propanal }(A)}{CH_3CH_2CHO}$$

$$CH_3CH_2CHO \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} \underset{\text{Propane }(C)}{CH_3CH_2CH_3}$$

$$CH_3—CCl_2—CH_3 \xrightarrow{aq.\ KOH} \underset{\text{Unstable}}{CH_3—C(OH)_2—CH_3} \xrightarrow{-H_2O} CH_3\overset{O}{\overset{\|}{C}}CH_3$$

$$\underset{\text{Propane }(C)}{CH_3CH_2CH_3} \xleftarrow[\text{Conc. HCl}]{\text{Zn-Hg}} \text{Acetone } (B)$$

11 Molecular mass of *R*COOAg

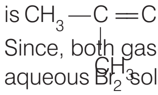
$$= \frac{108}{59.6} \times 100 = 181$$

$$RCOOH = RCOOAg - 108 + 1 = 74$$

Thus, acid *R*COOH is $CH_3—CH_2—COOH$ *(D)*.

Since, *D* is $CH_3—CH_2—COOH$, '*B*' will be $CH_3—CH_2—CH{=}O$ and hence, '*C*' will be

$$(CH_3)_2—C{=}O$$

On the basis of ozonolysis product *B* and *C*, we can say that hydrocarbon '*A*' is 

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

12 Since, both gases *P* and *Q* decolourise aqueous Br_2 solution, therefore both are unsaturated. Since, one of them gives a white ppt with ammoniacal $AgNO_3$ solution while the other does not, one of them is a terminal alkyne (but-1-yne), while the other is a non-terminal alkyne (but-2-yne).