13

Hydrocarbons

Facts that Matter

• Hydrocarbon

A compound of carbon and hydrogen is known as hydrocarbon.

• Saturated Hydrocarbon

A hydrocarbon is said to be saturated if it contains only C – C single bonds.
For example: Ethane CH_3-CH_3

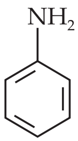
• Unsaturated Hydrocarbon

A hydrocarbon is said to be unsaturated if it contains C = C or C ≡ C multiple bonds.
Example: ethene $CH_2=CH_2$
ethyne $HC\equiv CH$

• Aromatic Hydrocarbon

Benzene and its derivatives are called aromatic compounds.
Example:

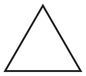
Benzene



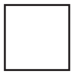
Aniline

• Alicyclic Compounds

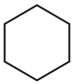
Cyclic compounds which consist only of carbon atoms are called alicyclic or carbocyclic compounds.



Cyclopropane



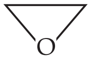
Cyclobutane



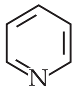
Cyclohexane

• Heterocyclic Compounds

Cyclic compounds in which the ring atoms are of carbon and some other element (For example, N, S, or O) are called heterocyclic compounds.



OXIRANE

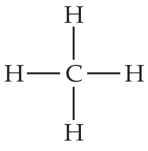


PYRIDINE

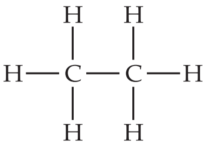
• Alkanes

Alkanes are the simplest organic compounds made of carbon and hydrogen only.
They have the general formula C_nH_{2n+2} (where n = 1, 2, 3, etc.)

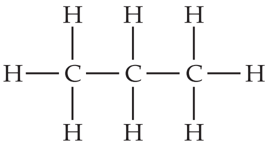
The carbon atoms in their molecules are bonded to each other by single covalent bonds. Since the carbon skeleton of alkanes is fully 'saturated' with hydrogens, they are also called saturated hydrocarbons. Alkanes contain strong C—C and C—H bonds. Therefore, this class of hydrocarbons are relatively chemically inert. Hence they are sometimes referred to as paraffins (Latin parum affinis = little affinity). First three members of this class can be represented as



Methane

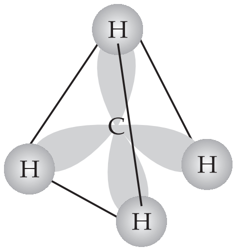


Ethane



propane

Structure:

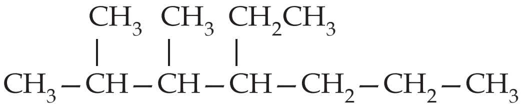


Structure of methane

In methane carbon forms single bonds with four hydrogen atoms. All H—C—H bond angles are of 109.5°. Methane has a tetrahedral structure. C—C and C—H bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1s orbitals of hydrogen atoms.

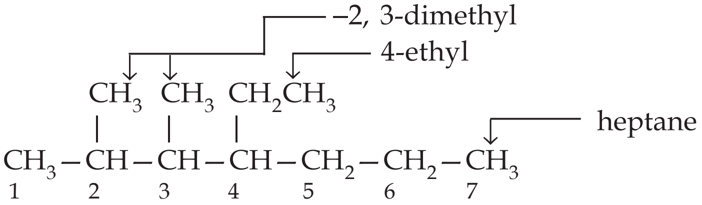
● Nomenclature Guidelines

Use the following step-by-step procedure to write the IUPAC names from the structural formulas. Consider the following structural formula:



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_2CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

Step 1. Identify the longest chain: In the given example, longest chain has seven carbons. The seven carbon chain is heptane.



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{4}{\overset{\overset{CH_2CH_3}{|}}{CH}}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

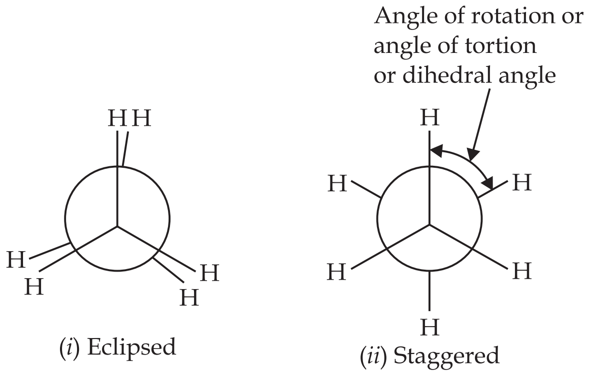
Step 2. Number the chain: The chain is numbered from left to right. This gives lowest numbers to the attached alkyl group.

Step 3. Identify the alkyl group: There are two methyl groups at *C*-2 and *C*-3, there is one ethyl group of *C*-4.

Step 4. Write the IUPAC name: In this case the IUPAC name is 4-Ethyl-2, 3-dimethyl heptane. Always keep in mind (*a*) Numbers are separated from each other by commas. (*b*) Numbers are separated from names by hyphens. (*c*) Prefixes di, tri are not taken into account in alphabetising substituent names.

• Newman Projections

In this projection, the molecule is viewed at the C—C bond head on.



Newman's projections of ethane

• Relative Stability of Conformations

In staggered form of ethane there are maximum repulsive forces, minimum energy and maximum stability of molecule. On the other hand, when the staggered form changes in the eclipsed form the electron clouds of the carbon hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions, molecule have to possess more energy and thus has lower stability.

Torsional Angle: Magnitude of torsional strain depends upon the angle of rotation about C—C bond. This angle is also called dihedral angle or torsional angle.

• Alkenes

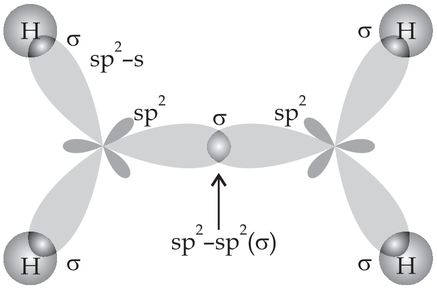
Alkenes are hydrocarbons that contain a carbon-carbon double bond (C═C) in their molecule. They have the general formula C_nH_{2n}.

Structure:

Let us consider ($H_2C{=}CH_2$) for illustrating the orbital make up of alkenes.

In ethylene the carbon atoms are sp^2 hybridized. They are attached to each other by a σ bond and a π bond.

The σ bond results from the overlap of two sp^2 hybrid orbitals. The π bond is formed from overlap of the unhybridized p-orbitals. Ethylene is a planar molecule.



Orbital picture of ethene depicting σ bonds only

Points to be noted

(*i*) The carbon-carbon double bond in alkenes is made up of one σ and one π-bond.

(*ii*) Alkenes are more reactive than Alkanes. This is due to the availability of π electrons.

• Nomenclature

In IUPAC system

(*i*) The name of the hydrocarbon is based on the parent alkene having the longest carbon chain of which double bond is apart.

(*ii*) This chain is numbered from the end near the double bond and its position is indicated by the number of the carbon atom not which the double bond originates.

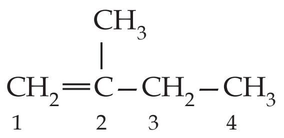
(*iii*) The name of the parent alkene with the position number of the double bond is written first and then the names of other substituents prefixed to it.

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

1-Butene

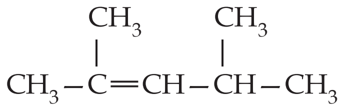
$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_3}$$

2-Butene



$$\underset{1}{CH_2}=\underset{2}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{3}{CH_2}-\underset{4}{CH_3}$$

2-Methyl-1-butene



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2, 4-Dimethyl-2-pentene

(*iv*) When there are two or three double bonds in a molecule, the ending-one of the corresponding alkane is replaced by-a diene to get the name.

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

1, 3-Butadiene

• Isomerism

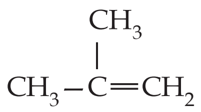
Structural Isomerism: Ethene and propene have no structural isomers, but there are three structures of butenes.

$$CH_3-CH_3-CH=CH_2$$

1-Butene

$$CH_3-CH=CH-CH_3$$

2-Butene



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

2-Methyl propene

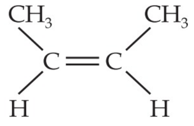
Of these, two are straight chain structures with the difference being in the position of double bond in the molecules.

These are position isomers and third structure is a branched-chain isomer.

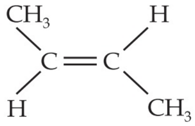
Geometrical Isomerism: It is known that a carbon-carbon double bond is made up of one σ bond and one π-bond. The π-bond presents free rotation about the double bond.

This presentation of rotation about the carbon-carbon double bond gives rise to the phenomenon of geometrical isomerism. An alkene having a formula RCH═CHR can have two stereoisomers, depending upon whether the two alkyl groups are on the same or opposite sides of the double bond. If they are on the same side, then it is called cis-isomer. If they are on opposite sides, then it is called trans-isomer.

Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility, etc.



cis-But-2-ene
(b.p. 277 K)



trans-But-2-ene
(b.p. 274 K)

• Alkynes

Alkynes are characterised by the presence of a triple bond in the molecule.

Their general formula is C_nH_{2n-2}.

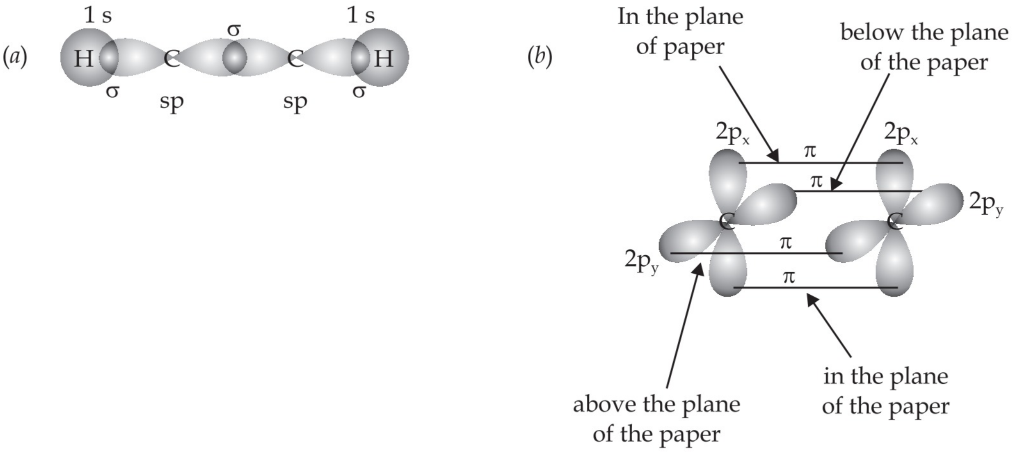
The first and the most important member of this series of hydrocarbons is acetylene, HC≡CH, and hence they are also called the Acetylenes.

Structure: Let us consider ethyne (HC≡CH) for illustrating the orbital make up of ethyne.

In ethyne, the carbon atoms are sp hybridized. They are attached to each other by a σ-bond and two π-bonds.

The σ-bond results from the overlap of two sp hybrid orbitals. The π bonds are formed from the separate overlap of the two p-orbitals from the two adjacent carbon atoms.

The other sp hybrid orbital of each carbon atom forms a σ bond with another carbon or hydrogen atom. Ethyne is a linear molecule.



Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.

Points to be noted:

(*i*) The carbon-carbon triple bond in alkynes is made up of one σ and two π bonds.

(*ii*) Like alkenes, alkynes undergo addition reaction. These reactions are due to the availability of more exposed π electrons.

• Nomenclature

IUPAC System: The IUPAC names of alkynes are obtained by dropping the ending-ane of the parent alkane and adding the suffix-yne. Carbon chain including the triple bond is numbered from the end nearest this bond. The position of the triple bond is indicated by prefixing the number of carbon preceding it to the name of the alkyne.

$H-C\equiv C-H$

Ethyne

$CH_3-C\equiv C-H$

Propyne

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

1-Butyne

Preparation:

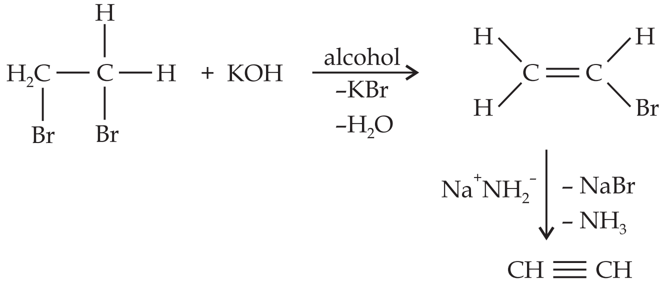
From calcium carbide: Ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared as follows:

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

$$CaO + 3C \longrightarrow CaC_2 + CO$$

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

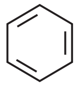
From vicinal dihalides: When reacted with vicinal dihalides, alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



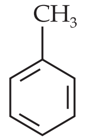
• Aromatic Hydrocarbons

These hydrocarbons are also known as 'arenes'. Most of such compounds were found to contain benzene ring.

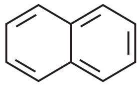
Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids. Some examples of arenes are given below.



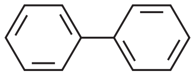
Benzene



Toluene

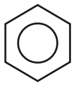


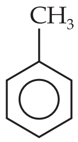
Naphthalene

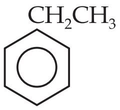


Biphenyl

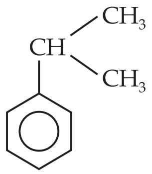
Nomenclature and Isomerism: Benzene and its homologous are generally called by their common names which are accepted by the IUPAC system. The homologous of benzene having a single alkyl group are named as Alkyl benzenes.


Benzene

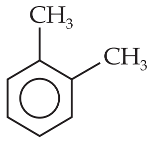

Toluene
(Methyl benzene)

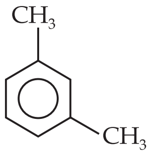


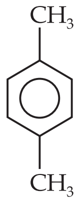
Ethyl Benzene


Cumene
(Isopropyl
benzene)

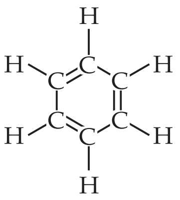
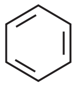
Dimethylbenzenes have the common name Xylenes. The three isomeric xylenes are


o – xylene

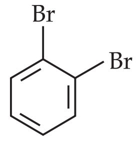

m – xylene

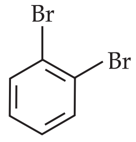

p – xylene

Structure of Benzene: By elemental analysis, it is found that molecular formula of benzene is C_6H_6. This indicates that benzene is a highly unsaturated compound. In 1865, Kekule gave the cyclic planar structure of benzene with six carbons with alternate double and single bonds.

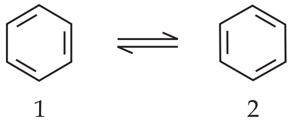

or


The Kekule structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other they are attached to the singly bonded carbon.



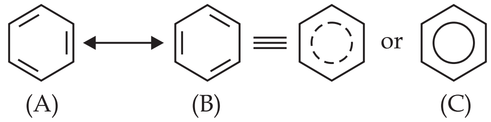


In fact, only one ortho-dibromobenzene could be prepared.
To overcome this problem Kekule suggested that benzene was a mixture of two forms.

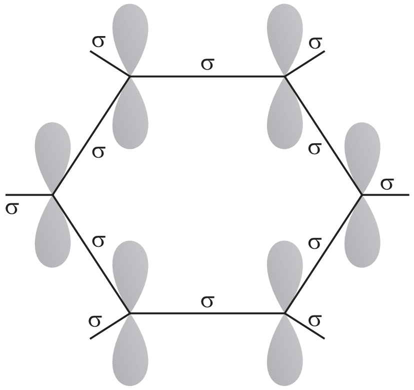

1 2

Failure of Kekule's structure: Kekule structure of benzene failed to explain the unique stability and its preference to substitution reaction than addition reactions.

Resonance Structure of Benzene: The phenomenon in which two or more structures can be written for a substance which involve identical positions of atoms is called resonance. In benzene's Kekule's structures (1) and (2) represent the resonance structures. Actual structure of the molecule is represented by hybrid of the these two structures.



Orbital structure of benzene: All six carbon atoms in benzene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with *s* orbitals of the six hydrogen atoms forming C—C and C—H σ-bonds.



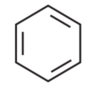
X-Ray diffraction data indicates that benzene is a planar molecule. The data indicates that all the six C—C bond length are of the same order (139 pm) which is intermediate between (C—C) single bond (154 pm) and C—C double bond (133 pm). Thus the presence of pure double bond in benzene gives the idea of reductance of benzene to show addition reaction under normal condition. Thus, it explains the unusual behaviour of benzene.

Aromaticity: It is a property of the *sp*^{2} hybridized planar rings in which the *p* orbitals allow cyclic delocalization of π electrons.

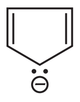
Conditions for Aromaticity:

(*i*) An aromatic compound is cyclic and planar.
(*ii*) Each atom in an aromatic ring has a *p* orbital. These *p* orbitals must be parallel so that a continuous overlap is possible around the ring.
(*iii*) The cyclic π molecular orbital (electron cloud) formed by overlap of *p* orbitals must contain ($4n + 2$) π electrons. Where n = integer (0, 1, 2, 3, etc.). This is known as Huckel rule.

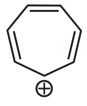
Some Examples of Atomic Compounds are given below:



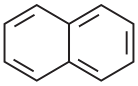
Benzene



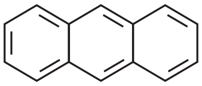
Cyclopentadienyl anion
(n=1, 6π electrons)



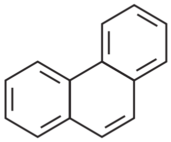
Cycloheptatrienyl cation



Naphthalene
(n = 2, 10 π electrons)



Anthracene

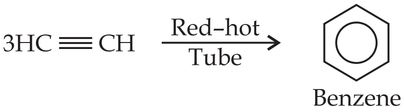


Phenanthrene

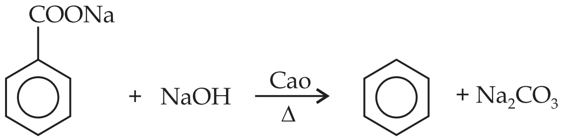
(n = 3, 14 π electrons)

Preparation of Benzene: Benzene is commercially isolated from coaltar. However, there are some synthetic methods which is applied in the laboratory for the preparation of benzene.

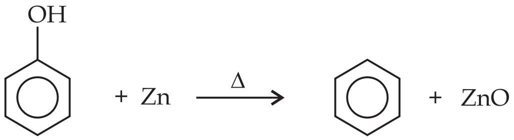
(*i*) By passing acetylene through red-hot tube at 500°C.



(*ii*) **Decarboxylation:** By heating sodium salt of benzoic acid with sodalime (NaOH + CaO).



(*iii*) By heating phenol with Zinc dust.



Physical Properties of Benzene:

(*i*) Benzene is a colourless liquid.
(*ii*) It is insoluble in water. It is soluble in alcohol, ether, chloroform etc.
(*iii*) Benzene itself is a good solvent for many organic and inorganic substances *e.g.*, fat, resins, sulphur and iodine.
(*iv*) It burns with a luminous, sooty flame in contrast to alkanes and alkenes which usually burn with a bluish flame.

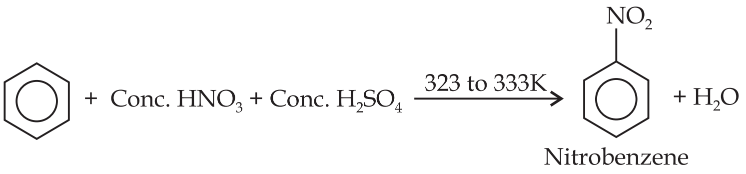
Chemical Properties:

Benzene undergeos following types of chemical reactions.

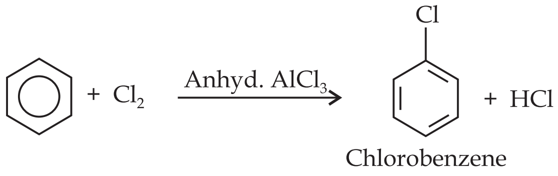
(*i*) Electrophillic Substitution Reaction
(*ii*) Addition Reaction
(*iii*) Oxidation Reaction

Electrophillic Substitution Reactions:

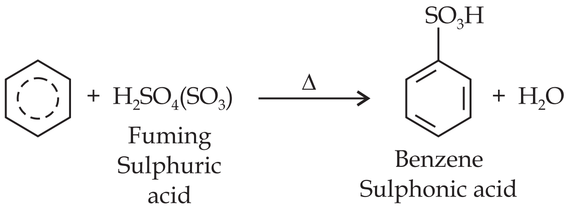
(*i*) **Nitration:**



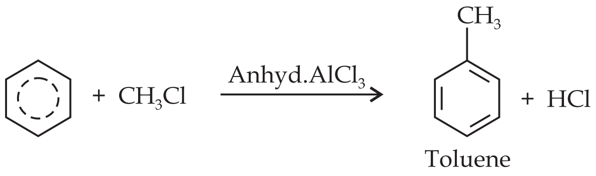
(*ii*) **Halogenation:**

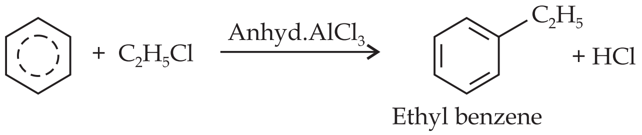


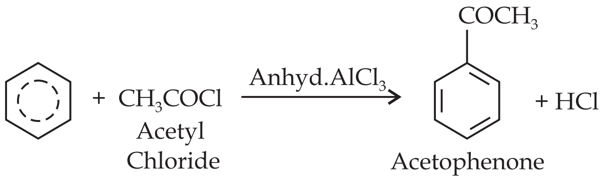
(*iii*) **Sulphonation:**

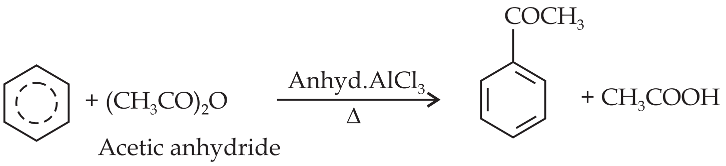


(*iv*) **Friedel-crafts alkylation reaction:**

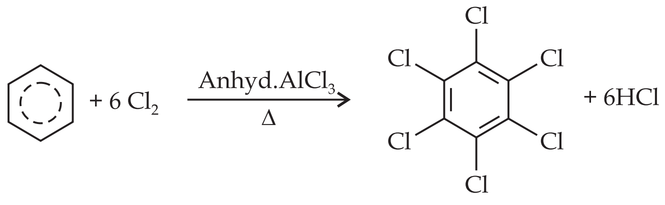








Benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ can be chlorinated to hexachlorobenzene (C_6Cl_6)

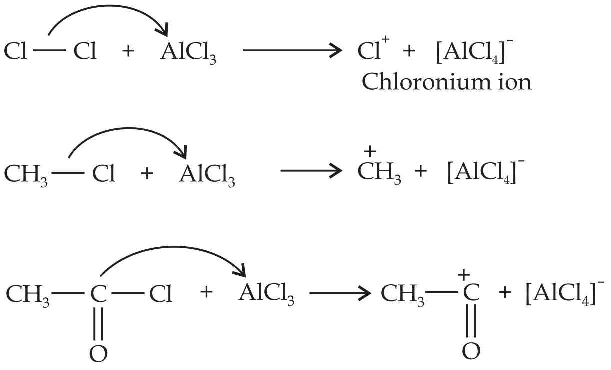


Hexachlorobenzene
(C_6Cl_6)

Mechanism of electrophilic substitution reactions:

All electrophilic substitution reactions follow the same three step mechanism.

Setp 1. Formation of an electrophile:



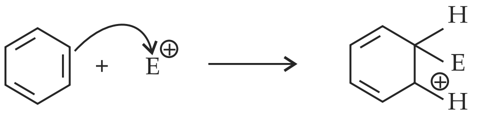
$$Cl-Cl + AlCl_3 \longrightarrow Cl^+ + [AlCl_4]^-$$

Chloronium ion

$$CH_3-Cl + AlCl_3 \longrightarrow \overset{+}{C}H_3 + [AlCl_4]^-$$

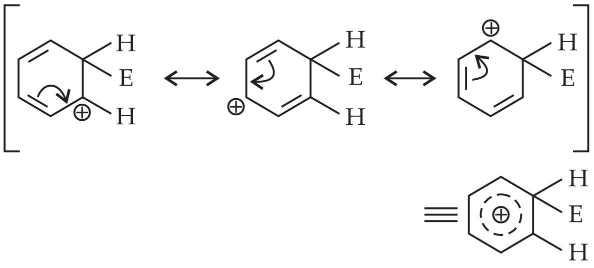
$$CH_3-\underset{\underset{O}{\|}}{C}-Cl + AlCl_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{\overset{+}{C}} + [AlCl_4]^-$$

Step 2. The electrophile attacks the aromatic ring to form a carbonium ion.



(Carbonium ion)
or
(arenium ion)

The arenium ion gets stabilised by resonance:



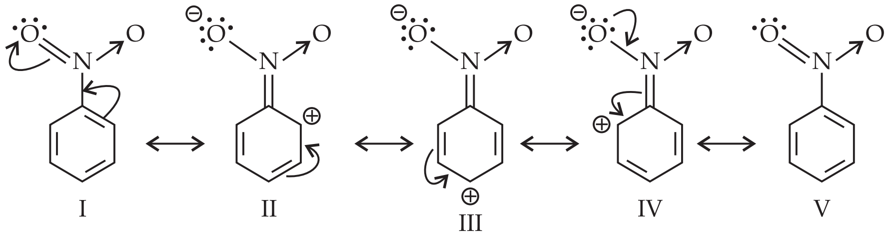
Step 3. Loss of proton gives the substitution product.

Activating groups: These group activates the benzene ring for the attack by an electrophile. Example, —OH, —NH_2, —NHR, —$NHCOCH_3$, —OCH_3, —CH_3, —C_2H_5 etc.

Deactivating groups: Due to deactivating group because of strong —I effect, overall electron density on benzene ring decreases. It makes further substitution difficult.

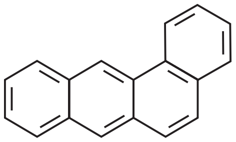
Metadirecting group: The groups which direct the incoming group to meta position are called meta directing groups. Some examples of meta directing groups are —NO_2, —CN, —CHO, —COR, —COOH, —COOR, —SO_3H etc.

Let us consider the example of nitro group: Since Nitro group due to its strong –I effect reduces the electron density in benzene ring. Nitrobenzene is a resonance hybrid of following structures.

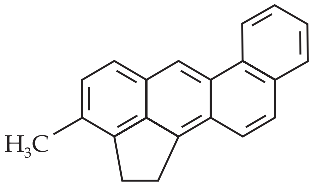


Carcinogenicity and Toxicity: Some polynuclear hydrocarbons containing more than two benzene rings fused together become toxic and they are having cancer producing property. They are actually formed due to incomplete combustion of some organic materials like tobacco, coal and petroleum, etc.

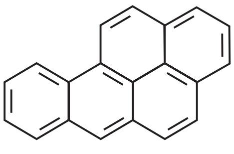
Some of the carcinogenic hydrocarbons are given below.



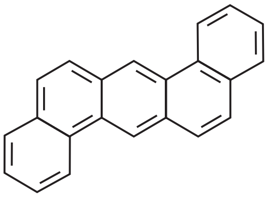
1 , 2-Benzanthracene



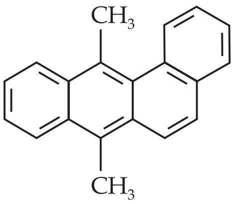
3-Methylcholanthrene



1 , 2-Benzpyrene



1,2,5,6-Dibenzanthracene



9,10-Dimethyl-1, 2-benzanthracene

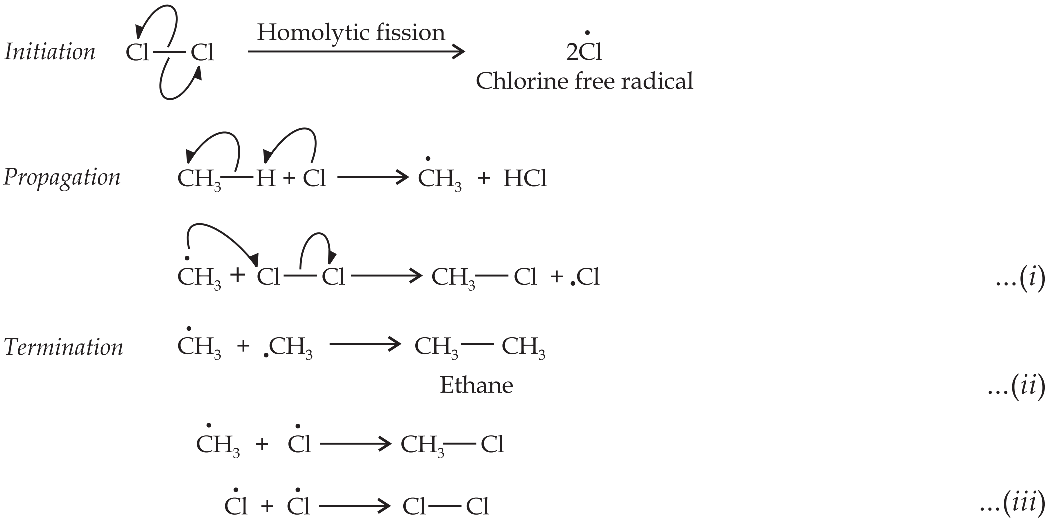
Words that Matter

- **Hydrocarbons:** They are compounds of carbon and hydrogen only.
  Open Chain saturated compound—Alkane
  Unsaturated Compound—Alkenes and Alkynes
  Aromatic Compound—Benzene and its derivatives
  Terminal alkynes are weakly acidic in nature.
- **Conformation:** Spatial arrangements obtained by rotation around sigma bonds.
- **Eclipsed Conformation:** Less stable because of more repulsion between bond pairs of electrons.
- **Staggered:** It is more stable since there is less repulsion between bond pairs of electrons.
- **Geometrical isomerism:** Observed only in compounds containing a double bond.
- **Stability of benzene.** Is explained on the basis of resonance hybrid.
- **Arenes:** Take part in electrophilic substitution reaction.
  Aromaticity is determined by Huckle's rule (4n + 2) rule

NCERT TEXTBOOK QUESTIONS SOLVED

Q1. *How do you account for the formation of ethane during chlorination of methane?*

Ans. Chlorination of methane is a free radical reaction which occurs by the following mechanism:



Initiation $Cl—Cl \xrightarrow{\text{Homolytic fission}} 2\dot{C}l$ Chlorine free radical

Propagation $CH_3—H + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$

$\dot{C}H_3 + Cl—Cl \longrightarrow CH_3—Cl + \dot{C}l$ ...(*i*)

Termination $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3—CH_3$ Ethane ...(*ii*)

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

$\dot{C}l + \dot{C}l \longrightarrow Cl—Cl$ ...(*iii*)

From the above mechanism, it is evident that during propagation step, $\dot{C}H_3$ free radicals are produced which may undergo three reactions, *i.e.*, (*i*)—(*iii*). In the chain termination step, the two CH_3 free radicals combine together to form ethane ($CH_3—CH_3$) molecule.

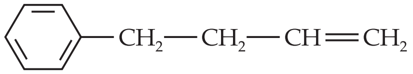
Q2. *Write IUPAC names of the following compounds:*

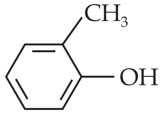
(*a*) $CH_3CH{=}C(CH_3)_2$

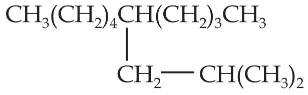
(*b*) $CH_2{=}CH—C{\equiv}C—CH_3$

(*c*)

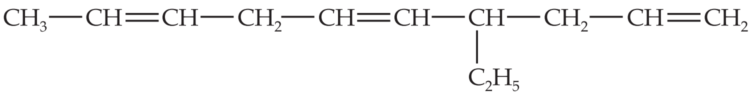
(*d*)



(*e*) 

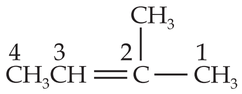
(*f*) 

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

(*g*) 

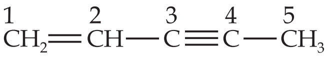
$$CH_3-CH=CH-CH_2-CH=CH-\underset{\substack{|\\ C_2H_5}}{CH}-CH_2-CH=CH_2$$

Ans.

(*a*) 

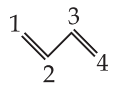
$$\overset{4}{C}H_3\overset{3}{C}H=\overset{\overset{CH_3}{|}}{\overset{2}{C}}-\overset{1}{C}H_3$$

2–Methylbut–2–ene

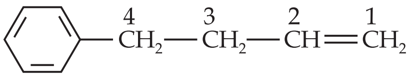
(*b*) 

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

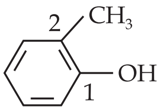
Pent – 1 – ene – 3 – yne

(*c*) 

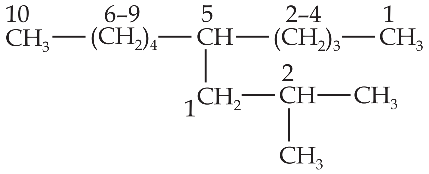
But–1,3–diene

(*d*) 

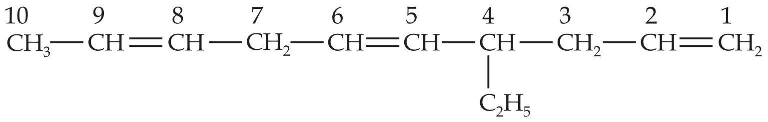
4 – Phenylbut – 1 – ene

(*e*) 

2 – Methyl phenol

(*f*) 

5–(2– Methylpropyl)decane

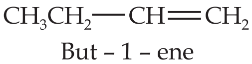
(*g*) 

$$\overset{10}{CH_3}-\overset{9}{CH}=\overset{8}{CH}-\overset{7}{CH_2}-\overset{6}{CH}=\overset{5}{CH}-\underset{\substack{|\\ C_2H_5}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

4–Ethyldeca – 1, 5, 8 – triene

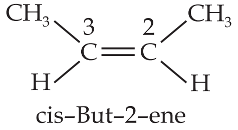
Q3. *For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated:*
(a) C_4H_8 (one double bond) (b) C_5H_8 (one triple bond)

Ans. (*a*) Isomers of C_4H_8 having one double bond are:

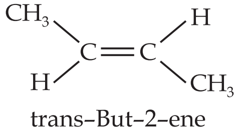
(*i*) 

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

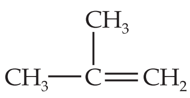
But – 1 – ene

(*ii*) 

cis–But–2–ene

(*iii*) 

trans–But–2–ene

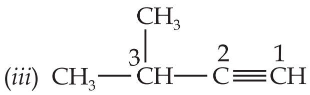
(*iv*) 

$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

2–Methylprop–1–ene

(*b*) (*i*) $CH_3CH_2CH_2\overset{2}{C}\equiv\overset{1}{CH}$
Pent–1–yne

(*ii*) $CH_3CH_2-C\equiv\overset{2}{C}-\overset{1}{CH_3}$
Pent–2–yne

(*iii*) 

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

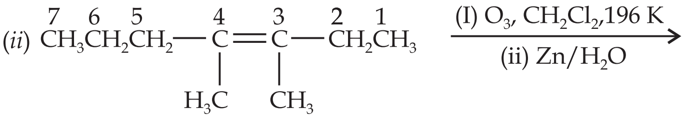
3–Methylbut–1–yne

Q4. *Write IUPAC names of the products obtained by the ozonolysis of the following compounds: (i) Pent-2-ene (ii) 3, 4-Dimethylhept-3-ene (iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene.*

Ans.

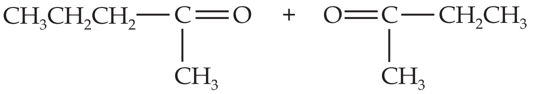
(*i*) $$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_3}\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2\text{,196 K}}CH_3-CH_2-CH=O+O=CH-CH_3$$

Pent–2–ene Propanal Ethanal

(*ii*) 

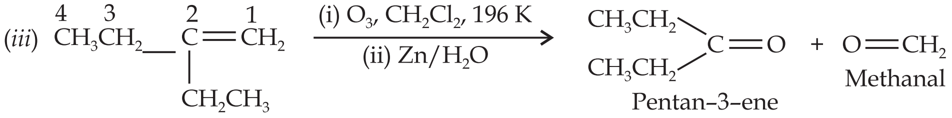
$$\overset{7}{CH_3}\overset{6}{CH_2}\overset{5}{CH_2}-\underset{\underset{H_3C}{|}}{\overset{4}{C}}=\underset{\underset{CH_3}{|}}{\overset{3}{C}}-\overset{2}{CH_2}\overset{1}{CH_3}\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(I) O}_3\text{, CH}_2\text{Cl}_2\text{,196 K}}$$

3,4–Dimethythept–3–ene



$$CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{C}=O\quad+\quad O=\underset{\underset{CH_3}{|}}{C}-CH_2CH_3$$

Pentane–2–ene Butane–2–ene

(*iii*) 

$$\overset{4}{CH_3}\overset{3}{CH_2}-\underset{\underset{CH_2CH_3}{|}}{\overset{2}{C}}=\overset{1}{CH_2}\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{, CH}_2\text{Cl}_2\text{, 196 K}}(CH_3CH_2)_2C=O\quad+\quad O=CH_2$$

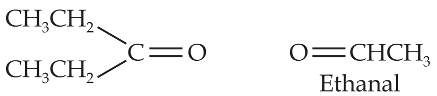
2–Ethylbut–1–ene Pentan–3–ene Methanal

(*iv*) $$\overset{4}{CH_3}\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}-C_6CH_5\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{, CH}_2\text{Cl}_2\text{, 196 K}}CH_3CH_2CH=O\quad+\quad O=CH-C_6H_5$$

1–Phenylbut–1–ene Propanal Benzaldehyde

Q5. *An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write the structure and IUPAC name of 'A'.*

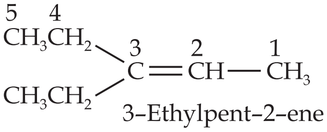
Ans. **Step 1.** Write the structure of the products side by side with their oxygen atoms pointing towards each other.



$$(CH_3CH_2)_2C=O\qquad O=CHCH_3$$

Pentan–3–ene Ethanal

Step 2. Remove the oxygen atoms and join the two ends by a double bond, the structure of the alkene 'A' is



$$(\overset{5}{CH_3}\overset{4}{CH_2})_2\overset{3}{C}=\overset{2}{CH}-\overset{1}{CH_3}$$

3–Ethylpent–2–ene (A)

Q6. *An alkene 'A' contains three C—C, eight C—H, σ-bonds, and one C—C π-bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write the IUPAC name of 'A'.*

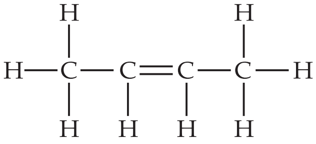
Ans. (*i*) An aldehyde with molar mass of 44 u is ethanal, $CH_3CH=O$

(*ii*) Write two moles of ethanal side by side with their oxygen atoms pointing towards each other.

$$\underset{\text{Ethanal}}{CH_3CH{=}O} \qquad \underset{\text{Ethanal}}{O{=}CHCH_3}$$

(*iii*) Remove the oxygen atoms and join them by a double bond, the structure of alkene 'A' is

$$\underset{\text{But–2–ene}}{CH_3—CH{=}CH—CH_3}$$ or



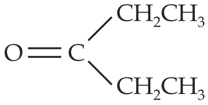
$$H—\overset{H}{\underset{H}{C}}—\underset{H}{C}{=}\underset{H}{C}—\overset{H}{\underset{H}{C}}—H$$

As required, but-2-ene has three C—C, eight C—H σ-bonds and one C—C π-bond.

Q7. *Propanal and pentan-3-ene are the ozonolysis products of an alkene. What is the structural formula of the alkene?*

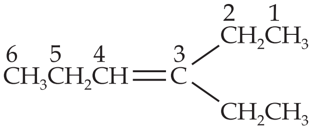
Ans. (*i*) Write the structures of propanal and pentan-3-ene with their oxygen atoms facing each other, we have,

$$\underset{\text{Propanal}}{CH_3CH_2CH{=}O}$$



Pentan–3–ene

(*ii*) Remove oxygen atoms and join the two fragments by a double bond, the structure of the alkene is



3–Ethylhex–3–ene

Q8. *Write chemical equations for the combustion reaction of the following hydrocarbons.*
(i) Butane (ii) Pentene (iii) Hexyne (iv) Toluene

Ans. (*i*) $$\underset{\text{Butane}}{C_4H_{10}(g)} + 13/2\ (g) \xrightarrow{\Delta} 4CO_2(g) + 5H_2O(g)$$

(*ii*) $$\underset{\text{Pentene}}{C_5H_{10}(g)} + 15/2O_2(g) \xrightarrow{\Delta} 5CO_2(g) + 5H_2O(g)$$

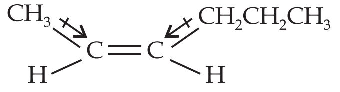
(*iii*) $$\underset{\text{Hexyne}}{C_6H_{10}(g)} + 17/2O_2(g) \xrightarrow{\Delta} 6CO_2(g) + 5H_2O(g)$$

(*iv*)  $—CH_3(g)$ or $C_7H_8(g) + 9O_2(g) \xrightarrow{\Delta} 7CO_2(g) + 4H_2O(g)$

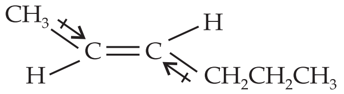
Toluene

Q9. *Draw the cis- and trans-structures for hex-2-ene. Which iosmer will have higher b.p. and why?*

Ans. The structures of cis- and trans-isomer of hex-2-ene are:



cis–Hex–2–ene
(Higher dipole moment, higher b.p.)

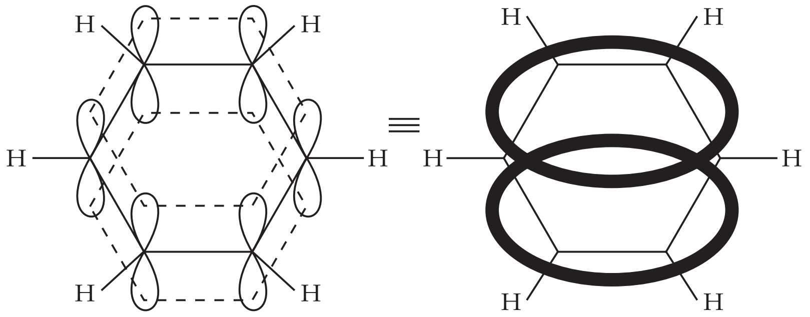


trans–Hex–2–ene
(Lower dipole moment, lower b.p.)

The boiling point of a molecule depends upon dipole-dipole interactions. Since cis-isomer has higher dipole moment, therefore, it has higher boiling point.

Q10. *Why is benzene extra-ordinarily stable though it contains three double bonds?*

Ans.



The six electrons of the *p*-orbitals cover all the six carbon atoms, and are said to be delocalized. As a result of delocalization there formed a stronger π-bond and a more stable molecule.

Q11. *What are the necessary conditions for any system to be aromatic?*

Ans. The necessary conditions for a molecule to be aromatic are:

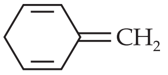
(*i*) It should have a single cyclic cloud of delocalised π-electrons above and below the plane of the molecule.

(*ii*) It should be planar. This is because complete delocalization of π-electrons is possible only if the ring is planar to allow cyclic overlap of p-orbitals.

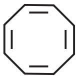
(*iii*) It should contain Huc̆kel number of electrons, *i.e.,* $(4n + 2)$ π-electrons where $n = 0, 1, 2, 3$ .... etc.

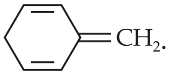
A molecule which does not satisfy any one or more of the above conditions is said to be **non-aromatic.**

Q12. *Explain why the following systems are not aromatic?*

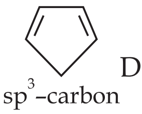
(*i*)


(*ii*)

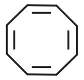

(*iii*)


Ans. (*i*)


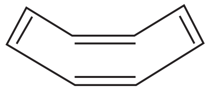
. Due to the presence of a sp^3-hybridized carbon, the system is *not planar*. It does contain six π-electrons but the system is not fully conjugated since all the six π-electrons do not form a single cyclic electron cloud which surrounds all the atoms of the ring. Therefore, it is not an aromatic compound.

(*ii*)


Due to the presence of a sp^3 -carbon, the system is not planar. Further, it contains only four π-electrons, therefore, the system is not aromatic because it does not contain planar cyclic cloud having $(4n + 2)$ π-electrons.

(*iii*) 

Planar



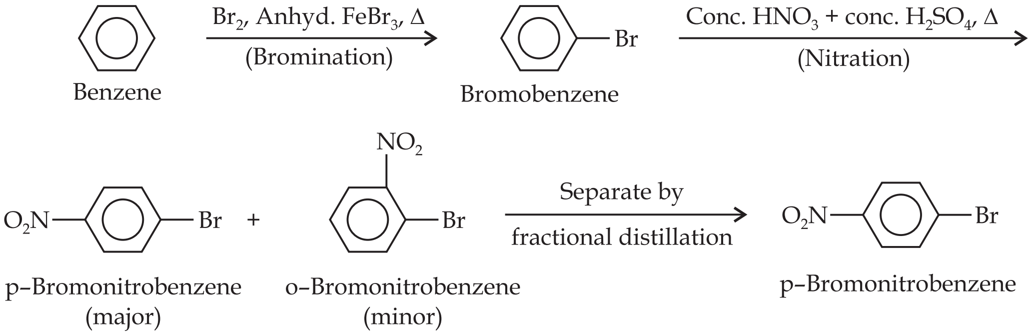
Tub shaped

Cyclo-octatetraene is not planar but is tub shaped. It is, therefore, a non-planar system having 8 π-electrons.

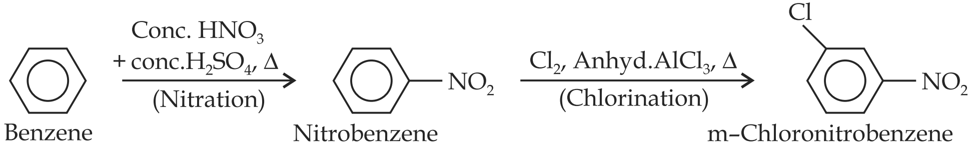
Therefore, the molecule is not aromatic since it does not contain a planar cyclic cloud having (4*n* + 2) π-electrons.

Q13. *How will you convert benzene into*
(i) p-nitrobromobenzene (ii) m-nitrochlorobenzene (iii) p-nitrotoluene (iv) acetophenone?

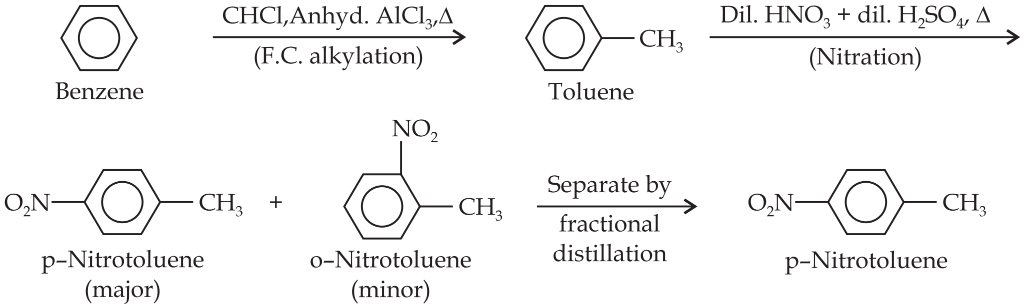
Ans. (*i*) The two substituents in the benzene ring are present at p-positions. Therefore, the sequence of reactions should be such that first an o, *p*-directing group, *i.e.,* Br atom should be introduced in the benzene ring and this should be followed by nitration. Thus,



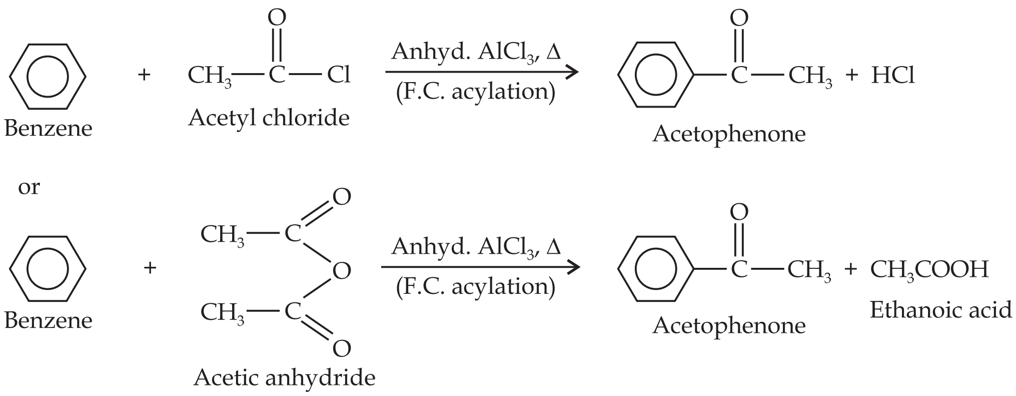
(*ii*) Here since the two substituents are at m-position w.r.t. each other, therefore, the first substituent in the benzene ring should be a m-directing group (*i.e.,* NO_2) and then other group (*i.e.,*Cl) should be introduced. Therefore, the sequence of reactions is:



(*iii*) Here since the two substituents are at *p*-position w.r.t. each other, therefore, the first substituent in the benzene ring should be a *o*, *p*-directing group (*i.e.,* CH_3) and then the other group (*i.e.,* NO_2) should be introduced.

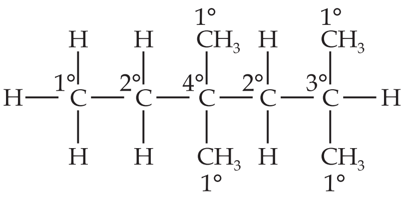


(*iv*) Acetophenone can be prepared by F.C. acylation using either acetyl chloride or acetic anhydride.



Q14. *In the alkane, $CH_3CH_2—C(CH_3)_2—CH_2—CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the number of H-atoms bonded to each one of these.*

Ans. The expanded formula of the given compound is

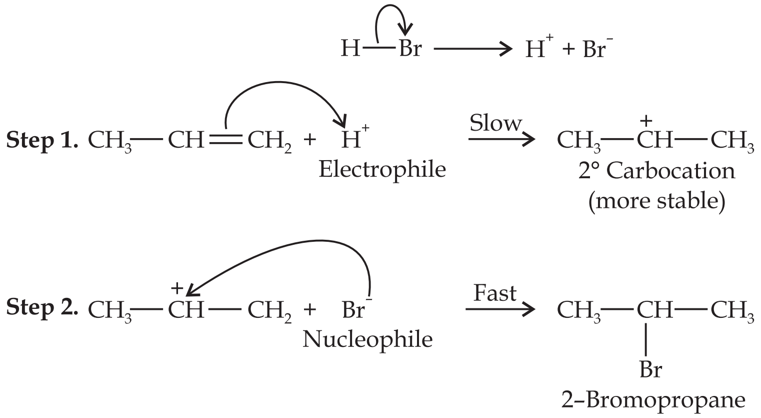


Q15. *What effect does branching of an alkane chain has on its boiling point?*

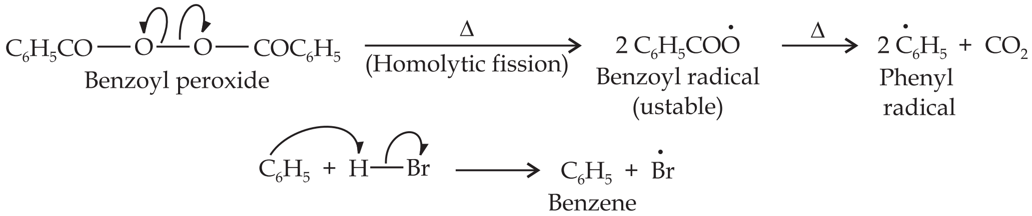
Ans. Branching of carbon atom chain decreases the boiling point of alkane.

Q16. *Addition of HBr to propene yields 2-bromopropane, while in presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.*

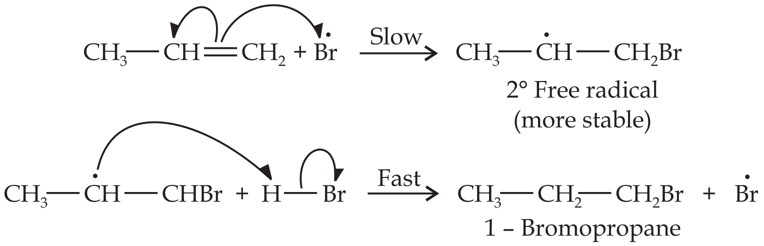
Ans. Addition of HBr to propene is an *ionic electrophilic addition reaction* in which the electrophile, *i.e.,* H^+ first adds to give a more stable 2° carbocation. In the 2nd step, the carbocation is rapidly attacked by the nucleophile Br^- ion to give 2-bromopropane.



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 benzoyl peroxide on HBr



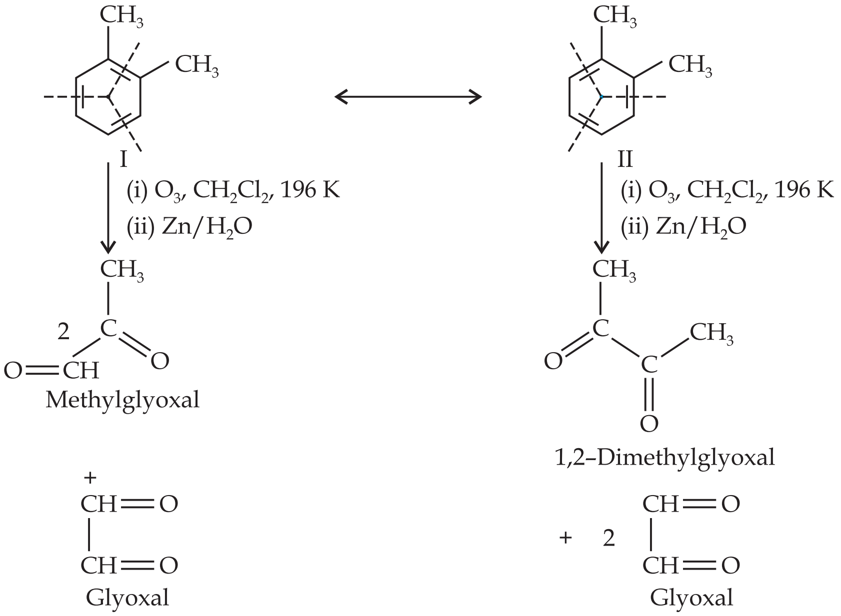
In the first step, Br radical adds to propene in such a way so as to generate the more stable 2° free radical. In the second step, the free radical thus obtained rapidly abstracts a hydrogen atom from HBr to give 1-bromopropane.



From the above discussion, it is evident that although both reactions are *electrophilic addition reactions* but it is due to different order of addition of H and Br atoms which gives different products.

Q17. *Write down the products of ozonolysis of 1, 2-dimethylbenzene (o-xylene). How does the result support Kekule structure of benzene?*

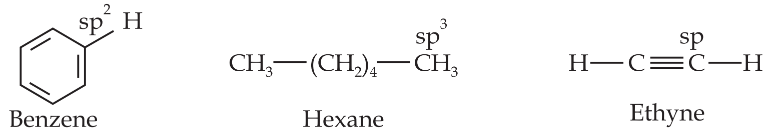
Ans. o-Xylene may be regarded as a resonance hybrid of the following two Kekule structures. Ozonolysis of each one of these gives two products as shown below:



Thus, in all, three products are formed. Since all the three products cannot be obtained from any one of the two Kekule structures, this shows that o-xylene is a resonance hybrid of the two Kekule structures (I and II).

Q18. *Arrange benzene, n-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.*

Ans. The hybridization state of carbon in these three compounds is:



Type of orbital:	sp^2	sp^3	sp
***s*-Character:**	33.3%	25%	50%

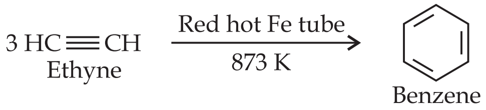
Since *s*-electrons are closer to the nucleus, therefore, as the *s*-character of the orbital making the C—H bond increases, the electrons of C—H bond lie closer and closer to the carbon atom. In other words, the partial +ve charge on the H-atom and hence the acidic character increases as the *s*-character of the orbital increases. Thus, the acidic character decreases in the order: *Ethyne* > *Benzene* > *Hexane.*

Q19. *Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?*

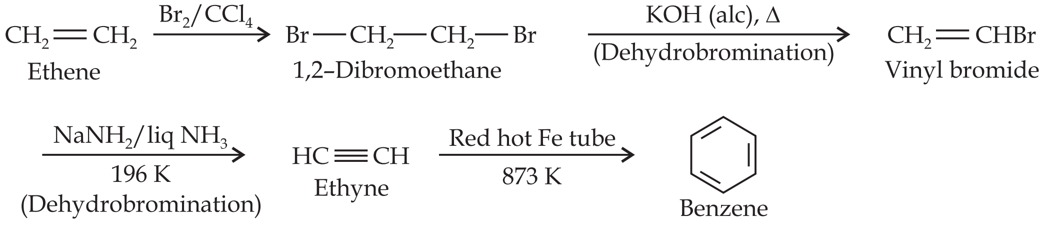
Ans. Due to the presence of an electron cloud containing 6 π-electrons above and below the plane of the ring, *benzene is a rich source of electrons*. Consequently, it attracts the electrophiles (electron-deficient) reagents towards it and repels nucleophiles (electron-rich) reagents. As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty.

Q20. *How will you convert the following compounds into benzene?*
(i) Ethyne (ii) Ethene (iii) Hexane.

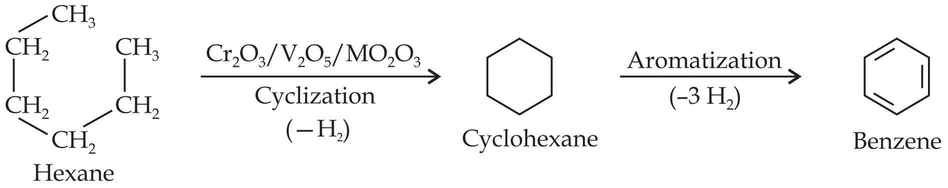
Ans. (*i*)



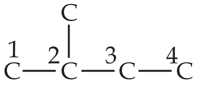
(*ii*) Ethene is first converted into ethyne and then to benzene as shown above.



(*iii*) When vapours of hexane are passed over heated catalyst consisting of Cr_2O_3, MO_2O_3 and V_2O_5 at 773 K under 10-20 atm pressure, cyclization and aromatization occurs simultaneously to afford benzene

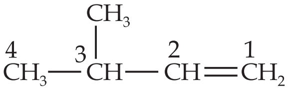


Q21. *Write structures of all the alkenes which on hydrogenation give 2-methylbutane.*

Ans. The basic skeleton 2-methylbutane is 

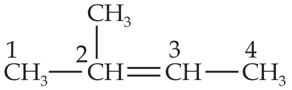
$\overset{1}{C}-\overset{\overset{C}{|}}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}$

Putting double bonds at various different positions and satisfying the tetracovalency of each carbon, the structures of various alkenes which give 2-methylbutane on hydrogenation are:



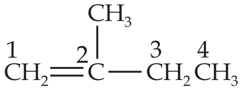
$\overset{4}{CH_3}-\overset{\overset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH}=\overset{1}{CH_2}$

3 – Methylbut–1–ene



$\overset{1}{CH_3}-\overset{\overset{CH_3}{|}}{\overset{2}{CH}}=\overset{3}{CH}-\overset{4}{CH_3}$

2–Methylbut–2–ene



$\overset{1}{CH_2}=\overset{\overset{CH_3}{|}}{\overset{2}{C}}-\overset{3}{CH_2}\overset{4}{CH_3}$

2–Methylbut–1–ene

Q22. *Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+.*

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

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

Ans. (*a*) The typical reactions of benzene are *electrophilic substitution reactions*. Higher the electron-density in the benzene ring, more reactive is the compound towards these reactions. Since NO_2 is a more powerful electron-withdrawing group than Cl, therefore, more the number of nitro groups, less reactive is the compound. Thus, the overall reactivity decreases in the order:

Chlorobenzene > *p-nitrochlorobenzene* > *2, 4-dinitrochlorobenzene*

(*b*) Here, CH_3 group is electron donating but NO_2 group is electron-withdrawing. Therefore, the maximum electron-density will be in toluene, followed by *p*-nitrotoluene followed by *p*-dinitrobenzene. Thus, the overall reactivity decreases in the order:

Toluene > p-$H_3C-C_6H_4-NO_2$ > $p-O_2N-C_6H_4-NO_2$

Q23. *Out of benzene, m-dinitrobenzene and toluene which will undergo nitration most easily and why?*

Ans. CH_3 group is electron-donating while—NO_2 group is electron-withdrawing. Therefore, maximum electron density will be in toluene, followed by benzene and least in *m*-dinitrobenzene. Therefore, the ease of nitration decreases in the order: *toluene* > *benzene* > *m*-dinitrobenzene.

Q24. *Suggest the name of another Lewis acid instead of anhydrous aluminium chloride which can be used during ethylation of benzene.*

Ans. Anhydrous Ferric Chloride ($FeCl_3$) is another Lewis acid which can be used.

Q25. *Why is Wurtz reaction not preferred for preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.*

Ans. For preparation of alkanes containing odd number of carbon atoms, a mixture of two alkyl halides has to be used. Since two alkyl halides can react in three different ways, therefore, a mixture of three alkanes instead of the desired alkane would be formed. For example, Wurtz reaction between 1-bromopropane and 1-bromobutane gives a mixture of three alkanes *i.e.,* hexane, heptane and octane as shown below:

$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2}\boxed{—Br + 2\,Na + Br}\underset{\text{1–Bromopropane}}{—CH_2CH_2CH_3} \xrightarrow[\Delta]{\text{Dry ether}} \underset{\text{Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3} + 2\,NaBr$$

$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2—}\boxed{Br + 2\,Na + Br}\underset{\text{1–Bromobutane}}{—CH_2CH_2CH_2CH_3} \xrightarrow[\Delta]{\text{Dry ether}}$$

$$\underset{\text{Heptane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_3} + 2\,Na\,Br$$

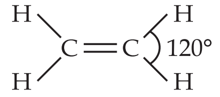
$$\underset{\text{1–Bromobutane}}{CH_3CH_2CH_2CH_2—}\boxed{Br + 2\,Na + Br}\underset{\text{1–Bromobutane}}{—CH_2CH_2CH_2CH_3} \xrightarrow[\Delta]{\text{Dry ether}}$$

$$\underset{\text{Octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2\,Na\,Br$$

MORE QUESTIONS SOLVED

I. VERY SHORT ANSWER TYPE QUESTIONS

Q1. *What are shapes of (i) $CH_2{=}CH_2$ (ii) $HC{\equiv}CH$*

Ans. (*i*)  (Planar)

(*ii*) $H—C{\equiv}C—H$ (Linear with bond angle 180°)

Q2. *What are conformations?*

Ans. Conformations are spatial arrangements which are obtained by rotation around sigma bonds.

Q3. *What is decarboxylation? Give an example.*

Ans. The process by which carbon dioxide is removed from sodium acetate (or any sodium salt of acid) with the help of sodalime is called decarboxylation.

$$CH_3COONa + NaOH \xrightarrow[\text{Cao}]{\text{heat}} CH_4 + Na_2CO_3$$

Q4. *What do you mean by pyrolysis?*

Ans. The decomposition of a compound by heat is called pyrolysis. This process when applied to alkanes is known as cracking.

Q5. *What happens when ethanol is heated with conc. H_2SO_4?*

Ans. Ethene is formed

$$CH_3\,CH_2\,OH \xrightarrow[\text{443 K}]{\text{Conc. }H_2SO_4} CH_2{=}CH_2 + H_2O$$

Q6. *Convert ethylene to ethane.*

Ans.

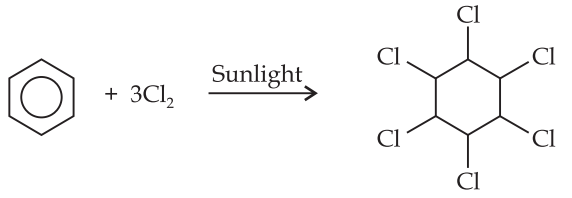
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow[\text{573 K}]{\text{Ni}} \underset{\text{ethane}}{CH_3—CH_3}$$

Q7. *What is Lindlar's catalyst? Give its use.*

Ans. $Pd/BaSO_4$ is known as Lindlar's catalyst. It is used in the conversion of alkynes to alkenes with the help of H_2.

Q8. *What happens when benzene is treated with excess of Cl_2 in presence of sunlight? Give chemical reaction.*

Ans.



BHC
(Benzene hexachloride)
is formed

Q9. *Why are alkanes called paraffins?*

Ans. Paraffins means little affinity. Alkanes due to strong C—C and C—H bonds are relatively chemically inert.

Q10. *Arrange the three isomers of pentane in increasing order of their boiling points.*

Ans. 2, 2–Dimethylpropane < 2-methylbutane < pentane.

Q11. *Arrange the following: HCl, HBr, HI, HF in order of decreasing reactivity towards alkenes.*

Ans. HI > HBr > HCl > HF

Q12. *Although benzene is highly unsaturated it does not undergo addition reactions. Why?*

Ans. It is due to delocalization of π-electrons in benzene it is highly stable.

Q13. *Why are Alkenes called olefins?*

Ans. Alkenes are commonly known as olefins because the lower members form oily products on treatment with chlorine or bromine.

Q14. *Which is more acidic: ethene or ethyne and why?*

Ans. Ethyne is more acidic than ethene because it has 'sp' hybridised 'C' which is more electronegative.

Q15. *What is Huckel rule?*

Ans. Huckel rule states that a compound is said to be aromatic if it has $(4n + 2)$ π electrons delocalized where n = an integer 0, 1, 2, 3, ...

Q16. *How will you distinguish between propene and propane?*

Ans. Pass them through dilute cold $KMnO_4$ solution (purple) or Br_2 in CCl_4 solution (red). Propene will decolourise both the solutions but propane does not react.

Q17. *How will you distinguish between acetylene and ethylene?*

Ans. Acetylene forms precipitate with ammoniacal silver nitrate solution, ethylene does not react with these reagents.

Q18. *What happens when benzene is treated with acetyl chloride in presence of $AlCl_3$?*

Ans. Acetophenone is formed.

Q19. *Which type of isomerism is exhibited by but-1-yne and but-2-yne?*

Ans. Position isomerism.

Q20. *What is electrophile in sulphonation?*

Ans. SO_3.

Q21. *What is the hybridisation of central carbon in 1,2-propadiene ($CH_2{=}C{=}CH_2$)?*

Ans. sp.

Q22. *What are Arenes?*

Ans. Arenes are aromatic hydrocarbons.

II. SHORT ANSWER TYPE QUESTIONS

Q1. *Define resonance energy. What is resonance energy of benzene?*

Ans. Resonance energy is the difference in energy between actual structure of compound and most stable resonating structure. The resonance energy of benzene is 150.325 J mol^{-1}.

Q2. *Explain the following with examples:*

(i) Wurtz reaction

(ii) Hydrogenation.

Ans. (*i*) **Wurtz reaction:** Alkanes are produced by heating an alkyl halide with sodium metal in dry ether solution.

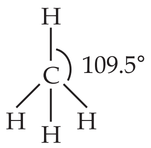
$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$

(*ii*) **Hydrogenation:** Alkenes react with hydrogen in presence of Ni or Pd catalyst to form saturated compounds.

$$CH_2{=}CH_2 + H_2 \xrightarrow[\text{373K}]{\text{Ni}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

Q3. *Discuss the shape of methane and ethane.*

Ans. In methane, carbon forms have single bonds with four hydrogen atoms. Since the carbon atom is attached to four other atoms, it uses sp^3 hybrid orbitals to form these bonds. Hybridization of 'C' is sp^3

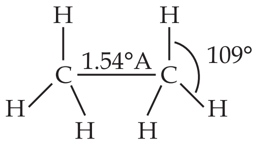


Shape—tetrahedral having bond angle = 109.5°

In ethane, there are six C—H covalent bonds and one C—C covalent bond.

The C—H bond is the result of overlap of an sp^3 hybrid orbital from carbon and s-orbital from hydrogen.

Orbital structure can be shown as



Orbital Structure of ethane

Q4. *Classify the following compounds into (i) alkanes (ii) alkenes (iii) alkynes (iv) arenes.*

(a) C_6H_6 *(b)* C_4H_8 *(c)* C_8H_{18} *(d)* C_5H_8 *(e)* C_6H_{14}

Ans. (*i*) Alkanes — C_6H_{14}, C_8H_{18}

(*ii*) Alkenes — C_4H_8

(*iii*) Alkynes — C_5H_8

(*iv*) Arenes — C_6H_6.

Q5. *What is polymerization? Give an example.*

Ans. The process by which simple molecules join together to form large molecules is known as polymerization.

Simple alkenes polymerize to form long chain addition polymers.

For example, ethylene gives polyethylene.

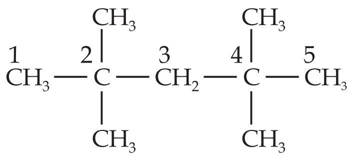
$$n\,CH_2{=}CH_2 \xrightarrow{\text{polymerization}} \!+\!CH_2-CH_2\!+$$

polyethylene

Q6. *Write the IUPAC names of the following compounds.*

(i) $(CH_3)CCH_2C(CH_3)_3$ *(ii)* $(CH_3)_2C(C_2H_5)_2$

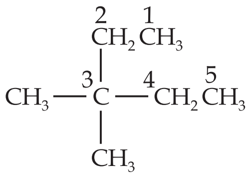
Ans. (*i*)



$$\overset{1}{CH_3}-\overset{2}{C}(CH_3)_2-\overset{3}{CH_2}-\overset{4}{C}(CH_3)_2-\overset{5}{CH_3}$$

2,2,4,4 – Tetramethyl pentane

(*ii*)



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

3 , 3 – Dimethyl pentane

Q7. *Write the structure and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10}.*

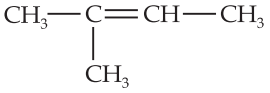
Ans.

$CH_2{=}CH-CH_2-CH_2-CH_3$

Pent-1-ene

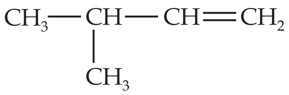
$CH_3-CH{=}CH-CH_2-CH_3$

Pent-2-ene



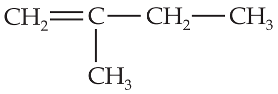
$$CH_3-C(CH_3){=}CH-CH_3$$

2-Methylbut-2-ene



$$CH_3-CH(CH_3)-CH{=}CH_2$$

3-Methylbut-1-ene



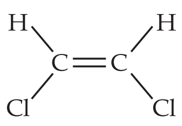
$$CH_2{=}C(CH_3)-CH_2-CH_3$$

2-Methylbut-1-ene

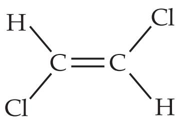
Q8. *Draw the structures of cis- and trans-isomers of the following compounds. Also write their IUPAC names.*

(i) $CHCl{=}CHCl$ *(ii)* $C_2HC(CH_3){=}C(CH_3)C_2H_5$

Ans. (*i*)

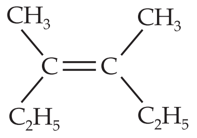


cis-1, 2-Dichloroethene

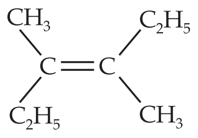


trans-1, 2-Dichloroethene

(*ii*)



cis-3, 4-Dimethylhex-3-ene



trans-3, 4-Dimethylhex-3-ene

Q9. *(a) What effect the branching of an alkane has on its melting point?*

(b) Which of the following has highest boiling point?

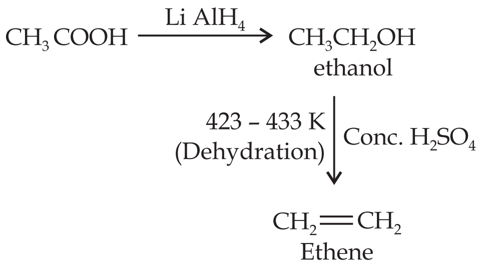
  (i) 2-methyl pentane
  (ii) 2, 3-diethyl butane
  (iii) 2, 2-dimethyl butane

Ans. (*a*) In general conception, as the branching increases packing of the molecules in the crystal lattices becomes less close and hence melting point decreases accordingly.

(*b*) As the branching increases, surface area decreases and thus magnitude of van der Waals forces of attraction decreases and hence the boiling point decreases. 2,2-dimethyl butane has lower surface area due to more branching and hence has lower boiling point.

Q10. *How will you convert ethanoic acid into ethene?*

Ans.



$$CH_3COOH \xrightarrow{Li\,AlH_4} \underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[\text{(Dehydration)}]{423-433\text{ K},\ \text{Conc. } H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2}$$

III. LONG ANSWER TYPE QUESTIONS

Q1. *Explain the term aromaticity. What are the necessary conditions for any compound to show aromaticity?*

Ans. The aromatic compounds apparently contain alternate double and single bonds in a cyclic structure, and resemble benzene in chemical behaviour. They undergo substitution reactions rather addition reactions. This characteristic behaviour is called Aromatic character or Aromaticity.

Conditions for Aromaticity:

(*i*) An aromatic compound is cyclic and planar.

(*ii*) Each atom in an aromatic ring has a *p*-orbital. These *p*-orbitals must be parallel so that a continuous overlap is possible around a ring.

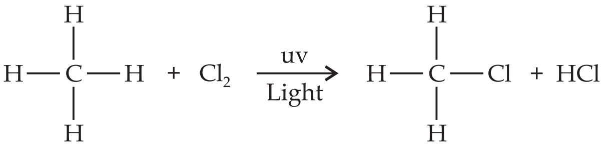
(*iii*) The cyclic π-molecular orbital formed by the overlap of *p*-orbitals must contain (4*n* + 2) π electrons, where (*n* = 0, 1, 2, 3, 4 etc.)

Q2. *(a) Define substitution reactions. Why do benzene undergo substitution reactions even though they contain double bonds?*

(b) What happens when benzene is treated with

- *(i) Br_2 in presence of anhydrous $AlCl_3$*
- *(ii) Conc. H_2SO_4 at 330K*
- *(iii) Mixture of conc. H_2SO_4 and conc. HNO_3 at 330 K*
- *(iv) Ethanoyl Chloride in presence of anhydrous $AlCl_3$.*

Ans. (*a*) Substitution reactions are those reactions in which an atom or group of atoms directly attached to carbon in the substrate molecule is replaced by another atom or group of atoms, for example,



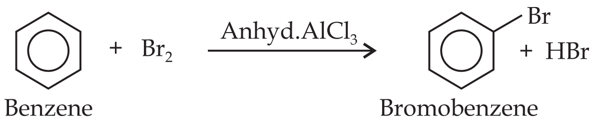
$$\mathrm{CH_4} + Cl_2 \xrightarrow[\text{Light}]{\text{uv}} \mathrm{CH_3Cl} + HCl$$

Methyl chloride

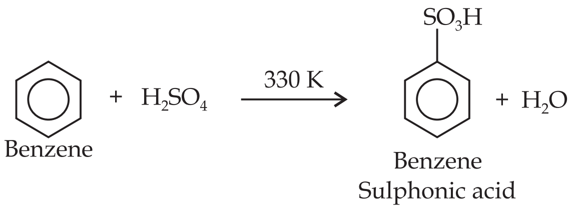
A hydrogen atom of the methane molecule is replaced by chlorine atom.

Benzene undergoes electrophilic substitution reactions because benzene ring has delocalized electrons is an electron-rich system. It is attacked by electrophiles giving substitution products.

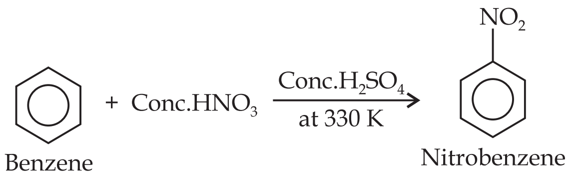
(*b*) (*i*)



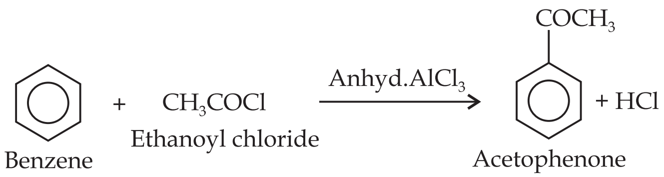
(*ii*)



(*iii*)



(*iv*)



Q3. *(a) What type of isomerism is shown by methoxymethane and ethanol?*

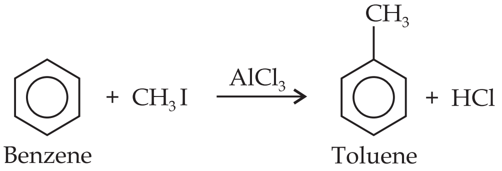
(b) How will you bring out the following conversions.

(i) Acetylene to ethane (ii) Benzene to Toluene (iii) Ethanol to ethene?

Ans. (*a*) Functional isomerism.

(*b*) (*i*) $\underset{\text{Acetylene}}{CH \equiv CH} + 2H_2 \xrightarrow[573\text{ K}]{Ni} \underset{\text{Ethane}}{CH_3-CH_3}$

(*ii*)



(*iii*) $CH_3CH_2OH \xrightarrow[\text{heat}]{\text{Conc.}H_2SO_4} CH_2=CH_2 + H_2O$

Q4. *Discuss the preparation of alkanes by Wurtz reaction. What is the limitation of the reaction?*

Ans. **Wurtz synthesis:** Higher alkanes are prepared by heating an alkyl halide (RX) with sodium metal in dry ether solution.

$$R-X + 2Na + XR \xrightarrow{\text{ether}} R-R + 2NaX$$

$$CH_3Br + 2Na + BrCH_3 \longrightarrow CH_3-CH_3 + 2NaBr$$

Limitations: Use of two different alkyl halides in Wurtz reaction always leads to a mixture of alkanes. The separation of these alkanes is difficult because there is only a little difference in their boiling points. Thus only symmetrical alkanes can be prepared by this method.

Q5. *(a) Why are alkenes called unsaturated hydrocarbons?*

(b) How will you test the presence of double bond in an alkene?

(c) Name the products formed when propene is subjected to ozonolysis.

Ans. (*a*) Alkenes contain two hydrogen atoms less than alkanes and thus they contain C—C double bond ($C=C$) in their molecule. Thus they are called unsaturated hydrocarbons.

(*b*) Alkenes react with cold dilute $KMnO_4$ solution to form gycols. Since bright purple colour of $KMnO_4$ disappears during the reaction it is used as a test for the presence of double bond.

(*c*) A mixture of acetaldehyde and formaldehyde is formed.

IV. MULTIPLE CHOICE QUESTIONS

1. Which of the following is correct regarding the stability of carbocation?

(*a*) 3° > 2° > 1° (*b*) 1° < 2° < 3° (*c*) 2° > 1° > 3° (*d*) 2° > 3° > 1°

2. A liquid hydrocarbon is converted to a mixture of gaseous hydrocarbon by

(*a*) hydrolysis (*b*) oxidation (*c*) distillation (*d*) cracking

3. The peroxide effect in anti-Markovnikov addition involves
(*a*) The heterolytic fission of the double bond
(*b*) The homolytic fission of the double bond
(*c*) a free radical mechanism
(*d*) an ionic mechanism

4. The catalyst required for the given reaction is

$$\mathrm{HC \equiv CH + dil\ H_2SO_4 \xrightarrow{Catalyst} CH_3CHO}$$

(*a*) $HgSO_4$ (*b*) Pt (*c*) $AlCl_3$ (*d*) Pd

5. Which conformation of ethane has the lowest potential energy?
(*a*) Eclipsed (*b*) Skewed
(*c*) Staggered (*d*) All will have equal PE

6. Baeyer's reagent is
(*a*) aqueous $KMnO_4$ (*b*) neutral $KMnO_4$
(*c*) alkaline $KMnO_4$ (*d*) aqueous bromine water

7. Benzene reacts with acetyl chloride in the presence of $AlCl_3$ to give
(*a*) acetophenone (*b*) toluene (*c*) benzophenone (*d*) ethyl benzene

8. An aqueous solution of compound A gives ethane on electrolysis, the compound A is
(*a*) Ethyl acetate (*b*) Sodium acetate (*c*) Sodium propionate (*d*) Sodium ethoxide

9. Tolueue reacts with chlorine in the presence of light to give
(*a*) benzyl choride (*b*) benzoyl chloride (*c*) p-chlorotoluene (*d*) o-chlorotoluene

10. Which of the following is less reactive than benzene towards electrophilic substitution reactions?
(*a*) Nitrobenzene (*b*) Aniline (*c*) Bromobenzene (*d*) Chlorobenzene

Ans. 1. (*a*) 2. (*d*) 3. (*c*) 4. (*a*) 5. (*c*)
6. (*c*) 7. (*a*) 8. (*b*) 9. (*a*) 10. (*a*)

V. HOTS QUESTIONS

Q1. *What effect does branching of an alkane chain has on its boiling point?*

Ans. As branching increases, the surface area of the molecule decrease which results in a small area of contact. As a result, the van der Waals force also decrease which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

Q2. *An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Deduce IUPAC name of 'A'.*

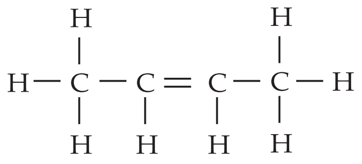
Ans. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms. Hence, the structure of 'A' can be represented as:

$$XC = CX$$

There are eight C–H σ bonds. Hence, there are 8 hydrogen atoms in 'A'. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of ‘A’.

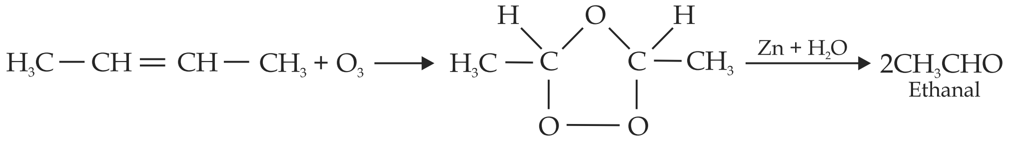
The IUPAC name of ‘A’ is But–2–ene.

Ozonolysis of ‘A’ takes place as:



$$\begin{array}{ccccccccc} & & H & & & & & & H & & \\ & & | & & & & & & | & & \\ H & - & C & - & C & = & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

(A)



The final product has molecular mass = 44*u*

Q3. *How will you demonstrate that double bonds of benzene are somewhat different from that of olefins?*

Ans. The double bonds of olefins decolourize bromine water and discharge the pink colour of Bayer’s reagent while those of benzene not.

Q4. *How will you separate propene from propyne?*

Ans. By passing the mixture through ammonical silver nitrate solution when propyne reacts while propene passes over.

Q5. *Write the structure of the alkene which on reductive ozonolysis gives butanone and ethanol.*

Ans. $CH_3CH_2C(CH_3) = CHCH_3$

❑❑❑