DAY SIXTEEN

Hydrocarbons

Learning & Revision for the Day

- Alkanes
- Conformations
- Alkenes
- Alkynes
- Aromatic Hydrocarbons
- Benzene

Hydrocarbons means compounds containing carbon and hydrogen only. Single bond containing hydrocarbons is saturated hydrocarbon and multiple bond hydrocarbons are called **unsaturated hydrocarbon**.

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

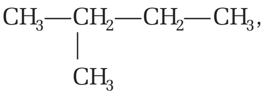
- These are the simplest organic compounds formed by carbon and hydrogen only. Chemically, these are almost inert that's why also called **Paraffins** (Latin, *Parum affinis* = Little affinity). The general formula for this series is C_nH_{2n+2}. Hence, the first member is CH_4 (methane).
- **Nomenclature** Alkanes are named on the basis of their chain structure and adding suffix 'ane' in the end. IUPAC names of some simple alkanes are given below :

Molecular Formula	IUPAC Name
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Decane	$C_{10}H_{22}$

- **Isomerism** Alkanes exhibit only chain isomerism. e.g. possible chain isomers of C_5H_{12} ar as follows :

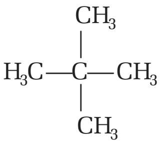
$CH_3—CH_2—CH_2—CH_2—CH_3$,

Pentane



$CH_3—\underset{CH_3}{\underset{|}{CH}_2}—CH_2—CH_3$,

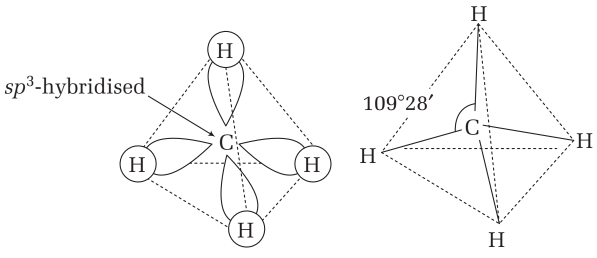
2–methylbutane



$H_3C—\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—CH_3$

2,2-dimethyl propane

- **Structure** All the carbon-carbon bonds in alkanes are sp^3-sp^3 hybridised where σ-bond is quite strong. They have three dimensional structures where all the four bonds are tetrahedrally arranged making a normal angle of $109°28'$, e.g. in CH_4, the carbon at the centre is bonded by four hydrogen atoms, where all the bonds lie in different planes giving it a three dimensional structure.



Structures of methane (CH_4) molecule

Methods of Preparation

These can be prepared by the following ways :

- Unsaturated hydrocarbons (alkenes or alkynes), reduction in the presence of finely divided catalyst (e.g. Pt/Pd/Ni) give alkanes. This reaction is known as **Sabatier-Sanderens** reduction.

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

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

- Alkyl halides (except fluorides) on reduction give alkanes in the presence of Zn and HCl.

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

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

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

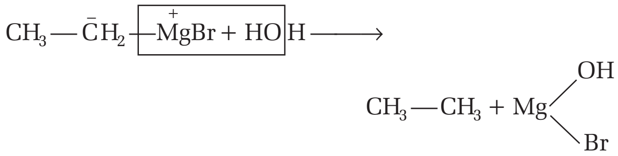
- Sodium salt of carboxylic acid (RCOONa) is heated with hot sodalime ($CaO + NaOH$) to give alkane and this reaction is called as **decarboxylation**.

$$CH_3COONa + NaOH \xrightarrow[\Delta]{\text{CaO}} CH_4 + Na_2CO_3$$

- Sodium or potassium salt of carboxylic acid on electrolysis gives alkane ($R{-}R$). This reaction is known as **Kolbe's electrolysis method.**

$$2CH_3COONa + 2H_2O \xrightarrow{\text{Electrolysis}} \underbrace{C_2H_6 + 2CO_2\uparrow}_{\text{Anode}} + \underbrace{H_2 + 2NaOH}_{\text{Cathode}}$$

- Grignard reagent (RMgX) when reacts with H_2O or ROH, gives alkane.



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

- 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 **methanoids**.

Physical Properties

Physical properties depend upon the intermolecular forces of attraction.

(i) **Boiling point** of alkanes increases steadily with increase in molecular mass. If molecular mass is same, as the contact surface area increases, boiling point increases. More branched chain has less contact surface area so, less has boiling point.

(ii) **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.

(iii) **Solubility** of a compound is governed by the principle that like dissolves like. As alkanes are non-polar, therefore soluble in non-polar solvents such as petroleum, benzene etc.

(iv) 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

Alkanes being saturated compounds undergo only substitution reactions at C—H bond. Some of these are discussed below :

Halogenation

- Halogenation of alkanes is a free radical substitution reaction which occurs in the presence of UV- light. Reactivity towards halogenation is

$$3°H > 2°H > 1°H$$

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow{Cl_2/h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} \xrightarrow{Cl_2/h\nu} \underset{\substack{\text{Trichloro}\\\text{methane}}}{CHCl_3} \xrightarrow{Cl_2/h\nu} \underset{\substack{\text{Tetrachloro}\\\text{methane}}}{CCl_4}$$

- Bromination and chlorination proceed approx by same way. Iodination is reversible but fluorination of alkanes is too vigorous.

Mechanism

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

(i) In **initiation** step, the homolysis of chlorine molecule takes place in the presence of light or heat.

$$Cl{-}Cl \xrightarrow[\text{Homolysis}]{h\nu} \underset{\substack{\text{Chlorine free}\\\text{radicals}}}{\overset{\bullet}{Cl} + \overset{\bullet}{Cl}}$$

(ii) In **propagation** step, chlorine free radical reacts with methane molecule and generates methyl free radical.

$$CH_4 + \overset{\bullet}{Cl} \xrightarrow{h\nu} \overset{\bullet}{C}H_3 + H—Cl$$

$$\overset{\bullet}{C}H_3 + Cl—Cl \xrightarrow{h\nu} CH_3—Cl + \overset{\bullet}{Cl}$$

$$CH_3Cl + \overset{\bullet}{Cl} \longrightarrow \overset{\bullet}{C}H_2Cl + HCl$$

$$\overset{\bullet}{C}H_2Cl + Cl—Cl \longrightarrow CH_2Cl_2 + \overset{\bullet}{Cl}$$

(iii) **Termination** step occurs as follows :

$$\overset{\bullet}{Cl} + \overset{\bullet}{Cl} \longrightarrow Cl—Cl$$

$$H_3\overset{\bullet}{C} + \overset{\bullet}{C}H_3 \longrightarrow CH_3—CH_3$$

$$H_3\overset{\bullet}{C} + \overset{\bullet}{Cl} \longrightarrow CH_3—Cl$$

Due to consumption of free radicals, chain is terminated.

Combustion

- Complete 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 fillers in tyre industry.

$$CH_4(g) + O_2(g) \xrightarrow[\text{combustion}]{\text{Incomplete}} C(s) + 2H_2O(l)$$

- On **controlled oxidation**, alkanes give different products as :

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

$$CH_4 + O_2 \xrightarrow{MoO,\ \Delta} \underset{\text{Methanal}}{HCHO} + H_2O$$

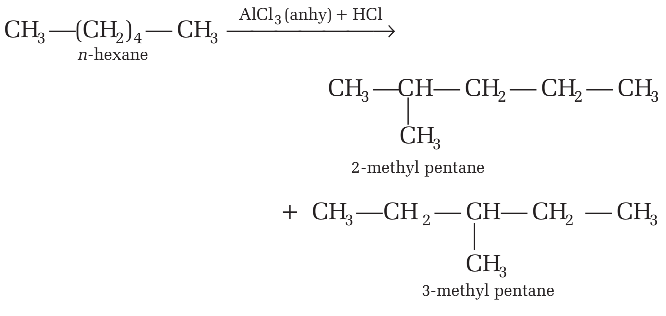
$$2CH_3—CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$$

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

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

Isomerisation

n-alkane on heating in the presence of $AlCl_3$ (anhydrous) and $HCl(g)$ isomerises to give branched chain alkanes. This reaction is called **isomerisation**.



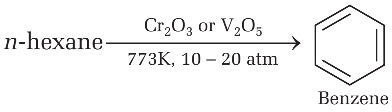
$$\underset{n\text{-hexane}}{CH_3—(CH_2)_4—CH_3} \xrightarrow{AlCl_3\,(anhy) + HCl} \underset{\text{2-methyl pentane}}{CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_2—CH_2—CH_3} + \underset{\text{3-methyl pentane}}{CH_3—CH_2—\underset{\substack{|\\CH_3}}{CH}—CH_2—CH_3}$$

Aromatisation

Aromatisation take place when alkanes get converted into benzene in the presence of Cr_2O_3 or V_2O_5.

It is applicable to alkanes from hexane to decane.

e.g.



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

Benzene

Reaction with Steam

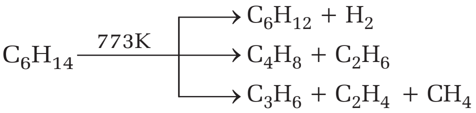
Alkanes reacts with **steam** as follows :

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

This method is used for industrial preparation of H_2 gas.

Pyrolysis or Cracking

Pyrolysis or cracking is a process in which higher alkanes on heating to higher temperature decompose into lower alkanes.



$$C_6H_{14} \xrightarrow{773K} C_6H_{12} + H_2$$

$$C_6H_{14} \xrightarrow{773K} C_4H_8 + C_2H_6$$

$$C_6H_{14} \xrightarrow{773K} C_3H_6 + C_2H_4 + CH_4$$

Octane Number

The quality of petrol or gasoline is measured in terms of octane number while that of diesel is measured in terms of cetane number. Octane number gives the percentage of *iso*-octane (by volume) in a mixture of n-heptane and *iso*-octane while cetane number gives the percentage of octane (by volume) in a mixture of octane ($C_{16}H_{34}$) and α-methyl naphthalene.

Conformations (or Rotamers or Conformers)

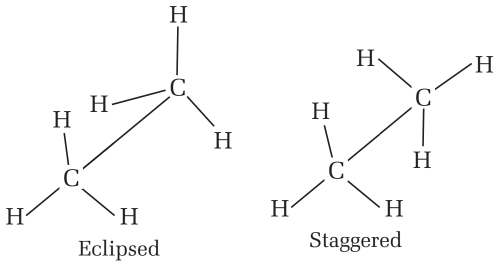
Spatial arrangements of atoms which can be converted into one another by rotation around a C—C single bond.

Ethane has three main conformations:

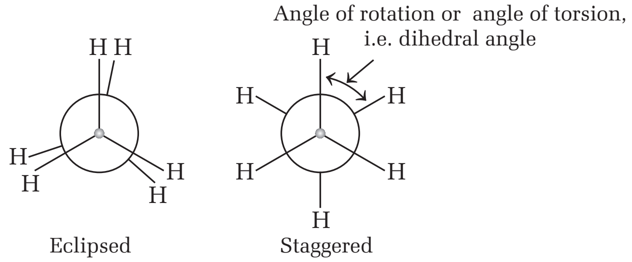
(i) **Eclipsed conformations** are those in which the hydrogen atoms attached to two carbons are as closed together as possible. This conformation is highly unstable and has maximum energy.

(ii) **Staggered conformations** are those in which hydrogens are as far apart as possible. It is highly stable and has minimum energy.

(iii) **Skew conformation** is an intermediate conformation of the above two conformations.



Sawhorse projection of ethane



Newman projection 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

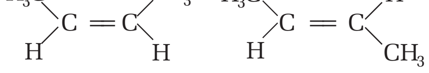
- These are unsaturated hydrocarbons containing at least one double bond. Their general formula is C_nH_{2n}.
- **Nomenclature** Following rules are followed for nomenclature of alkenes in IUPAC system.
  - (i) The longest chain of carbon atom containing double bond is selected.
  - (ii) Numbering of the chain is done from the end nearer to the double bond.
  - (iii) Compound is named by adding suffix 'ene' to the root word.

  IUPAC names of a few members of alkenes are given below :

Structure	IUPAC Name
$\underset{3}{CH_3} - \underset{2}{CH} = \underset{1}{CH_2}$	Propene
$\overset{4}{CH_3} - \overset{3}{CH_2} - \overset{2}{CH} = \overset{1}{CH_2}$	But–1–ene
$\overset{4}{CH_2} = \overset{3}{CH} - \overset{2}{CH} = \overset{1}{CH_2}$	Buta–1,3–diene
$CH_2 = CH - \underset{\substack{\vert \\ CH_3}}{CH} - CH_3$	3–methylbut –1–ene

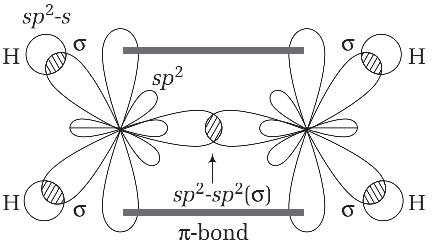
- **Isomerism** Alkenes show structural as well as geometrical isomerism. For exhibiting of geometrical isomerism, restricted rotation of double bond should be present.

e.g.



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

- In **structure of alkenes**, double bond between two carbon atoms. Consists of one strong σ- bond and one weak. π-bond. The orbital diagram of ethene molecule is shown as :

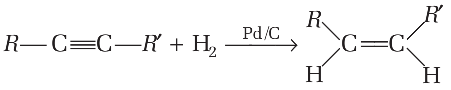


Methods of Preparation

Methods of preparation of alkenes are given below :

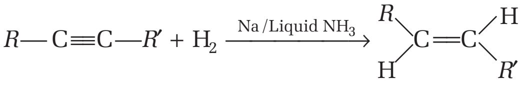
- Alkynes when treated with Lindlar's catalyst$[Pd/C/H_2(g)]$ give *cis*-alkenes while on reduction with Na/liquid NH_3 give *trans*-alkenes.

e.g.



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

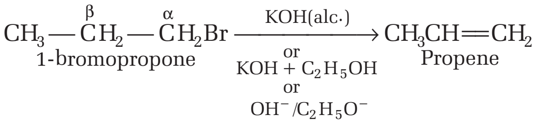
cis-alkene



$R-C\equiv C-R' + H_2 \xrightarrow{Na/Liquid\ NH_3}$

trans -alkene

- Alkyl halides on dehydrohalogenation (β-elimination reaction) give alkenes.



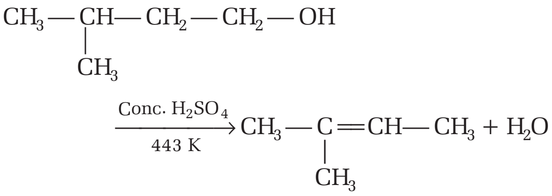
$$\underset{\text{1-bromopropone}}{CH_3-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2Br} \xrightarrow[\substack{\text{or} \\ KOH + C_2H_5OH \\ \text{or} \\ OH^-/C_2H_5O^-}]{KOH(alc.)} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

Ease of reaction

∴ 3° alkyl halide > 2° > 1°.

$RI > RBr > RCl$

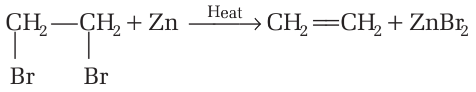
- Alcohols on dehydration give alkenes. In this reaction intermediate carbocation is formed and rearrange, therefore double bond is formed at maximum degree of carbon.



$$CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-CH_2-CH_2-OH \xrightarrow[443\ K]{Conc.\ H_2SO_4} CH_3-\underset{\substack{\vert \\ CH_3}}{C}{=}CH-CH_3 + H_2O$$

- 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.

- *Vicinal* dihalides when treated with zinc metal give alkenes. This reaction is known as **dehalogenation**.



$$\underset{Br}{CH_2}-\underset{Br}{CH_2} + Zn \xrightarrow{Heat} CH_2=CH_2 + ZnBr_2$$

Physical Reaction

The physical properties of alkenes are listed below:

(i) The **melting point** of alkenes do not show regular gradation. Alkenes have higher melting point than corresponding alkanes.

(ii) The **boiling point** of alkenes vary in the same manner as in alkanes. Their boiling points are higher than that of the corresponding alkanes.

(iii) Solubility of a compound is governed by the principle that like dissolves like. Being non-polar, alkenes are quite soluble in **non-polar solvents** such as benzene, CCl_4 etc.

Chemical Reaction

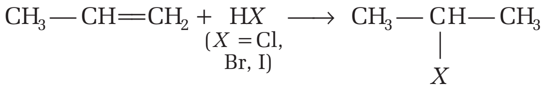
Alkenes show different types of reactions such as:

Electrophilic Addition Reactions

- Symmetrical alkenes undergo addition reaction with **hydrogen halides** (HCl, HBr or HI) to form alkyl halides.

$$\underset{\text{Ethene}}{CH_2=CH_2} + HBr \longrightarrow \underset{\text{Bromoethane}}{H_3C-CH_2Br}$$

In case of unsymmetrical alkenes, addition takes place 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.



$$CH_3-CH=CH_2 + \underset{(X = Cl,\ Br,\ I)}{HX} \longrightarrow CH_3-\underset{X}{CH}-CH_3$$

Mechanism of Electrophilic Addition

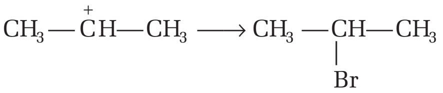
- HBr provides an electrophile, H^+ which attacks the double bond to form carbocation.

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H-Br$$

$$\underset{(1° \text{ carbocation})}{CH_3-CH_2-\overset{+}{C}H_2} + Br^- \text{ (less stable)}$$

$$\underset{(2° \text{ carbocation})}{CH_3-\overset{+}{C}H-CH_3} + Br^- \text{ (more stable)}$$

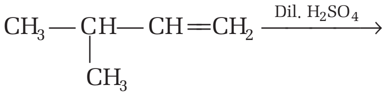
- 2° carbocation is formed at a faster rate and it is attacked by Br^- ion to form product.



$$CH_3-\overset{+}{C}H-CH_3 \longrightarrow CH_3-\underset{Br}{CH}-CH_3$$

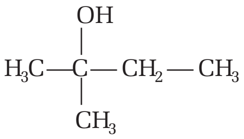
2-bromopropane
major product)

- Alkene when treated with dil. H_2SO_4 gives alcohol and —OH gets attached to that carbon atom which has maximum degree.



$$CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow{\text{Dil. } H_2SO_4}$$

2-methyl-but-1-ene



$$H_3C-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$$

2-methyl butan-2-ol

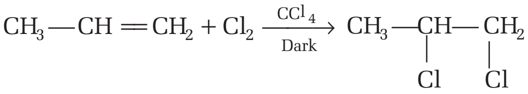
In this reaction intermediate carbocation is formed, which rearrange to form an alcohol.

Free Radical Addition Reactions

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

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

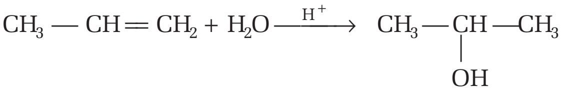
- Alkenes readily undergo **addition reactions with halogens** to give *vicinal* dihalides, such as



$$CH_3-CH=CH_2 + Cl_2 \xrightarrow[\text{Dark}]{CCl_4} CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

1, 2-dibromopropane

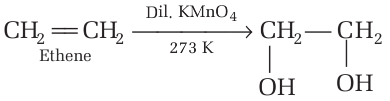
- Alkenes undergo **addition reaction with water** to yield alcohols. This reaction also follow **Markownikoff's addition**.



$$CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{OH}{CH}-CH_3$$

2-propanol

- Cold dilute $KMnO_4$ (Baeyer's reagent) when treated with alkene gives glycol (*vicinal* dihydric alcohol). This is a type of **oxidation reaction** of alkene.



$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[273\text{ K}]{\text{Dil. } KMnO_4} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

Ethan-1, 2-diol
(Ethylene glycol)

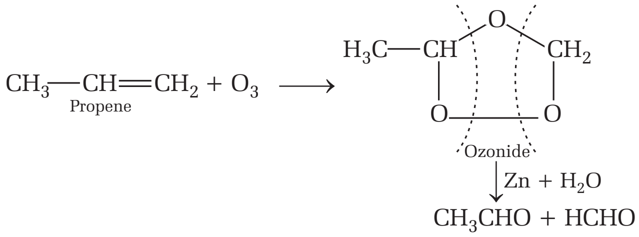
(i) It is a test for unsaturation as purple colour of $KMnO_4$ disappears during the reaction and a brown precipitate of MnO_2 is obtained.

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

$$\underset{\text{2-methyl propene}}{(CH_3)_2C=CH_2} \xrightarrow{KMnO_4/H^+} (CH_3)_2C=O + CO_2 + H_2O$$

- Alkenes undergo addition reaction with hydrogen to form alkanes.

- Alkenes react with ozone to give ozonides, which on further reaction with water in the presence of water gives aldehyde or ketones. This reaction is called **ozonolysis**.



Ozonolysis is used to locate the position of double bond in an alkene.

- Alkenes have the ability to form gaint molecules called polymer and the process is called **polymerisation**.

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

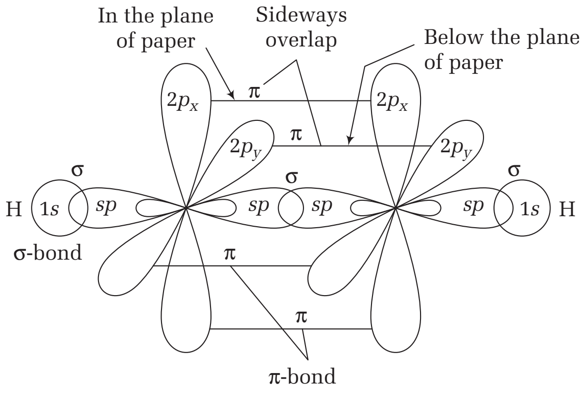
Alkynes

- These are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. Their general formula is C_nH_{2n-2}.
- **Nomenclature** The IUPAC name of alkynes is written by replacing-'ane' of alkane by a suffix -'yne'. The position of triple bond is indicated by arabic numbers, the numbering being started from that end which lies closer to the triple bond.

  Some examples of few member of alkynes with their IUPAC names are given below :

Structure	IUPAC Name
$HC \equiv CH$	Ethyne
$\underset{3}{H_3C}—\underset{2}{C}\equiv\underset{1}{CH}$	Prop–1–yne
$H_3\underset{4}{C}—\underset{3}{C}\equiv\underset{2}{C}—\underset{1}{CH_3}$	But–2–yne
$H_3\underset{1}{C}—\underset{2}{C}\equiv\underset{3}{C}—\underset{4}{CH_2}—\underset{5}{CH_3}$	Pent-2-yne

- **Structure** In structure of alkyne, triple bond is present between two adjacent carbon atom. In triple bond, one C— C bond is σ- bond whereas the remaining two bonds are π-bonds. The structure of ethyne can be shows as :



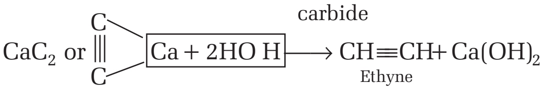
Methods of Preparation

Different methods of preparation of alkynes are as follows :

- Alkyne (ethyne) is obtained by treating calcium carbide with water.

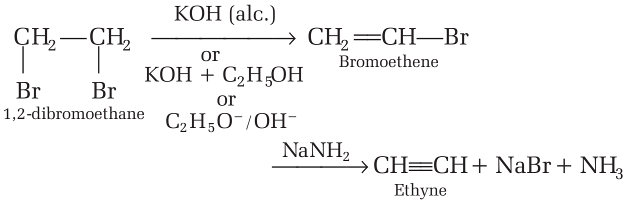
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

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



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

- These are obtained by treating *vicinal* dihalides with alcoholic KOH followed by reaction with sodium amide.



$$\underset{\text{1,2-dibromoethane}}{\underset{Br}{\underset{|}{CH_2}}—\underset{Br}{\underset{|}{CH_2}}} \xrightarrow[\substack{\text{or} \\ KOH + C_2H_5OH \\ \text{or} \\ C_2H_5O^-/OH^-}]{\text{KOH (alc.)}} \underset{\text{Bromoethene}}{CH_2═CH—Br} \xrightarrow{NaNH_2} \underset{\text{Ethyne}}{CH\equiv CH} + NaBr + NH_3$$

- Lower alkynes on treatment with Na metal in liquid NH_3 give the sodium salt. Which further react with primary alkyl halide to give higher alkynes.

$$R—C\equiv CH \xrightarrow{NaNH_2,\ \text{liq. } NH_3} R—C\equiv C—Na \xrightarrow{R'X} R—C\equiv C—R'$$

Physical Properties

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

Chemical Reactions

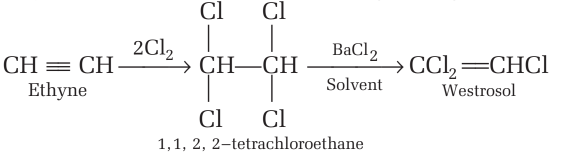
The alkynes exhibit the chemical properties as given below:

Addition Reactions

- Alkynes undergo addition reaction with hydrogen to give alkenes or alkanes.

$$CH\equiv CH + H_2 \xrightarrow{Pt} CH_2═CH_2 + H_2 \xrightarrow{Pt} \underset{\text{(alkane)}}{CH_3—CH_3}$$

- Alkynes gives addition reaction with halogens in which they react with two molecules of halogens to give tetrahalides.



$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow{2Cl_2} \underset{\text{1,1, 2, 2–tetrachloroethane}}{\overset{Cl}{\underset{Cl}{CH}}—\overset{Cl}{\underset{Cl}{CH}}} \xrightarrow[\text{Solvent}]{BaCl_2} \underset{\text{Westrosol}}{CCl_2═CHCl}$$

- **Addition of hydrgen halides** (HCl, HBr or HI) to alkynes follows Markownikoff's addition in case of unsymmetrical alkynes, to give haloalkene or haloalkane.

$$CH\equiv CH + HX \longrightarrow CH_2═CH—X \xrightarrow{HX} CH_3CHX_2$$

$(X = Cl, Br, I)$

- The **addition of water** to alkynes (unsymmetrical) follows Markownikoff's rule to give an adduct called enol which undergo tautomerism to give stable product having carbonyl group.

$$\mathrm{CH{\equiv}CH + H_2O \xrightarrow[1\%,\ HgSO_4]{40\%,\ H_2SO_4} \underset{\text{Vinyl alcohol (enol)}}{CH_2{=}CH{-}OH}}$$

$$\underset{\text{Enol}}{\mathrm{[CH_2{=}CH{-}OH]}} \xrightleftharpoons{\text{Tautomerises}} \underset{\text{Acetaldehyde}}{\mathrm{CH_3CHO}}$$

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

- Terminal alkynes have acidic character because C—H bond has ionic nature due to hybridisation.
  Therefore, alkyne react with strong bases to form salts.

$$\mathrm{CH{\equiv}CH + NaNH_2 \xrightarrow{196\ K} \underset{\text{Sodium acetylide}}{CH{\equiv}\overset{-}{C}\overset{+}{Na}} + NH_3}$$

- **Acidic Nature of Alkynes** Alkynes with terminal H-atom are acidic due to *sp*-hybridisation of C-atom attached to hydrogen.
- Due to **acidic nature of H–atoms**, attached to a triple bond, acetylenes and terminal alkynes, form metal acetylides with heavy metals salts such as Tollen's reagent, Cu_2Cl_2 solution.

$$\mathrm{CH{\equiv}CH + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\substack{\text{Silver acetylide}\\\text{(white ppt.)}}}{AgC{\equiv}CAg\downarrow} + 2H_2O + 4NH_3}$$

- Terminal alkynes give carboxylic acids on oxidation with cold alk. $KMnO_4$ (Baeyer's reagent).

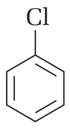
$$R\mathrm{{-}C{\equiv}C{-}}R' \xrightarrow[\text{Heat}]{\mathrm{KMnO_4/H^+}} R\mathrm{COOH} + R'\mathrm{COOH}$$

NOTE Wilkinson's catalyst reduces alkenes and alkynes without affecting common functional groups such as $C{=}O$, $—CN$ and $—NO_2$ etc.

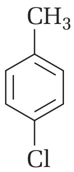
Aromatic Hydrocarbons

- These are specialised cyclic compounds which are known for their characteristic unique smell (Aroma = fragrance). The group is also called **arenes.**
- **Nomenclature** According to IUPAC system of nomenclature, the prefixes 1,2; 1,3 and 1,4 are used.

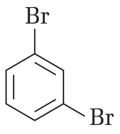
  e.g.



Chloro benzene

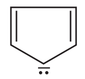


1-chloro-4-methyl benzene



1, 2-dibromo benzene

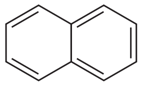
- **Aromaticity** of aromatic compounds whether having benzene ring or not is characterised by following points:
  - (i) Planarity
  - (ii) Contain one or more rings that have cyclic arrangement of π-orbitals.
  - (iii) Complete delocalisation of the π-electrons in the ring.
  - (iv) Presence of $(4n+2)$ π-electrons in the ring, where, n is an integer $(n = 0, 1, 2)$.



Cyclopentadienyl anion

$n = 1$

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



Naphthalene

$n = 2$

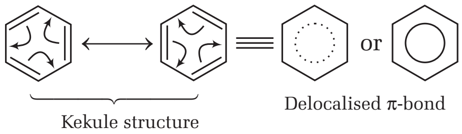
$(4n+2) = 10\pi$- electrons

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.

Resonance

When single Lewis dot structure is unable to explain all the properties of a compounds, two or more structure called the **canonical forms** or **resonating structures**. The drawn to explain all the properties of that compound then the actual structure of the compound is in the between these canonical form and is called the resonance.

Structure of benzene can be explained on the basis of concept of resonance.



There is complete delocalisation of π-electrons.

It is aromatic, $(4n+2) = 6$, Here, $n =$ number of π-electrons delocalised (Huckel's rule is followed).

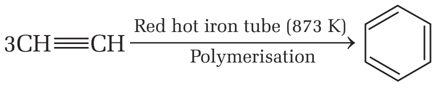
Benzene

Benzene is the first member of aromatic-hydrocarbon having formula C_6H_6, i.e. 

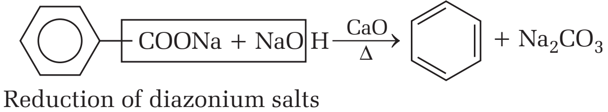
Methods of Preparation

Benzene can be prepared by following ways :

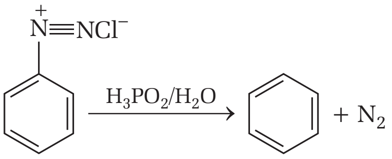
- From acetylene



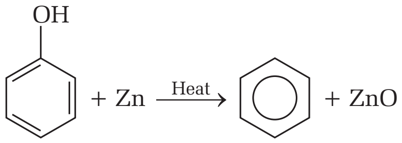
- Decarboxylation



- Reduction of diazonium salts



- Reduction of phenol



Chemical Properties

Benzene exhibit the following chemical properties may be given as :

Electrophilic Substitution Reactions

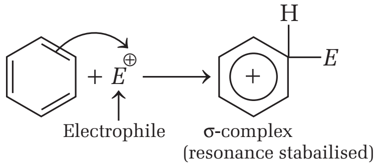
Benzene shows electrophilic substitution reactions due to 6π-electrons and resonance.

Mechanism of Electrophilic Substitution

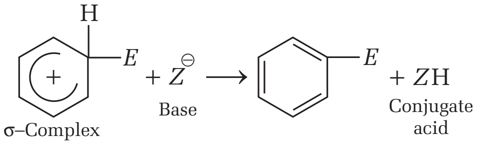
- **Generation of Electrophile** First of all electrophile is generated with the help of catalyst provided.

$$E — \text{Nu} \longrightarrow E^+ + \text{Nu}^-$$

- **Formation of Carbocation Intermediate** The electrophile E^+ approaches the π- electron cloud of the aromatic ring and forms a bond with carbon creating a positive charge on ring. This results in the formation of σ- complex.



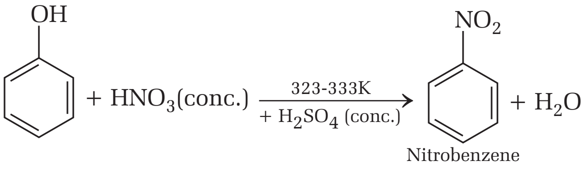
- **Elimination of Proton** In this step, one H^+ from the same carbon atom of ring is removed to which the electrophile was attached.



$Z^- = \text{Fe}X_4^-$ $(X = \text{Cl, Br})$ in halogenation; HSO_4^- in nitration; H_2O in sulphonation, $\text{Al}X_4^-$ $(X = \text{Cl, Br})$ in Friedel-Crafts alkylation/ acylation.

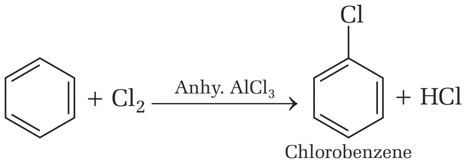
Some of the important electrophilic substitution reaction are as follows:

- **Nitration** is carried out with a mixture of conc.HNO_3 and conc. H_2SO_4 (nitrating mixture).



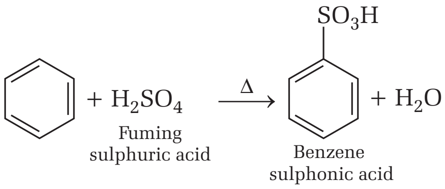
Attacking reagent (electrophile) is NO_2^+.

- **Halogenation** is carried out with Cl_2 or Br_2 in the presence of anhyd. $AlCl_3$.



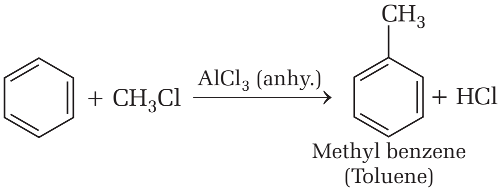
Attacking electrophile is Cl^+.

- **Sulphonation** is carried out with conc. H_2SO_4.



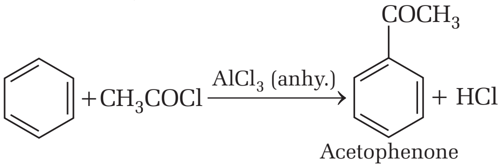
Attacking electrophile is SO_3.

- In **Friedel-Crafts alkylation reaction**, benzene ring reacts with alkyl halide to given alkylbenzene.



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

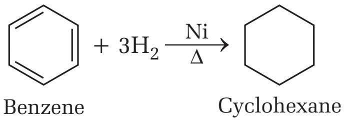
- **Friedel-Crafts Acylation Reaction**



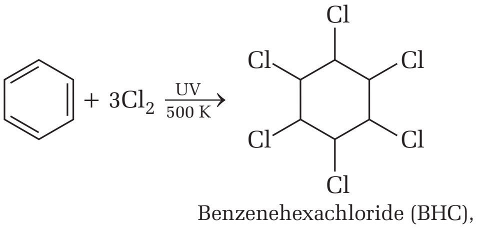
Addition Reactions

Addition reactions of benzene are given below :

- Gives addition reaction with hydrogen to produce cyclohexane.

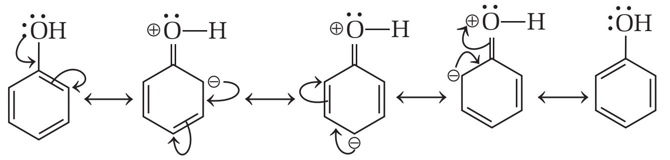


- It gives addition reaction with chlorine to produce benzene hexachloride.



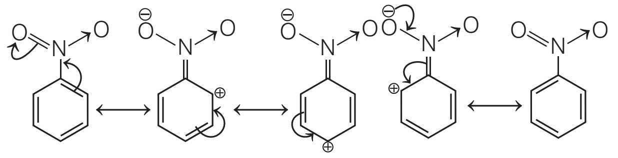
Directive Influence of Functional Group in Monosubstituted Benzene

- The ability of a group allready present on the benzene ring to direct the incoming group to a particular position is called **directive influence of functional group.** According to the nature of functional groups, they can be of two types:
  - (i) o, *p*-directing groups activate the benzene ring.
  - (ii) *m*-directing groups deactivate the benzene ring. e.g. —OH group is *ortho-para* directing.
- ***o*, *p*-directing groups** have tendency to release electrons e.g.


Resonating structures of phenol

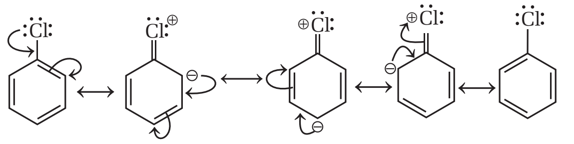
$—NH_2$, $—NHR$, $—NHCOCH_3$, $—OCH_3$, $—CH_3$, $—C_2H_5$ are *o* and *p*-directing groups.

- ***m*-directing groups** decrease the over all electron density over the benzene ring due to their strong *I*- effect. e.g $—NO_2$ group is *meta* directing.


Resonating structures of nitrobenzene

$—NO_2$, $—CN$, $—CHO$, $—COR$, $—COOH$, $—COOR$, $—SO_3H$ are meta directing groups.

NOTE In case of haloarenes, halogens are highly deactivating because of $-I$-effect but due to resonance, electron density on *o*-and *p*-position increases, hence halogens are *o* -, *p* -directing.


Resonating structures of chlorobenzene

Carcinogenicity and Toxicity

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together, are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic material like tobacco, coal and petroleum.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 When ethyl bromide is heated with sodium in dry other, it gives

(a) C_4H_{10} (b) C_2H_6 (c) C_3H_8 (d) C_2H_5OH

2 Aqueous solution of potassium acetate is electrolysed. Possible organic products is/are

(a) CH_3CH_3
(b) CH_3COCH_3
(c) $CH_3CH_2CH_2CH_3$
(d) Both (a) and (b)

3 Iodoethane reacts with sodium in the presence of dry ether. The main product is

(a) ethane (b) propyne (c) butane (d) butyne

4 In alkanes, the boiling point decreases as branching increases. This is due to

(a) dipole–dipole interactions
(b) decreased surface area for intermolecular attraction
(c) Both (a) and (b)
(d) None of the above

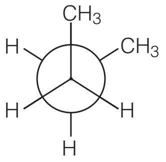
5 Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by → **CBSE-AIPMT 2010**

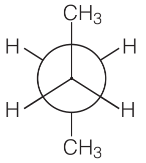
(a) oxidation
(b) cracking
(c) distillation under reduced pressure
(d) hydrolysis

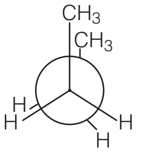
6 Cracking of hexane gives mixture of

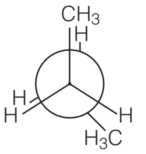
(a) C_4H_{10} and CH_4
(b) C_4H_8 and C_2H_6
(c) H_2 and C_5H_2
(d) C_3H_6 and C_2H_4

7 In the following the most stable conformation of *n*-butane is → **CBSE-AIPMT 2010**

(a)


(b)


(c)


(d)


8 The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is → **NEET 2016, Phase I**

(a) The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain

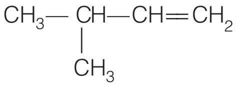
(b) The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
(c) The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
(d) The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain

9 The reaction of 2- methyl-propanol in the presence of conc. H_2SO_4 at 443 K temperature gives

(a) but-1-ene
(b) 2-methyl-propene
(c) 2-methyl-propane
(d) 2-methyl-propyne

10 Which does not follow Markownikoff's rule?

(a) $CH_3-CH=CH_2$
(b) $CF_3CH=CH_2$
(c)



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

(d) $CH_3-CH_2-CH=CH_2$

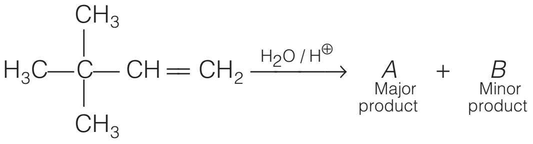
11 Addition of HI on double bond of propene yields isopropyl iodide as major product. It is because the addition proceeds through

(a) more stable carbocation
(b) more stable carboanion
(c) homolysis
(d) more stable free radical

12 Acid catalysed hydration of alkenes except ethene leads to the formation of

(a) primary alcohol
(b) secondary or tertiary alcohol
(c) mixture of primary and secondary alcohols
(d) mixture of secondary and tertiary alcohols

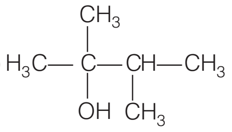
13 In the following reaction, **→ CBSE-AIPMT 2012**



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{H_2O\,/\,H^{\oplus}} \underset{\text{Major product}}{A} + \underset{\text{Minor product}}{B}$$

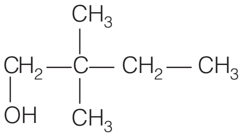
The major product is

(a)



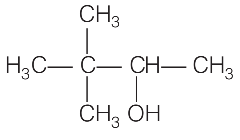
$H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(b)



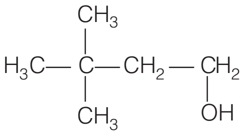
$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$

(c)



$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-CH_3$

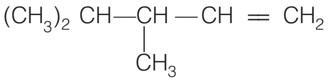
(d)



$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{OH}{|}}{CH_2}$

14 2,3-dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid? **→ NEET 2016, Phase I**

(a)

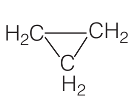


$(CH_3)_2\,CH-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

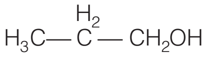
(b) $(CH_3)_3C-CH=CH_2$
(c) $(CH_3)_2C=CH-CH_2-CH_3$
(d) $(CH_3)_2CH-CH_2-CH=CH_2$

15 Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction? **→ NEET 2016, Phase II**

(a)

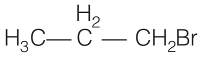


(b)



$H_3C-\overset{H_2}{C}-CH_2OH$

(c) $H_2C=C=O$
(d)



$H_3C-\overset{H_2}{C}-CH_2Br$

16 Ozonolysis of an organic compounds gives formaldehyde as one of the products. This confirms the presence of

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

17 $CaC_2 + H_2O \longrightarrow A \xrightarrow{H_2SO_4/HgSO_4} B$

Identify A and B in the given reaction

(a) C_2H_2 and CH_3CHO
(b) CH_4 and HCOOH
(c) C_2H_4 and CH_3COOH
(d) C_2H_2 and CH_3COOH

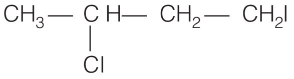
18 Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne? **→ CBSE-AIPMT 2012**

(a) $NaNH_2$
(b) HCl
(c) O_2
(d) Br_2

19 Predict the product C obtained in the following reaction of butyne-1.

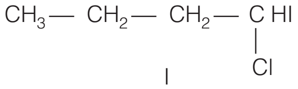
$$CH_3CH_2-C\equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$$

(a)



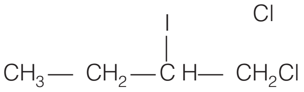
$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2I$

(b)



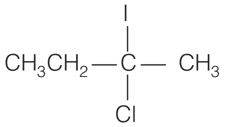
$CH_3-CH_2-CH_2-\underset{\underset{Cl}{|}}{CHI}$

(c)



$CH_3-CH_2-\overset{\overset{I}{|}}{CH}-CH_2Cl$

(d)



$CH_3CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{I}{|}}{C}}-CH_3$

20 When acetylene is passed through dil. H_2SO_4 in presence of $HgSO_4$, the compound formed is

(a) ether
(b) ketone
(c) acetic acid
(d) acetaldehyde

21 Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. A is **→ NEET 2018**

(a) CH_3-CH_3
(b) $CH_2=CH_2$
(c) $CH\equiv CH$
(d) CH_4

22 Which of the following molecules represents the order of hybridisation sp^2, sp^2, sp, sp from lift to right atoms?

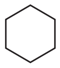
→ **NEET 2018**

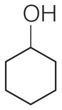
(a) $CH_2 = CH - CH = CH_2$
(b) $CH_2 = CH - C \equiv CH$
(c) $CH \equiv C - C \equiv CH$
(d) $CH_3 - CH = CH - CH_3$

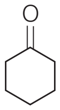
23 Which one is the correct order of acidity? → **NEET 2017**

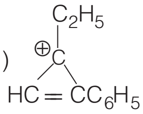
(a) $CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - C \equiv CH > CH \equiv CH$
(b) $CH \equiv CH > CH_3 - C \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$
(c) $CH \equiv CH > CH_2 = CH_2 > CH_3 - C \equiv CH > CH_3 - CH_3$
(d) $CH_3 - CH_3 > CH_2 = CH_2 > CH_3 - C \equiv CH > CH \equiv CH$

24 Which of the following compounds is aromatic?

(a) 

(b) 

(c) 

(d) 

25 Which one of the following is aromatic?

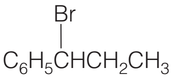
(a) Cyclopentadienyl cation
(b) Cyclooctatetraene
(c) Cycloheptatriene
(d) Cycloheptatrienyl cation

26 Select the true statement about benzene amongst the following.

(a) Because of unsaturation benzene easily undergoes addition
(b) There are two types of C—C bonds in benzene molecule
(c) There is cyclic delocalisation of pi-bonds in benzene
(d) Monosubstitution of benzene gives three isomeric products

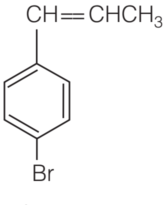
27 The reaction of $C_6H_5CH = CHCH_3$ with HBr produces

→ **CBSE-AIPMT 2015**

(a) 
$C_6H_5\overset{Br}{C}HCH_2CH_3$

(b) $C_6H_5CH_2CHCH_3$

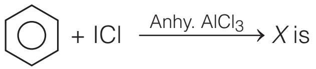
(c) $C_6H_5CH_2CH_2CH_2$

(d) 

28 The function of $AlCl_3$ in Friedel-Crafts reaction is

(a) to absorb HCl
(b) to absorb water
(c) to produce nucleophile
(d) to produce electrophile

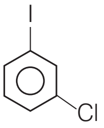
29 The compound X in the reaction,



(a) 

(b) 

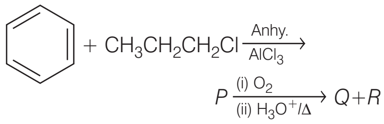
(c) 

(d) 

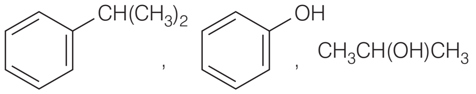
30 Which of the following compounds will not undergo Friedel-Crafts reaction easily? → **NEET 2013**

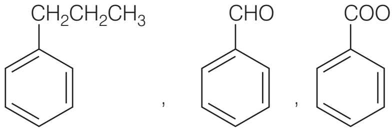
(a) Xylene (b) Nitrobenzene
(c) Toluene (d) Cumene

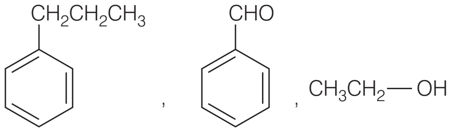
31 Identify the major products P, Q and R in the following sequence of reactions : → **NEET 2018**

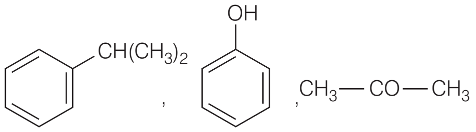


P Q R

(a) 

(b) 

(c) 

(d) 

Direction (Q. Nos. 32) *Following question contains two statements : Assertion and 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) Assertion is true, Reason is true; Reason is a correct explanation for Assertion
(b) Assertion is true, Reason is true; Reason is not a correct explanation for Assertion
(c) Assertion is true, Reason is false
(d) Assertion is false, Reason is true

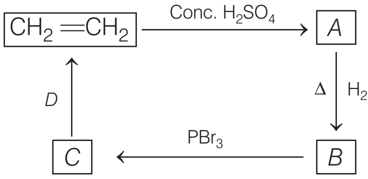
32 **Assertion** (A) C—H bond in ethyene is shorter than C—H bond in ethene.

Reason (R) Carbon atom in ethene is sp-hybridised, while it is sp^2 hybridised in ethyne.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Identify *B* and *D* in the following sequence of reactions.



(a) Methanol and bromoethane
(b) Ethyl hydrogen sulphate and alcoholic KOH
(c) Ethyl hydrogen sulphate and aqueous KOH
(d) Ethanol and alcoholic KOH

2 In the presence of platinum catalyst, hydrocarbon *A* adds hydrogen to form *n*-hexane. When hydrogen bromide is added to *A* instead of hydrogen only a single bromo compound is formed. Which of the following is *A*?

(a) $CH_3-CH_2-CH=CH-CH_2-CH_3$
(b) $CH_3-CH_2-CH_2-CH=CH-CH_3$
(c) $CH_3-CH=CH-CH_2-CH_2-CH_3$
(d) $CH_2=CH-CH_2-CH_2-CH_2-CH_3$

3 Which would be the best sequence of reactions used to prepare is non–3–ene from 1–butyne?

(a) (1) $NaNH_2$ in NH_3; (2) 1– bromopentane (3) H_2, Lindlar catalyst
(b) (1) $NaNH_2$ in NH_3; (2) 1– bromopentane (3) Na, NH_3
(c) (1) H_2, Lindlar catalyst; (2) $NaNH_2$ in NH_3; (3) 1–bromopentane
(d) (1) Na, NH_3; (2) $NaNH_2$ in NH_3; (3) 1– bromopentane

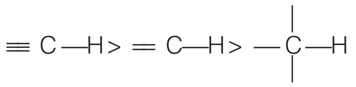
4 6 L of an alkene require 27 of oxygen at constant temperature and pressure for complete combustion. The alkene is

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

5 Which of the following reaction statements best explains the greater acidity of terminal alkynes compared with monosubstituted alkenes?

(a) The *sp*- hybridised carbons of the alkyne are less electronegative than the sp^2- carbons of the alkene
(b) The two π- bonds of the alkyne are able to stabilise better the negative charge of the anion by resonance
(c) The *sp*-hybridised carbons of the alkynes are more electronegative than sp^2- carbons of the alkene
(d) The question is incorrect alkenes are more acidic than alkynes

6 Different hydrocarbons release proton in the following order.



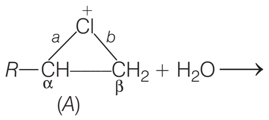
$$\equiv C-H > = C-H > -\overset{|}{\underset{|}{C}}-H$$

I II III

Which factor causes easy removal of proton?

(a) Bond strength of C — H bond: I<II<III
(b) Electronegativity of C in I>II>III
(c) Bond strength of C — H bond: I>II> III
(d) Electronegativity of C in I<II<III

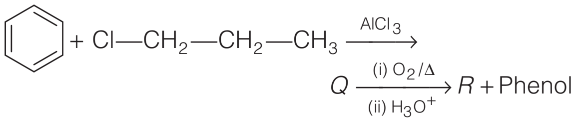
7 Intermediate (*X*) changes to chlorohydrin due to attack of H_2O (nucleophile). Select correct statement about this reaction.



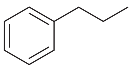
(*A*)

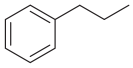
(a) H_2O attacks β – carbon and bond (*a*) is cleaved
(b) H_2O attacks α – carbon and bond (*a*) is cleaved
(c) H_2O attacks β – carbon and bond (*b*) is cleaved
(d) H_2O attacks α – carbon and bond (*a*) is cleaved

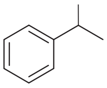
8

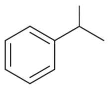


In the above reaction, benzene reacts with chloropropane in the presence of anhy. $AlCl_3$ to give *Q*, which further reacts with O_2 to give *R*. *Q* and *R* are respectively.

(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_2COCH_3

(d)  and CH_3CH_2CHO

9 Reaction of one molecule of HBr with one molecule of 1,3- butadiene at 40°C gives predominantly.

(a) 3-bromobutene under kinetically controlled conditions
(b) 1-bromo-2-butene under thermodynamically controlled conditions
(c) 2-bromobutene under kinetically controlled conditions
(d) 1-bromobutene under thermodynamically controlled conditions

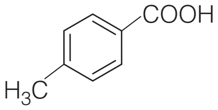
10 Identify the correct order of reactivity in electrophile substitution reactions of the following compounds. Benzene (1), toluene (2), chlorobenzene (3) nitrobenzene (4).

(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1
(c) 2 > 1 > 3 > 4 (d) 2 > 3 > 1 > 4

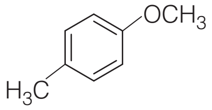
11 Ozonolysis of an organic compound *A* produces acetone and propionaldehyde in equimolar mixture. Identify '*A*' from the following compounds

(a) 1–pentene
(b) 2– methyl–1–pentene
(c) 2–methyl–2–pentene
(d) 2– pentene

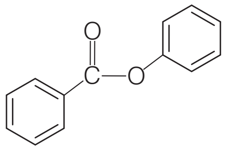
12 The compounds *P*, *Q* and *S*



P



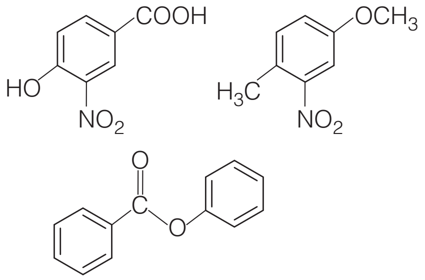
Q



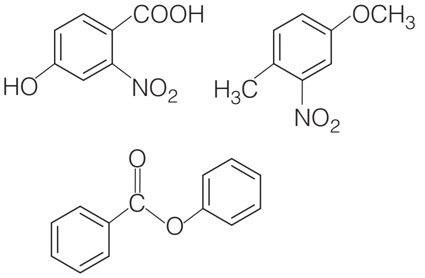
S

separately subjected to nitration using HNO_3/H_2SO_4 mixture.
The major product formed in each case respectively is

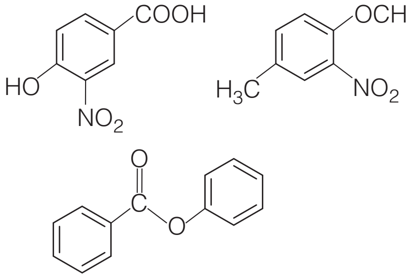
(a)



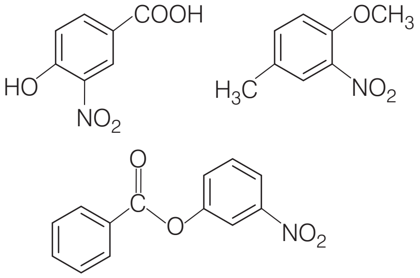
(b)



(c)



(d)



13 In the following sequence of reactions, the alkene affords the compound '*B*'.

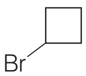
$$CH_3CH{=}CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$$

The compound *B* is

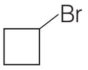
(a) CH_3CH_2CHO
(b) CH_3COCH_3
(c) $CH_3CH_2COCH_3$
(d) CH_3 CHO

14 What would be the product formed when 1-bromo-3-chlorocyclo-butane reacts with two equivalents of metallic sodium in ether?

(a)



(b)



(c)

(d)

15 An organic compound having molecular formula C_7H_{12} in catalytic hydrogenation over platinum gives C_7H_{16}. The parent hydrocarbon adds bromine and also reacts with $[Ag(NH_3)_2]$ OH to give a precipitate. The parent hydrocarbon is

(a) $CH_3—CH_2—C\equiv C—CH(CH_3)_2$
(b) $CH_3—CH{=}CH—CH_2—CH{=}CH—CH_3$
(c) $(CH_3)_3C—CH_2—C\equiv CH$
(d) $CH_3—CH{=}CH—CH{=}CH—CH_2—CH_3$

ANSWERS

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

SESSION 2	**1** (d)	**2** (a)	**3** (a)	**4** (b)	**5** (c)	**6** (b)	**7** (b)	**8** (c)	**9** (b)	**10** (c)
	11 (c)	**12** (c)	**13** (d)	**14** (d)	**15** (c)					

Hints and Explanations

SESSION 1

1 $2\,C_2H_5Br \xrightarrow[\text{Dry ether}]{2Na} CH_3CH_2CH_2CH_3 (C_4H_{10})$

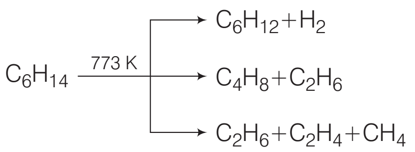
2 $2CH_3COOK + 2H_2O \xrightarrow{\text{Electrolysis}} C_2H_6 + 2CO_2 + H_2 + 2NaOH$

3 $\underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow{\text{Na/Dryether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$

4 More branched chain has less contact surface area and so lesser the boiling point.

5 On cracking or pyrolysis, the hydrocarbon with higher molecular mass gives a mixture of hydrocarbons having lower molecular mass. Hence, we can say that by cracking a liquid hydrocarbon can be converted into a mixture of gaseous hydrocarbons.

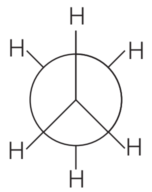
6



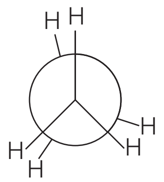
$$C_6H_{14} \xrightarrow{773\text{ K}} \begin{cases} C_6H_{12}+H_2 \\ C_4H_8+C_2H_6 \\ C_2H_6+C_2H_4+CH_4 \end{cases}$$

7 Among the given conformations of *n*-butane, the conformation shown in option (b), i.e. anti conformation is most stable as in it the bulkier group, i.e. $-CH_3$ group are present at maximum possible distance and get lower energy.

8 Due to the absence of torsional strain staggered conformation of ethane is more stable than eclipsed conformation of it.

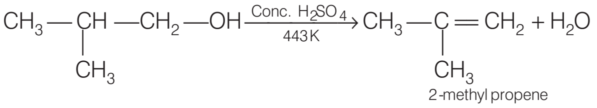


Staggered conformation



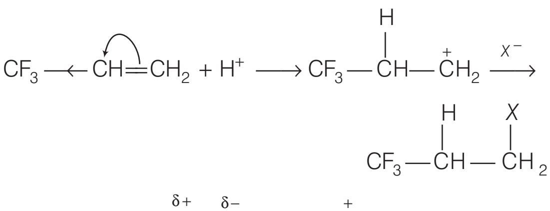
Eclipsed conformation

9



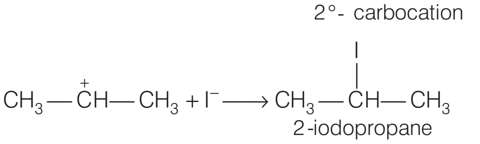
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH \xrightarrow[443K]{\text{Conc. }H_2SO_4} \underset{\text{2-methyl propene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} + H_2O$$

10



$$CF_3 \leftarrow CH=CH_2 + H^+ \longrightarrow CF_3-\overset{\overset{H}{|}}{CH}-\overset{+}{C}H_2 \xrightarrow{X^-} CF_3-\overset{\overset{H}{|}}{CH}-\overset{\overset{X}{|}}{CH_2}$$

11

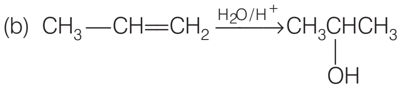


$$CH_3CH=CH_2 + \overset{\delta+}{H}-\overset{\delta-}{I} \longrightarrow \underset{\text{2°- carbocation}}{CH_3\overset{+}{C}H-CH_3} + I^-$$

$$CH_3-\overset{+}{C}H-CH_3 + I^- \longrightarrow \underset{\text{2-iodopropane}}{CH_3-\overset{\overset{I}{|}}{CH}-CH_3}$$

12 (a) $CH_2=CH_2 \xrightarrow{H_2O/H^+} \underset{\text{1°- alcohol}}{CH_3CH_2OH}$

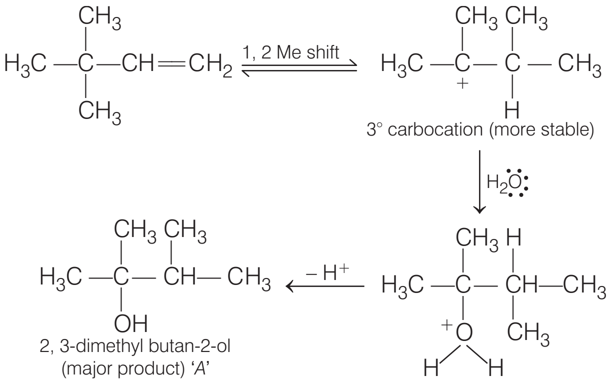
(b)



$$CH_3-CH=CH_2 \xrightarrow{H_2O/H^+} CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

2°- alcohol through 2°- carbocation ($CH_3\overset{\oplus}{C}HCH_3$).

13



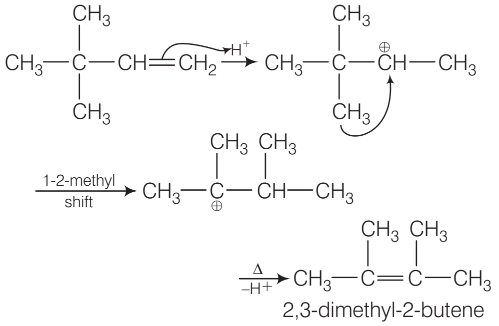
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \overset{\text{1, 2 Me shift}}{\rightleftharpoons} H_3C-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

3° carbocation (more stable)

$$\xrightarrow{H_2\ddot{O}:} H_3C-\underset{\underset{H\quad H}{{}^+O}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{CH}}-CH_3 \xrightarrow{-H^+} H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2, 3-dimethyl butan-2-ol
(major product) '*A*'

14



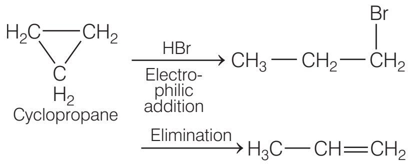
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{H^+} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H-CH_3$$

$$\xrightarrow[\text{shift}]{\text{1-2-methyl}} CH_3-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow[-H^+]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$$

2,3-dimethyl-2-butene

15 The said reactions can be visualised as :

(a)



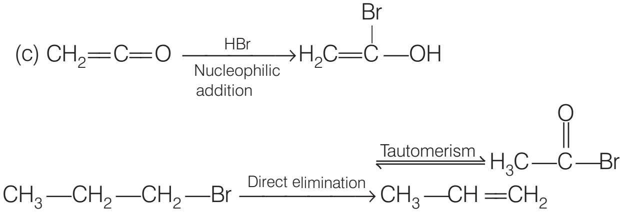
Cyclopropane

$$\xrightarrow[\text{Electrophilic addition}]{HBr} CH_3-CH_2-\overset{\overset{Br}{|}}{CH_2}$$

$$\xrightarrow{\text{Elimination}} H_3C-CH=CH_2$$

(b) $\underset{\text{Propanol}}{CH_3-CH_2-CH_2-OH} \xrightarrow[\text{Electrophilic addition}]{HBr} \underset{\text{Bromopropane}}{CH_3-CH_2-CH_2-Br} \xrightarrow{\text{Elimination}} H_3C-CH=CH_2$

(c)

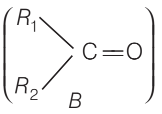


$$CH_2=C=O \xrightarrow[\text{Nucleophilic addition}]{HBr} H_2C=\overset{\overset{Br}{|}}{C}-OH \overset{\text{Tautomerism}}{\rightleftharpoons} H_3C-\overset{\overset{O}{\|}}{C}-Br$$

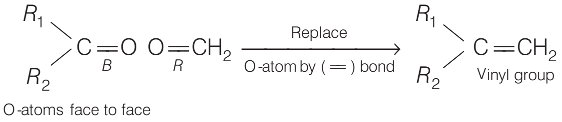
$$CH_3-CH_2-CH_2-Br \xrightarrow{\text{Direct elimination}} CH_3-CH=CH_2$$

Thus, option (c) is correct answer.

16 Alkene $\xrightarrow{O_3/Zn/H_2O} \underset{A}{HCHO}$ + other carbonyl compound



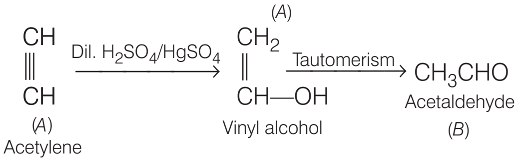
To determine alkene, place carbonyl compounds with their O-atom face to face, i.e. Replace O-atom by a double bond.



$$\underset{B}{R_1R_2C{=}O}\ \ \underset{R}{O{=}CH_2} \xrightarrow[\text{O-atom by }(=)\text{ bond}]{\text{Replace}} \underset{\text{Vinyl group}}{R_1R_2C{=}CH_2}$$

O-atoms face to face

17 $CaC_2 + 2H_2O \longrightarrow \underset{(A)}{C_2H_2} + Ca(OH)_2$



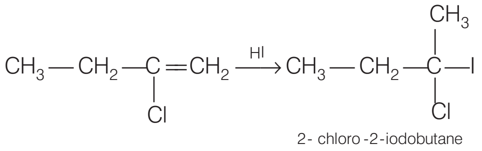
$$\underset{\substack{(A)\\ \text{Acetylene}}}{CH{\equiv}CH} \xrightarrow{\text{Dil. } H_2SO_4/HgSO_4} \underset{\text{Vinyl alcohol}}{CH_2{=}CH{-}OH} \xrightarrow{\text{Tautomerism}} \underset{\substack{\text{Acetaldehyde}\\ (B)}}{CH_3CHO}$$

18 $NaNH_2$ is used to distinguish between 1-butyne and 2-butyne.

$$\underset{\text{1-butyne}}{CH_3CH_2C\equiv CH} \xrightarrow{NaNH_2} CH_3CH_2C\equiv \bar{C}Na + \frac{1}{2}H_2\uparrow$$

$$\underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3} \xrightarrow{NaNH_2} \text{No reaction}$$

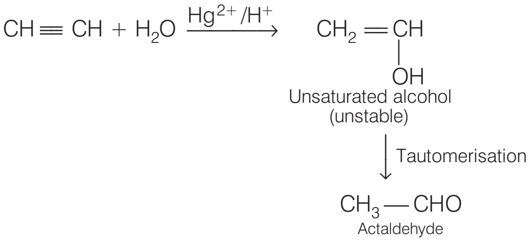
19 $CH_3-CH_2-C\equiv CH + HCl \longrightarrow$

or 

$$CH_3-CH_2-\underset{\substack{|\\ Cl}}{C}{=}CH_2 \xrightarrow{HI} CH_3-CH_2-\underset{\substack{|\\ Cl}}{\overset{\substack{CH_3\\ |}}{C}}-I$$

2- chloro -2 -iodobutane

20 Hydration of alkyne,



$$CH\equiv CH + H_2O \xrightarrow{Hg^{2+}/H^+} \underset{\substack{|\\ OH}}{CH_2{=}CH}$$

Unsaturated alcohol (unstable)

$\downarrow$ Tautomerisation

$$\underset{\text{Actaldehyde}}{CH_3-CHO}$$

21 The given reaction takes place as follows :

$$\underset{(A)}{CH_4} \xrightarrow[\text{Step 2}]{Br_2/h\nu} CH_3Br \xrightarrow[\substack{\text{Wurtz reaction}\\ \text{(Step2)}}]{\text{Na/dry ether}} \underset{(A)}{CH_3-CH_3}$$

***Step* I** Alkyl halide is formed by free radical halogenation of alkane in the presence of UV-light.

***Step* II** The formed alkyl halide reacts with sodium in presence of dry ether to form alkane containing double number of carbon atoms present in alkyl halide. This reaction is known as Wurtz reaction.

22 Key Idea While judging the hybridisation in the given type of organic molecules always look for the number of σ and π-bonds formed by C-atom involved.

The hybridisation of the given molecules are.

(i) $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$

(ii) $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv\overset{sp}{CH}$ (iii) $\overset{sp}{CH}\equiv\overset{sp}{C}-\overset{sp}{C}\equiv\overset{sp}{CH}$

(iv) $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp^3}{CH_3}$

Therefore, the correct option is (b).

23 Greater the *s*-character of C-atom in hydrocarbons, greater the electronegativity of that carbon and thus greater the acidic nature of the H attached to electronegative carbon.

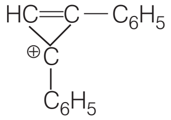
	$CH\equiv CH$	$CH_2=CH_2$	CH_3-CH_3
Hybridisation :	*sp*	sp^2	sp^3
s-character :	50%	33%	25%

Electronegativity : $\xleftarrow{\text{Max.}\qquad\qquad\qquad\qquad}$

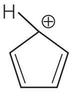
Acidic character of terminal H $\xleftarrow{\text{Max.}\qquad\qquad\qquad\qquad}$

Thus, $CH\equiv CH > CH_3C\equiv CH > CH_2=CH_2 > CH_3-CH_3$

24 It is aromatic because the compound is cyclic and number of π-electrons is 2, which is in accordance with the Huckel's rule, $(4n+2)\ \pi$. When $n=0$, according to this rule, number of π- electrons is $4\times 0+2=2$.



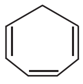
25 According to Huckel, an aromatic compound must be cyclic planar having $(4n+2)\pi$ -electrons.

(a) 

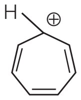
Cyclopentadienyl cation ($4\pi e^-$) (non-aromatic)

(b) 

Cyclooctatetraene ($8\pi e^-$) (anti-aromatic)

(c) 

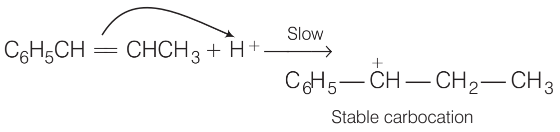
Cycloheptatriene ($6\pi e^-$ but non-planar, so non-aromatic)

(d) 

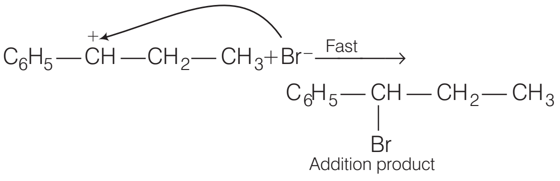
Cycloheptatrienyl cation ($6\pi e^-$ and planar, so aromatic)

26 According to the orbital concept, each carbon atom in benzene is sp^2-hybridised and one *p*-orbital of each carbon remains unhybridised. The π-electron charge in benzene is not confined to space between two carbon atoms as in ethylene, but is spread over a greater area. This is known as the delocalisation of the electron charge.

27

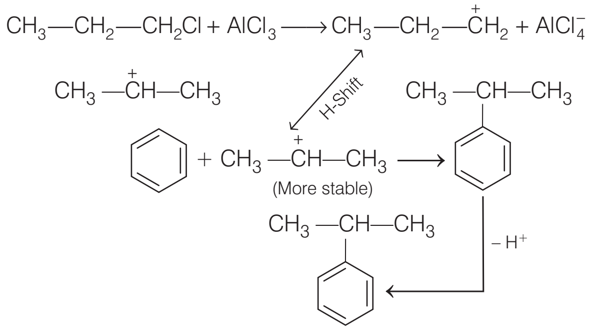


$$C_6H_5CH=CHCH_3 + H^+ \xrightarrow{\text{Slow}} \underset{\text{Stable carbocation}}{C_6H_5-\overset{+}{C}H-CH_2-CH_3}$$

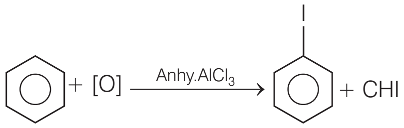


$$C_6H_5-\overset{+}{C}H-CH_2-CH_3+Br^- \xrightarrow{\text{Fast}} \underset{\text{Addition product}}{C_6H_5-\underset{\substack{|\\ Br}}{CH}-CH_2-CH_3}$$

28 The function of $AlCl_3$, in Friedel-Crafts reaction, is to produce electrophile, which later add to benzene nucleus.

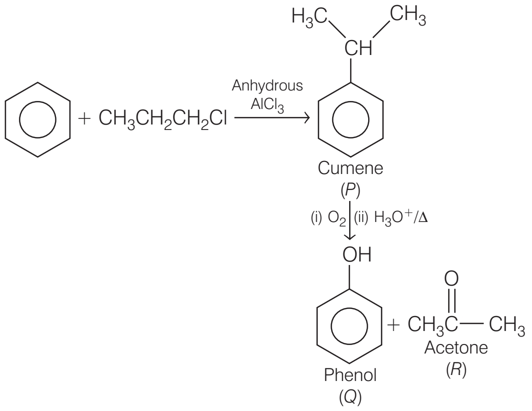


29 The ICl on reaction with anhydrous $AlCl_3$ produces I^+ (electrophile) consequently the final product is iodobenzene.



30 Due to the presence of most deactivating NO_2 group, Nitrobenzene does not undergo Friedel-Crafts reaction easily.

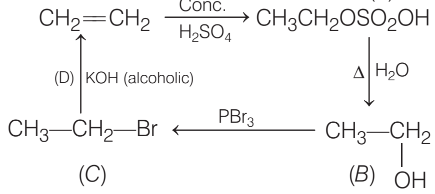
31 The given reaction takes place as follows :



32 The correct reason is the carbon atom is sp^2- hybridised in ethene and sp- hybridised in ethyne.

SESSION 2

1



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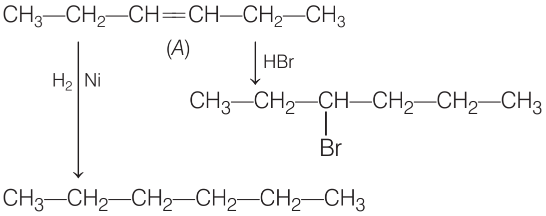

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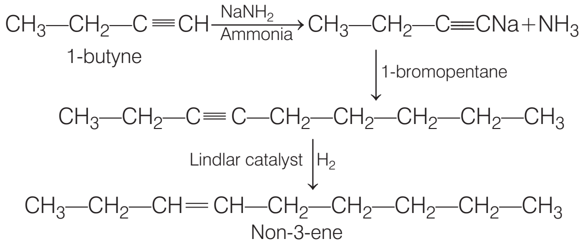


4 General reaction for the combustion of alkene is

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow n\,CO_2 + nH_2O$$

Given, 6 L 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. $\frac{3n}{2} = \frac{9}{2}$

$\therefore$ $3n = 9$ or $n = 3$

On putting the value of n in general formula of alkene, we get $[C_nH_{2n}] \times 3 = C_3H_6$. Hence, the alkene is propene $(CH_3CH═CH_2)$.

5 The sp-hybridised carbons of the alkynes are more electronegative than sp^2-carbons of the alkenes. Electro negativity of the carbon atom depends upon the 's' character present in it.

Hybridisation–	sp^3	sp^2	sp
% s character–	25%	33%	50%

Hence, order of their electronegativity is as follows sp-hybridised carbon > sp^2 hybridised carbon > sp^3 hybridised carbon

6 Acidic strength (tendency to release proton) of carbon atom depends upon its electronegativity which directly depends on its hybridisation.

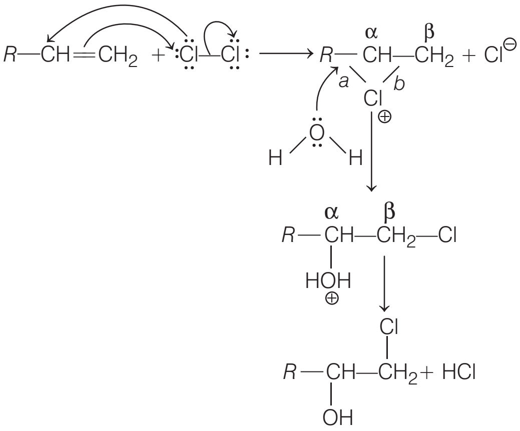
sp- hybridised carbon is more electronegative than sp^2 and sp- hybridised carbon atoms.

There order of electonegativity is as $sp > sp^2 > sp^3$

Hence, there tendency to release proton will be – $sp > sp^2 > sp^3$

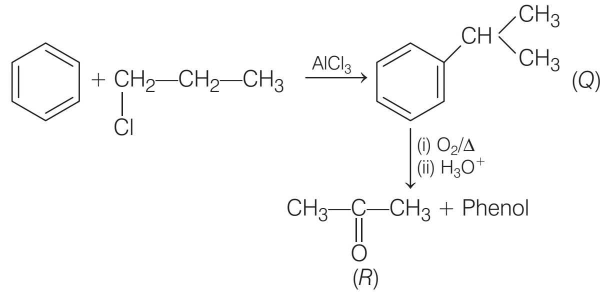
Therefore, option (b) is correct.

7 The mechanism for reaction is as follows



Hence, H_2O attacks α-carbon and bond (a) is cleaved.

8



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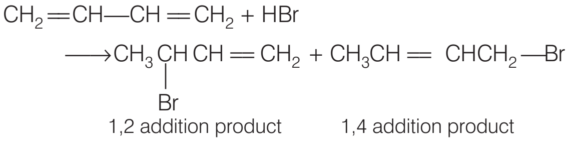
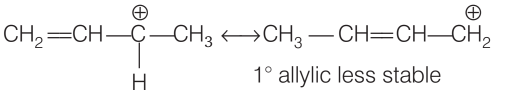


$$CH_2{=}CH{-}CH{=}CH_2 + HBr \longrightarrow CH_3\underset{\underset{Br}{|}}{C}H\,CH{=}CH_2 + CH_3CH{=}CHCH_2{-}Br$$

1,2 addition product 1,4 addition product

Addition is through the formation of allylic carbocation.



$$CH_2{=}CH{-}\overset{\oplus}{\underset{\underset{H}{|}}{C}}{-}CH_3 \longleftrightarrow CH_3{-}CH{=}CH{-}\overset{\oplus}{C}H_2$$

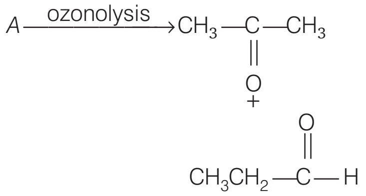
1° allylic less stable

2° allylic more stable

Under mild conditions (temp ≈ −80°C) kinetic product is the 1,2-addition product and under vigorous conditions (temp ≈ −40°C) thermodynamic product is the 1,4, addition product. Thus, under given conditions 1- bromo–2–butene is the major product.

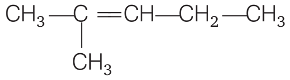
10 Toluene is highly reactive towards electrophite substitution reaction among the given compounds because toluene has —CH_3 group which increases electron density at *o*/*p* position of the ring. While in case of (3) and (4), both have electron withdrawing groups i.e. —Cl and —NO_2 respectively. —NO_2 has more capacity to attract or to withdraw the electrons from ring. Hence, their reactivity order will be $2 > 1 > 3 > 4$.

11



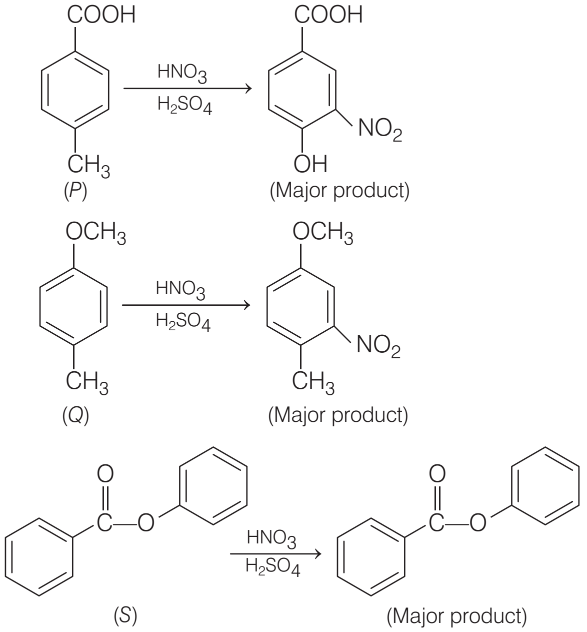
$$A \xrightarrow{\text{ozonolysis}} CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + CH_3CH_2{-}\overset{\overset{O}{\|}}{C}{-}H$$

To obtain or to identify '*A*' we need to remove oxygen atom replace it with double bond. Hence, '*A*' is,



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

12



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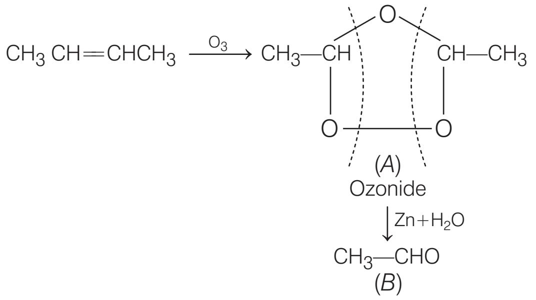

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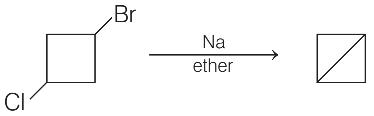

15 As the hydrocarbon can react with Tollen's reagent $\{[Ag(NH_3)_2]\ OH\}$ and gives ppt, therefore it is alkyne because only alkyne's having terminal triple bond gives white ppt with Tollen's reagent.

As its molecular formula is C_7H_{12} and it has terminal triple bond, hence the hydrocarbon is (c) among the given options as only option (c) has terminal triple bond.