9

Hydrocarbons

Hydrocarbons are essential in our daily lives. We all use it in some way every day. Plastic, for example, is a petrochemical industry product that is vital to our daily lives. Plastic is now ubiquitous throughout the world! Everything, including your table, chair, grocery bags, straws, etc.

Topic Notes

- ☐ *Classification of Hydrocarbons and Aliphatic Hydrocarbons*
- ☐ *Aromatic Hydrocarbons and Carcinogenicity*

CLASSIFICATION OF HYDROCARBONS AND ALIPHATIC HYDROCARBONS

1

TOPIC 1

CLASSIFICATION

Based on the types of carbon-carbon bonds present in hydrocarbons, they are classified under three categories:

(1) Saturated hydrocarbons

(2) Unsaturated hydrocarbons

(3) Cyclic hydrocarbons

(4) Aromatic hydrocarbons

Saturated Hydrocarbons

They contain carbon-carbon and carbon-hydrogen single bonds. If carbon atoms are joined together in an open chain manner through a single bond, then that hydrocarbon is called an alkane.

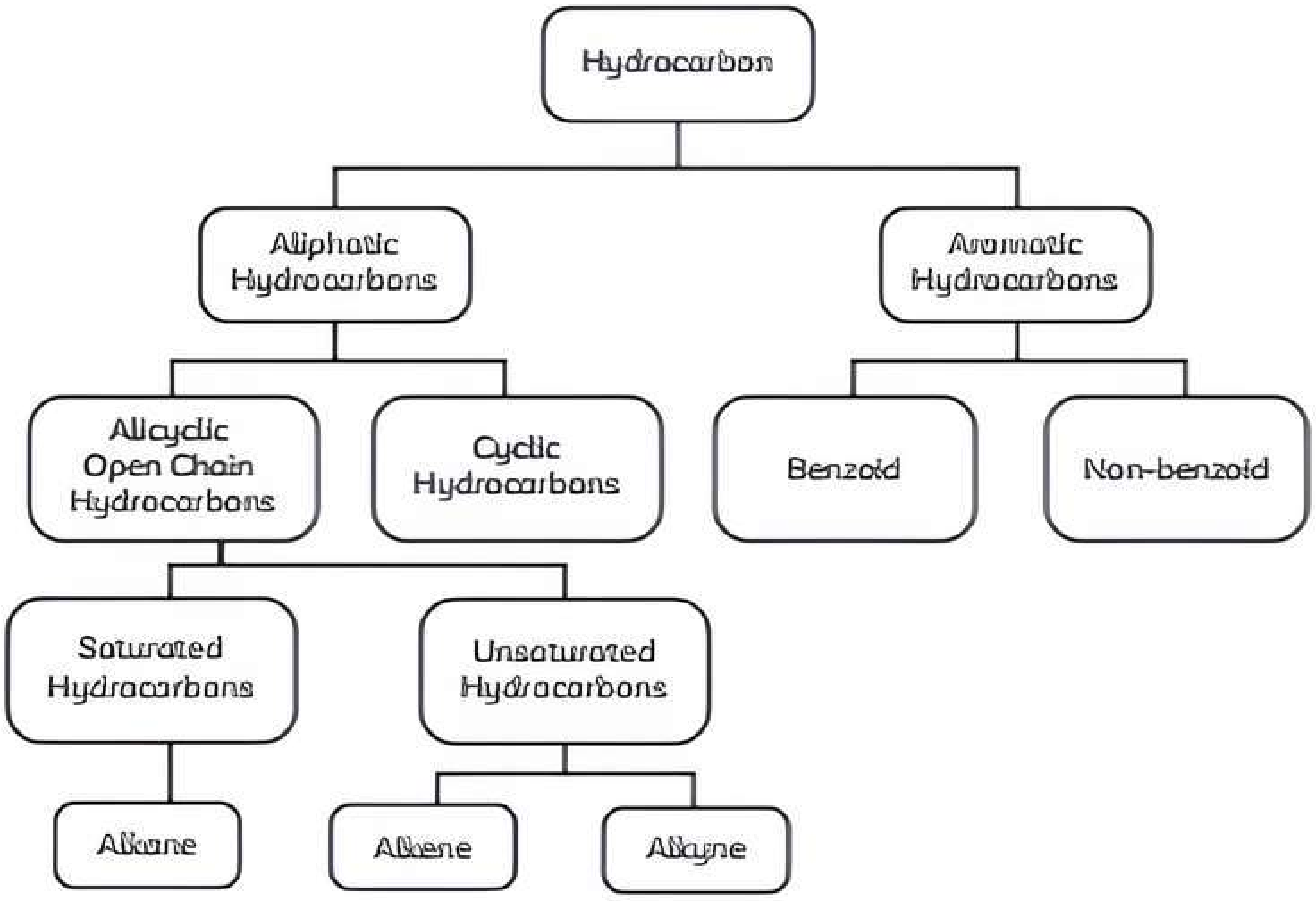
Unsaturated Hydrocarbons

They are hydrocarbons that have double or triple covalent bonds between adjacent carbon atoms. The term "unsaturated" means more hydrogen atoms may be added to the hydrocarbon to make it saturated (*i.e.*, consisting of all single bonds). The configuration of unsaturated carbons includes straight chains, such as alkenes and alkynes, as well as branched chains and aromatic compounds.

Cyclic Hydrocarbons

They are carbon chains in a ring structure. They may contain multiple carbon atoms and may have single, double or triple bonds. The cyclic hydrocarbons have saturated single rings. Bridged cycloalkanes contain one or more pairs of carbon atoms common to two or more rings. The inclusive terms for any cyclic hydrocarbons having any number of such multiple bonds are cyclic olefins or cyclic acetylenes.

Aromatic hydrocarbons are circularly structured organic compounds that contain sigma bonds along with delocalized pi electrons. They are also referred to as arenes or aryl hydrocarbons. Aromatic hydrocarbons are a special type of cyclic compound.



Classification of hydrocarbons

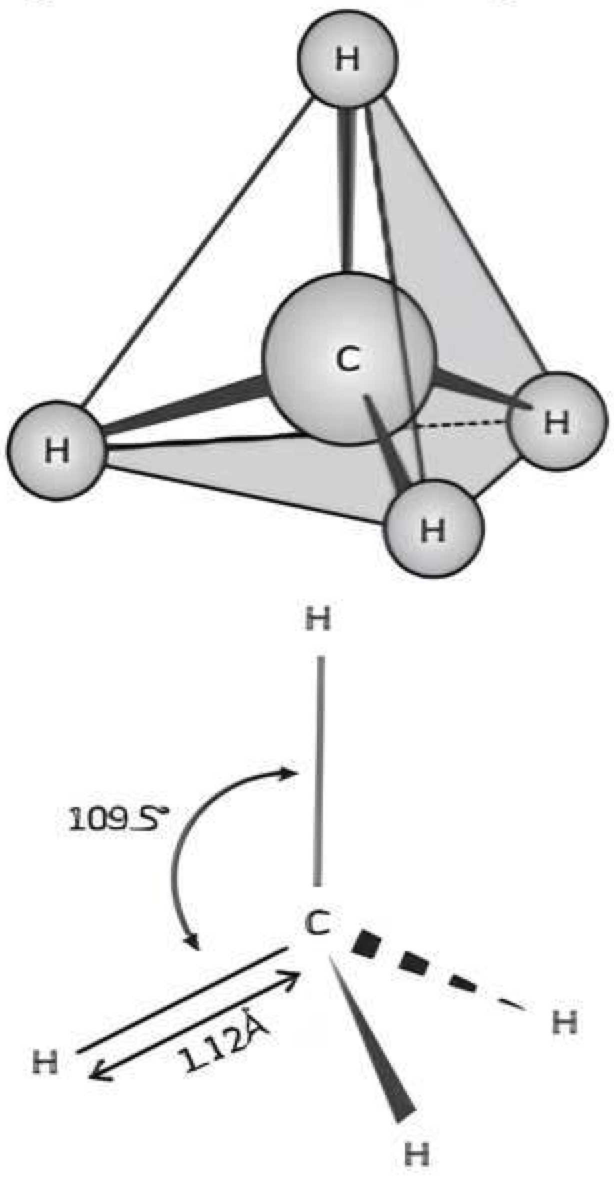
TOPIC 2

ALKANES

These are saturated open-chain hydrocarbons consisting of carbon-carbon single bonds. Methane is the first member of the alkane family. It is found in coal mines and marshy places. These hydrocarbons are inert under normal conditions because they do not react with acids, bases and other reagents. Hence, they are called paraffins (*Latin: Parum: little, affins: affinity*). General formula of alkanes: C_nH_{2n+2} where n stands for a number of C–atoms and $2n + 2$ stands for the number of hydrogen atoms in a molecule. When we replace one hydrogen from the methane molecule with carbon, the tetra valency of carbon should be satisfied by hydrogens. *Eg.*, The ethane molecule C_2H_6 can be formed by replacing one hydrogen with a carbon atom in the methane molecule CH_3.

Structure of Alkane

Each carbon of alkanes is sp^3 hybridized with a tetrahedral structure. The carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All the C–C and C–H bonds are joined together by a single bond with bond (σ bond) lengths of 154 pm and 112 pm respectively. All the H–C–H bond angles are 109.5°.

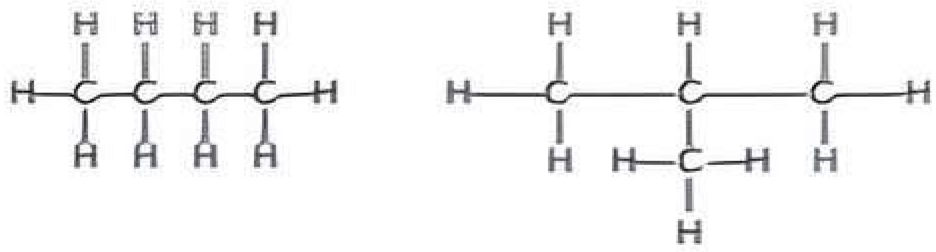


Structure of methane

Nomenclature and Isomerism

We have already learnt about the nomenclature of different classes of organic compounds in Unit 8. The names of all alkanes end with -ane. Alkanes are the simplest family of hydrocarbons - compounds containing carbon and hydrogen only. Alkanes only contain carbon-hydrogen and carbon-carbon single bonds. All of the alkanes which contain four or more carbon atoms show structural isomerism. Thus these compounds show chain isomerism. The first three alkanes (Methane, ethane and propane) have only one structure but other higher alkanes have more than one structure.

The four carbon atoms C_4H_{10} can be joined either in a continuous or with a branched chain manner in the following two ways:



Butane (C_4H_{10})
(Continuous chain alkane)
(b.p. 273 K)

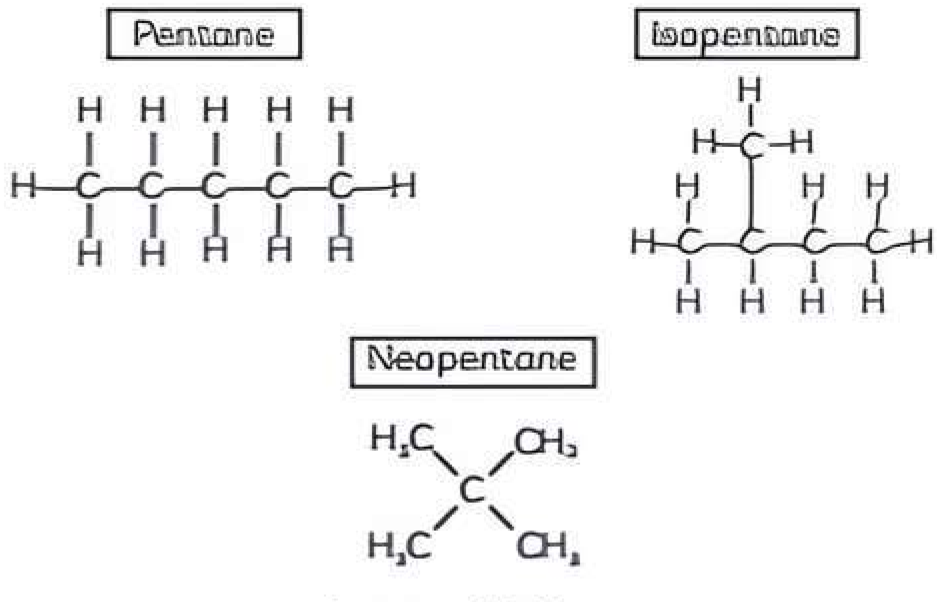
2-methyl propane (C_4H_{10})
(Branched chain alkane)
(b.p. 261 K)

The Isomers of C_4H_{10}

Important

- *A **substituent** is one or a group of atoms that replaces (one or more) hydrogen atoms on the parent chain of a hydrocarbon, thereby becoming a moiety in the resultant (new) molecule. These groups or substituents are known as alkyl groups as they are derived from alkanes by the removal of one hydrogen atom.*
  The general formula for alkyl groups is C_nH_{2n+1}

Let's consider the structure of C_5H_{12}. The five carbons in C_5H_{12} can be joined either by continuous or branched chain; represented as follows:



Isomers of C_5H_{12}

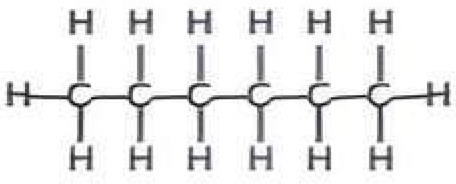
This phenomenon of hydrocarbons in which a compound possesses the same molecular formula but different structures are known as isomerism. Since the difference in properties arises due to the difference in their structures so, it is called as structural isomers.

pentane, isopentane and neopentane have the same molecular formula but different chains hence these are known as chain isomers.

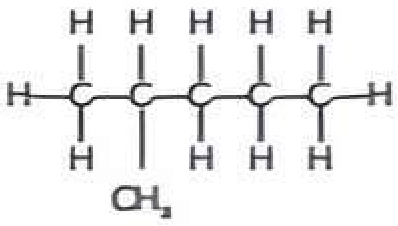
The C_6H_{14} has got five isomers and C_7H_{16} has nine and 75 isomers are possible for $C_{10}H_{22}$.

Example 1.1: **Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also, write their IUPAC names.**

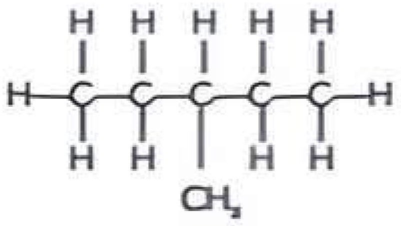
Ans.



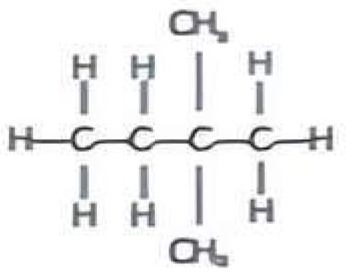
n-Hexane



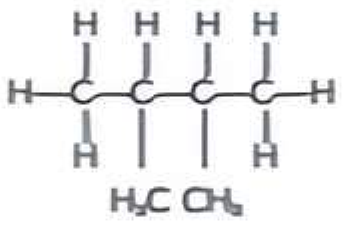
2- Methyl pentane (Isohexane)



3-Methyl pentane



2,2 Dimethyl butane (Neohexane)



2,3-Dimethyl butane

The possible chain isomers of C_6H_{14}

A carbon atom is classified as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°) depending on the number of carbon atoms linked to it. A primary carbon atom is connected to no other carbon atom, as in methane, or to only one carbon atom, as in ethane. Carbon atoms at the end of a chain are always primary. Secondary carbon atoms are those that are connected to two other carbon atoms. Three carbon atoms are attached to tertiary carbon, while four carbon atoms are attached to neo or quaternary carbon.

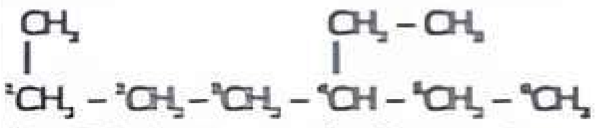
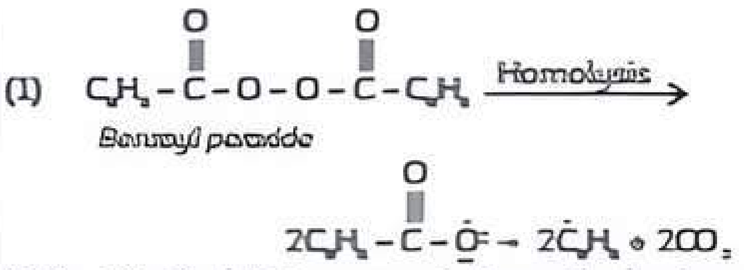
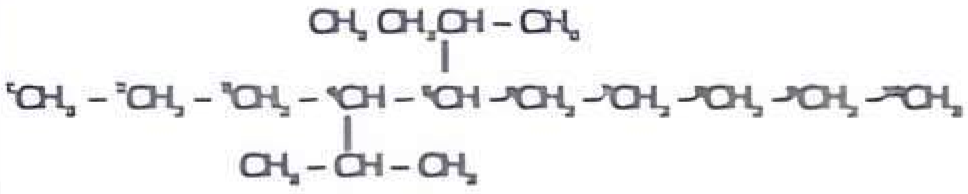
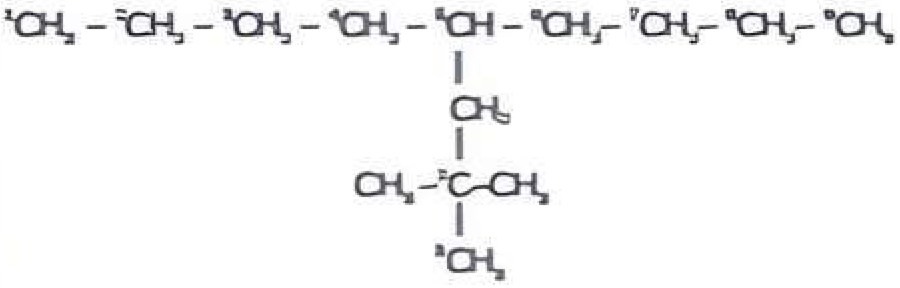
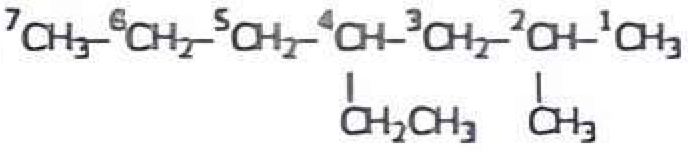
Example 1.2: **Write the structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of —OH at different carbons of the alkyl chain.**

Ans.

S. No.	Structure of – C_5H_{11} Group	Corresponding Alcohols	Name of Alcohols
(i)	$CH_3-CH_2-CH_2-CH_2-CH_2-$	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	Pentan-1-ol
(ii)	$CH_3-\underset{\vert}{CH}-CH_2-CH_2-CH_3$	$CH_3-\underset{\underset{OH}{\vert}}{CH_2}-CH_2-CH_2-CH_3$	Pentan-2-ol
(iii)	$CH_3-CH_2-\underset{\vert}{CH}-CH_2-CH_3$	$CH_3-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_3$	Pentan-3-ol
(iv)	$CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-$	$CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-OH$	3- Methyl-butan-1-ol
(v)	$CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-$	$CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-OH$	2- Methyl-butan-1-ol
(vi)	$CH_3-CH_2-\underset{\vert}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$	$CH_3-\underset{\underset{OH}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_3$	2- Methyl-butan-2-ol
(vii)	$CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-$	$CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-OH$	2,2- Dimethyl-propan-1-ol
(viii)	$CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\vert}{CH}-CH_3$	$CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{OH}{\vert}}{CH}-CH_3$	3- Methyl-butan-2-ol

The isomers of C_5H_{11}

Table: Nomenclature of few Alkanes

S. No.	Structure and IUPAC Name	Remarks
(i)	 (4 - Ethyl - 2 - methylhexane)	Lowest sum and alphabetical arrangement
(ii)	 (3,3 - Diethyl-5-isopropyl-4-methyloctane)	Lowest sum and alphabetical arrangement
(iii)	 (5-sec - butyl - 4 - isopropyl decane	sec is not considered while arranging alphabetically isopropyl is taken as one word
(iv)	 5 -(2, 2-Dimethylpropyl) nonane	Further numbering to the substituents of the side chain
(v)	 (4 - Ethyl - 2 - methylheptane	Alphabetical priority order

Example 1.3: Write IUPAC names of the following compounds :

(A) $(CH_3)_3\,C\,CH_2\,C(CH_3)_3$

(B) $(CH_3)_2\,C(C_2H_5)_2$

(C) tetra –tert butylmethane

Ans. (A) 2,2,4,4 – Tetramethyl pentane

(B) 3,3 – Dimethyl pentane

(C) 3,3–Di–tert–butyl–2,2,4,4–tetramethyl-pentane

To write the correct structure from the given IUPAC name, first choose the longest chain of carbon atoms corresponding to the parent alkane is written. Then number it, the substituents are attached to the correct carbon atoms and finally valency of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be understood by writing the structure of 3–ethyl –2, 2– dimethylpentane in the following steps:

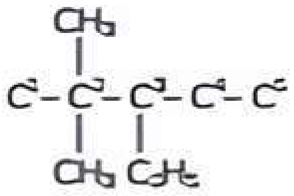
(1) Draw the chain of five carbon atoms:

C – C – C – C – C

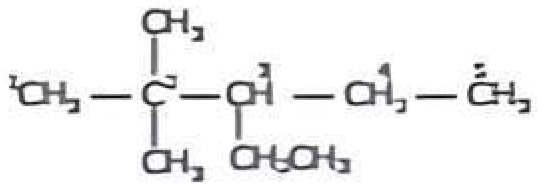
(2) Give number to carbon atoms

$C^1 - C^2 - C^3 - C^4 - C^5$

(3) Attach ethyl group at carbon 3 and two methyl groups at carbon 2



(4) Satisfy the valence of each carbon atom by putting a requisite number of hydrogen atoms:

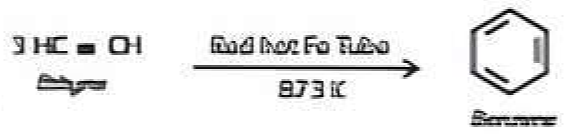


3-Ethyl-2,2-dimethyl pentane

Example 1.4: Write the structural formulas of the following compounds:

(A) 3,4,4,5 – Tetramethylheptane

(B) 2, 5 – Dimethylhexane

Ans. (A) 

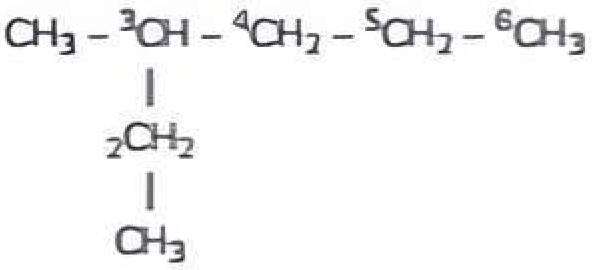
(B) 

Example 1.5: Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names.

(A) 2 – Ethylpentane

(B) 5 – Ethyl -3-Methyl-heptane

Ans. (A)

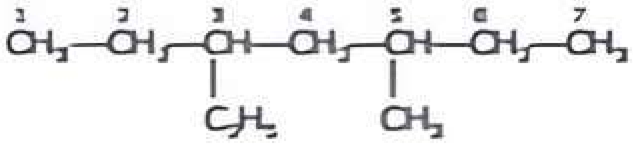


$$CH_3-{}^3CH(-{}_2CH_2-CH_3)-{}^4CH_2-{}^5CH_2-{}^6CH_3$$

2-Ethylpentane

Longest chain is of six carbon atoms and not that of five. Hence, the correct name is 3-Methyl hexane.

(B) Numbering is to be started from the end which gives lower number to ethyl group. Hence, the correct name is 3-ethyl-5-methyl heptane.



$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H(C_2H_5)-\overset{4}{C}H_2-\overset{5}{C}H(CH_3)-\overset{6}{C}H_2-\overset{7}{C}H_3$$

3-Ethyl 5-methyl heptane

Physical Properties

Some important physical properties of alkanes are:

(1) Alkanes are colourless and odourless.

(2) Alkanes having 1-4 carbon atoms are gases, then from 5-17 carbon atoms they are liquid and alkanes having 18 or more carbon atoms are solid at 298K. This is due to the presence of weak van der Waal's forces.

(3) Boiling point increases with the increasing molecular weight as the van der Waals forces increase with the increasing molecular weight. Straight chain alkanes have a higher boiling point than their structural isomers.

(4) Melting point also increases with increasing molecular weight because it is difficult to break the intermolecular forces of attraction between higher alkanes as they are generally solids. Even-numbered alkanes have better packing in the solid phase than the odd ones as they form a well-organised structure which is difficult to break hence even-numbered alkanes have a higher melting point than odd-numbered ones.

(6) Alkanes are generally insoluble in water as they are non-polar molecules because of the covalent bonds between C-C and C-H and also because of the very small difference between the electronegativities of carbon and hydrogen.

(7) Alkanes have a lower density than water, they float on water. Density increases with an increase in molecular mass.

Chemical Properties

Alkanes are inert towards acids, bases, oxidising and reducing agents. But they undergo the following reactions under certain conditions:

Substitution reactions

Halogens, nitro groups, and sulphonic acid groups can be used to substitute one or more hydrogen atoms in alkanes. Such reactions are known as substitution reactions. Alkanes undergo several substitution reactions like halogenation, nitration and sulphonation.

Halogenation

Halogenation occurs when a substance is heated to a higher temperature or when diffused sunlight or ultraviolet radiation is present. Nitration and sulphonation processes do not occur in lower alkanes. Substitution reactions are those in which hydrogen atoms in alkanes are replaced with other hydrogen atoms. For example

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

Chloromethane

$$CH_3-Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + HCl$$

Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$$

Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

Tetrachloromethane

$$CH_3-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-CH_2Cl + HCl$$

Chloroethane

Rate of reaction of alkanes with different halogens is $F_2 > Cl_2 > Br_2 > I_2$

Rate of replacement of hydrogens of alkanes is $3^\circ > 2^\circ > 1^\circ$

Fluorination is too violent to be controlled. Iodination is a very slow and reversible reaction. It can be carried out in the presence of oxidising agents like HIO_3 and HNO_3 .

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$HIO_3 + 5HI \rightleftharpoons 3I_2 + 3H_2O$$

Halogenation is done by a free radical mechanism. It involves three steps:

(1) Initiation

(2) Propagation

(3) Termination

(1) **Initiation:** The reaction is initiated by the homolysis of chlorine molecules in presence of light or heat. The bond is weaker than the C–H bond and hence is easiest to break.

$$Cl_2 \xrightarrow{\text{Light}} 2Cl$$

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

The methyl radical thus obtained attacks the second molecule of chlorine to form CH_3Cl with the liberation of another chlorine free radical by homolysis of the chlorine molecule.

$$Cl\cdot + CH_4 \longrightarrow HCl + \cdot CH_3$$
$$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

(3) **Termination:** The reaction stops after some time due to the consumption of reactants due to the following side reactions.

The possible chain-terminating steps are:

$$2Cl\cdot \longrightarrow Cl_2$$
$$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$
$$2\cdot CH_3 \longrightarrow CH_3CH_3$$

Though in (3). $CH_3 - Cl$ one of the products is formed free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a by-product during the chlorination of methane.

Combustion

Alkanes completely oxidise to carbon dioxide and water with the evolution of large amounts of heat on heating in presence of air or dioxygen. Since a large amount of heat is evolved during the combustion of alkanes, therefore they are used as fuels.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}\ \Delta H_c = -890\ kJ\,mol^{-1}$$

$$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)}$$

$$\Delta H_c = -2875.84\ kJ\,mol^{-1}$$

The general combustion equation for any alkane is :

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

The incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed. It is used in the manufacture of ink, printer ink, black pigments and as filters.

$$CH_{4(g)} + O_{2(g)} \xrightarrow[\text{Combustion}]{\text{Incomplete}} C_{(s)} + 2H_2O_{(l)}$$

Controlled oxidation

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalyst give different oxidation products.

$$2CH_{4(g)} + O_{2(g)} \xrightarrow[100\,atm]{Cu/523K} 2CH_3OH$$

Methanol

$$CH_{4(g)} + O_{2(g)} \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$$

Methanal

$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

Ethanoic acid

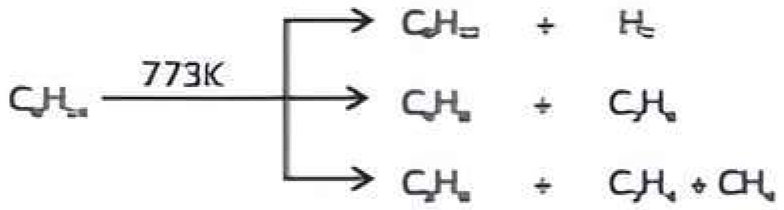
Alkanes do not undergo oxidation but alkanes having the tertiary hydrogen atom are oxidized to alcohols by potassium permanganate.

$$(CH_3)_3OH \xrightarrow[\text{Oxidation}]{KMnO_4} (CH_3)_3COH$$

2-methylpropane 2-methylpropan-2-ol

Pyrolysis

Higher alkanes decompose into lower alkanes, alkenes, and other compounds when heated to higher temperatures. Pyrolysis, or cracking, is a breakdown reaction that uses heat to split into smaller particles. It follows a free radical reaction.



Pyrolysis of alkane

Important

➥ *(1) Petrol is a mixture of hydrocarbons and is used as fuel in automobiles.*

(2) Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains.

(3) Preparation of oil gas or petrol gas from kerosene oil or petrol involves the pyrolysis principle. In the presence of platinum, palladium or nickel Dodecane gives a mixture of heptane and pentene.

$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{Other products}$$

Conformations

In alkanes, the distribution of electrons in sigma molecular orbital is symmetrical around the internuclear axis of the C-C bond. Thus, it permits the possibility of free rotation about the C-C single bond. The spatial arrangement of atoms in space that allows free rotation of groups around C–C bond axis is called conformers or rotamers or conformational isomers.

Torsional strain

It is a weak repulsive interaction between the adjacent bonds of a molecule due to which the rotation around C–C bond is slightly hindered. The rotation around C–C is not completely free, it is hindered by a small energy barrier which is due to the repulsive interaction with adjacent bonds.

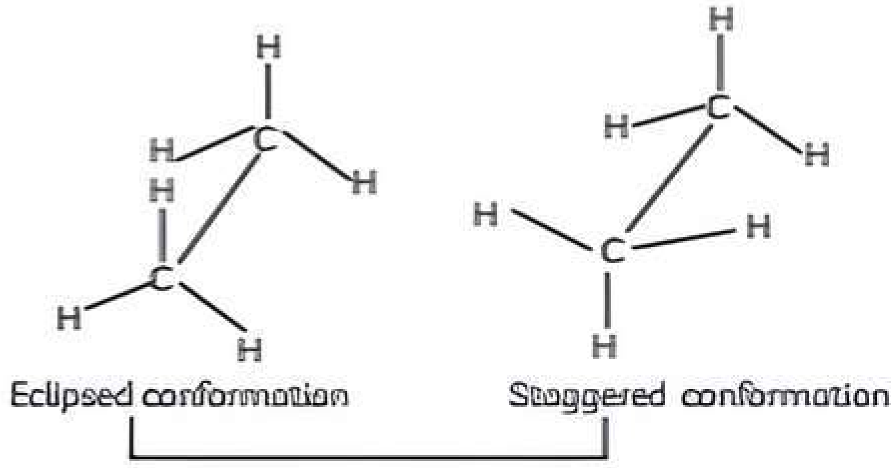
Conformations of ethane

Each carbon atom is connected to three hydrogen atoms in the ethane molecule C_2H_6, which has a single carbon-carbon bond. Keep one carbon atom immobile and spin the other carbon atom around the C–C axis using the ball and stick model of *ethane*. An infinite number of spatial arrangements of hydrogen are obtained with respect to carbon and hydrogen which are called conformational isomers. The conformation in which hydrogen atoms attached to two carbons are close to each other is called *eclipsed* conformation and in which the hydrogens are far apart is known as *staggered* conformation. Other intermediate conformations are skew conformations. All conformations have the same bond length and bond angles.

The eclipsed and staggered conformations are represented by Sawhorse and Newman projections.

Sawhorse Projections

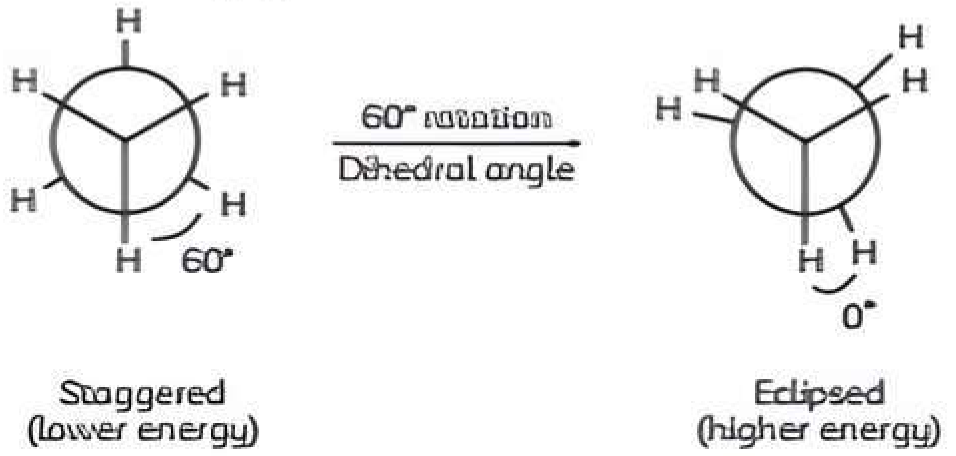
In this projection, the molecules are viewed along the molecular axis and projected on paper by drawing the central C–C bond as a longer straight line. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other, with the upper end slightly tilted towards the right or left-hand side. Sawhorse projections of conformations of ethane are depicted in the following figure.



Sawhorse projections of ethane

Newmann Projections

The molecule is viewed at C–C bond head-on, in this projection. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 60° to each other. A circle represents the rear carbon atom (the carbon atom away from the eye), and three shorter lines drawn at an angle of 60° to each other depict the three hydrogen atoms linked to it. The staggered and eclipsed Newman projections of ethane are shown in the following figure.

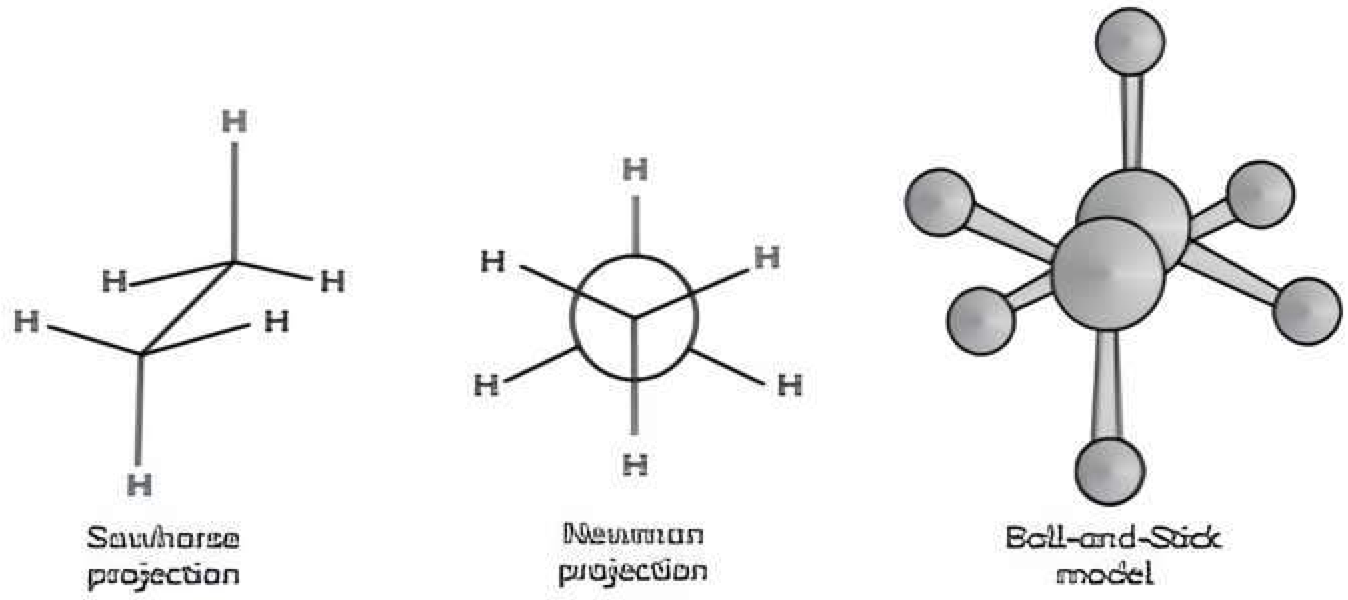


Newman projection of ethane

Relative stability of conformations

In the staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy, and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in an increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects the stability of a conformation, is called torsional strain. The magnitude of torsional strain depends upon the angle of rotation about the C–C bond. This angle is also called as **dihedral angle or torsional angle.** The rotation of C–C is not completely free. Therefore, staggered conformation is more stable than eclipsed conformation.

The potential energy difference among the conformers of the ethane is about 3 kcal/mol or 12.5 kJ/mol called torsional strain (or energy barrier). this energy barrier can be overcome by gaining thermal or kinetic energy through intermolecular collisions. Due to the small difference in the energy, the two conformers are readily interconvertible and that's why it is not possible to separate the two conformations of ethane.



Newman, Sawhorse and Projections Ball and Stick

TOPIC 3

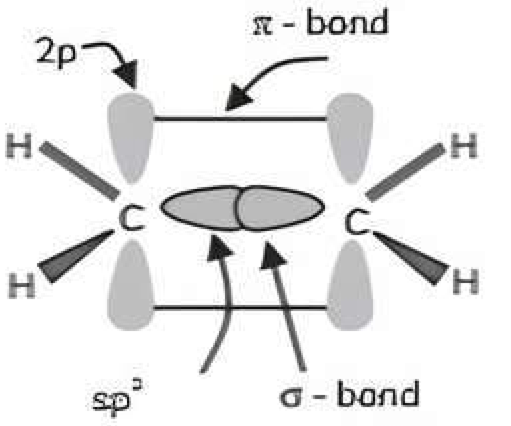
ALKENES

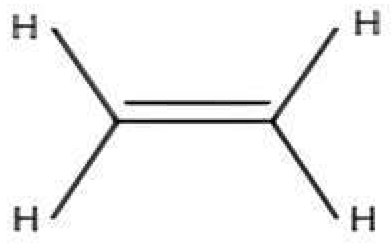
Alkenes are unsaturated hydrocarbons having at least one double bond between two carbon atoms and they possess two hydrogens less than alkanes (C = C). General formula of alkenes is (C_nH_{2n}). The first member of alkenes is ethylene or ethene (C_2H_4) which is an oily liquid that's why alkenes are also known as olefins (oil forming).

Structure of Double Bond

The double bond in alkenes consists of one strong sigma σ bond and one weak pi (π) bond due to the head-on overlapping of sp^2 hybridised orbitals and sideways overlapping of sp^2 orbitals of two carbon atoms respectively. The double bonds (C = C) have a shorter bond length of 134 *pm* than the single bonds (C – C).

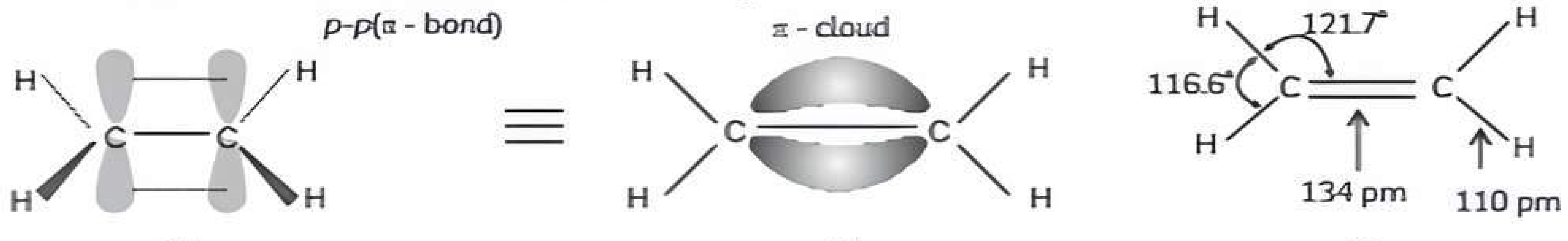
The π – bonds are formed by poor overlapping of p orbitals, thus the electron in the alkenes are loosely bound mobile electrons. These alkenes can be readily attacked by electron-accepting reagents that are electrophilic reagents. The presence of a weaker π bond in alkene makes it unstable when compared to alkanes and thus alkenes can be easily converted to alkanes by reacting with electrophilic reagents. Bond enthalpy of the double bond is 681 kJ mol^{-1} and the (C – C) bond enthalpy of bond is 348 kJ mol^{-1}.





Ethene

Orbital picture of ethene



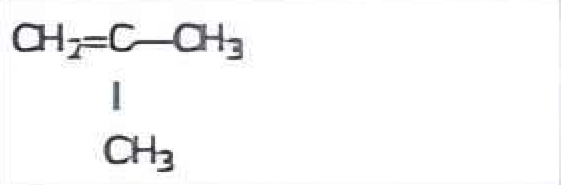
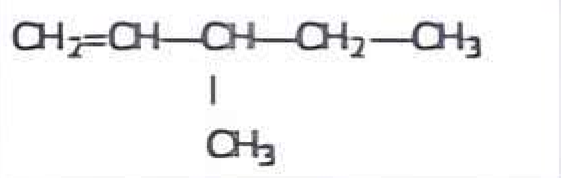
(a) *(b)* *(c)*

Orbital picture of ethene showing (a) π - bond, (b) π cloud and (c) bond angle and bond lengths

Nomenclature

The IUPAC nomenclature of alkenes is done by selecting the longest chain containing the double bond. Numbering is done from the end which is nearer to the double bond. The IUPAC names of simple alkenes are derived from the simple alkanes only by replacing the suffix –one to –ene. The first stable member of the alkene series is C_2H_4 ethylene (common name) or ethene (IUPAC).

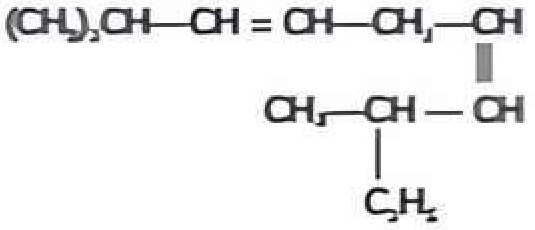
Table: Structure and IUPAC names of some alkenes

S. No	Structure	IUPAC Name
(1)	$CH_3—CH=CH_2$	Propene
(2)	$CH_3—CH=CH—CH_3$	2-Butene
(3)	 $CH_2=\underset{\underset{CH_3}{\mid}}{C}—CH_3$	2-Methyl-1-propene
(4)	 $CH_2=CH—\underset{\underset{CH_3}{\mid}}{CH}—CH_2—CH_3$	3-Methyl-1-pentene

Structure and IUPAC names

Example 1.7: Write the IUPAC names of the following alkenes.

(A)

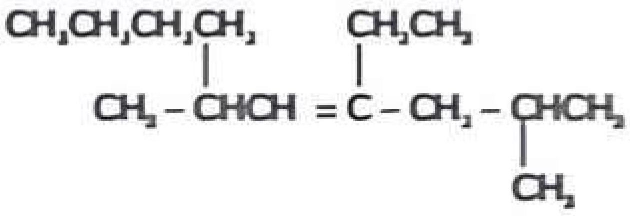


$$\begin{array}{l}(CH_3)_2CH—CH=CH—CH_2—CH\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad CH_3—CH—CH\\ \qquad\qquad\qquad\qquad\quad\ \mid \\ \qquad\qquad\qquad\qquad C_2H_5\end{array}$$

(B)

(C) $CH_2=C(CH_2CH_2CH_3)_2$

(D)



$$CH_3-\overset{\overset{CH_3CH_2CH_2CH_2}{\mid}}{CH}CH=\overset{\overset{CH_2CH_3}{\mid}}{C}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}CH_3$$

Ans. (A) 2,8 – Dimethyl – 3,6 – decadiene

(B) 1,3,5,7 – Octatetraene

(C) 2-Propylpent – 1 – ene

(D) 4 - Ethyl –2,6 – dimethyl – dec –4 – ene

Example 1.8: Calculate the number of sigma bonds (σ) and pi bonds (π) in the above structures

Ans. (A) σ bonds : 33, π bonds : 2

(B) σ bonds : 17, π bonds : 4

(C) σ bonds : 23, π bonds : 1

(D) σ bonds : 41, π bonds : 1

Isomerism

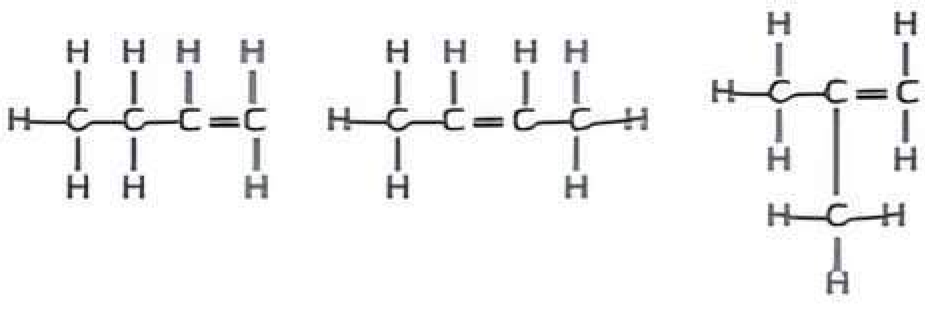
Alkenes show two types of isomerism:

(1) Structural isomerism

(2) Geometrical isomerism

Structural Isomerism

Alkenes higher than *propene* show structural isomers like chain and position isomers. Example: Structural isomers of *butene* (C_4H_8) are:



But-1-ene But-2-ene 2-Methylprop-1-ene

Structural Isomers of Butene

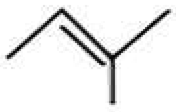
Structures first and third, and second and third are examples of chain isomerism whereas structures first and second are position isomers.

Example 1.9: **Write structures and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10}.**

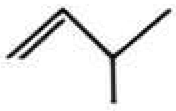
Ans.

Pent-1-ene

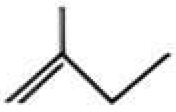
Pent-2-ene



2-Methylbut-2-ene



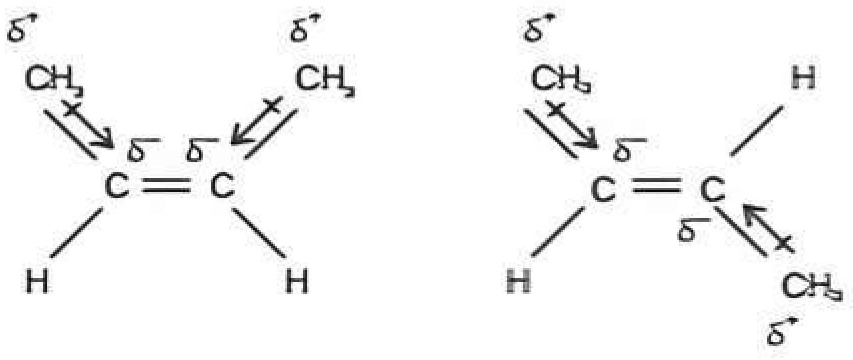
3-Methylbut-1-ene



2-Methylbut-1-ene

Geometrical Isomerism

The double-bonded carbon atoms satisfy the remaining valencies by joining with two atoms or groups. By considering their linkage geometrical isomers can be of two forms namely: *cis*– and *trans*–isomers. *cis*–isomers- in which the two identical groups lie on the same side of the double bond whereas *trans*-isomers are those in which the two identical groups lie on the opposite sides of the double bond.



cis-But-2-ene (μ = 0.33D) *trans*-But-2-ene (μ = 0)

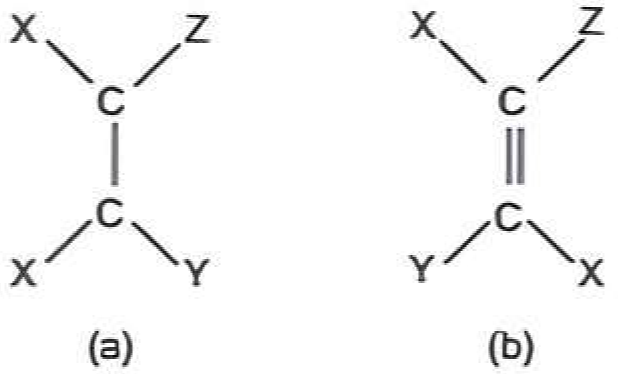
Geometrical Isomers representing the dipole moments.

These two isomers differ in physical properties:

Trans-isomers are non-polar because they have zero dipole moment. For example: the dipole moment of *cis*–2–butene is 0.33D whereas the dipole moment of *trans*–2–butene is almost zero because it is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in the *trans*–2–butene, the two methyl groups are in opposite directions. Therefore, dipole moments of C–CH_3 bonds cancel, thus making the *trans* form non-polar.

trans– form has higher melting point than *cis*– form in case of solids.

Geometrical or *cis-trans* isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW. They can represented in two ways, where figure (a) is a *cis* isomer and figure (b) is a *trans* isomer.

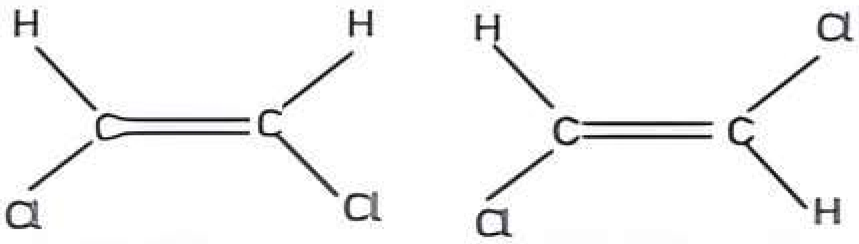


(a) (b)

Geometrical Isomerism

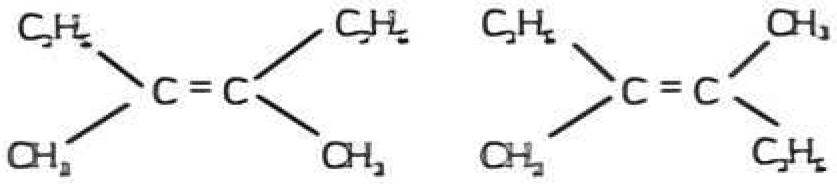
Example 1.10: **Draw *cis*– and *trans*– isomers of the following compounds. Also, write their *IUPAC* names: (A) CHCl=CHCl (B) $C_2H_5CCH_3 = CCH_3C_2H_5$**

Ans.



cis-1,2-dichloroethene *trans*-1, 2-dichloroethene

Isomers of dichloro ethene



cis-form *trans*-form

Isomers of 3,4-dimethyl hex-3-ene

Example 1.11: **Which of the following compounds will show geometrical isomerism?**

(i) $(CH_3)_2C = CH - C_2H_5$

(ii) $CH_2 = CBr_2$

(iii) $C_6H_5CH = CH - CH_3$

(iv) $C_6H_5CH = CH - C_6H_5$

Ans. Structures (iii) and (iv) will show geometrical isomerism as non-identical groups are linked to each doubly bonded carbon atom. In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atoms hence these will not show geometrical isomerism.

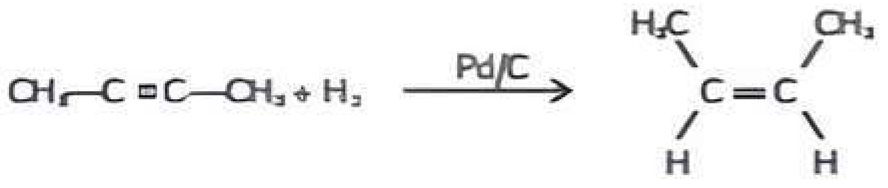
Preparation

From Alkynes

Alkynes on partial reduction in the presence of dihydrogen and palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes.

(1) Alkynes on reduction with this reagent give *cis*–alkenes.

Reagent: Partially deactivated palladised charcoal.



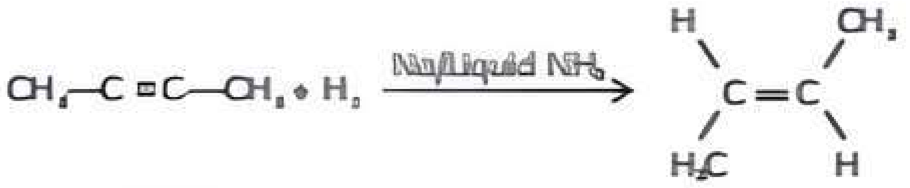
2- Butyne

cis - 2 - Butene

(2) Birch reduction:

Reagent- Sodium in liquid ammonia

Alkynes on reduction with this reagent gives *trans*– alkenes.

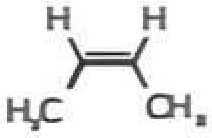


2- Butyne

trans-2-Butene

(3) Hydrogenation of an alkyne with Pd/ C and H_2 gives the alkane.

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2]{Pd/C} CH_3-CH_2-CH_2-CH_3$$

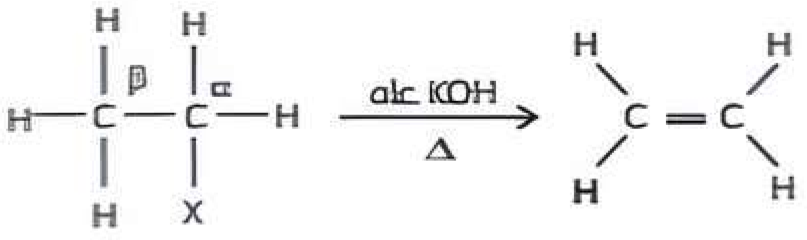
proceeds via 

(4) Hydrogenation of propyne to propene

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

From Alkyl halides

Dehydrohalogenation: Alkyl halides on reaction with alcoholic potash in presence of heat eliminate one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation. It is an example of β elimination reaction.



(X = Cl, Br, I)

Important

➥ *Reactivity order of halides: I > Br > Cl*

Reactivity order of alkyl groups: 3° > 2° > 1°

From vicinal dihalides

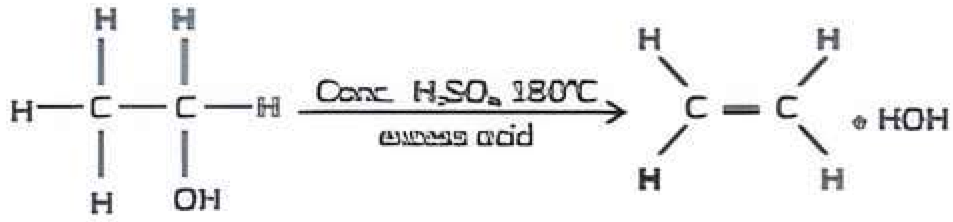
Two halogen atoms attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on reaction with zinc metal forms alkene by the elimination of ZnX_2 molecule. This reaction is also known as dehalogenation.

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

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

From alcohols by acidic dehydration

Alcohols on treatment with concentrated sulphuric acid form alkenes with the elimination of one water molecule. This is also a β elimination reaction.



Properties

Physical Properties

The first three members of alkenes are gases, the next fourteen members are liquids and the higher alkene are solids. Alkenes are colourless and odourless. But ethene is a colourless gas with a faint sweet smell. All alkenes are insoluble in water but fairly soluble in a non-polar solvent like benzene, petroleum or ether. Boiling point of alkenes increases with size by straight chains have a higher boiling point than isomeric branched chain compounds.

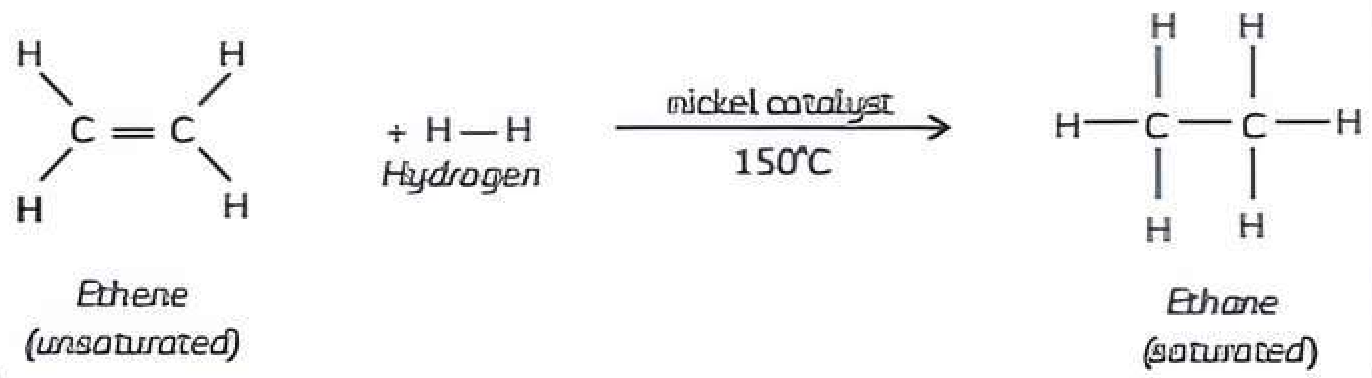
Chemical Properties

Alkenes are a rich source of loosely held π-electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents are also added by the free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of the different reactions of alkenes is given below:

(1) Addition of dihydrogen

Alkenes in presence of finely divided nickel, platinum and palladium, form alkanes by the addition of one molecule of dihydrogen gas to it.

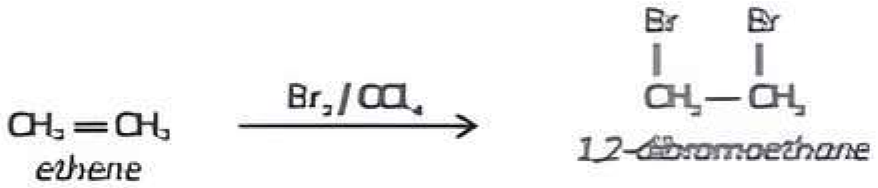
$$C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$$



Addition of dihydrogen in ethene

(2) Addition of halogens

Addition of bromine and chlorine to alkenes forms vicinal dihalides. Iodine does not show an addition reaction. When bromine is added to unsaturated compounds a reddish-orange colour of bromine solution is discharged which is used for the tests for unsaturation. This is an electrophilic addition reaction involving cyclic halonium ion formation.

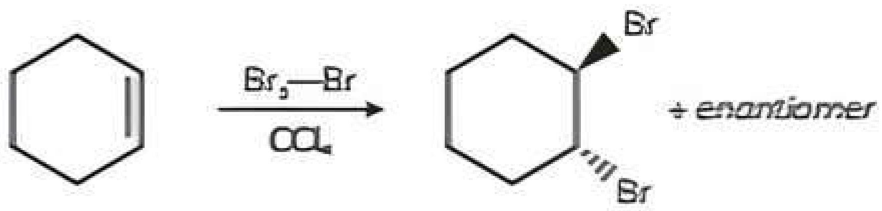


$$\underset{\text{ethene}}{CH_2=CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{1,2-dibromoethane}}{\overset{Br}{CH_2}-\overset{Br}{CH_2}}$$

Bromination of ethene

$$CH_3-CH=CH_2 + Cl_2 \longrightarrow CH_3-CHCl-CH_2Cl$$

Propene to 1,2-dichloropropane



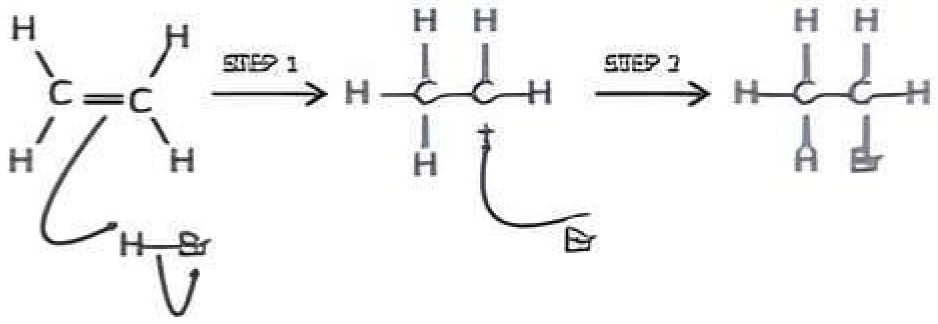
Addition of halogens in alkene

(3) Addition of hydrogen halides

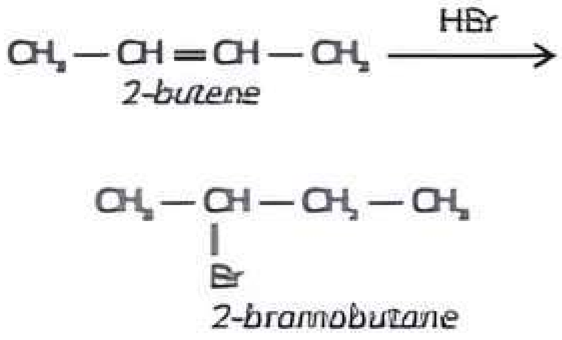
Hydrogen halides add up to alkenes to form alkyl halides. It is an electrophilic addition reaction. Reactivity order of hydrogen halide: HI > HBr > HCl

(i) Addition of HBr to symmetrical alkenes

The hydrogen bromide gets added to the symmetrical alkenes. This follows the electrophilic addition mechanism.



HBr addition to symmetrical alkenes



$$\underset{\text{2-butene}}{CH_3-CH=CH-CH_3} \xrightarrow{HBr} \underset{\text{2-bromobutane}}{CH_3-\underset{Br}{CH}-CH_2-CH_3}$$

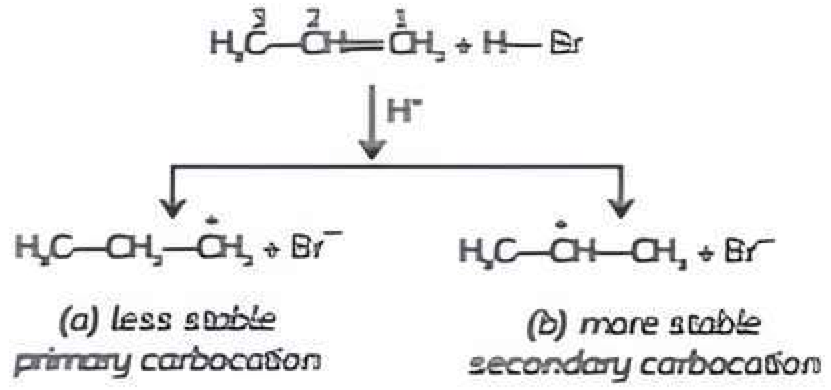
Addition of hydrogen bromide to 2-butene

(ii) Addition of HBr to unsymmetrical alkenes (Markovnikov rule)

Addition of HBr to an unsymmetrical alkene follows Markonikov's rule. According to this rule, the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses a lesser number of hydrogen atoms.

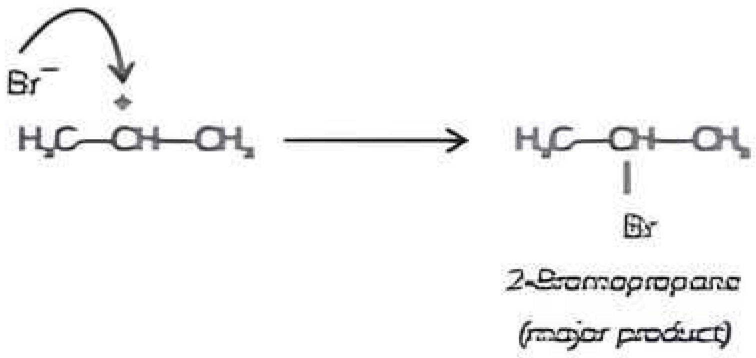
Mechanism:

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



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

(2) The carbocation (b) is attacked by Br^- ion to form the product as follows:



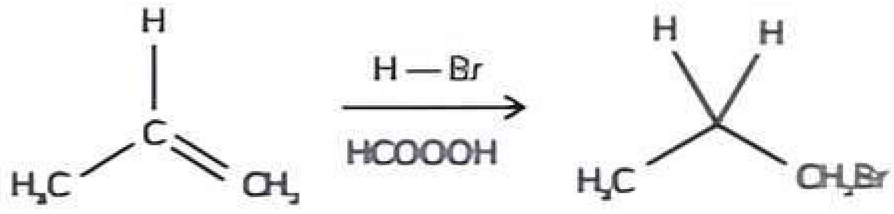
$$H_3C-\overset{+}{C}H-CH_3 + Br^- \longrightarrow H_3C-\underset{Br}{CH}-CH_3$$

2-Bromopropane
(major product)

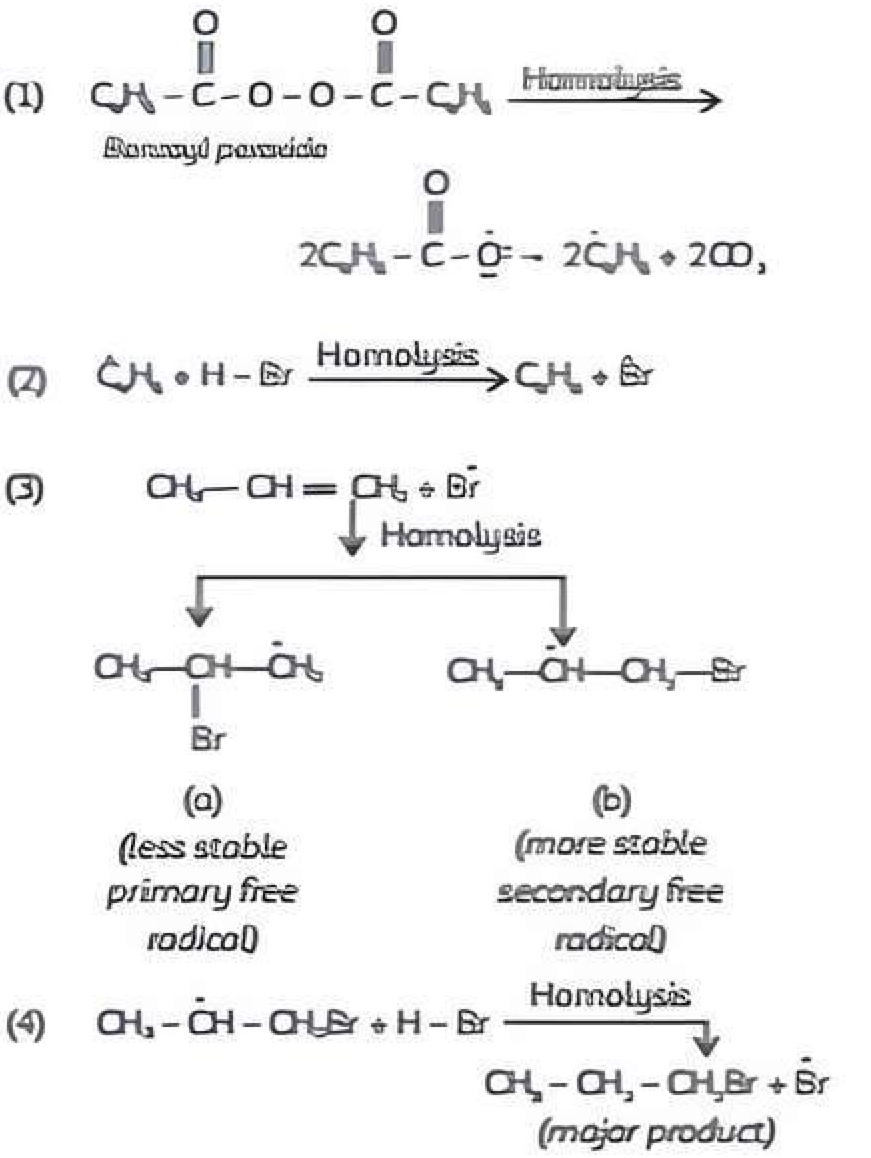
(iii) Anti-Markovnikov rule or Kharash effect or peroxide effect

Addition of HBr to unsymmetrical alkenes in the presence of peroxide (HCOOOH) is done according to karash or peroxide effect (opposite to the Markovnikov rule). This effect follows a free radical mechanism.

For example: The addition of *HBr* to *Propene* in presence of peroxide gives 1–*bromopropane*.



Mechanism: Peroxide effect proceeds via free radical chain mechanism:



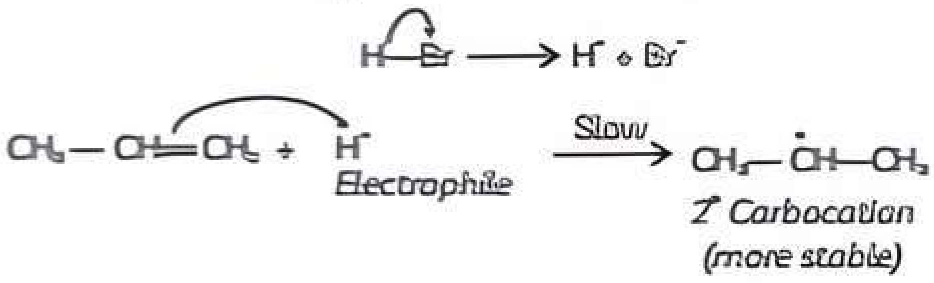
Important

➥ *The anti-Markovnikov addition is applicable for HBr only not for HCl or HI.*
This could be because the H–Cl bond is stronger (430.5 kJ mol^{-1}) than the H–Br bond (363.7 kJ mol^{-1}), and the free radical does not leave it, whereas the H–I bond is weaker (296.8 KJ mol^{-1}), and iodine free radicals combine to produce iodine molecules instead of adding to the double bond.

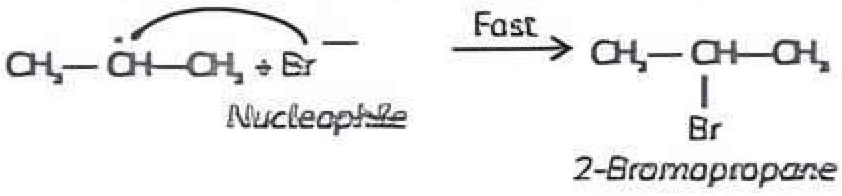
Example 1.12: Addition of HBr to propene yields 2-bromopropane, while in presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give the mechanism. **[NCERT]**

Ans. The addition of HBr to propene yield 2-bromopropane, is an electrophilic addition reaction.

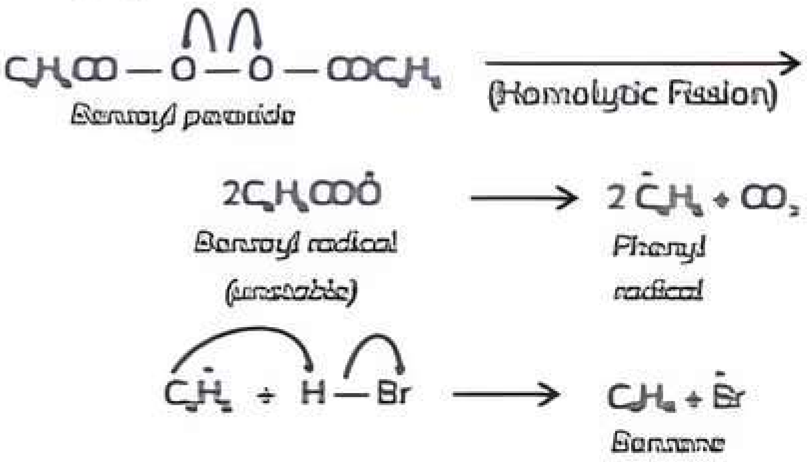
Ist step: The electrophile i.e. H^+ is first substituted to give a more stable B carbocation.



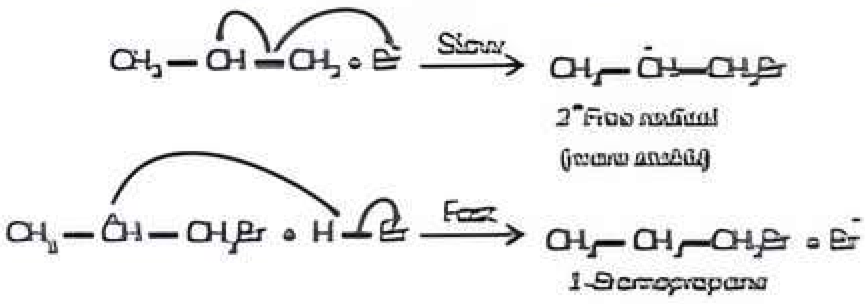
IInd step: The carbocation is attacked by the nucleophile Br^- ion to give 2–*bromopropane*.



In presence of benzoyl peroxide the reaction is still electrophilic but the electrophile here is a *Br•* free radical which is obtained by the action of $C_6H_5^\bullet$ on HBr.



In the first step, the *Br•* radical reacts with propene to produce the more stable 2° free radical. The free radical thus formed promptly abstracts a hydrogen atom from *HBr* in the second step, yielding 1–*bromopropane*.



Although both reactions are electrophilic addition reactions, it is clear from the previous description that the products differ due to the order of addition of *H* and *Br* atoms.

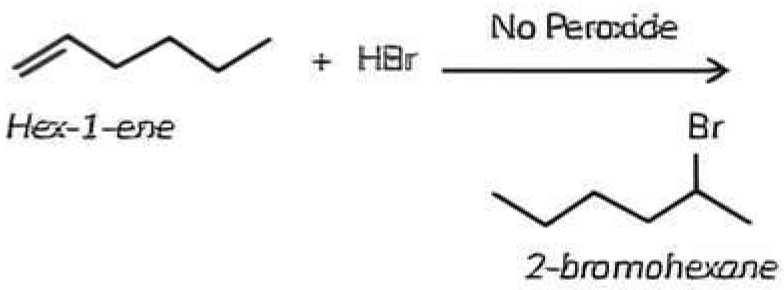
Example 1.13: Write the names of the products obtained by the addition reaction of hydrogen bromide to hex-1-ene:

(A) In the absence of peroxide

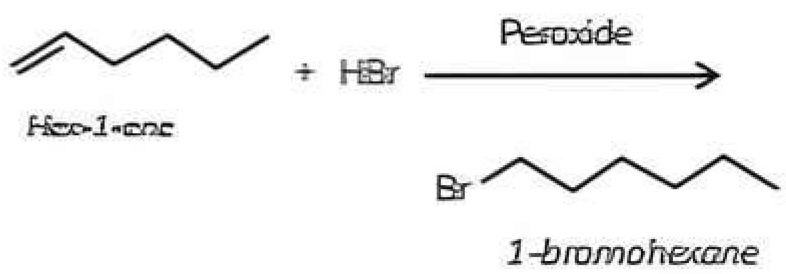
(B) In the presence of peroxide.

Ans.

(A)

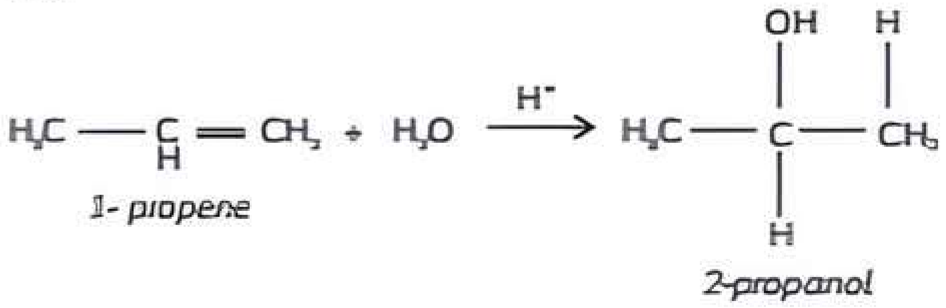


(3)



(4) Addition of water

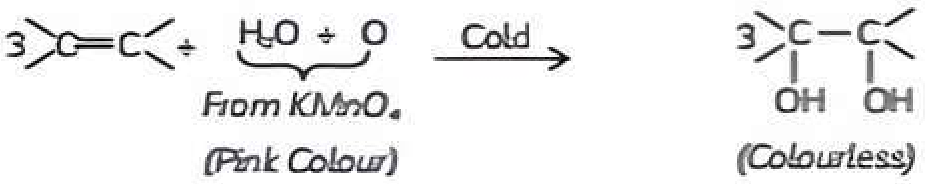
Alkenes react with water in the presence of acid and water to form alcohols, following the Markovnikov rule.

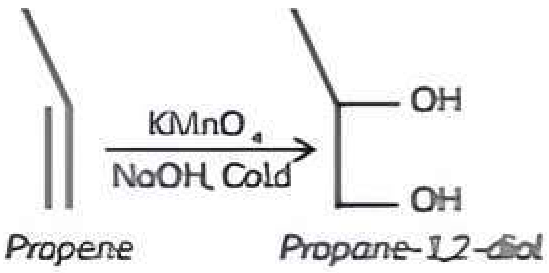


(5) Oxidation

Alkenes on reaction with a cold dilute aqueous solution of potassium permanganate (Bayer's reagent) produce vicinal glycols.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$





Oxidation reaction with potassium permanganate

Alkenes on reaction with acidic potassium permanganate oxidise to ketones and acids depending upon the nature and condition of alkenes.

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

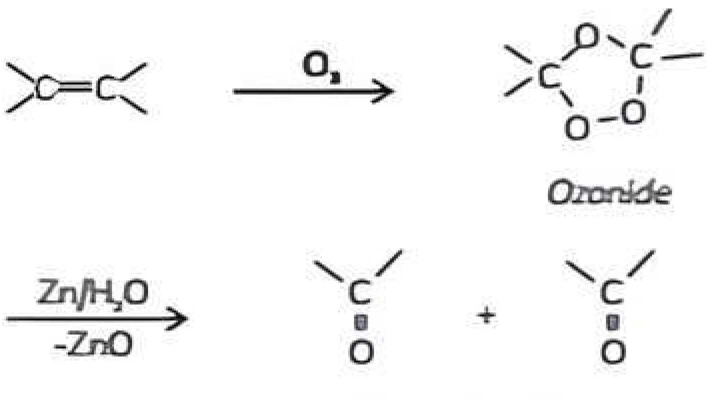
2- methylpropene Propane- 2 - one

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

But - 2 ene Ethanoic acid

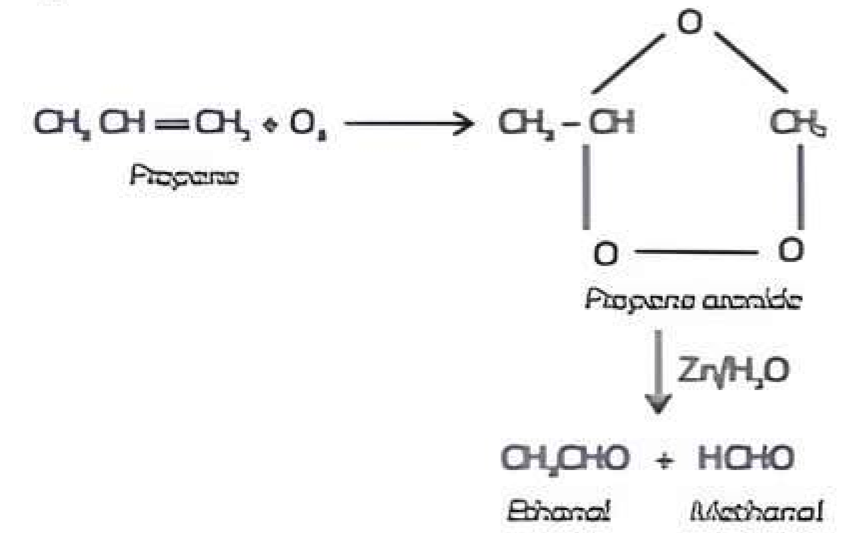
(6) Ozonolysis

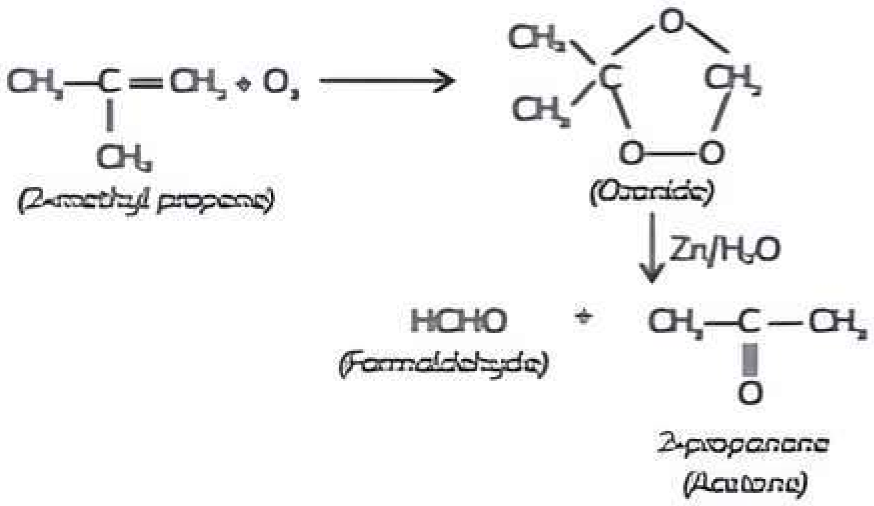
Ozonolysis of alkenes comprises the addition of an ozone molecule to the alkene to generate an ozonide, which is subsequently cleaved into smaller molecules by Zn – H_2O. The position of the double bond in alkenes or other unsaturated compounds can be determined using this reaction.



(Aldehyde or ketones)

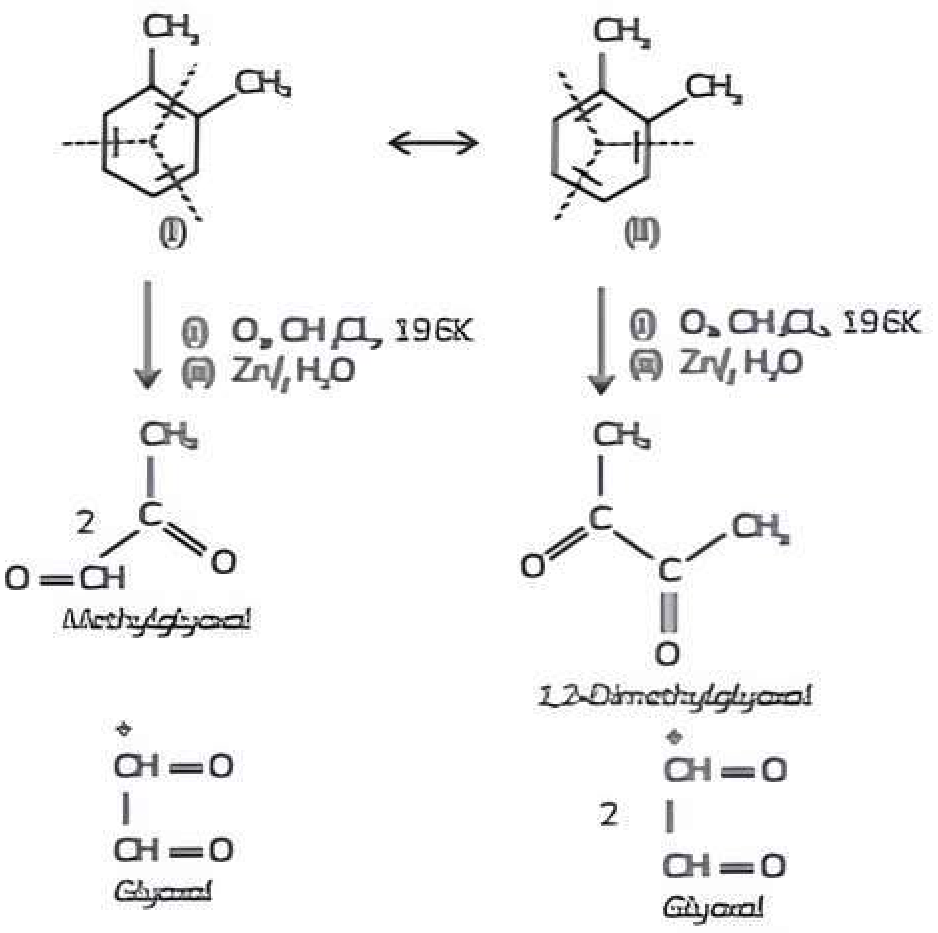
Example:





Example 1.14: Write down the products of ozonolysis of 1, 2– dimethyl benzene (o–xylene). How does the result support the Kekule's structure of benzene?

Ans. 1,2 – dimethyl benzene (o–xylene) may be regarded as a resonance hybrid of the following two Kekule structures. Ozonolysis of each one of these gives two products as shown below:



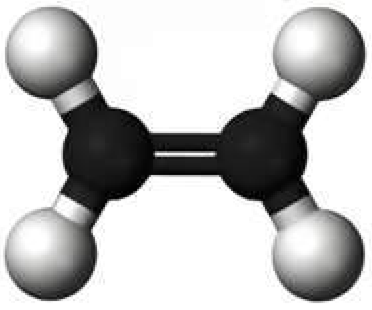
As a result, three products are formed. Because none of the three products can be formed from any of the two Kekule structures, this shows that (o–xylene) is a resonance hybrid of the two (I and II).

Example 1.15: Case Based:

Alkene is frequently used interchangeably with olefin, which refers to any hydrocarbon with one or more *double bonds. Monoalkenes are divided into two categories: terminal and internal. Terminal alkenes are more helpful. Alkenes are less stable than alkanes, but they are more reactive. The majority of alkene reactions involve additions to the pi bond, resulting in new single bonds. Because alkenes may participate in a wide range of processes, including polymerization and alkylation, they are used as feedstock in the petrochemical industry.*

Alkenes, with the exception of ethylene, contain two reactive sites: the carbon–carbon pi-bond and the presence of allylic centres. The former is more crucial, although the allylic site is also important.

Hydrocarbon cracking is used to make alkenes. Another major approach for the production of alkenes is the construction of a new carbon–carbon double bond by coupling a carbonyl compound (such as an aldehyde or ketone) to a carbanion equivalent. Olefination is a term used to describe such reactions. The Wittig reaction is the most well-known of these techniques. The stereoselective synthesis of disubstituted alkenes can be accomplished by reducing alkynes.



Molecular diagram of alkenes

(A) Which of the following is a Bayer's reagent?

- (a) Neutral potassium permanganate
- (b) Alkaline potassium permanganate
- (c) Acidic potassium dichromate
- (d) Acidic sodium dichromate

(B) Which of the following shows geometrical isomerism?

- (a) $CHCl = CHCl$
- (b) $CH_2 = CCl_2$
- (c) CCl2 = l give the structures of cis-and transforms
- (d) $CH_2=CH_2$

(C) Which is more acidic out of ethylene and acetylene. State the reason.

(D) How will you convert ethanoic acid to ethene?

(E) Assertion (A): In $CH_2 = C = CH_2$ all the hydrogen atoms lie in one plane.

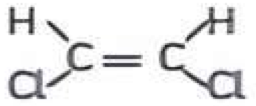
Reason (R): All the carbons in it are sp^2 hybridised.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

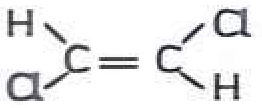
Ans. **(A)** *(b) Alkaline potassium permanganate*

(B) *(a) $CHCl = CHCl$*

Explanation:



cis 1, 2-dichloroethene



trans- 1, 2-dichloroethene

(C) Acetylene, ethylene and acetylene have sp^2, sp hybridized C atoms respectively. Due to the 50% s-Character of the C-H bond of acetylene rather than the 33% s-Character of the C-H bond in ethane, acetylene is more acidic.

(D) For the conversion of ethanoic acid to ethene following sequential reactions are involved:

$$CH_3COOH \xrightarrow{\text{NaOH(aq)}} CH_3COONa \xrightarrow[\Delta]{\text{Soda lime}}$$

$$CH_4 \xrightarrow[hv]{Cl_2} CH_3Cl \xrightarrow[\text{Wurtz reaction}]{\text{Na/dry ether}} C_2H_6$$

$$\xrightarrow{Cl_2} C_2H_5Cl \xrightarrow{\text{alc KOH}} CH_2 = CH_2$$

(E) *(d) (A) is false but (R) is true.*

Explanation: The two H–atoms on the first carbon and the two H–atoms on the third carbon atom in $CH_2 = C = CH_2$ lie perpendicular to the planes. The central carbon atoms are sp^2 hybridised.

TOPIC 4

ALKYNES

Alkynes are also unsaturated (–C ≡ C–) compound, having at least one triple bond. General formula of alkynes is C_nH_{2n-2}. The first stable member of alkyne series is ethyne which is popularly known as acetylene.

Nomenclature and Isomerism

Alkynes are name as derivatives of *acetylene* in common system. In *IUPAC* system they are named as derivatives of alkanes replacing suffix –one to yne. Acetylene is used for arc welding purposes in the form of oxyacetylene with oxygen gas. Alkynes are starting material for many organic compounds.

Table: Common and IUPAC names of alkynes

Value of n	Formula	Structure	Common Name	IUPAC Name
2	C_2H_2	$H\text{-}C \equiv CH$	Acetylene	Ethyne
3	C_3H_4	$CH_3 - C \equiv CH$	Methylacetylene	Propyne
4	C_4H_6	$CH_3\,CH_2 - C \equiv CH$	Ethylacetylene	But-1-yne
4	C_4H_6	$CH_3 - C \equiv C - CH_3$	Dimethylacetylene	But-2-yne

Ethyne and *propyne* have one structure and butyne have two structures namely *but-1-yne* and *but-2-yne*.

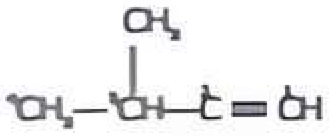
These two compounds differ in structure due to the position of the triple bond. So, they are called the position isomers. The C_5H_8 compound have the following possible position and chain isomers.

$CH_3-CH_2-CH_2-C\equiv CH$

1-pentyne

$CH_3-CH_2-C\equiv C-CH_3$

2-pentyne



$^4CH_3-\overset{\overset{CH_3}{|}}{^3CH}-{^2C}\equiv {^1CH}$

3-methyl-1-butyne

Position and chain isomers of C_5H_8

Example 1.16: **Write structures of different isomers corresponding to the fifth member of alkyne series. Also, write the IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers.**

Ans. The 5th member of alkyne has the molecular formula C_6H_{10}. The possible isomers are:

$CH\equiv C-CH_2-CH_2-CH_2-CH_3$

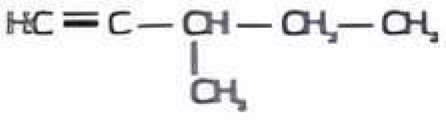
Hex-1-yne

$CH_3-C\equiv C-CH_2-CH_2-CH_3$

Hex-2-yne

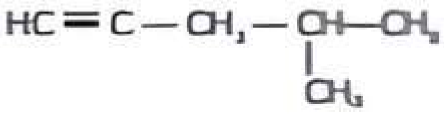
$CH_3-CH_2-C\equiv C-CH_2-CH_3$

Hex-3-yne



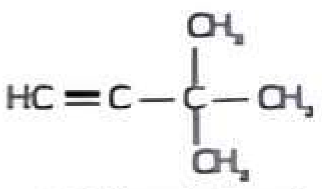
$HC\equiv C-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

3-Methylpent-1-yne



$HC\equiv C-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

4-Methylpent-1-yne



$HC\equiv C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

3,3-Dimethylbut-1-yne

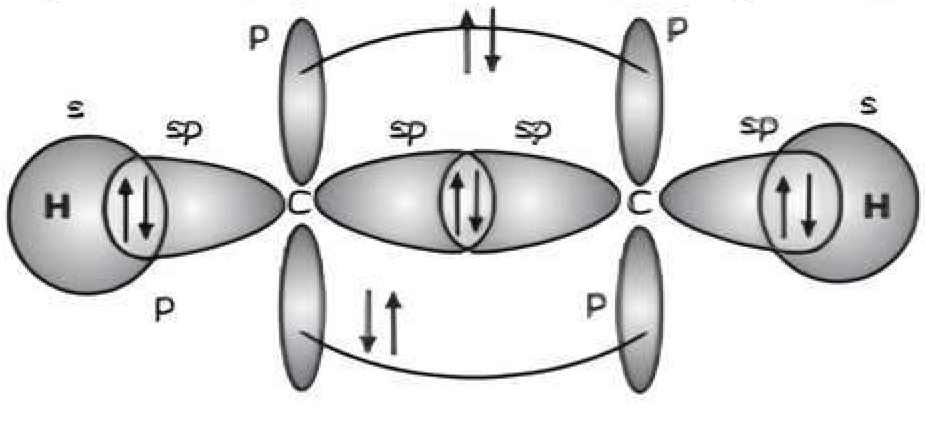
$CH_3-C\equiv C-\underset{\underset{CH_3}{|}}{CH}-CH_3$

4-Methylpent-2-yne

Position and chain isomers of C_6H_{10}

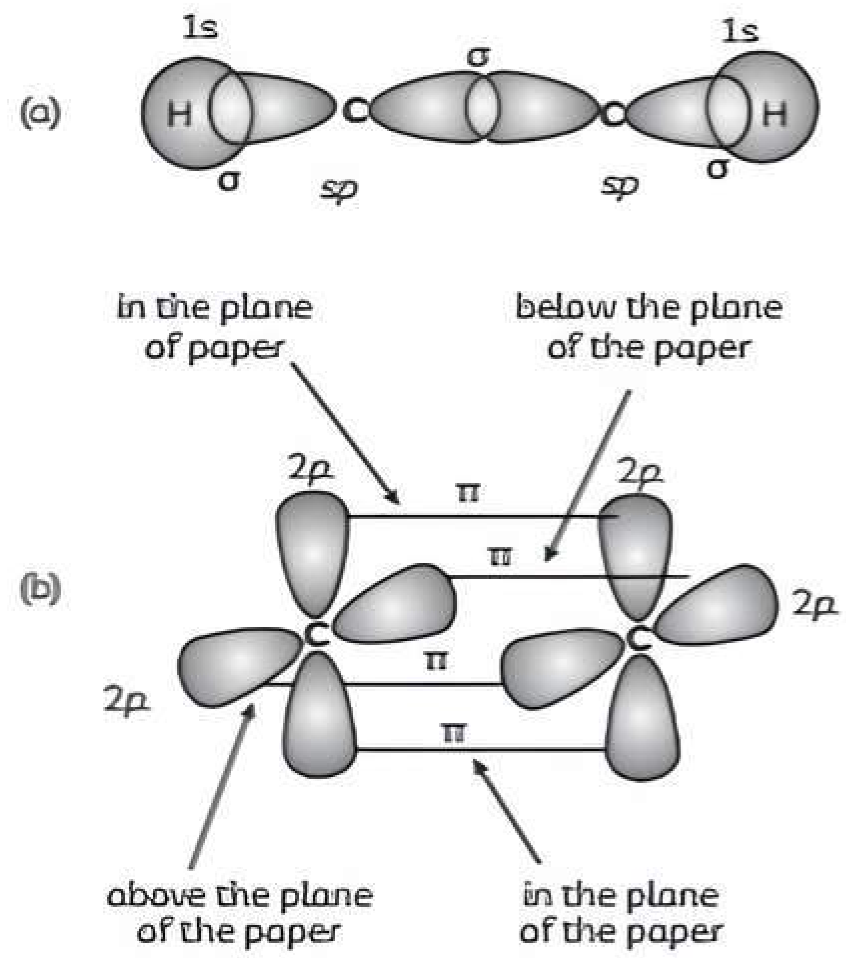
Structure of Triple Bond

Ethyne is the simplest molecule of the alkyne series.



Each carbon atom of ethyne has two *sp* hybridised orbitals. Carbon-carbon sigma bond is obtained by the head-on-overlapping of two *sp* hybridised orbitals of the two carbon atoms. The remaining *sp* hybridised orbitals of each carbon undergo overlapping along internuclear axis with 1s orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised *p* orbitals which are perpendicular to each other as well as to the plane of C-C sigma bond. The 2*p* orbitals of one carbon atom are parallel to the 2*p* orbitals of other carbon atom, which undergo lateral or sideways overlapping to form two π – bonds between two carbon atoms. Thus ethyne molecule consists of one *C–C* σ – bond, two *C–H* σ bonds and two *C–C* π – bonds.

The strength of C ≡ C bond (bond enthalpy 823 kJ mol^{-1}) is more than C=C (bond enthalpy 681 kJ mol^{-1}) and C-C (bond enthalpy 348 mol^{-1}). The bond length of C≡C is shorter than the bond length of C=C and C–C . Around the internuclear axis, the electron cloud between two carbon atoms is cylindrically symmetrical. It is thus a linear molecule.



Orbital picture of ethyne showing sigma and pi overlaps

Preparation

From calcium carbide

Ethyne is prepared by treating calcium carbide with water on an industrial scale. Quick lime is heated with coke to manufacture calcium carbide. The following reactions show how to make quick lime by heating limestone.

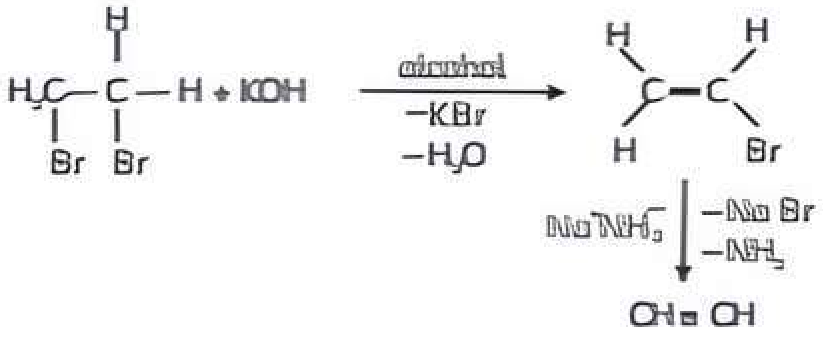
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \rightarrow \underset{\text{Calcium Carbide}}{CaC_2} + CO$$

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

From vicinal dihalides

Vicinal dihalides are dehydrohalogenated when exposed to alcoholic potassium hydroxide. One hydrogen halide molecule is removed to form *alkenyl halide*, which is then treated with soda amide to produce alkyne.



Properties

Physical Properties

Alkynes have the same physical properties as alkenes and alkanes. All alkynes are colourless. The odour of ethyne is distinctive. Other members have no odour. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. With an increase in molar mass, their melting point, boiling temperature, and density increase.

Chemical Properties

Alkynes show acidic nature, addition reactions and polymerisation reactions as follows:

(1) Acidic character of alkyne

Sodium metal and sodamide are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. In comparison to *ethene* and *ethane*, hydrogen atoms in ethyne can be released more easily as protons. The hydrogen atoms in ethyne are attached to the *sp* hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene and sp^3 hybridised carbons in ethane. Due to the maximum percentage of s-character, the *sp* hybridised orbitals of carbon atoms in ethyne molecules have the highest electronegativity, hence these attract the shared electron pair of the *C—H* bond of ethyne to a greater extent than that of the sp^2 hybridised orbitals of carbon in ethene and sp^3 hybridised orbitals of ethane. Hence, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. As a result, hydrogen atoms of ethyne, connected to a triply bonded carbon atom are acidic in nature. The hydrogen atoms connected to the triply bonded carbons are acidic but not all hydrogen atoms in alkynes.

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

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

These reactions are not shown by alkenes and alkanes.

Important

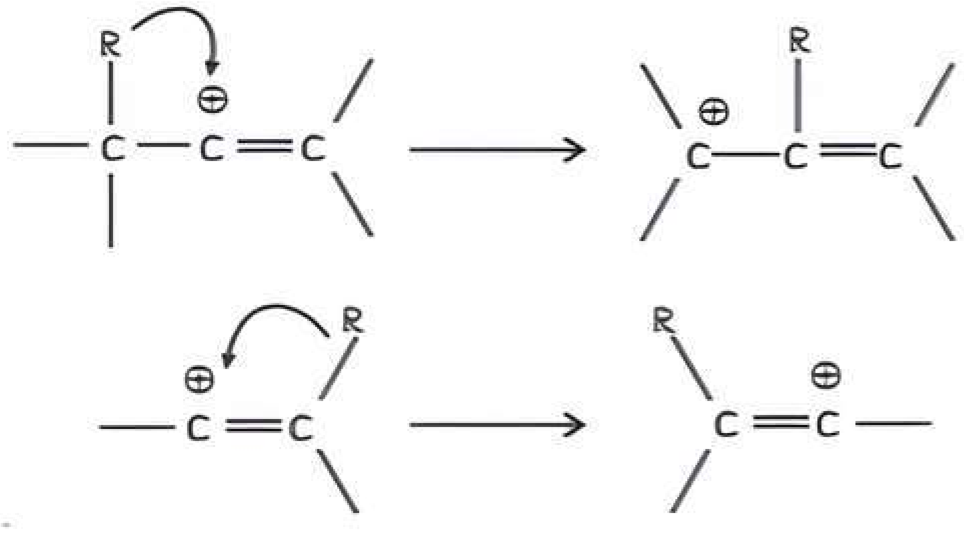
➥ *Acidic nature of alkane, alkene and alkyne are as follows:*

(1) $HC \equiv CH > H_2C = CH_2 > CH_3 - CH_3$

(2) $HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$

(2) Addition reactions

Alkyne contains a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides, etc. The formation of additional products takes place through the following steps:



Vinylic cation generation

The additional product formed depends upon the stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to The Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions are given below:

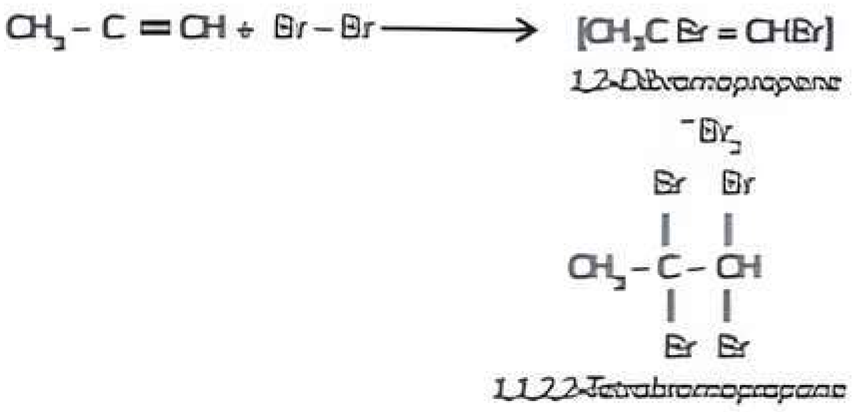
(i) Addition of dihydrogen

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

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

(ii) Addition of halogens

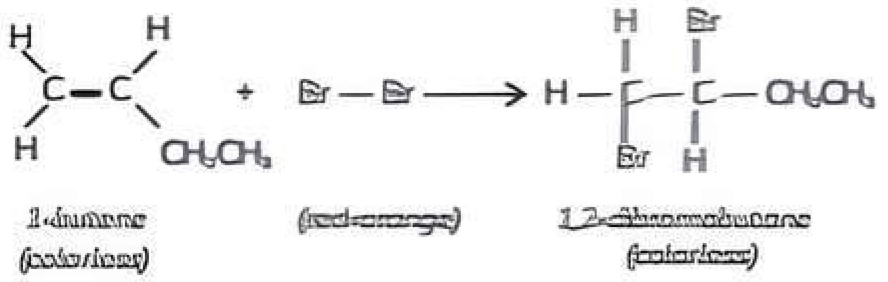
This method is used as a test for unsaturation where the reddish-orange colour of the solution of bromine in carbon tetrachloride is decolourised.

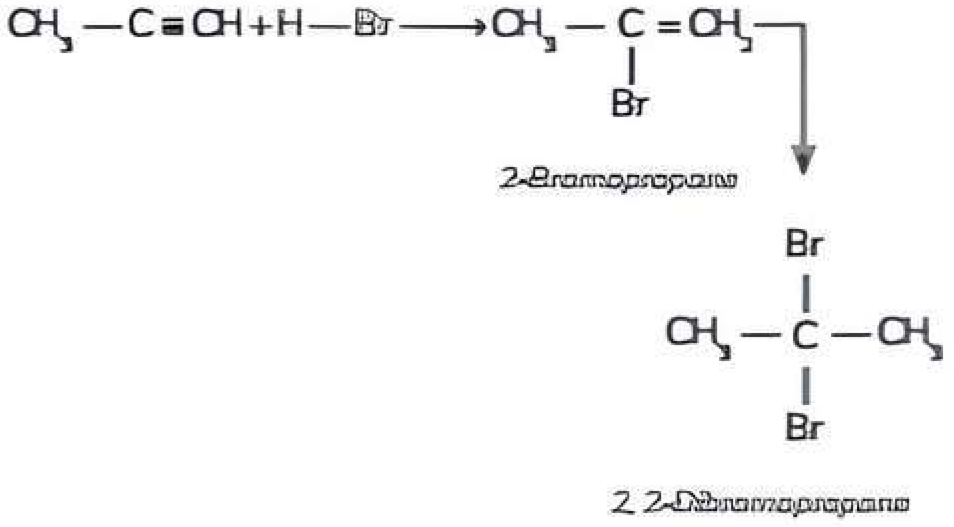


$$CH_3 - C \equiv CH + Br - Br \longrightarrow \underset{\text{1,2-Dibromopropene}}{[CH_3CBr = CHBr]} \xrightarrow{Br_2} \underset{\text{1,1,2,2-Tetrabromopropane}}{CH_3 - CBr_2 - CHBr_2}$$

(iii) Addition of hydrogen halides

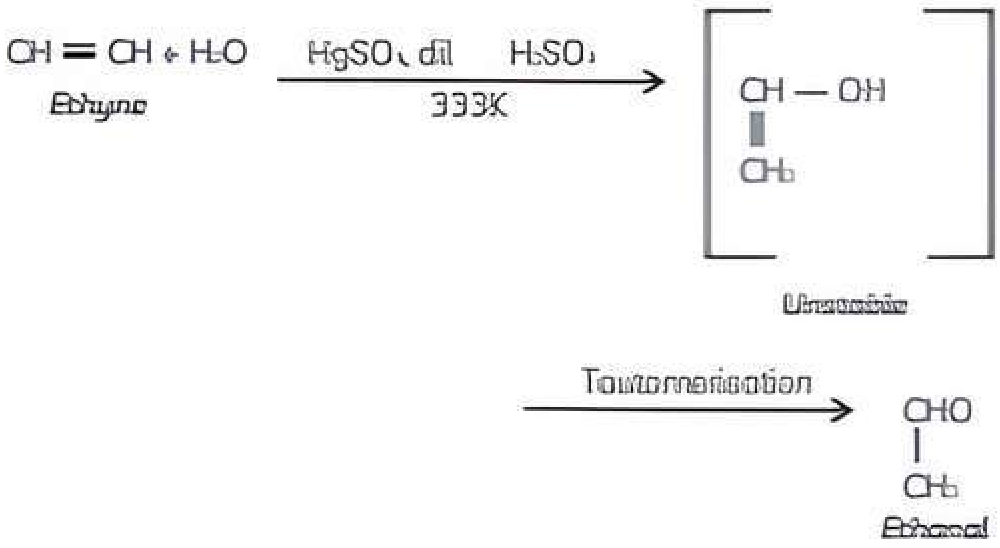
Two molecules of hydrogen halides are added to alkynes to form *gem – dihalides* (in which two halogens are attached to the same carbon atom).

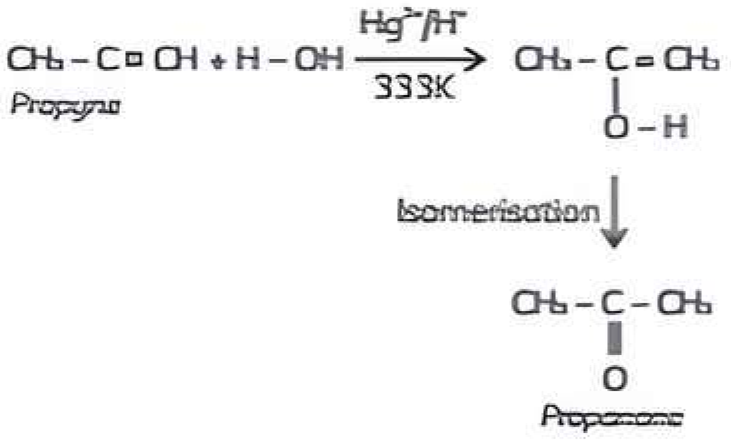




(iv) Addition of water

Like alkanes and alkenes, alkynes are also immiscible and have no reaction with water. However, when alkynes are heated with mercuric sulphate and dilute sulphuric acid at 333 K, one molecule of water is added forming carbonyl compounds.





Example 1.17: How will you convert the following compounds into benzene?

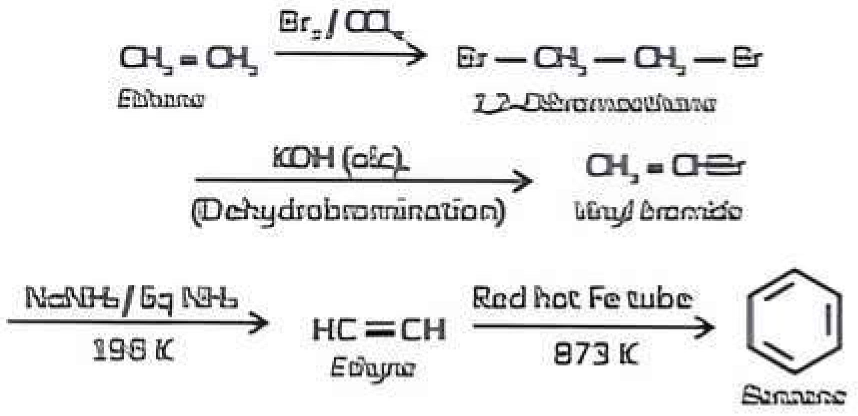
(A) Ethyne

(B) Ethene

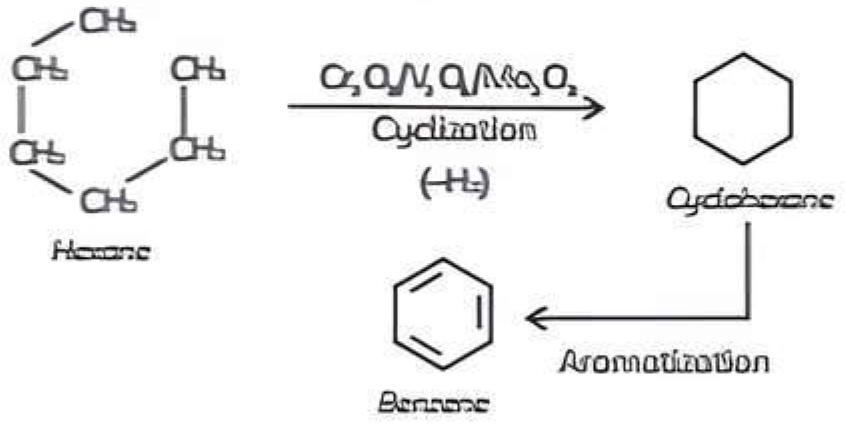
(C) Hexane

Ans. (A)

(B) Ethene is first converted into ethyne and then to benzene as shown above.



(C) When vapours of hexane are passed overheated catalyst consisting of Cr_2O_3, MO_2O_3 and V_2O_5 at 773 K under 10-20 atm pressure, cyclization and aromatization occur simultaneously to afford benzene.



Example 1.18: Case Based:

Hydrocarbons are colourless and hydrophobic with a mild odour. Because of their different chemical structures, it's impossible to generalise any more. The majority of anthropogenic hydrocarbon emissions come from the burning of fossil fuels. Plants emit hydrocarbons such as ethylene, isoprene, and monoterpenes. An alkyne is an unsaturated hydrocarbon with at least one carbon-carbon triple bond in organic chemistry. Alkynes, like other hydrocarbons, are hydrophobic in nature. The word acetylene is most usually used to refer to ethyne. It is the most basic of the alkynes, with two carbon atoms joined by a triple bond and each carbon atom capable of bonding to one hydrogen atom. Ethyne is often used in oxyacetylene gas welding and oxyacetylene gas cutting because it has a very hot flame. When ethyne is combined with oxygen, the ensuing flame has a temperature of approximately 3600 Kelvin. Millions of kilogrammes of acetylene are produced annually through fractional oxidation of natural gases, with the dominant alkyne being used as fuel. Some of these alkynes are used to make chemical compounds including ethanoic acid, acrylic acid, and ethanol. It's also utilised to create polymers and polymer raw materials.

(A) Which one of the following compounds forms salt on reaction with $NaNH_2$?

(a) C_2H_2 (b) C_2H_6

(c) C_6H_6 (d) C_2H_4

(B) The number of σ bonds and π bonds present in pent-4-ene-1-yne:

(a) 12, 3 (b) 10, 3

(c) 3, 9 (d) 12, 4

(C) The product formed in the reaction of propyne with dilute H_2SO_4 and $HgSO_4$ is:
   (a) Propyl hydrogen sulphate
   (b) Propanone
   (c) Propanal
   (d) Propanol

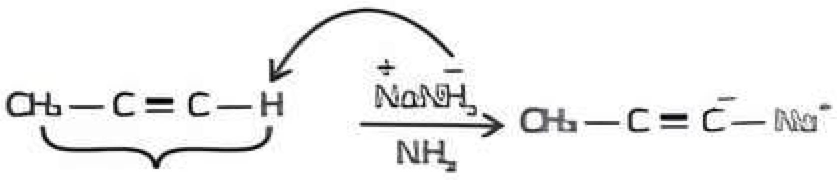
(D) What products are obtained by oxidative ozonolysis of Propyne?

(E) Assertion (A): $CH \equiv C^-$ is more stable than $CH_2 = CH^-$.

Reason (R): $CH \equiv C^-$ has more s character than $CH_2 = CH^-$.
   (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
   (b) Both (A) and (R) are true but (R) is not the true explanation of (A).
   (c) (A) is true but (R) is false.
   (d) (A) is false but (R) is true.

Ans. (A) *(a)* C_2H_2

Explanation: Only terminal alkynes react with $NaNH_2$ to form a salt.



(B) *(b)* 10. 3

Explanation: $\overset{1}{C}H \equiv \overset{2}{C} - \overset{3}{C}H_2 - \overset{4}{C}H = \overset{5}{C}H_2$

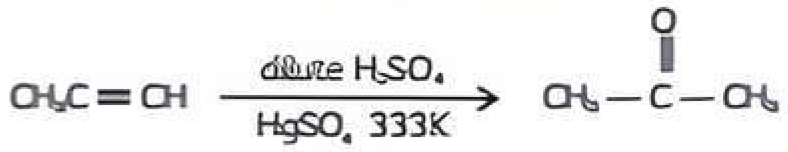
Pent-4-ene-1-yne

No of σ bonds = 4 $(C-C)$ + 6 $(C-H)$ = 10

No of π bonds = 1 $(C-C)$ + 2 $(C=C)$ = 3

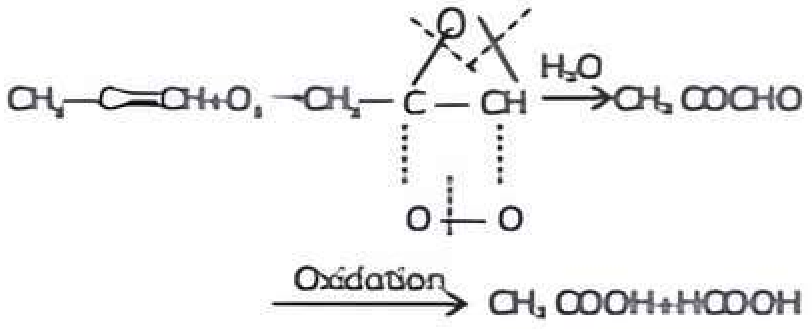
(C) *(b) Propanone*

Explanation: Propyne reacts with dilute H_2SO_4 and $HgSO_4$ to give propanone.



$$CH_3C \equiv CH \xrightarrow[HgSO_4,\ 333K]{\text{dilute } H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(D) Propyne with ozonolysis gives ethanoic acid and methanoic acid



(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: $CH \equiv C^-$ has 50% characters and $CH_2 = CH^-$ has 33% s – characters. Stability of carbanions increases with the increase in s – character at the carbanion. So. $CH \equiv C^-$ is more stable than $CH_2 = CH^-$. So. both the assertion and reason is true and reason is the correct explanation of assertion.

Related Theory

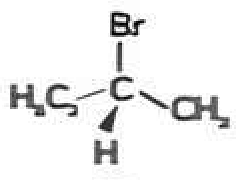
- *Acidity order is alkyne > alkene > alkane. Alkyne and alkanes have maximum and minimum acidic character respectively due to presence of maximum and minimum s character.*

OBJECTIVE Type Questions

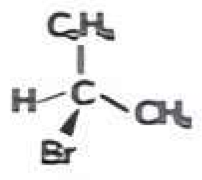
[1 mark]

Multiple Choice Questions

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



(A)



(B)

$CH_3-CH_2-CH_2-CH_2-Br$

(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, C as major products [NCERT Exemplar]

Ans. *(a) A and B as major and C as minor products.*

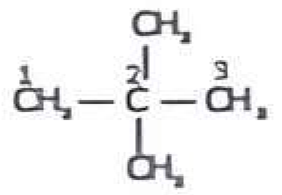
Explanation: Butene-1 is asymmetrical. Markovnikov's rule states that 2-Bromobutane is the major product and 1-Bromobutane is the minor product. Because 2-Bromobutane possesses chiral carbon, it has two enantiomers that are mirror images of one another. As a result, the mixture contains *A* and *B* as major and *C* as minor products.

2. .... has highest boiling point.
   (a) n-hexane
   (b) n-pentane
   (c) 2-methyl butane
   (d) 2, 2-dimethyl propane [Diksha]

Ans. *(a) n-hexane*

Explanation: The boiling point depends upon the molecular mass and branching. The boiling point increases with the increase in molecular mass and decreases with the branching. In the given options *n*-hexane have the highest molecular mass and 2, 2-dimethyl propane shows maximum branching. Therefore, the highest boiling point is shown by *n*-hexane.

n-hexane



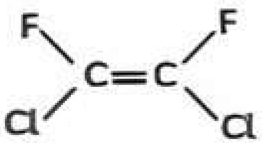
$$\overset{1}{C}H_3-\overset{2}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{3}{C}H_3$$

2, 2 dimethylpropane

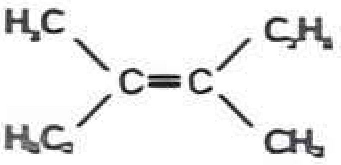
3. Which of the following will not show geometrical isomerism?

(a)

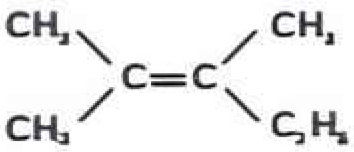
(b)



(c)

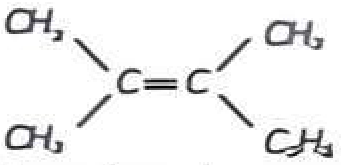


(d)

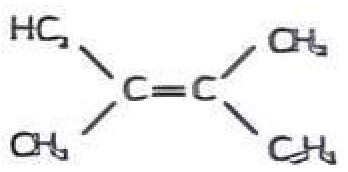


[NCERT Exemplar]

Ans. *(d)*



Explanation: In geometrical isomers, each carbon atom of the double bond must have different substituents. In option (d) a carbon with a double bond has two same functional groups (CH_3) attached. The rotation around the carbon will not produce a new compound. Hence, geometrical isomerism is not possible for



4. Cyclohexane on chlorination gives:

(a) Chlorocyclohexane

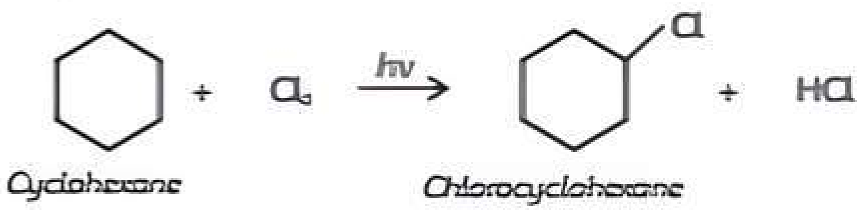
(b) 1, 2 – Dichlorocyclohexane

(c) 1,4 – Dichlorocyclohexane

(d) 2,2 – Dichlorocyclohexane

Ans. *(a) Chlorocyclohexane*

Explanation:



5. Action of acetylene on dilute H_2SO_4 gives:

(a) Acetic acid

(b) Acetone

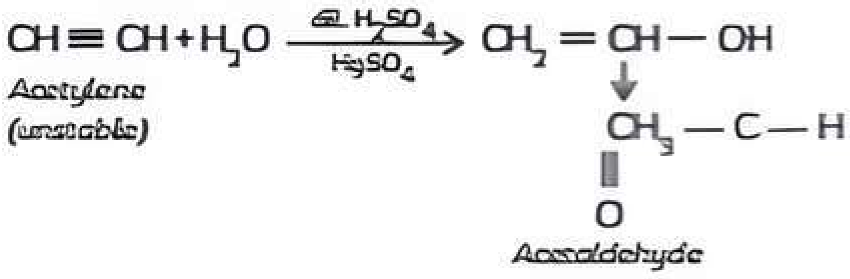
(c) Acetaldehyde

(d) Ethyl alcohol

[Delhi Gov. QB 2022]

Ans. *(c) Acetaldehyde*

Explanations: First water molecule gets added to acetylene, the product formed undergoes tautomerization and finally we get acetaldehyde.



$$\underset{\substack{\text{Acetylene}\\\text{(unstable)}}}{CH\equiv CH}+H_2O\xrightarrow[HgSO_4]{dil\ H_2SO_4}CH_2=CH-OH\ \downarrow\ \underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{O}{\|}}{C}-H}$$

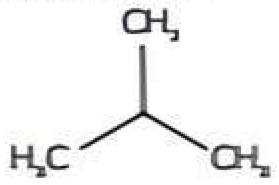
6. Which of the following compound cannot be obtained from single alkane by Wurtz reaction?

(a) Ethane *(b)* Butane

(c) Isobutane *(d)* hexane

Ans. *(c) Isobutane*

Explanation: Unsymmetrical alkanes are not formed by the Wurtz reaction. Only the higher and symmetrical alkanes are formed by this process. So, according to the options isobutane is an unsymmetrical alkane. Hence it cannot be formed by this mechanism.



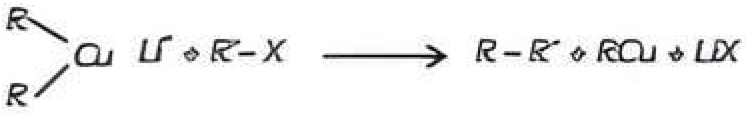
Related Theory

➥ *Corey-House synthesis*

The method is suitable for the formation of both symmetrical and unsymmetrical alkanes.

$$R{-}X+2\,Li\xrightarrow[\text{ether}]{\text{Dry}}\underset{\substack{\text{alkyl}\\\text{lithium}}}{R{-}Li}+LiX$$

$$2R-Li+CuI\longrightarrow[R_2Cu]^-\ Li^+ + LiI$$



$$R_2Cu^-\ Li^+ + R'-X\longrightarrow R-R'+RCu+LiX$$

7. Bromination of alkane as compared to chlorination proceeds:

(a) At a slower rate

(b) At a faster rate

(c) With equal rates

(d) With equal or different rates depending upon the temperatures.

Ans. *(a) At a slower rate*

Explanation: The rate of bromination of an alkane is slower than the rate of chlorination of an alkane. Halogenation, as we all know, involves the production of a carbon-halogen bond. The strength of the carbon-halogen bond will now determine how easy it is to undergo halogenation.

8. **The products formed when ethene reacts with bromine in an aqueous sodium chloride solution are:**
   - **(a) Ethylene dibromide and 1-bromo-2-chloro ethane**
   - **(b) Ethylene dibromide only**
   - **(c) Ethylene dichloride**
   - **(d) 1-bromo-2-chloroethane**

Ans. *(a) Ethylene dibromide and 1-bromo-2-chloro ethane*

Explanation: When *ethene* reacts with bromine in aqueous sodium chloride solution products formed are ethylene dibromide and 1-bromo-2-chloro ethane.

$$C_2H_4 + Br_2\ BrCH_2CH_3Br$$

$$C_2H_4Br^{+} + Cl^{-} \rightarrow Br^{-}CH_2CH_2{-}Cl$$

Hence first the process of bromination occurs to form Ethylene dibromide then further reaction with aqueous sodium chloride forms 1-bromo-2-chloroethane.

9. **Which of the following alkynes is used as rocket fuel?**

(a) Ethyne	**(b) Propyne**
(c) But-1-yne	**(d) Pent-1-yne**

[Diksha]

Ans. *(B) Propyne*

Explanation: European space companies have researched using light hydrocarbons with liquid oxygen, a relatively high-performing liquid rocket propellant combination that would also be less toxic than the commonly used monomethylhydrazine/nitrogen tetroxide. Their research showed that propyne would be highly advantageous as a rocket fuel for craft intended for low Earth orbital operations.

Assertion-Reason (A-R)

In the following question (Q. No. 10-13) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

- **(a) Both (A) and (R) are true and (R) is the correct explanation of (A).**
- **(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).**
- **(c) (A) is true but (R) is false.**
- **(d) (A) is false but (R) is true.**

10. **Assertion (A): Among isomeric pentanes, 2, 2-dimethyl propane has the lowest boiling point.**

Reason (R): Branching does not affect the boiling point.

Ans. *(c) (A) is true but (R) is false.*

Explanation: 2, 2–dimethylpropane has the lowest boiling point because branching affects the boiling point. As the branching increases, the boiling point decreases simultaneously. So, Assertion is true but Reason is false.

11. **Assertion (A): Sodium acetate on Kolbe's electrolysis give methane.**

Reason (R): Methyl free radical is formed at the anode.

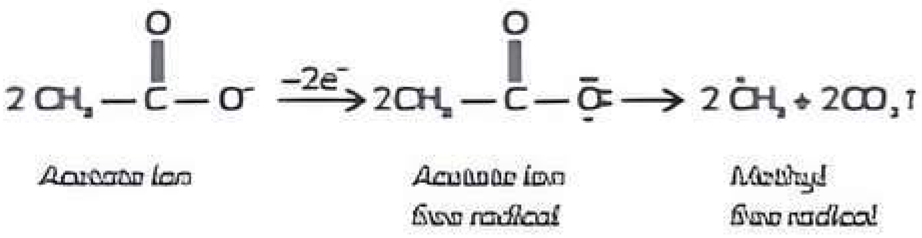
Ans. *(d) (A) is false but (R) is true.*

Explanation: Sodium acetate on Kolbe electrolysis gives ethane. It is formed at the anode.

Kolbe electrolysis reaction:

$$2CH_3COO^{-}Na^{+} + 2H_2O \xrightarrow{\Delta} CH_3CH_3 + 2CO_2 + H_2 + 2NaOH$$

At anode:



$$2\,CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{-} \xrightarrow{-2e^{-}} 2CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\dot{\bar{O}}: \longrightarrow 2\,\dot{C}H_3 + 2CO_2\uparrow$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3\uparrow$$

12. **Assertion (R): The IUPAC name of $CH_3CH = CH - C \equiv CH$ is pent-3-en-1-yne and not pent-2-en-4-yne.**

Reason (R): While deciding the locants of double and triple bonds, the lowest sum rule is always followed.

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Lowest sum rule is always followed. if both double and triple bonds are on same position then preference is given to the triple bond.

$$\overset{5}{C}H_3\overset{4}{C}H = \overset{3}{C}H - \overset{2}{C} \equiv \overset{1}{C}H \quad \text{(Lowest sum 1+3 =4)}$$

pent-3-en-1-yne (correct)

$$\overset{1}{C}H_3\overset{2}{C}H = \overset{3}{C}H - \overset{4}{C} \equiv \overset{5}{C}H \quad \text{(Sum 2+4 =6)}$$

pent-2-en-4-yne (incorrect)

13. **Assertion (A): Propene reacts with HBr in presence of benzyol peroxide to yield 1-bromopropane.**

Reason (R): In presence of peroxide, the addition of HBr to propene follows ionic mechanism.

Ans. *(c) (A) is true but (R) is false.*

Explanation: Propene reacts with HBr in presence of benzoyl peroxide to give 1–bromopropane. In presence of peroxide, the addition of HBr to propane occurs by a free radical mechanism.

CASE BASED Questions (CBQs)

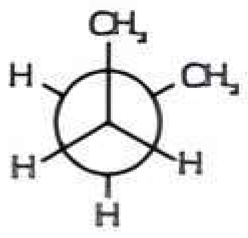
[**4** & **5** marks]

Read the following passages and answer the questions that follow:

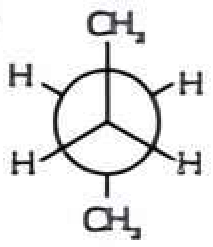
14. *Conformational isomerism is a type of stereoisomerism in chemistry in which isomers can be interconverted simply by rotating them around formally single bonds. While any two atomic configurations in a molecule that differ by rotation about single bonds are called distinct conformations. conformations that correspond to local minima on the potential energy surface are called conformational isomers or conformers. When hydrogen atoms are connected to two carbon regions as close to one other as possible, the conformation is called eclipsed. To further explain, the closest proximity of two substituents X and Y on adjacent atoms A and B indicates that the torsion angle X – A – B – Y is 0°. Another type of conformation is called a staggered conformation, which occurs when hydrogen atoms connected to two carbons are spaced as far apart as feasible. These conformations can be found in any open chain single chemical bond connecting two* sp^3 *hybridized atoms and have low conformational energy. For some compounds, such as n-butane, there are specialised kinds of staggered conformations called gauche and anti.*

(A) In the following, the most stable conformation of *n-butane* is:

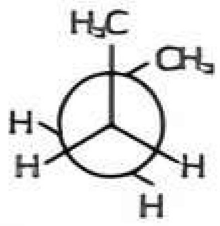
(a)



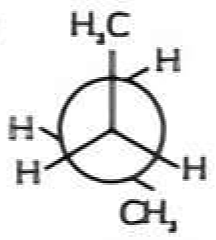
(b)



(c)



(d)



(B) With respect to conformers of ethane, which of the following is true?

(a) Bond length remains the same but the bond angle changes.

(b) Both length and bond angle changes.

(c) Bond angle and bond length remains the same.

(d) Bond angle remains the same and the bond length changes.

(C) Increasing order of stability of the three conformers of ethane is:

(a) eclipsed > gauche > staggered

(b) eclipsed < gauche < staggered

(c) gauche > staggered > eclipsed

(d) eclipsed > staggered > gauche

(D) Increasing order of stability of the three conformers of ethylene glycol is:

(a) eclipsed > gauche > staggered

(b) eclipsed < gauche < staggered

(c) gauche > staggered > eclipsed

(d) eclipsed < staggered > gauche

(E) The magnitude of torsional strain depends upon the:

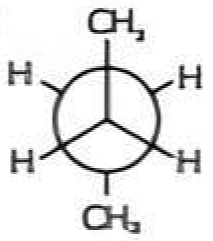
(a) dihedral angle

(b) staggered conformer

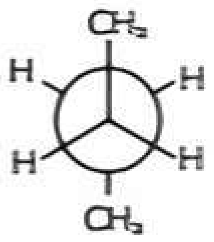
(c) eclipsed conformer

(d) none of the above

Ans. (A) *(b)*



Explanation: The anti-conformation is the most stable conformer of *n-butane*. The bulky methyl groups are spaced as widely apart as possible, reducing steric repulsions to a minimum and hence, increasing the stability.



(B) *(c) Bond angle and bond length remains the same.*

Explanation: Conformers are isomers that exist as a result of rotation around single bonds without any bond cleavage. An infinite number of conformations are possible in *ethane*. The two important forms are the *staggered* conformation, which is the most stable, and the eclipsed conformation of *ethane* that have the same bond angle and bond length but have different energy, stability, and dihedral angles.

(C) *(b) eclipsed < gauche < staggered*

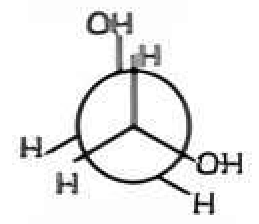
Explanation: The eclipsed conformer is the least stable because the hydrogen and bonding electron pairs on adjacent carbon are close to one another. This causes maximum repulsion and hence the least stability of the conformer. In *staggered* form, because the hydrogen and bonding electron pairs on adjacent carbon are far apart at *anti–position* to one another. Thus, gaining the minimum repulsion and maximum stability. The gauche form lies in between these two conformers. So, the order of stability is: eclipsed < gauche < staggered.

(D) *(c) gauche > staggered > eclipsed*

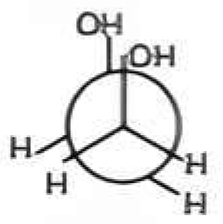
Explanation: In *ethylene glycol*, the gauche conformer is most stable due to the presence of *H–bonding* between the –OH groups of two carbons.

Related Theory

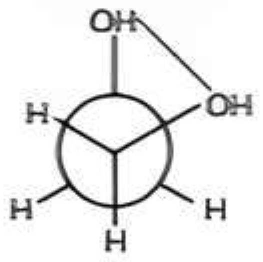
- *The different conformers of glycol are:*



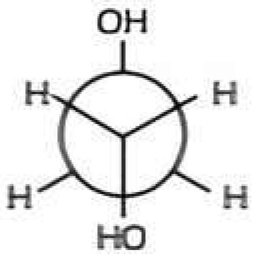
Partially Eclipsed



Eclipsed



Gauche

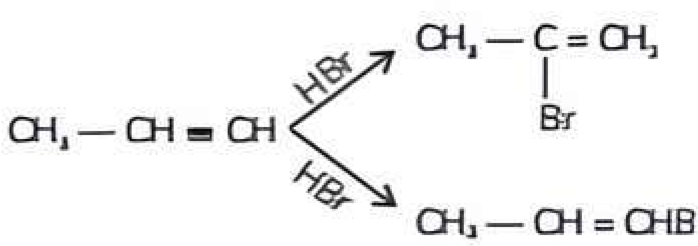


(E) *(a) dihedral angle*

Explanation: The magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is known as dihedral angle or torsional angle.

15. *Alkenes are made up of a lot of weakly held pi bonds. They display additional reactions due to the presence of such bonds. Electrophiles (Electron-seeking species) are added to the double-bonded molecules in this reaction, resulting in the production of a new product. It also has the ability to undertake free radical substitution reactions under certain conditions. Ozonolysis and oxidation reactions are also vividly displayed. HX (HBr, HBr, HI) and alkenes undergo two types of addition reactions: Markovnikov and Anti-Markovnikov. The Markovnikov reaction occurs when HX is added to an alkene or alkyne, with H–bonding to the double bond's less substituted carbon atom and X bonding to the other double-bonded carbon atom via an ionic mechanism. When HBr (not HCl, HI) is introduced to an alkene or alkyne, Br attaches to the less substituted double-bonded carbon, whereas H links to the other carbon atom, resulting in the anti-Markovnikov reaction. This is where the Markovnikov and Anti-Markovnikov.*

(A) What would be the major product in the given figure, if the following reaction obeys Markovnikov rule?



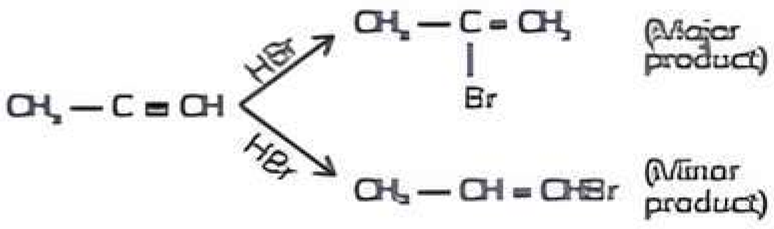
(B) How will you prepare prop–1–ene to propane–1,2–diol?

(C) Complete the following reactions:

(i) $CH = CH \xrightarrow{NaNH_2} A \xrightarrow{CH_3Br} B$

(ii) 2 methyl pent-2-ene $\xrightarrow[Zn/H_2O]{O_3}$ C + D

Ans. (A) As per Markovnikov's rule, the product in which bromine is attached to the secondary carbon atom will be the major product. The $CH_3CH = CHBr$ product would be the minor product as per Markovnikov's Rule. (The secondary carbocation forms during the reaction and it is more stable than the primary carbocation as per Markovnikov's rule).



Caution

- *Always take care about the addition of halogen in the Markovnikov's and anti-Markovnikov's rules.*

(B) Prop–1–ene can be converted into propane–1,2–diol by the reaction with dilute potassium permanganate.

$$\underset{\text{Prop-1-ene}}{CH_3\text{-}CH=CH_2} + H_2O \xrightarrow{\text{dil. }KMnO_4/273K} \underset{\text{propane-1,2-diol}}{CH_3CH(OH)CH_2OH}$$

(C) (i) $CH \equiv CH \xrightarrow{NaNH_2} NaC \equiv CNa \xrightarrow{2CH_3Br} CH_3C \equiv CCH_3$

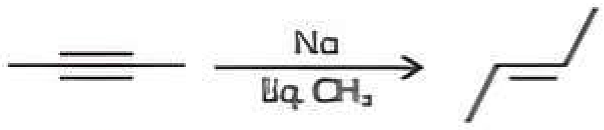
(ii) $CH_3CH_2CH = C(CH_3)_2 \xrightarrow{\text{Ozonolysis}} \underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Propanone}}{CH_3COCH_3}$

VERY SHORT ANSWER Type Questions (VSA)

[**1** mark]

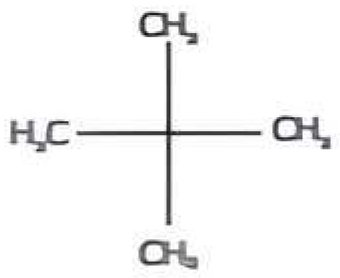
16. **Alkynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on the reduction of the 2-butyne show the geometrical isomerism? [NCERT Exemplar]**

Ans. In geometrical isomerism when the same groups are on the same side then it is cis-form and if same groups are on the opposite side, then it is *trans*- form. *Trans-2-butene* is formed by the reduction of *2-butyne*, is capable of showing the geometrical isomerism. The reaction is called Birch reduction.



17. **Give the I.U.P.A.C. name of the lowest molecular weight alkane that contains a quaternary carbon.**

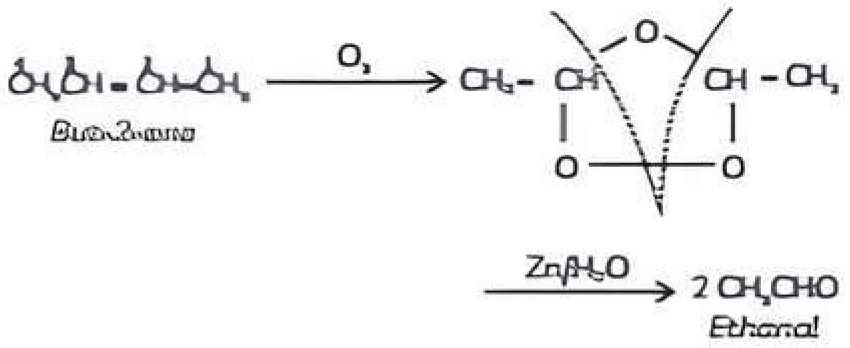
Ans. 2,2-Dimethylpropane is the lowest molecular weight alkane that contains quaternary carbon. It is also known as Neopentane.



18. **Complete the following reaction.**

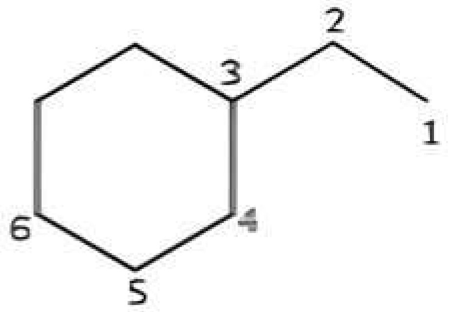
$$CH_3-CH=CH-CH_3 \xrightarrow[\text{[illegible]}]{O_3} A$$

Ans. The compound *A* will be Ethanal.



19. **How many products are formed from the monochlorination of ethylcyclohexane? Ignore the stereoisomers.**

Ans. The addition of a chlorine atom is known as monochlorination. When a chlorine atom is introduced into the structure below, one of the hydrogens will be replaced by chlorine. In Ethylcyclohexane, there are six different sorts of hydrogen atoms. As a result, there are six monochlorinated products.

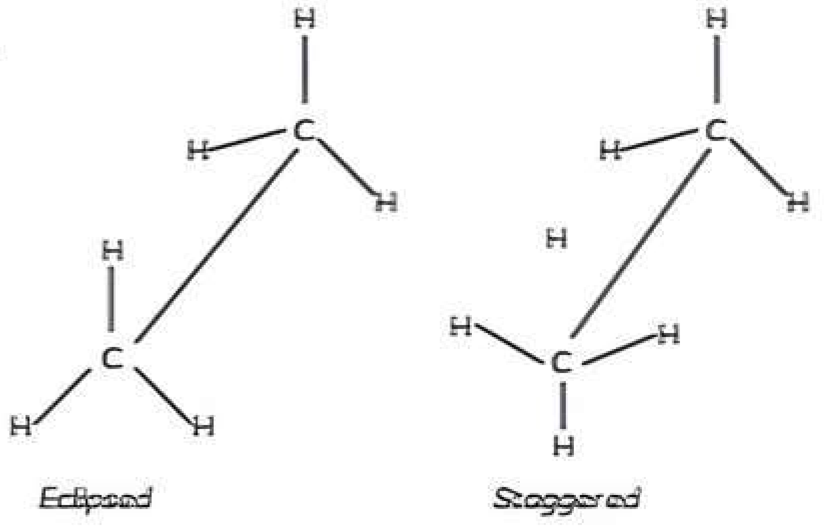


SHORT ANSWER Type-I Questions (SA-I)

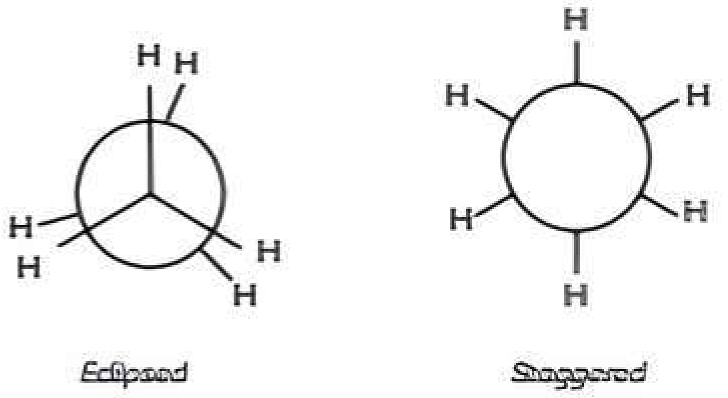
[**2** marks]

20. **Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why? [NCERT Exemplar]**

Ans.



Sawhorse projection of ethane



Newman projection of ethane

Staggered form of ethene is more stable than the eclipsed conformation by about 12.55 kJ/mol. This is because any two hydrogen atoms on adjacent carbon atoms of staggered configuration are maximum apart while in eclipsed conformation they cover or eclipse each other is space. In staggered from, there is a minimum repulsive force, minimum energy and, maximum stability of the molecule.

21. Which reagent is used to distinguish between 1-butyne and 2-butyne?

Ans. The reagent used for distinguishing 1-butyne and 2-butyne is $NaNH_2$.

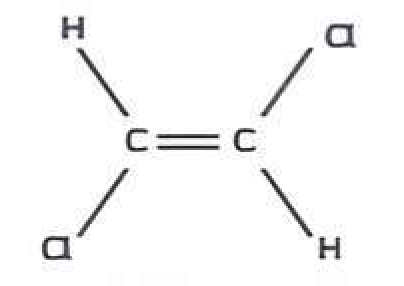
$CH_3CH_2C \equiv CH \xrightarrow{NaNH_2} CH_3CH_2C \equiv CNa$

$CH_3-C \equiv C-CH_3 \xrightarrow{NaNH_2}$ No reaction

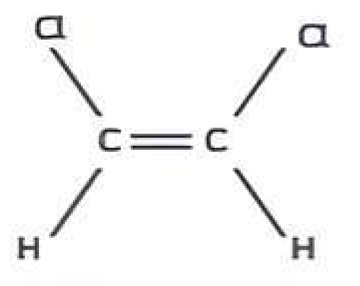
Because the terminal carbon atom of 1-butyne includes one acidic hydrogen, it will react with sodium and sodamide $NaNH_2$, to produce sodium acetylide, releasing hydrogen gas. Due to the absence of acidic hydrogen, 2-butyne does not conduct such a reaction.

22. ***cis*** **1,2– Dichloroethene has a lower dipole moment than the trans 1,2 – dichloroethene isomer. Explain.**

Ans. The *trans* 1,2– dichloroethene isomeric structure is more symmetrical than the *cis 1,2–dichloroethene* structure. In the *trans*– isomer, the dipole moments of the polar *C–Cl* bonds should cancel out, resulting in a molecule with a almost zero dipole moment. In the *cis*–isomer, however, these do not cancel. As a result, the *cis*– isomer has a distinct moment from the *trans*– isomer. The following are the structures:



trans-1,2-Dichloroethene



cis-1,2-Dichloroethene

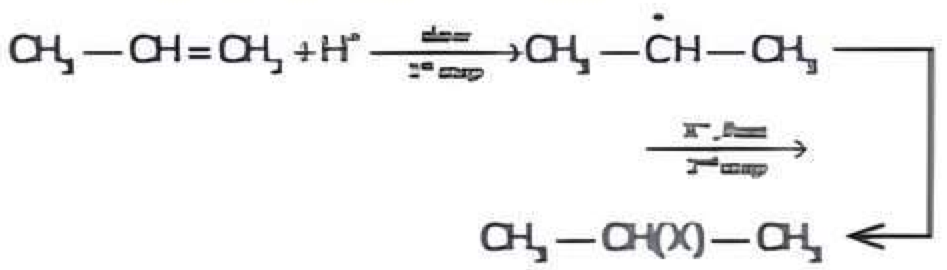
SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

23. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HI, HBr and HCl is 430.5 kJ mol⁻¹, 363.7 kJ mol⁻¹ and 296.8 kJ mol⁻¹ respectively. What will be the order of reactivity of these halogen acids?

[NCERT Exemplar]

Ans. Addition of halogen acids to an alkene is an electrophilic addition reaction.



$$CH_3-CH=CH_2+H^+ \xrightarrow[1^{st}\ step]{slow} CH_3-\overset{+}{C}H-CH_3 \xrightarrow[2^{nd}\ step]{X^-,\ fast} CH_3-CH(X)-CH_3$$

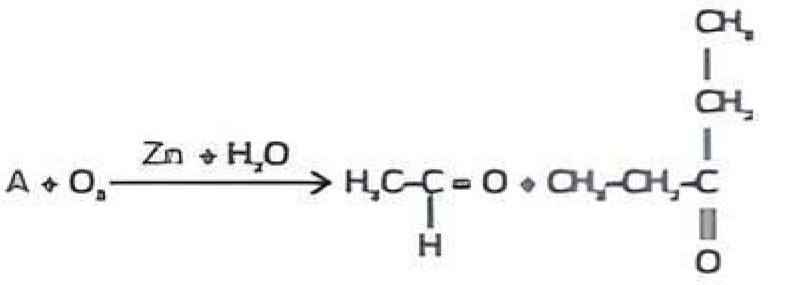
The first step is slow and it is a rate-determining step. The rate of step depends upon the availability of proton. This in turn depends upon the bond dissociation enthalpy of the H–X molecule.

Lower is the dissociation enthalpy of the H–X molecule, the greater is the reactivity of halogen halide. So, the bond dissociation enthalpy increases in the order: HI < HBr < HCl

Therefore, the reactivity of halogen decreases as: HI > HBr > HCl

24. An alkene 'A' on ozonolysis gives a mixture of *ethanal* and *pentan-3-one*. Write the structure and IUPAC name of 'A'.

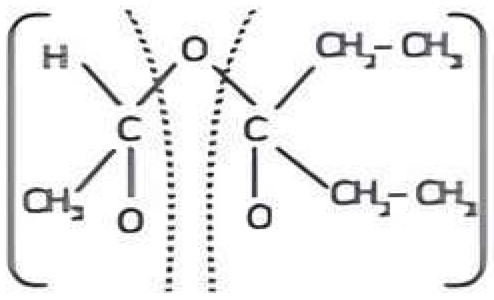
Ans.



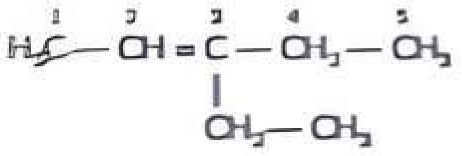
$$A + O_3 \xrightarrow{Zn + H_2O} H_3C-\underset{H}{C}=O + CH_3-CH_2-\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{\overset{CH_2}{C}}}$$

Ethanal *Pentan-3-one*

In the path of ozonolysis, an *ozonide* is produced as an intermediate that has a cyclic structure; it undergoes cleavage to provide the final products *ethanal* and *pentan–3–one*. These products are obtained from the *ozonide* intermediates. The possible *ozonide* structure will be:



This ozonide is made by adding ozone to 'A' as a transitional product, which then cleaves into final products. By eliminating the ozone from the *ozonide*, the preferred 'A' arrangement can be achieved. As a result, the structural formula for "A" is:



$$\overset{1}{H_3C}-\overset{2}{C}H=\overset{3}{\underset{\underset{CH_2-CH_3}{|}}{C}}-\overset{4}{C}H_2-\overset{5}{C}H_3$$

3-Ethylpent-2-ene

25. Why is ethyne acidic in nature in comparison to ethene and ethane?

Ans. Hydrogen atoms are connected to *sp* hybridized carbon atoms in ethyne, whereas they are joined to sp^2 hybridized carbon atoms in ethene, and sp^3 hybridized carbon atoms in ethane.

Because of the highest percentage of s–character (50%) in ethyne molecules, the sp hybridized orbitals of carbon atoms have the highest electronegativity 5. This attracts the C–H bond of ethyne to a greater extent than the sp^2 hybridized orbitals of carbon in ethyne and the sp^3 hybridized orbitals of carbon in ethyne. Thus, In comparison to ethyne and ethyne, hydrogen atoms in the ethyne molecule are more easily liberated as protons.

LONG ANSWER Type Questions (LA)

[**4** & **5** marks]

26. How would you explain the formation of ethane during chlorination of methane?

Ans. The methane chlorination process works through a free radical chain mechanism.

Step 1: Initiation:

The initiation process begins with the homolytic cleavage of $Cl - Cl$ bond as:

$$Cl — Cl \longrightarrow \dot{Cl} + \dot{Cl}$$

Step 2: Propagation:

In the propagation step, chlorine-free radicals attack methane molecules and the C–H bond collapses to form methyl radicals as:

$$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + H — Cl$$

Methyl chloride is formed next to the liberation of a chlorine-free radical when these methyl radicals react with other chlorine radicals other radicals are formed.

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

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

$$\dot{C}H_2Cl + Cl — Cl \longrightarrow CH_2Cl_2 + \dot{Cl}$$

Step 3: Termination:

The formation of *ethane* is the result of the chain reactions being terminated as a result of the consumption of methyl radicals.

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl — Cl$$

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

27. An alkyl halide $C_5H_{11}Br$ 'A' reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 (in CS_2) to give a compound 'C', which on dehydrobromination provides an alkyne 'D'. On treatment with sodium metal in liquid ammonia, one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight-chain alkane. Identify *A*, *B*, *C* and *D*. Give the reactions involved. **[NCERT Exemplar]**

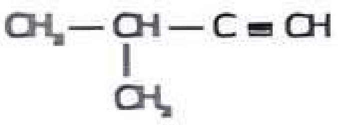
Ans.

$$\underset{(A)}{C_5H_{11}Br} \xrightarrow{\text{alc.KOH}} \underset{(B)}{\text{Alkene } (C_5H_{10})} \xrightarrow{Br_2 \text{ in } CS_2} \underset{(C)}{C_5H_{10}Br_2}$$

$$\xrightarrow[-2HBr]{\text{alc.KOH}} \underset{\substack{(D)\\ \text{Alkyne}}}{C_5H_8} \xrightarrow{\text{Na-liq.}NH_3} \underset{\substack{\text{Sodium}\\ \text{alkylide}}}{C_5H_7\text{–}Na} + \frac{1}{2} H_2$$

The reaction of alkyne 'D' form sodium salt which proves that it is a terminal alkyne. This means a triple bond is at the end of the chain. It could be either *(I)* or *(II)*. Alkyne 'D' on hydrogenation yields straight-chain alkane. So, the structure *(I)* is alkyne 'D'.

(I) 

(II) 

$$CH_3 — \underset{\substack{|\\ CH_3}}{CH} — C \equiv CH$$

It is important to note that alkyl halide 'A' cannot be 2-bromopentane because debromination of 'A' would give 2-pentene as a major product according to Markovnikoff's rule.

Therefore, the structures are:

(A) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2Br$

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

(C) $CH_3 - CH_2 - CH_2 - CH(Br) - CH_2Br$

(D) $CH_3 - CH_2 - CH_2 - C \equiv CH$

28. Answer the following questions:

(A) An alkene C_4H_8 reacts with HBr both in the presence and absence of peroxide to give the same product. Identify the alkene.

(B) Complete the following reactions

(I) $CH = CH \xrightarrow{NaNH_2, CH_3Br}$

(ii) $CH \equiv CH \xrightarrow{H_2O, HgSO_4/H_2SO_4}$

(iii) $CH_3C \equiv CH \xrightarrow{Pt/H_2}$

Ans. (A) As the alkene (C_4H_8) on reaction with HBr in the presence and in the absence of peroxide to give the same product, thus the alkene should be symmetrical. A symmetrical alkene with 4 carbon atoms is 2-butene.

$CH_3 - CH = CH - CH_3 + HBr \rightarrow$

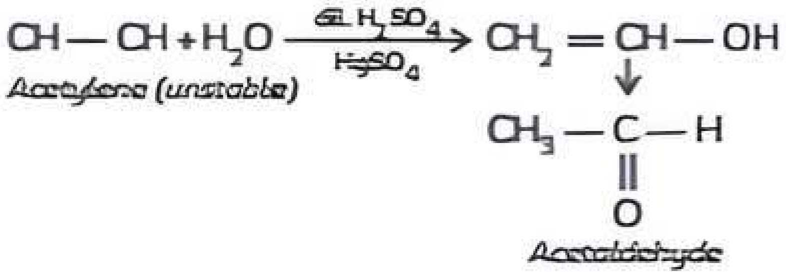
$CH_3 - CH_2 - CHBr - CH_3$

(B) (i) $CH \equiv CH \xrightarrow{NaNH_2} CH \equiv CNa \xrightarrow{CH_3Br}$

$CH \equiv C - CH_3$

(Propyne)

(ii)



$$CH \equiv CH + H_2O \xrightarrow[HgSO_4]{dil.\ H_2SO_4} CH_2 = CH - OH \rightarrow CH_3 - \underset{\underset{O}{\|}}{C} - H$$

Acetylene (unstable)

Acetaldehyde

(iii) $CH_3C \equiv CH \xrightarrow{Pt/H_2} CH_3CH_2CH_3$

(Propane)

AROMATIC HYDROCARBONS AND CARCINOGENICITY

2

TOPIC 1

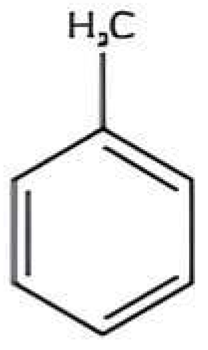
AROMATIC HYDROCARBON

The class of compounds was named 'aromatic compounds' because the majority of them have a pleasant odour, which means aroma - pleasant smelling and these compounds are discovered with a benzene ring. The benzene ring is highly unsaturated, but the unsaturation of the benzene ring is retained in the majority of reactions. These hydrocarbons are also referred to as 'arenes'.

Aromatic compounds with a benzene ring are referred to as benzenoids, while those without a benzene ring are referred to as non-benzenoids.

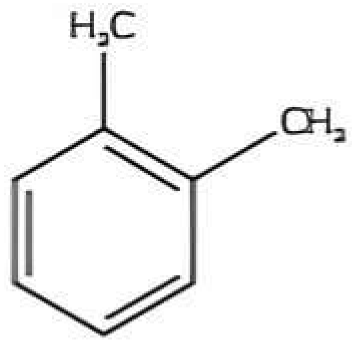
Nomenclature and Isomerism

Because all six hydrogen atoms in the benzene ring are equivalent, it can only form one type of monosubstituted product. Three different position isomers are possible when two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups. The ortho (*o*) di substituted compounds are 1, 2 or 1, 6, the Meta (*m*) disubstituted compounds are 1, 3 or 1, 5 and the para (*p*) di substituted compounds are 1, 4. Here are a few examples of benzene derivatives:



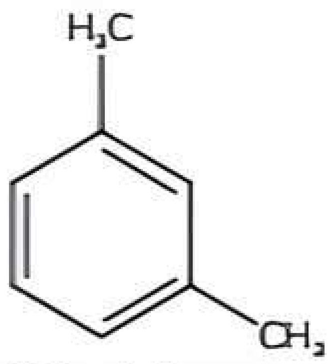
Methylbenzene

(Toluene)



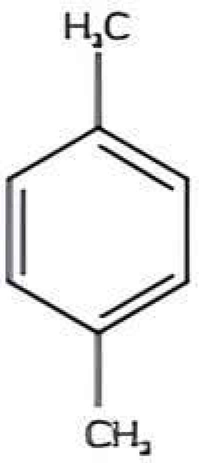
1, 2-Dimethybenzene

(o-Xylene)



1, 3-Dimethylbenzene

(m-Xylene)



1, 4-Dimethylbenzene

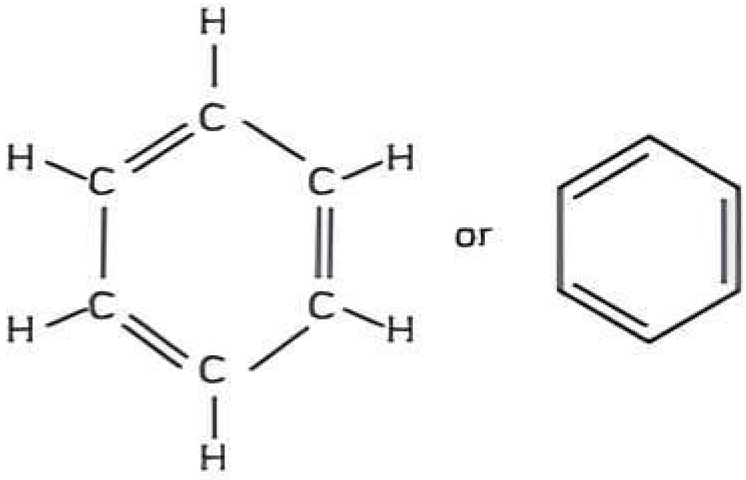
(p-Xylene)

Friedrich August Kekule, a German chemist was born in 1829 at Darmstadt in Germany. He made a major contribution to structural organic chemistry by proposing that carbon atoms can join to one another to form chains and later he found the answer to the problem of benzene structure by suggesting that these chains can also form closed rings. He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure. One hundred years later, on the occasion of Kekule's centenary celebrations a group of compounds having poly benzenoid structures has been named as kekulenes.

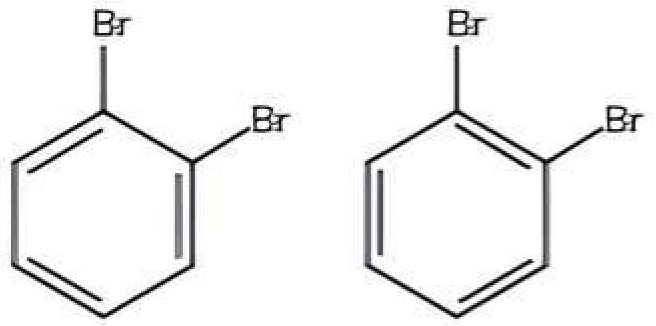
Friedrich August Kekule

Structure of Benzene

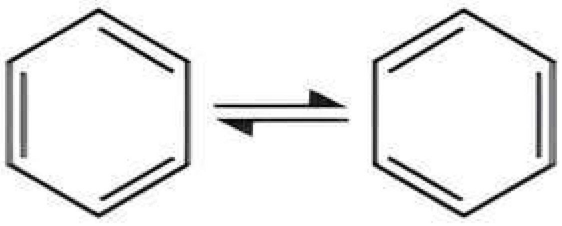
Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene is C_6H_6 as determined by elemental analysis. As a result, benzene is a highly unsaturated compound. It took several years to assign its structure due to its unique properties and unusual stability. Benzene was discovered to be a stable molecule that forms a triozonide, indicating the presence of three double bonds. Benzene was also discovered to produce only one monosubstituted derivative, indicating that all six carbon and six hydrogen atoms in benzene are identical. On the basis of this observation, August Kekulé proposed the cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom in 1865.



The Kekulé structure suggests the presence of two isomeric 1, 2-dibromobenzenes. The bromine atoms are attached to the doubly bonded carbon atoms in one isomer, while they are attached to the singly bonded carbons in the other.



However, only one ortho disubstituted product of benzene was discovered. Kekulé solved this problem by proposing the concept of oscillating double bonds in benzene, as shown below.

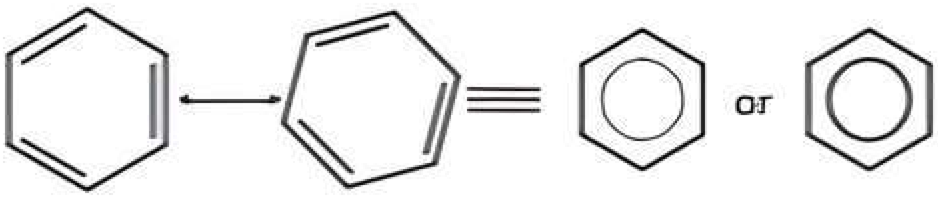


Even with this modification, the Kekulé structure of benzene fails to explain its unusual stability and preference for substitution reactions over addition reactions, which could be explained later by resonance.

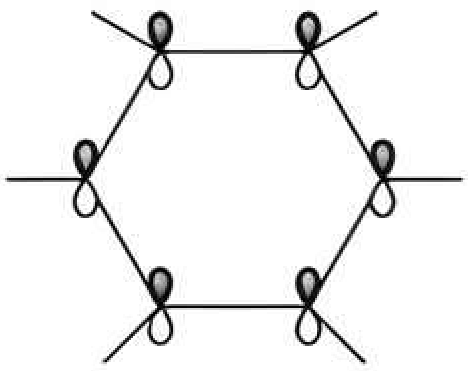
TOPIC 2

RESONANCE AND STABILITY OF BENZENE

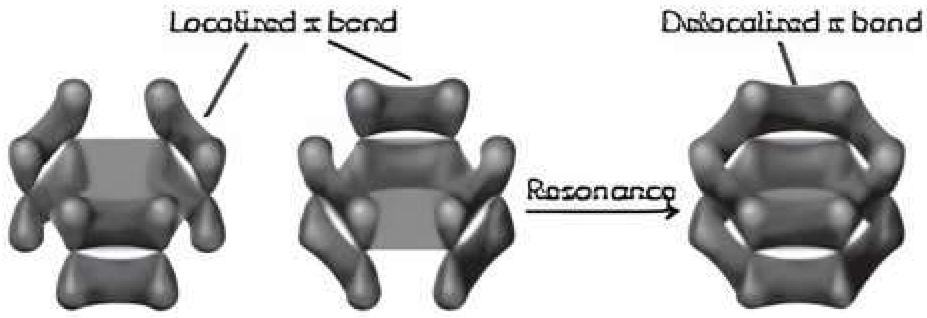
The oscillation of double bonds in benzene can be explained by the concept of VSEPR theory. Resonance is the phenomenon in which two or more structures for a substance can be written that involve identical atomic positions. The resonance structures in benzene are represented by Kekulé structures (1) and (2). The hybrid structure can be represented by inserting a circle or a dotted circle in the hexagon. The molecule's actual structure is represented by a hybrid of these two structures.



The orbital overlapping provides a clearer picture of benzene's structure. In benzene, all six carbon atoms are sp^2 hybridised. In each carbon atom, two sp^2 hybrid orbitals overlap with the sp^2 hybrid orbitals of the adjacent carbon atoms to form six $C-C$ sigma bonds in the hexagonal plane. Six $C-C$ sigma bonds are formed when a carbon atom remaining sp^2 hybrid orbital overlaps with a hydrogen atom's s orbital. As shown below, each carbon atom now has one unhybridised orbital perpendicular to the ring plane:

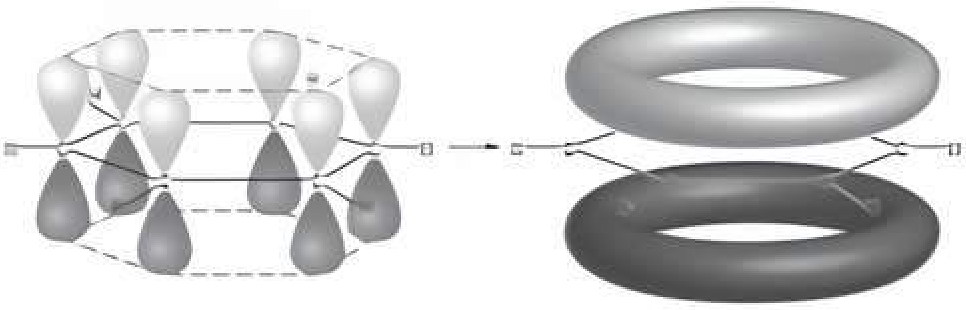


The unhybridised *p* orbital of carbon atoms is enough to form a lateral overlap. There are two possibilities of forming bond by overlap of C_1–C_2, C_3–C_4, C_5–C_6 or C_2–C_3, C_4–C_5, C_6– C_1 as shown in the following figures:



Delocalised □ bonds in benzene

The internuclear distance between all the carbon atoms in the ring was found to be the same confirmed by *X*-ray diffraction studies and there is also equal probability for the *p orbitals* of each carbon atom overlapping with of *p orbitals* adjacent carbon atoms. This can be represented in the form of two doughnuts (rings) of electron clouds one above and one below the plane of the hexagonal ring.



Electron cloud of benzene

As a result, the six □ electrons are delocalised and can freely move around the six carbon nuclei. The nuclei of the carbon atoms attract the delocalised electron cloud more strongly than the electron cloud localised between two carbon atoms. As a result, the appearance of delocalised □ electrons in benzene increases its stability.

According to X-ray diffraction data, benzene is a planar molecule. According to the data, all six $C-C$ bond lengths are of the same order (139 pm), which is intermediate between ($C-C$) single bond (154 pm) and $C=C$ double bond (133 pm). Thus, the absence of a pure double bond in benzene accounts for reductance to show an addition reaction under normal conditions. It explains benzene's unusual behaviour.

Aromaticity

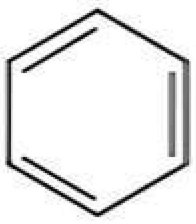
Benzene was assumed to be the parent 'aromatic' compound. The name is now applied to all ring systems, whether or not they contain a benzene ring, which exhibits the following characteristics:

(1) Planarity

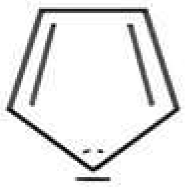
(2) The pi electrons in the ring have been completely delocalised.

(3) The presence of electrons in the ring, where n is an integer ($n = 0, 1, 2...$). This is known as the Hückel Rule.

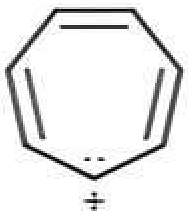
Few examples of aromatic compounds are as follows-



Benzene

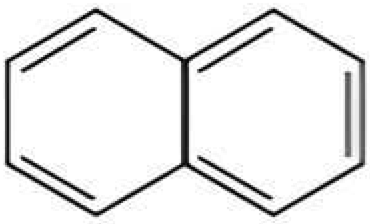


Cyclopentadienyl anion



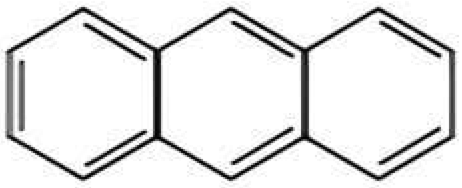
Cycloheptatrienyl cation

($n = 1$, 6π electrons)

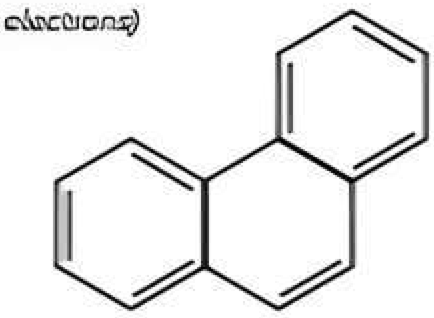


Naphthalene

($n = 2$, 10π electrons)



Anthracene



Phenanthrene

($n = 3$, 14π electrons)

Important

➡ *Compounds which have 4 pi-conjugated electrons are anti-aromatic while compounds which don't have a conjugated electron system are non-aromatic compounds.*

Example 2.1: Case Based:

Aromatic compounds are organic compounds also known as "mono- and polycyclic aromatic hydrocarbons". The parent member is benzene. Heteroarenes are closely related, since at least one carbon atom of CH group is replaced by one of the heteroatoms oxygen, nitrogen, or sulfur. Aromatics require satisfying Huckel's rule. Plants and micro-organisms have an exclusive route to benzene-ring compounds. The great majority of aromatic compounds are produced by plants and micro-organisms and animals.

(A) Which of the following is wrong about aromatic compounds?

(a) Aromatic hydrocarbons are also known as arenes.

(b) They are pleasant to smell.

(c) Benzene is simplest hydrocarbon in aromatic group.

(d) None of the above.

(B) Which of the following is correct regarding aromatic compounds?

(a) They have only sigma bonds.

(b) They have only pi bonds.

(c) They have a sigma bond and delocalised pi bond.

(d) They have pi and delocalized sigma bonds.

(C) How do you define benzene's unusual stability?

(D) Why  is not aromatic?

(E) Assertion (A): Aromatic hydrocarbons are stable.

Reason (R): Due to resonance hybrid they have more than one structure which lowers their energy and thus makes it stable.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

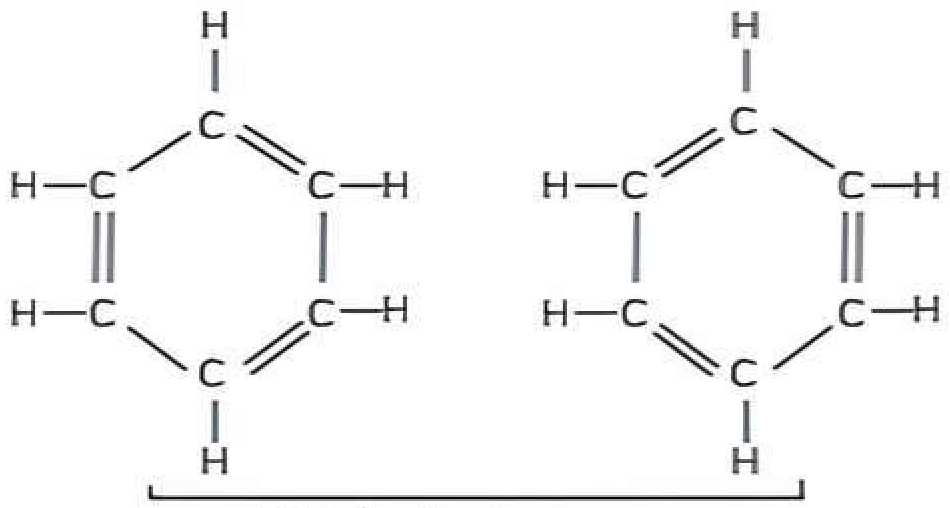
Ans. (A) *(d) None of the above*

Explanation: Aromatic compounds are also known as arenes and have pleasant odour. Among aromatic compounds benzene is the simplest in them

(B) *(c) They have sigma bond and delocalised pi bond.*

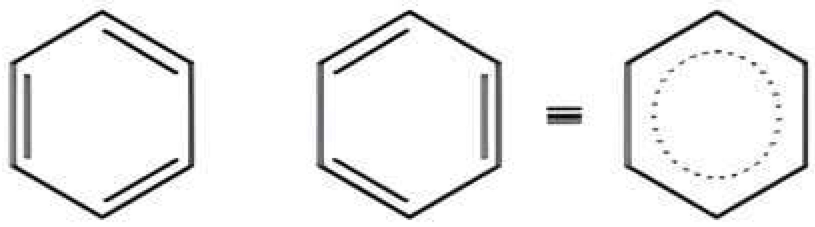
Explanation: Between the carbon atoms of an aromatic hydrocarbon, there is always a sigma bond and a delocalized pi bond.

(C) When benzene is forced to react by raising the temperature and adding a catalyst, it undergoes substitution reactions instead of the addition reactions seen in alkenes. Benzene's unusual stability was attributed to the resonance stabilisation of a conjugated cyclic triene. Benzene molecule is a resonance hybrid of the following two main contributing structures:



Contributing structures

Or



Due to resonance in benzene, the carbon-carbon bonds in benzene acquire an intermediate character of carbon-carbon single and double bonds.

(D) As cyclopentadiene has $(4n)\pi$ electrons not $(4n+2)\pi$ electrons thus it is not aromatic.

Related Theory

Aromatic compounds are those that have the following characteristics:

(1) Planarity

(2) The electrons in the ring have been completely delocalised.

(3) The presence of (4n+2)□ electrons in the ring, where n is an integer (n = 0, 1, 2...). This is known as the Hückel Rule.

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Aromatic hydrocarbons are stable due to resonance hybrid they have more than one structure which lowers their energy and thus makes it stable.

Properties

Physical properties

Aromatic hydrocarbons are non-polar molecules that typically exist as colourless liquids or solids with a distinct aroma. Example: Naphthalene balls are used in toilets and in clothes as an insect repellant. Aromatic hydrocarbons are insoluble in water but readily miscible in organic solvents. They emit a sooty flame.

Chemical properties

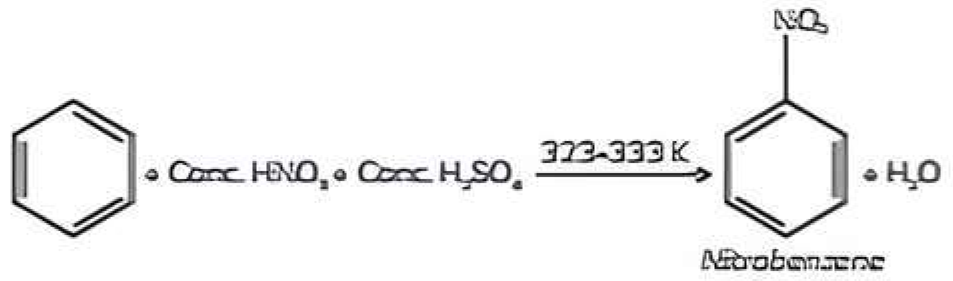
Electrophilic substitution reactions distinguish arenes. They can however, undergo addition and oxidation reactions under certain conditions.

(1) Electrophilic substitution reactions

The most common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel-Crafts alkylation and acylation reactions in which the attacking reagent is an electrophile.

Nitration

When benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture), a nitro group is introduced into the benzene ring.



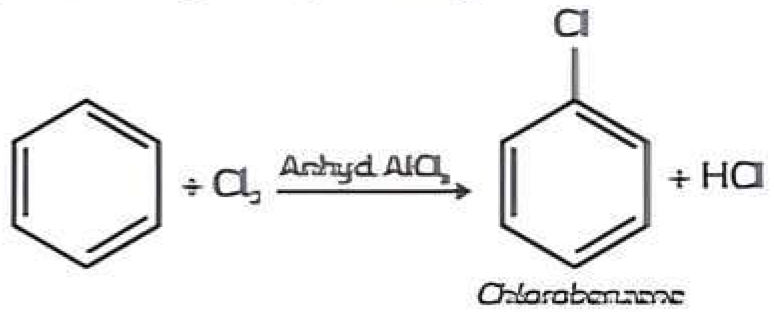
Example 2.2: Out of benzene, m-dinitrobenzene and toluene which will undergo nitration most easily and why?

Ans. The CH_3 group donates electrons, whereas the NO_2 group withdraws electrons. As a result, toluene has the highest electron density, followed by benzene, and *m*-dinitrobenzene has the lowest. As a result, the ease of nitration decreases as follows:

toluene > benzene > *m*-dinitrobenzene.

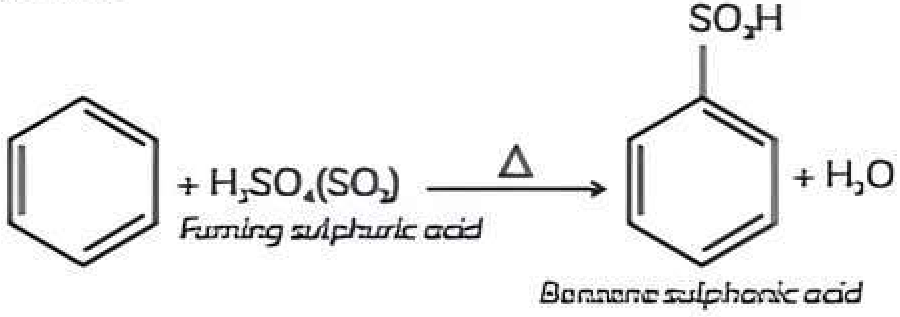
Halogenation

Haloarenes are formed when arenes react with halogens in the presence of a Lewis acid, such as anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$.



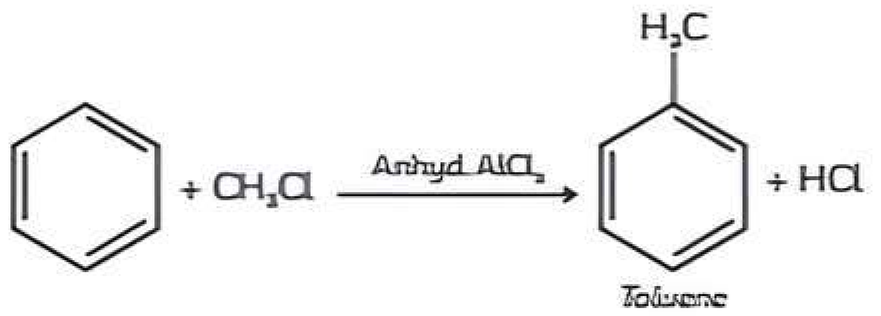
Sulphonation

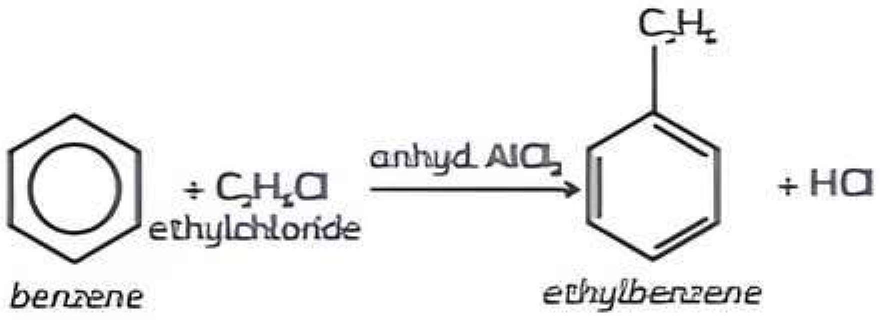
Sulphonation is the replacement of a hydrogen atom in a ring by a sulphonic acid group. It is accomplished by heating benzene with fuming sulphuric acid (oleum).



(2) Friedel-Craft alkylation reaction:

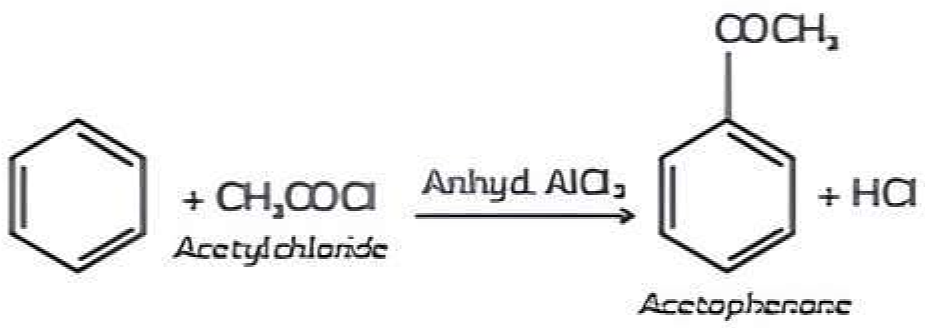
Alkylbenzene is formed when benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride.

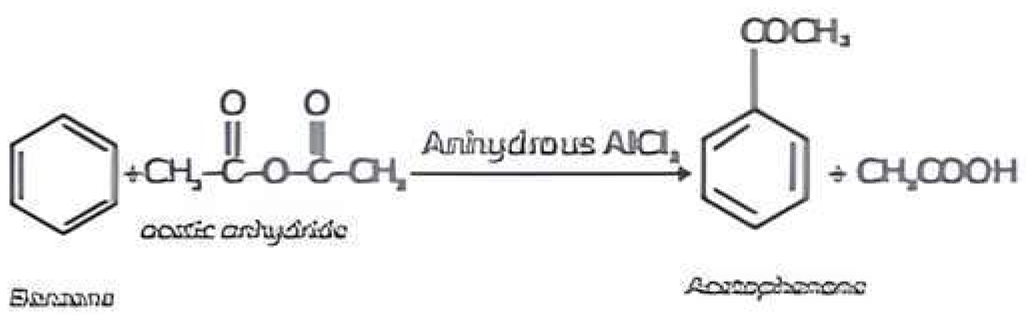




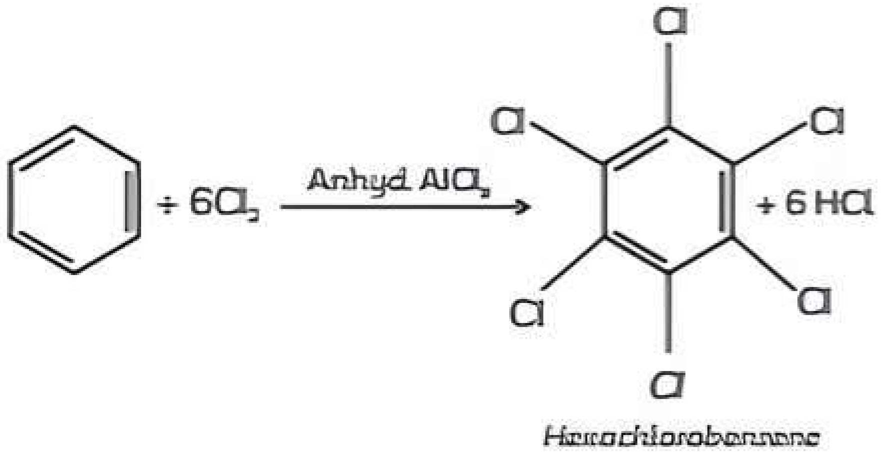
(3) Friedel-Craft acylation reaction:

In the presence of Lewis acids ($AlCl_3$), the reaction of benzene with either an acyl halide or acid anhydride yields acyl benzene.





If an excessive amount of electrophilic reagent is used, a further substitution reaction may occur in which other hydrogen atoms of the benzene ring are successively replaced by the electrophile. Example: Benzene on treatment with an excess of chlorine in presence of anhydrous aluminium chloride forms hexachlorobenzene.



Mechanism of electrophilic substitution reactions

Arenes are distinguished by electrophilic substitution reactions, which take the following three steps:

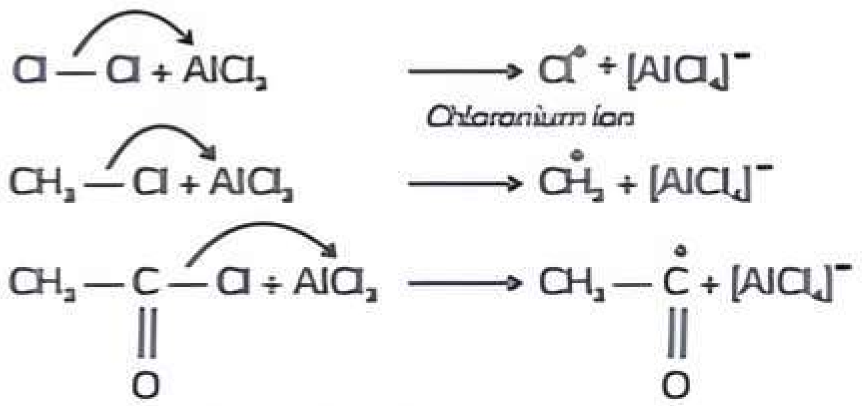
(1) Generation of the electrophile

(2) Formation of the carbocation intermediate

(3) Removal of the proton from the carbocation intermediate.

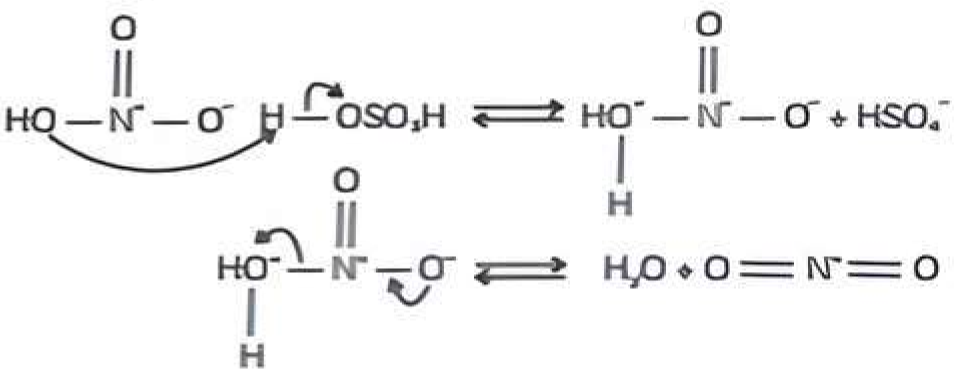
(1) Generation of the electrophile E^+

Anhydrous $AlCl_3$ acts as a Lewis acid aids in the generation of the electrophile Cl^+, R^+, RCO^+ (acylium ion) during chlorination, alkylation and acylation of benzene by combining with the attacking reagent.



Generation of electrophile

In the case of nitration, the nitronium ion $\overset{+}{N}O_2$ is produced by the transfer of a proton from sulphuric acid to nitric acid as shown below:

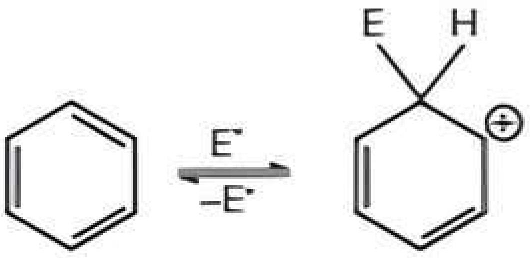


Generation of nitronium ion

Interestingly during the generation of nitronium ion, the sulphuric acid serves as acid and nitric acid as the base. It is a simple acid-base equilibrium.

(2) Formation of the carbocation intermediate

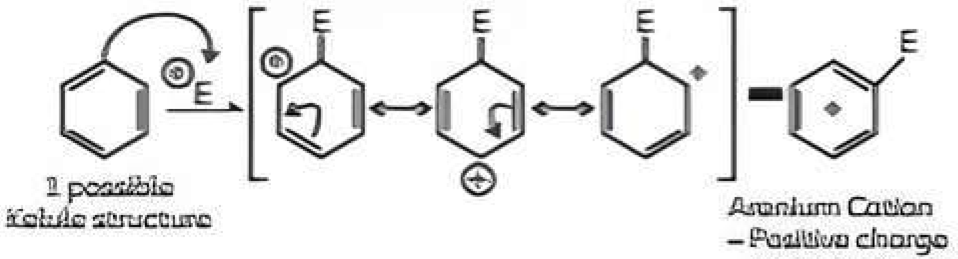
The attack of an electrophile results in the formation of σ-complex or arenium ion, with one of the carbons sp^3 hybridised.



Arenium ion (sigma complex)

Electrophilic attack

Formation of intermediate Cation:

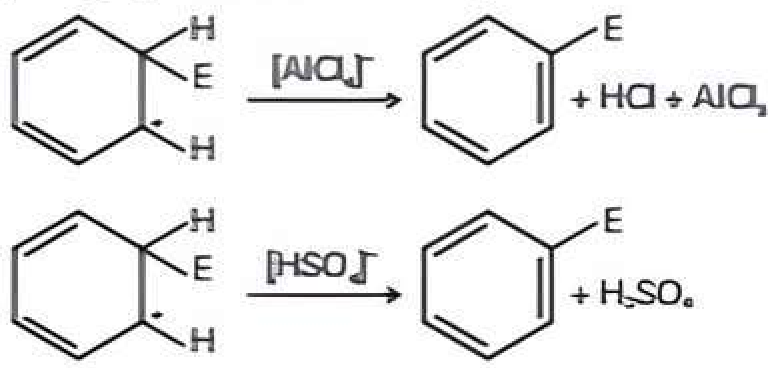


Arenium ion resonance stabilized

Because electron delocalisation stops at sp^3 hybridised carbon, the σ-complex or arenium ion loses its aromatic character.

(3) Removal of the proton from the carbocation intermediate

To restore the aromatic character, the σ-complex releases proton from the sp^3 hybridised carbon when attacked by $[AlCl_4]^-$ (in the case of halogenation, alkylation and acylation) and $[HSO_4]^-$ (in case of nitration).



Example 2.3: **Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?**

Ans. Benzene is a rich source of electrons due to the presence of an electron cloud containing 6 electrons above and below the plane of the ring. As a result, it attracts electrophiles (electron-deficient reagents) while repelling nucleophiles (electron-rich reagents). As a result, benzene easily undergoes electrophilic substitution reactions but struggles with nucleophilic substitutions.

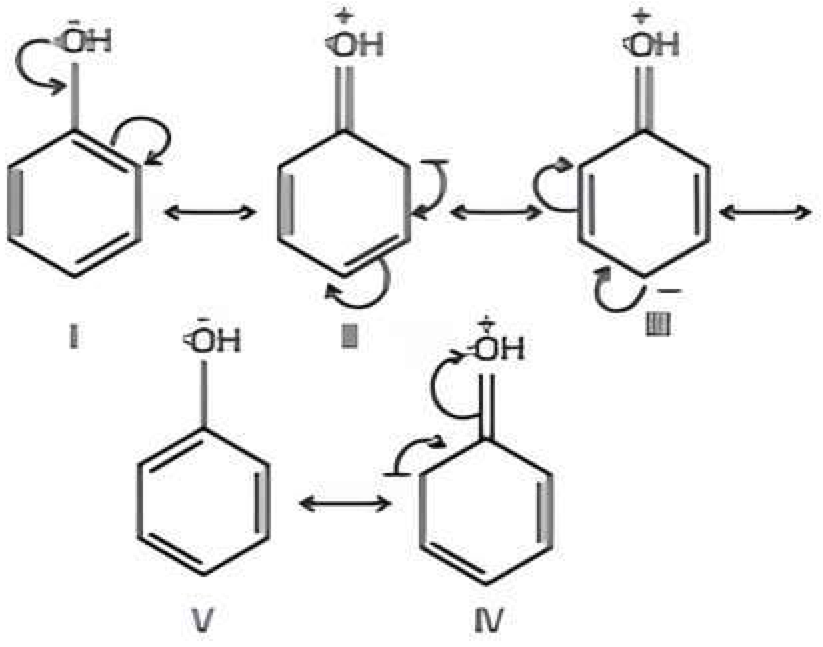
Directive Influence of a Fundamental Group in Monosubstituted Benzene

When a substitution reaction takes place in mono- substituted benzene, three types of disubstituted products are formed with unequal amounts which are ortho, para and meta. Two types of behaviour is majorly observed either in ortho and para products or meta products. This behaviour is dependent on the nature of the substituent already present in the benzene ring not depending on the nature of the entering group. This is known as the directive influence of substituents. The reasons for their position is discussed below:

Ortho and Para Directing Groups

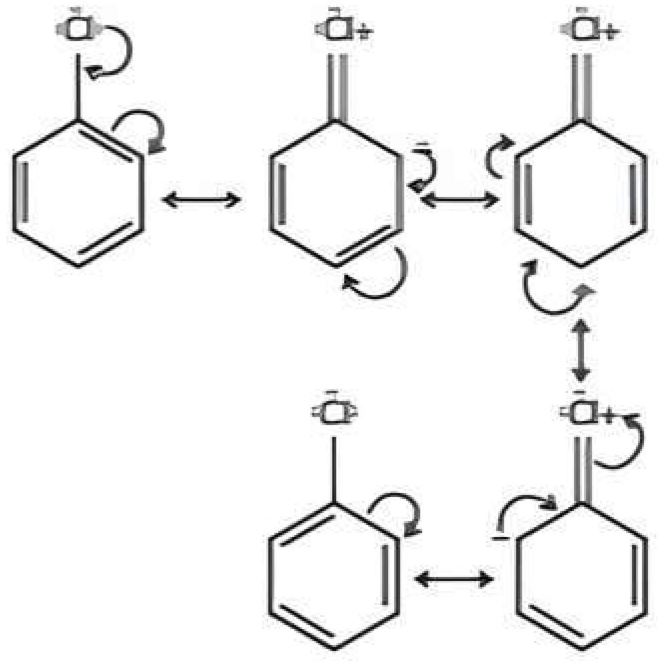
The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups. Example: The phenolic groups have the following resonating structure which increases the electron density on the ortho and para position, hence the substitution will take place at o–and p-positions. It is noted that –I effect of –OH also operates due to which electron density on ortho and para positions of benzene ring is slightly reduced. But the overall electron density is increased due to resonance. Therefore OH group activates the benzene group at the ortho and para positions.

OH, – NH_2, NHR, $NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$ are ortho and para directing and activating groups.



Resonance structures of phenol

In case of aryl halides, halogens are deactivating groups due to the strong –I effect, the overall electron density at benzene will decreases due to the above effect. It makes substitution difficult. However, due to resonance the electron density at ortho and para positions are greater than that of meta position. Hence, they are also ortho and para-directing groups.



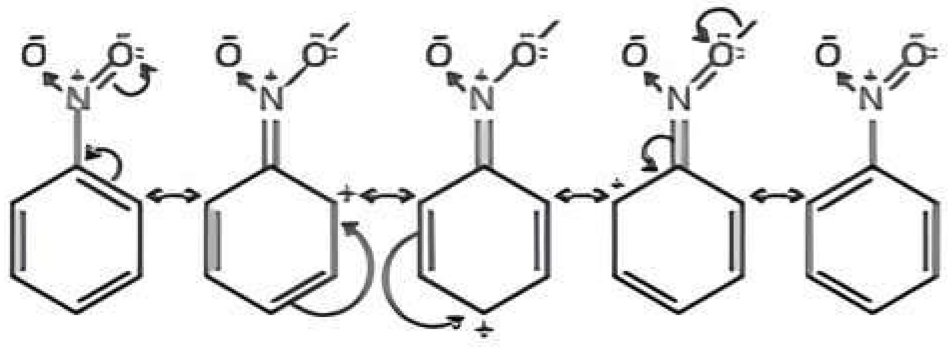
Resonance structures of chlorobenzene

Meta directing groups

Meta directing groups are one which directs the incoming group at meta position.

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

Example: In nitrobenzene, the nitro group reduces the electron density in the benzene due to the strong effect.



Resonance structures of nitrobenzene

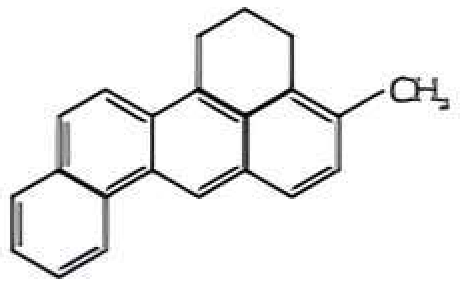
So, the overall electron density at the benzene ring decreases which makes substitution more difficult so, these groups are called deactivating groups. The electron density at the ortho and para positions is less when compared to the meta position. So substitution takes place at the meta position.

TOPIC 3

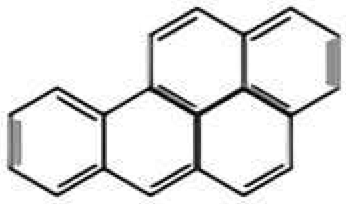
CARCINOGENICITY AND TOXICITY

Benzene and some polynuclear hydrocarbons with more than two benzene rings fused together are toxic and have cancer-causing properties. They are formed as a result of the incomplete combustion of organic materials such as tobacco, coal, and petroleum, among others. They enter into the human body and cause various biochemical reactions and damage DNA finally and cause cancer.

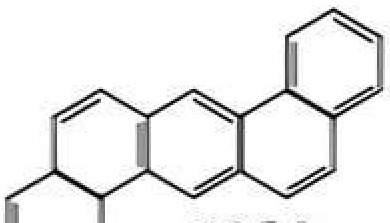
The following are some of the carcinogenic hydrocarbons.



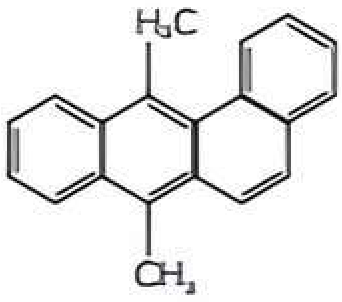
3 - Methylcholanthrene



1, 2-Benzpyrene



1,2,5,6-
Dibenzanthracene



9, 10- Dimethyl-

Example 2.5: Case Based:

Cancer that starts anywhere in the body's lymphatic system is called lymphoma. If they have the ability to spread, they are called malignant. The systema lymphatica runs throughout our bodies and consists of lymphatic tissue, vessels, and fluid. Lymphatic tissue contains lymph nodes, which are a part of the system. The immune system's job is to supply blood cells and protect against harm from invading germs. Cancers that begin in other organs and tissues, and then spread to the system lymphatica aren't lymphomas. Lymphoma can, however, spread to other parts of the body.

Benzene has also found limited application in medicine for the treatment of certain blood disorders, like polycythemia and malignant lymphoma. Exposure to benzene, an important industrial chemical and component of gasoline, is a widely recognized cure to minimize the destruction caused by malignant lymphoma.

Doctor diagnosing problem

(A) **Arenes are:**
- (a) Non -carcinogenic
- (b) Mostly gases
- (c) Volatile
- (d) Water soluble

(B) Which of the following compounds is carcinogenic?
- (a) 1, 2-Benzanthracene
- (b) Cyclohexane
- (c) Ethyne
- (d) Nitrobenzene

(C) What is the general formula of the aromatic compound?

(D) Give a few examples of meta-directing groups.

(E) Assertion (A): A butter stain on a tablecloth can be removed with benzene.

Reason (R): Butter has a strong affinity for benzene.
- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) *(c) Volatile*

Explanation: Because arenes have a very low boiling point, they are highly volatile in nature.

(B) *(a) 1, 2-Benzanthracene*

Explanation: Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are carcinogenic.

(C) Aromatic compounds are classified into several series based on the number of fused benzene rings in their molecules. C_nH_{2n-6m} is their general formula, where n is the number of carbon atoms and m is the number of rings.

(D) $-NO_2$, $-CN$, CHO, $-COR$, $-COOH$, COOR, $-SO_3H$ etc. are a few meta-directing groups.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: A polar solvent is a benzene. Butter is made up of organic compounds with low polarity. As a result, it dissolves in benzene.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. Aromatic hydrocarbons are also known as:

(a) Cyclic compounds

(b) Arenes

(c) Alkynes

(d) Alkenes

Ans. *(b) Arenes*

Explanation: Aromatic hydrocarbons are also known as arenes. Compounds which have at least one triple bond between carbons are known as alkynes and compounds that have at least one double bond between carbons are known as alkenes.

2. Which of the following acts as an electrophile in the chlorination of benzene?

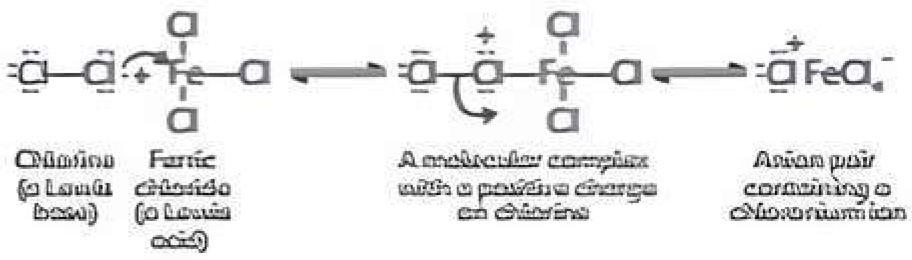
(a) Cl^+	**(b) Cl^-**
(c) Cl	**(d) $FeCl_3$**

Ans. *(a) Cl^+*

Explanation: In the chlorination of benzene, the electrophile is chloronium ion (Cl^+).

Related Theory

During chlorination anhydrous $AlCl_3$ being a Lewis acid helps in the generation of the electrophile Cl^+ by combining with the attacking reagent.



3. Arenes does not possess:

(a) Delocalisation of pi-electrons

(b) Greater stability

(c) Resonance

(d) Electrophilic additions

Ans. *(d) Electrophilic additions*

Explanation: Electrophilic substitution reactions occur in Arenes. Due to resonance stabilisation, arenes do not give an electrophilic addition reaction in their natural state.

4. Among the following compounds, the one which is most reactive towards electrophilic nitration is:

(a) Benzoic acid	**(b) Nitrobenzene**
(c) Toluene	**(d) Benzene**

[Delhi Gov. QB 2022]

Ans. *(C) Toluene*

Explanation: If the group attached to the benzene ring is electron donating, then it will the release electrons to benzene and the electron density of the benzene ring will increase. If the group attached to benzene ring is electron withdrawing, then it will attract an electron from the benzene ring and the electron density of the benzene ring will decrease.

Higher the electron density, higher will be the reactivity towards electrophilic substitution (or nitration).

Thus the order of reactivity towards electrophilic nitration for the given compound is:

Toluene > Benzene > Benzoic acid > Nitrobenzene

5. Carcinogenic compounds are toxic because they:

(a) cause heart failure

(b) damage the kidney

(c) damage the retina

(d) damage DNA and cause cancer [DIKSHA]

Ans. *(d) damage DNA and cause cancer*

Explanation: Some polynuclear hydrocarbons with more than two benzene rings fused together are toxic and have cancer-causing properties. They are formed as a result of the incomplete combustion of organic materials such as tobacco, coal, and petroleum, among others.

6. When benzene reacts with CH_3COCl in the presence of $AlCl_3$, the result is:

(a) $C_6H_5CH_3$	**(b) C_6H_5Cl**
(c) $C_6H_5COCH_3$	**(d) C_6H_5COCl**

Ans. *(c) $C_6H_5COCH_3$*

Explanation: In the presence of $AlCl_3$, benzene reacts with CH_3COCl to form $C_6H_5COCH_3$. Friedel - Crafts acylation of benzene is the name of this reaction.

Related Theory

In the presence of Lewis acids ($AlCl_3$), the reaction of benzene with either an acyl halide or acid anhydride yields acyl benzene.

7. In an electrophilic substitution reaction of nitrobenzene, the presence of the nitro group.

(a) Deactivates the ring by an inductive effect.

(b) Activates the ring by an inductive effect.

(c) Decreases the charge density at the ortho and para position of the ring relative to the meta position by resonance.

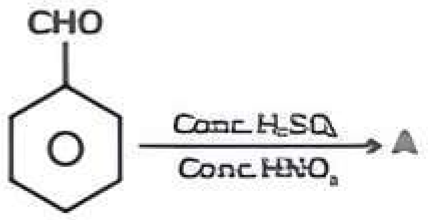
(d) Increases the charge density at the meta position relative to the ortho and para position of the ring by resonance.

[NCERT Exemplar]

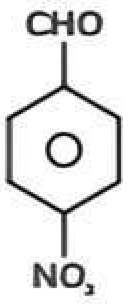
Ans. *(c) Decreases the charge density at the ortho and para position of the ring relative to the meta position by resonance.*

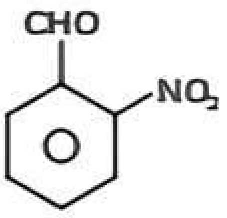
Explanation: The NO_2 is an ortho and para activating group and also possesses an effect which tends to increase the electron density at the ortho and para position of the benzene ring when compared to the the meta position.

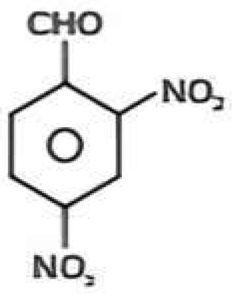
8. In the given reaction

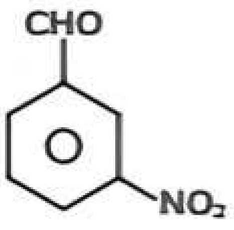


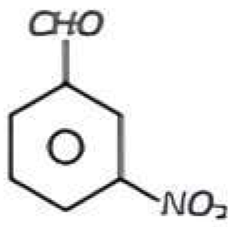
A is:

(a)


(b)


(c)


(d)


Ans. *(d)*


Explanation: Aldehyde is an electron-withdrawing and hence meta directing group. Thus in benzaldehyde incoming electrophile (NO_2^+) will attack at the meta position, giving m-nitro benzaldehyde as a major product.

9. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring

(I) deactivates the ring by inductive effect

(II) deactivates the ring by resonance

(III) increases the charge density at the ortho and para position relative to meta position by resonance

(IV) directs the incoming electrophile to the meta position by increasing the charge density relative to the ortho and para position.

Choose the correct option:

(a) (I) and (IV) (b) (I) and (III)

(c) (II) and (IV) (d) (II) and (III)

Ans. *(b) (I) and (III)*

Explanation: The presence of a halogen atom in the benzene ring deactivates the ring by inductive effect and tends to increase the charge density at ortho and para positions relative to meta position by resonance in an electrophilic substitution reaction.

Assertion-Reason (A-R)

In the following question no. (10-12) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

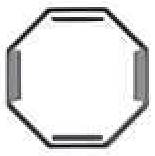
(a) Both (A) and (R) are true but (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

10. Assertion (A): The compound cyclooctane has the following structural formula:



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

Reason (R): (4n+2)□ electron rule does not hold good and ring is not planar. [NCERT Exemplar]

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Aromaticity is demonstrated by compounds with the following properties: planarity, complete delocalization of the electrons in the ring, and the presence of $(4n + 2)\pi$ electrons in the ring, where n is an integer ($n = 0, 1, 2...$). This is known as the Hückel rule.

The given compound is antiaromatic, according to Huckel's rule.

Related Theory

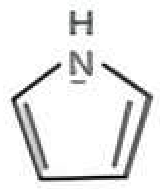
- *Students apply the formula as $(4n)$ π electron which is an invalid formula for Aromaticity.*

11. Assertion (A): Pyrrole is an aromatic heterocyclic organic compound.

Reason (R): It has 6π electrons that are cyclic and delocalised.

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Pyrrole is a five-membered ring heterocyclic compound. It contains 6π electrons. As 4π electrons in the ring and 2π electrons donated by the nitrogen atom in ring.



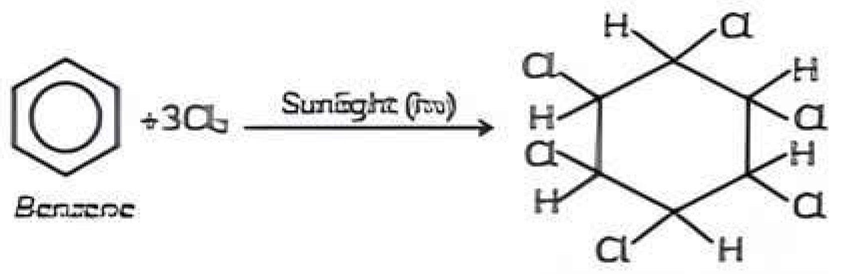
Pyrrole

12. Assertion (A): Benzene reacts with chlorine in the form of light to form BHC.

Reason (R): BHC is also called gammexane or 666. [Delhi Gov. QB 2022]

Ans. *(b) Both (A) and (R) are true but (R) is not correct explanation for (A).*

Explanation:



Benzene

Benzene hexachloride (BHC)

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

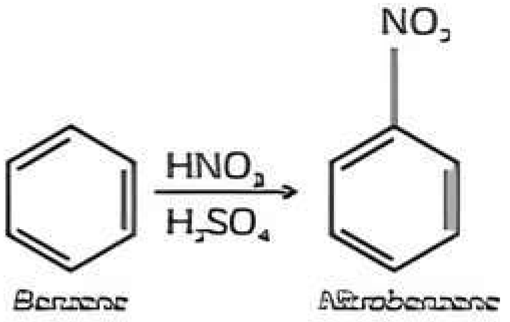
13. *The molecular formula of benzene is determined by elemental analysis. As a result, benzene is a highly unsaturated compound. It took several years to assign its structure due to its unique properties and unusual stability. Benzene was discovered to be a stable molecule that forms a triozonide, indicating the presence of three double bonds. A compound 'A' contains a meta-directing group. This compound is produced when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid.*

(A) Identify the compound 'A'.

(B) What are meta-directing groups?

(C) Comment on the structure of benzene.

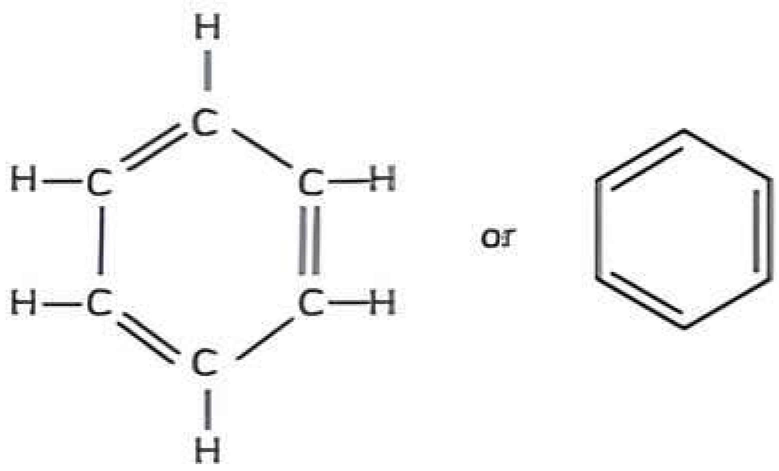
Ans. (A) *Compound 'A' is nitrobenzene*



Benzene *Nitrobenzene*

(B) Meta directors are also referred to as deactivators. Meta directors are substituents in an electrophilic aromatic substitution that aids in the electrophilic attack of the Meta substituent. For example- nitro groups, sulphonic groups, and carbonyl compounds.

(C) The molecular formula of benzene is C_6H_6 as determined by elemental analysis. As a result, benzene is a highly unsaturated compound. Benzene was discovered to be a stable molecule that forms a triozonide, indicating the presence of three double bonds. Benzene was also discovered to produce only one monosubstituted derivative, indicating that all six carbon and six hydrogen atoms in benzene are identical.



14. *Benzene has six π electrons which are delocalised and can freely move around the six carbon nuclei. The nuclei of the carbon atoms attract the delocalised electron cloud more strongly than the electron cloud localised between two carbon atoms. As a result, the appearance of delocalised π electrons in benzene increases its stability.*

According to X-ray diffraction data, benzene is a planar molecule. According to the data, all six (C–C) bond lengths are of the same order (139 pm), which is intermediate between (C–C) single bond (154 pm) and C = C double bond (133 pm). This behaviour can be explained on the basis of delocalisation of p-electrons.

(A) Benzene has .... pi electrons.

(a) 0 (b) 6

(a) 3 (a) 1

(B) What is the hybridisation of carbon atoms in the benzene ring?

(a) sp^3 (b) sp^2

(c) sp (d) dsp^3

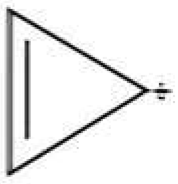
(C) Which of the following compounds is formed when benzene reacts with hydrogen gas in presence of Nickel?

(a) Hexyne (b) Hexene

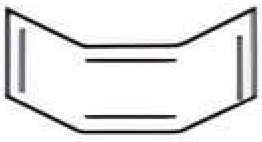
(c) Cyclohexane (d) Cyclopentane

(D) Four structures are given in options (i) to (iv). The correct option which represents the aromatic structures is

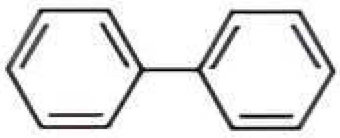
(I)



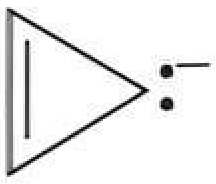
(II)



(III)



(IV)



Options:

(a) (I) and (II) (b) (I) and (III)

(c) (II) and (III) (d) (II) and (IV)

(E) Benzene reacts with anhydrous aluminium chloride in the dark and cold atmosphere to form ....

(a) chlorobenzene

(b) toluene

(c) hexachlorobenzene

(d) acetylene

Ans. (A) *(b) 6*

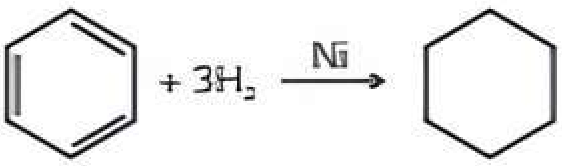
Explanation: Benzene has 6 pi electrons. Six pi electrons in benzene are delocalized in six p-orbitals that overlap across each plane of the ring. Because of the loosely held pi electrons, the benzene ring becomes electron-rich, allowing it to react with electrophiles. Because benzene adheres to Huckel's rule, it is exceptionally stable. As a result, reactions that preserve the aromatic ring are preferred.

(B) (b) sp^2

Explanation: Carbon atoms in the benzene ring have a trigonal planar geometry around them, and thus the hybridization is sp^2.

(C) *(c) Cyclohexane*

Explanation: Hydrogenation of benzene produces cyclohexane under vigorous conditions, *i.e.*, at high temperature and pressure in the presence of a nickel catalyst.



(D) *(b) (I) and (III)*

Explanation: For a compound to be aromatic it should follow Huckel Rule.

That is

(1) It should have $(4n+2)$ π electrons.

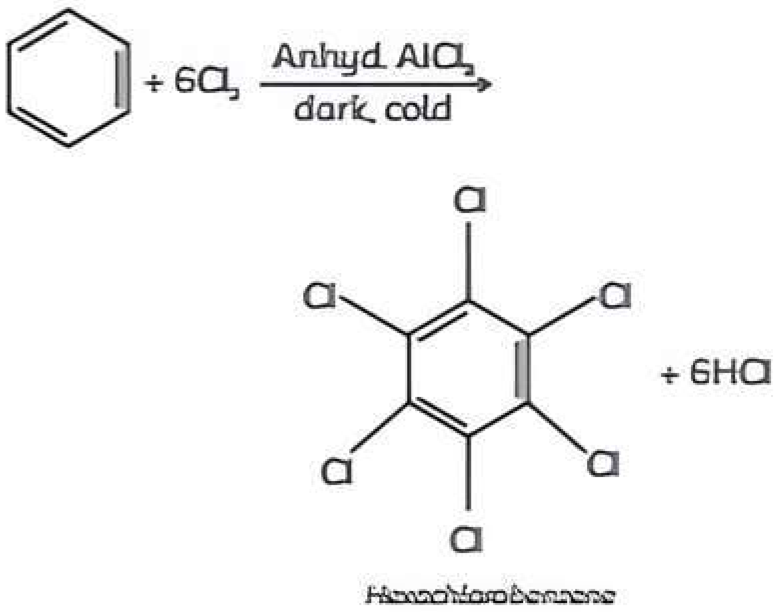
(2) It should be planar.

(3) π-electrons must be delocalised.

These conditions are fulfilled by (I) and (III) only hence these two are aromatic.

(E) *(c) hexachlorobenzene*

Explanation: If an excessive amount of electrophilic reagent is used, a further substitution reaction may occur in which other hydrogen atoms of the benzene rings are successively replaced by the electrophile.

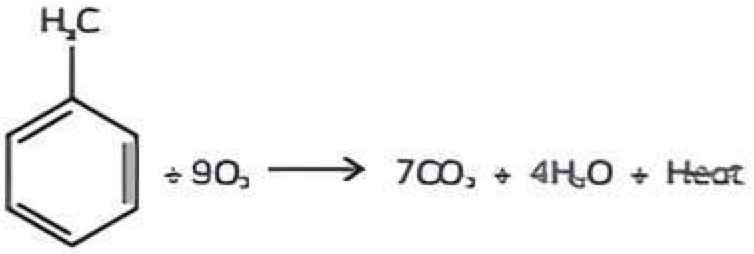


VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

15. **Write a chemical equation for toluene combustion.**

Ans.



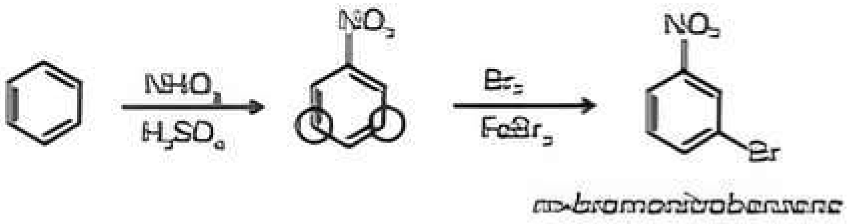
16. **What does Hückel rule state?**

Ans. It states that for any compound being aromatic it should accomplish $(4n + 2)$□ electrons.

17. **Starting from benzene, how would you synthesize m-Bromonitrobenzene.**

[Delhi Gov. QB 2022]

Ans.



18. **What is the colloquial term for aromatic hydrocarbon?**

Ans. Aromatic hydrocarbons are also known are Arenes.

19. **State whether toluene is aromatic or not.**

Answ. Toluene is classified as an aromatic hydrocarbon. In chemical structure, it is a mono-substituted benzene derivative composed of a CH_3 group attached to a phenyl group and it follows Hückel's rule of Aromaticity.

20. **Why does the presence of a nitro group make the benzene ring less reactive in comparison to unsubstituted benzene ring? Explain.**

[NCERT Exemplar]

Ans. Nitro group has a nitrogen bonded to two highly electronegative oxygen atoms. This results in the decrease of electron density around the nitrogen atom and nitrogen possess a partial positive charge which makes the benzene ring less reactive.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

21. **What conditions must a compound meet in order for it to be aromatic? Give a few examples also.**

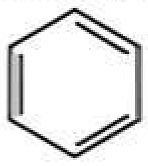
Ans. Aromatic compounds are those that have the following characteristics.

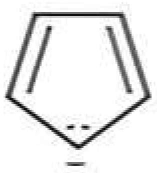
(1) Planarity

(2) The electrons in the ring have been completely delocalised.

(3) The presence of electrons in the ring, where n is an integer (n = 0, 1, 2...). This is known as the Hückel Rule.

Some of the aromatic compounds are as follows:


Benzene

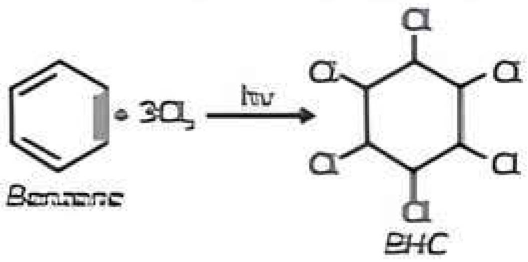

Cyclopentadienyl anion


Cycloheptatrienyl cation

22. **What happens when Chlorine is passed through benzene in the presence of sunlight and absence of halogen carrier?**

[Delhi Gov. QB 2022]

Ans. When chlorine is passed through warm benzene in presence of the sunlight, the product obtained is Gammexane. It is also called benzene hexachloride (BHC) or 666 or gamma- Lindone. It is an insecticide.

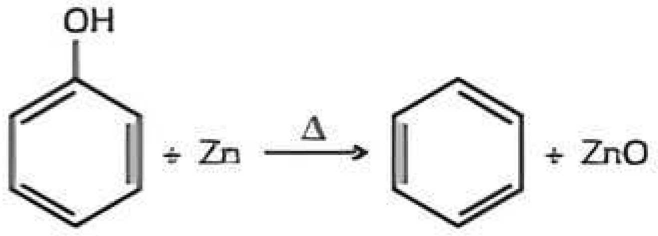


23. **What is the difference between benzenoids and non- benzenoids compounds?**

Ans. Aromatic compounds with a benzene ring are referred to as benzenoids, while those without a benzene ring are referred to as non-benzenoids.

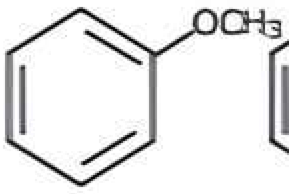
24. **Establish a procedure for converting phenol to benzene.**

Ans. In the presence of zinc and heat, it will reduce to benzene.

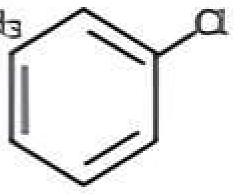


25. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. Give reason.

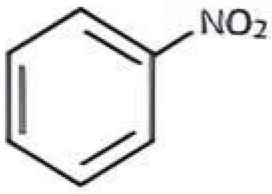
[NCERT Exemplar]



(I)



(II)



(III)

Ans. The +R effect of —OCH_3 > —Cl and —NO_2 has a – R effect. As the electron density increases on the benzene ring its reactivity towards electrophile increases.

Hence the reactivity order of the substituted benzene rings is as follows :

$C_6H_5—OCH_3 > C_6H_5—Cl > C_6H_5–NO_2$

26. Despite their effect, halogens are ortho and para directing in halo arenes. Explain.

[NCERT Exemplar]

Ans. Halogens in the benzene ring have the –*I* effect that deactivates the ring but effect increases the electron density on ortho and para positions when compared to the meta position. So, the halogens are ortho and para-directing groups.

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

27. What do the terms ortho, meta, and para mean?

Ans. The aromatic compounds containing the two groups at adjacent positions, *i.e.* the 1, 2–positions, are known as ortho and are denoted by the symbol '*o*'.

The aromatic compounds containing the two groups in alternate positions, *i.e.* the 1, 3–positions, are known as meta and are denoted by the symbol '*m*'.

The aromatic compounds with the two groups at the diagonal positions, *i.e.* the 1, 4–positions, are referred to as para-, denoted as 'p'.

28. What are the properties of aromatic hydrocarbons?

Ans. Few properties of aromatic hydrocarbons are as follows:

(1) These compounds have high aromaticity.

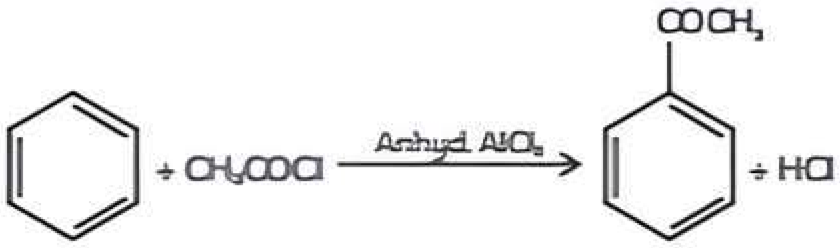
(2) Because of resonance, these compounds have excellent stability.

(3) There is a significant carbon-to-hydrogen ratio.

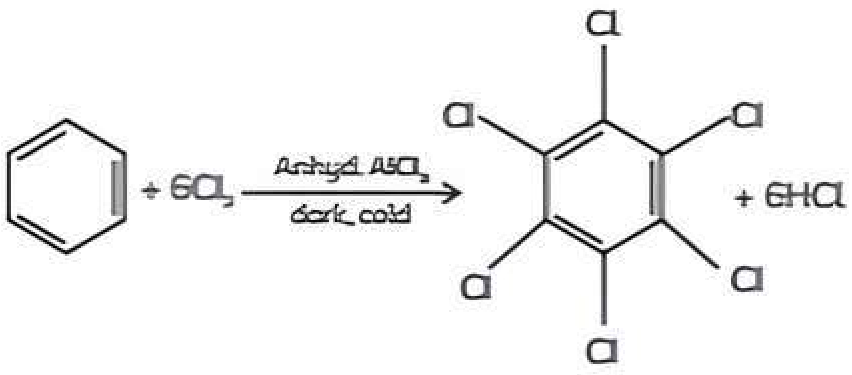
(4) Aromatic hydrocarbons can be aromatically substituted in both electrophilic and nucleophilic ways.

29. Write about Friedel craft acylation reaction.

Ans. In the presence of Lewis acids ($AlCl_3$), the reaction of benzene with either an acyl halide or acid anhydride yields acyl benzene.

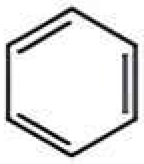


If an excessive amount of electrophilic reagent is used, a further substitution reaction may occur in which other hydrogen atoms of the benzene ring are successively replaced by the electrophile.

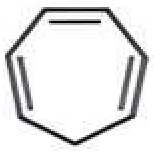


30. The ring systems having the following characteristics are aromatic (i) planar ring containing pi conjugated bonds (ii) Complete delocalisation of pi electrons (iii) The presence of (4n +2)□ electrons in the ring, where n is an integer (n = 0, 1, 2...). This is known as the Hückel Rule.

Using this information classify the following compounds as aromatic and non-aromatic.

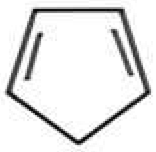


(A)

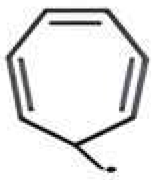


(B)

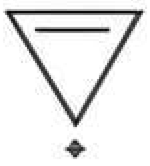
(C)



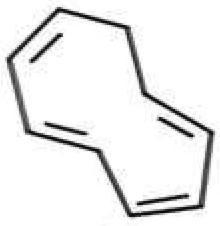
(D)



(E)



(F)



(G)

[NCERT Exemplar]

Ans. Aromatic compounds: A, E and F. This is because these compounds follow all the characteristics required for a compound to be aromatic.

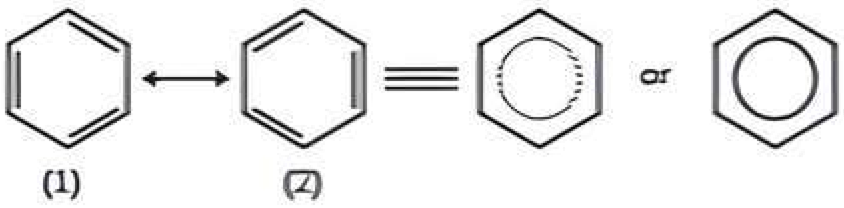
Non-aromatic compounds: B, C, D and G . This is because these compounds do not follow all the characteristics required for a compound to be aromatic.

LONG ANSWER Type Questions (LA)

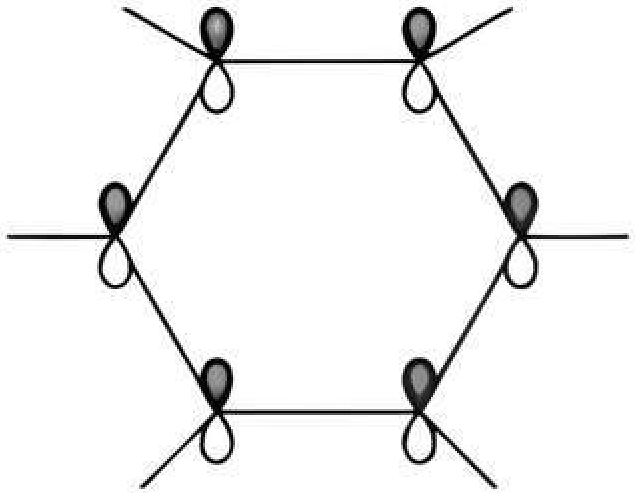
[**4** & **5** marks]

31. Explain the resonance and stability of benzene.

Ans. Resonance is the phenomenon in which two or more structures for a substance can be written that involve identical atomic positions. The resonance structures in benzene are represented by Kekulé structures (1) and (2). The molecule's actual structure is represented by a hybrid of these two structures.



The orbital overlapping provides a clearer picture of benzene's structure. In benzene, all six carbon atoms are sp^2 hybridised. Each carbon atoms two sp^2 hybrid orbitals overlap with the sp^2 hybrid orbitals of adjacent carbon atoms to form six $C–C$ sigma bonds in the hexagonal plane. Six $C–H$ sigma bonds are formed when a carbon atom remaining sp^2 hybrid orbital overlaps with a hydrogen atom s-orbital. As shown below, each carbon atom now has one unhybridised *p*-orbital perpendicular to the ring plane:



As a result, the six electrons are delocalised and can freely move around the six carbon nuclei. The nuclei of the carbon atoms attract the delocalised electron cloud more strongly than the electron cloud localised between two carbon atoms. As a result, the appearance of delocalised electrons in benzene increases its stability.

According to X-ray diffraction data, benzene is a planar molecule. According to the data, all six C–C bond lengths are of the same order (139 *pm*), which is intermediate between (C–C) single bond (154 *pm*) and C=C double bond (133 *pm*). Thus, the presence of a pure double bond in benzene lends itself to the idea of benzene's reductance to show addition reaction under normal conditions. It explains benzene's unusual behaviour.

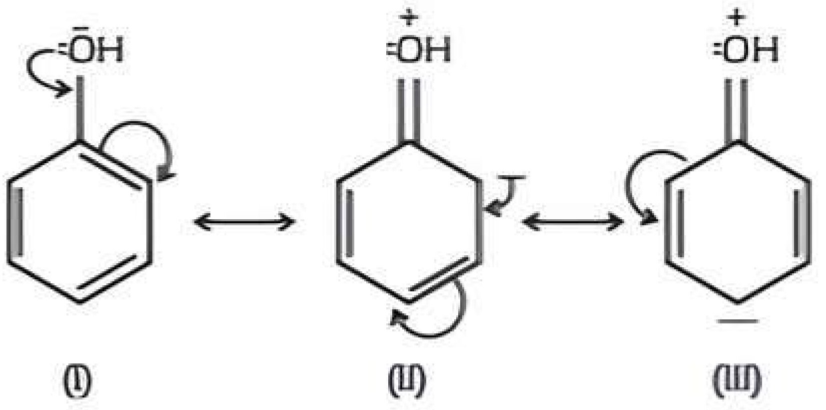
32. What is the directive influence of a fundamental group in monosubstituted benzene?

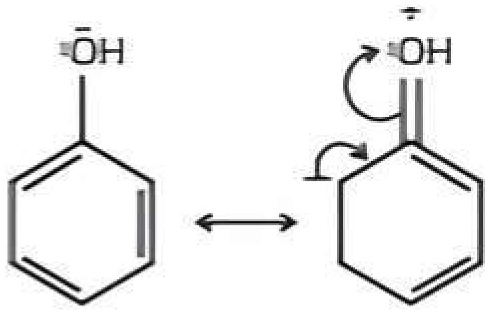
Ans. There is mainly two types of influence which are as follows:

When substitution reaction takes place in mono-substituted benzene three types of disubstituted products are formed with unequal amounts which are ortho, para and meta. Two types of behaviour are majorly observed either ortho and para products or meta products. This behaviour is dependent on the nature of substituent already present in the benzene ring not depending on the nature of the entering group. This is known as directive influence of substituents. The reasons for their position are discussed:

Ortho and para directing groups: The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups. Example: The phenolic groups have the following resonating structure which increases the electron density on the ortho and para position, hence the substitution will takes place in this position. It is noted that –I effect of –OH also operates due to which electron density on ortho and para positions of the benzene ring is slightly reduced. But the overall electron density is increased due to resonance. Therefore –OH group activates the benzene group at the ortho and para positions.

OH, –NHR, $NHCOCH_3$, $–OCH_3$, $–CH_3$, C_2H_5 are ortho and para directing and activating groups.





(V) (IV)

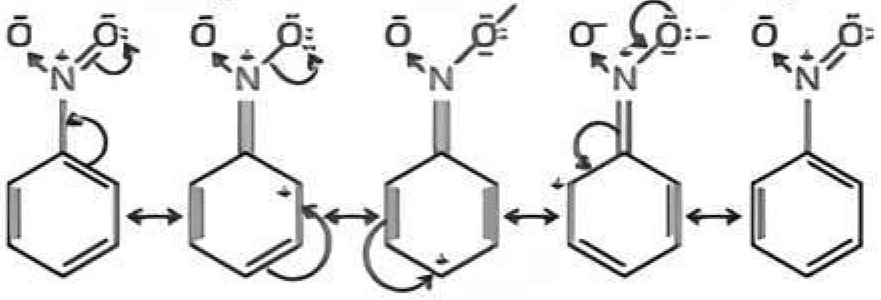
Resonance structures of phenol

Meta-directing groups:

Meta-directing groups are one which directs the incoming group at meta position.

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

Example: In nitrobenzene, the nitro group reduces the electron density in the benzene due to the strong effect.



Resonance hybrid of Nitrobenzene

So, the overall electron density at the benzene ring decreases which makes substitution more difficult so, these groups are called deactivating groups. The electron density at the ortho and para positions is less when compared to the meta position. So substitution takes place at the meta position.