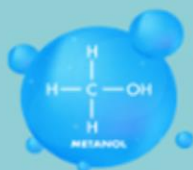
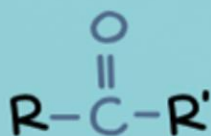
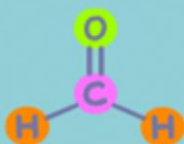
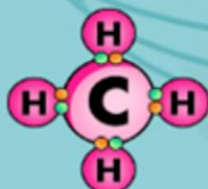




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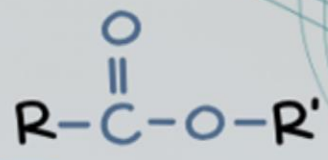
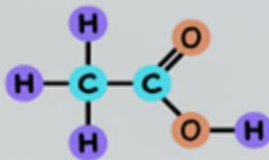
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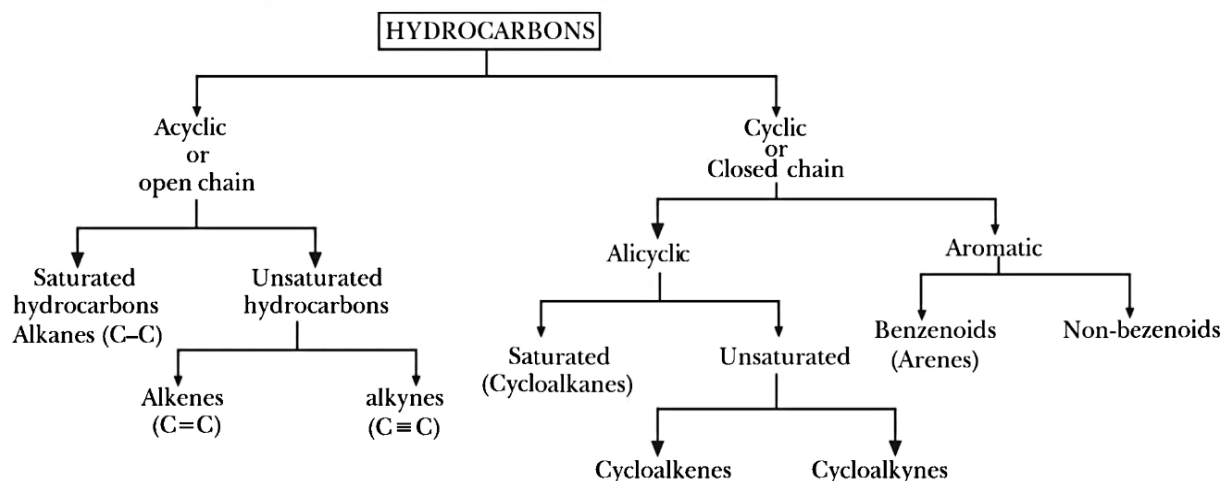
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2ND FLOOR, SATKOUDI COMPLEX, THANA CHOWK, RAMGARH - 829122-JH



BASIC CONCEPTS

- Hydrocarbons:** Hydrocarbons are the organic compounds containing carbon and hydrogen only, *e.g.*, alkanes, alkenes and alkynes.
- Classification of Hydrocarbons**



- Alkanes:** Acyclic saturated hydrocarbons are called alkanes. They contain only carbon-carbon single bonds in their molecules. They are also called paraffins. Alkanes have the general formula C_nH_{2n+2} .

(a) **Structure of Alkanes:** Alkanes (saturated hydrocarbons) contain only carbon-carbon (C—C) and carbon-hydrogen (C—H) single covalent bonds formed by the overlap of sp^3 hybrid orbital between carbon atoms and sp^3 hybrid orbital of carbon and s orbital of hydrogen atoms, respectively.

For example, in methane (CH_4) molecule carbon lies at the centre of the tetrahedron while the four hydrogen atoms are present at the corners (vertices) of the regular tetrahedron. This implies that each face of the tetrahedron is an equilateral triangle ($109^\circ 28'$) as has three bonds as shown in Fig. 6.1. Average C—C bond length is 154 pm and C—H bond length 112 pm (1.12 \AA).

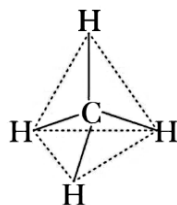


Fig. 6.1 Structure of Methane

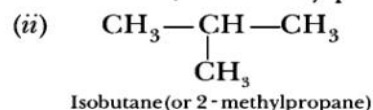
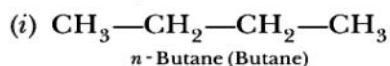
(b) **Nomenclature:** In IUPAC system of nomenclature, acyclic saturated hydrocarbons are called alkanes.

Some examples of IUPAC names of alkanes are given in the table below:

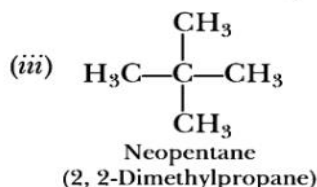
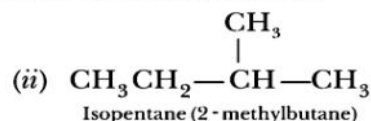
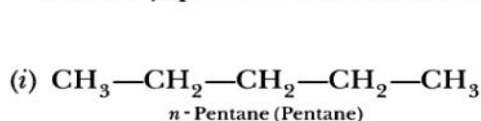
Table 6.1: IUPAC names of some alkanes

Structural Formula	IUPAC Name
CH ₄	Methane
C ₂ H ₆	Ethane
C ₃ H ₈	Propane
C ₄ H ₁₀	Butane
C ₅ H ₁₂	Pentane
C ₆ H ₁₄	Hexane
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	2, 2-Dimethylpropane
$ \begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \qquad \qquad \qquad \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array} $	4-Ethyl-3-methylheptane

(c) **Isomerism:** First three members of alkane series viz., methane (CH₄), ethane (C₂H₆) and propane (C₃H₈) do not exhibit isomerism. Other members of this series show chain isomerism. Thus, the fourth member of the alkane series—*n*-butane (C₄H₁₀) exhibits chain isomerism; it has two isomers—*n*-butane and isobutane (or 2-methylpropane).



Similarly, pentane exhibits three chain isomers as shown below:



(d) **Conformations of Alkanes:** Conformation Isomerism is defined as a kind of stereoisomerism in which there is different spatial arrangement of atoms or groups around each carbon atom bonded by a single covalent bond due to free rotation about C—C bond. This isomerism is shown by alkanes and cycloalkanes. Each structure is called as a **conformational isomer or conformer or rotamer**. These isomers can't be isolated. Due to rotation around bond, infinite number of conformers are produced, but they are not equivalent from energy point of view.

CONFORMATIONS OF ETHANE

Let's take an example of ethane and discuss the various methods adopted to project the molecule in order to study the conformational isomers.

(i) **Sawhorse projection:** The eclipsed and staggered conformations of ethane are better represented by sawhorse projection formula. In this projection, the molecule is viewed

down a particular C—C bond and the atoms or groups bonded to the both front and back 'C' atoms are drawn at 120° angles. In eclipsed conformation, the atoms or groups of front carbon is overlapping with the atoms or groups of back carbon. So the bond pair of electrons come very close and strongly repel each other, as a result the molecule becomes very unstable. Hence "eclipsed structure is highly unstable structure."

In staggered structure, the atoms or groups of front and back carbon atom are 60° apart from each other. So, the molecule becomes highly stable.

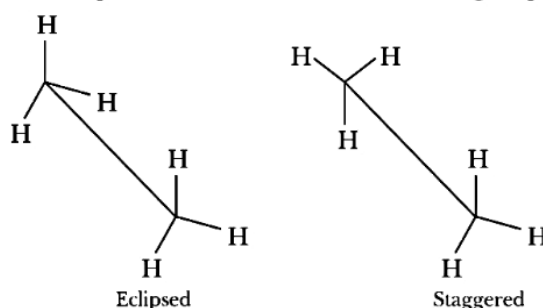


Fig. 6.2 Sawhorse Projection formula of ethane

- (ii) **Newmann projection formula:** It is the better projection formula to represent eclipsed, staggered and skew conformations of different alkanes. In this projection the molecule is viewed along the C—C bond axis, so that the two C-atoms look like one carbon atom, *i.e.*, the front carbon completely covers the back carbon. The front carbon is represented as a thick dot (●) and the back carbon, a circle (○).

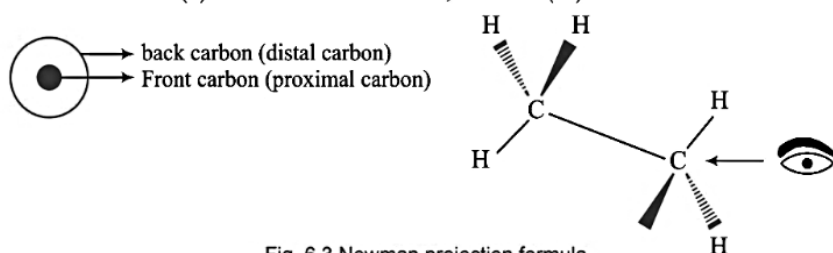


Fig. 6.3 Newman projection formula

The positions of different atoms or groups of both front and back carbons can be better represented in eclipsed, skew and staggered conformations.

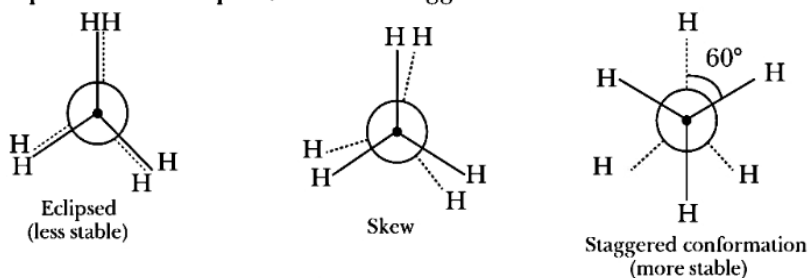


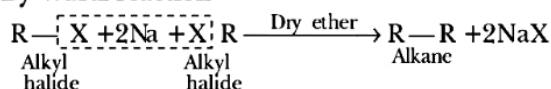
Fig. 6.4 Eclipsed Skew and Staggered conformation

The relative stability among different conformations is staggered > skew > eclipsed.

(e) Preparation of Alkanes

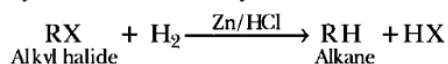
(i) From Alkyl Halides

1. By Wurtz reaction



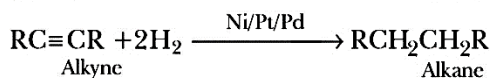
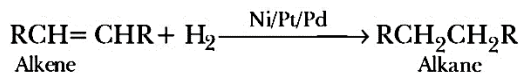
Note: This reaction is used for the preparation of higher alkanes containing even number of carbon atoms.

2. By Reduction of Alkyl halides



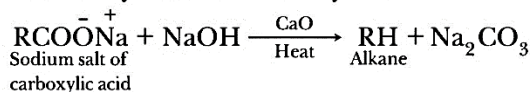
Note: Alkyl fluorides do not undergo this reaction.

(ii) From Unsaturated Hydrocarbons (Hydrogenation Reaction)



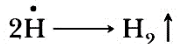
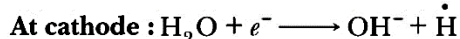
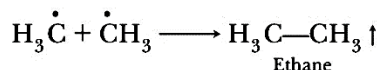
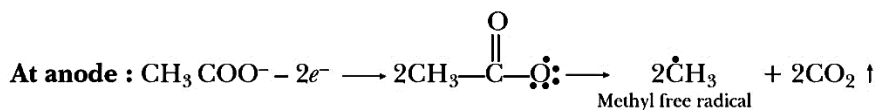
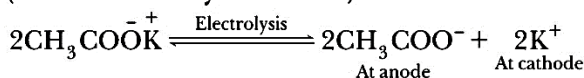
(iii) From Carboxylic Acids

1. Decarboxylation of Carboxylic acids



2. Electrolysis of sodium or potassium salt of carboxylic acid

(Kolbe's electrolytic method)



Note: Methane cannot be prepared by this method, also this method is used for preparation of alkanes having even number of carbon atoms.

(f) Physical Properties

(i) **Physical State:** With the increase in molecular weight, the physical state of alkanes changes from gaseous to liquid to solid. The first four alkanes (C₁ to C₄) are gases, the next thirteen alkanes from C₅ to C₁₇ are liquids while the higher alkanes from C₁₈ onwards are waxy solids at 298 K. They are colourless and odourless.

(ii) **Boiling point:** Alkanes are non-polar and the molecules are held by weak van der Waals forces (also called London dispersion forces) with increase in number of carbon atoms, the molecular mass as well as molecular size increases and thus the boiling point increases due to increased surface area.

The branched chain isomeric alkanes have relatively low boiling point as compared to their corresponding straight chain isomers. Also greater the branching of the chain, lower is the boiling point of the alkanes.

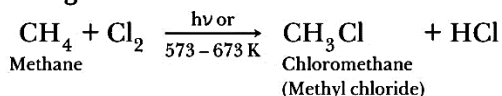
(iii) **Melting point:** Like boiling point, the melting point of alkanes also increases with the increase in the size of carbon chain but the variation is not regular.

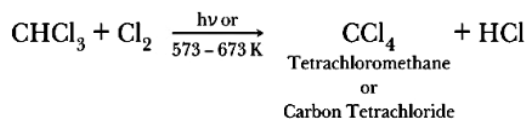
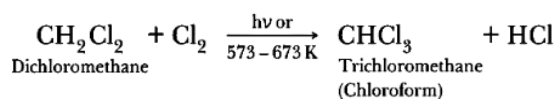
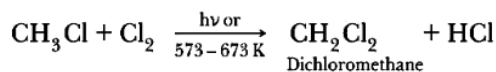
(iv) **Solubility:** Alkanes are predominantly non-polar compounds. They are, therefore, soluble in non-polar solvents such as ether, benzene, carbon tetrachloride, etc. but are insoluble in polar solvents such as water, alcohols, etc.

(v) **Density:** The alkanes are lighter than water.

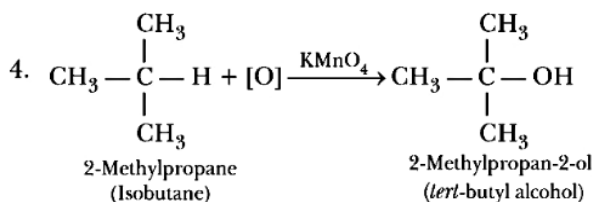
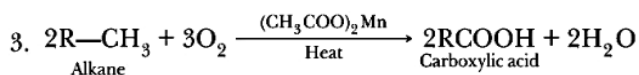
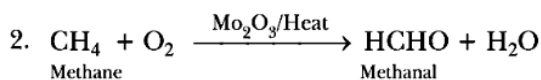
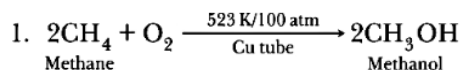
(g) Chemical Properties

(i) Halogenation of Alkanes

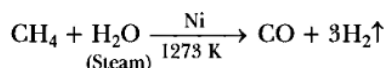




(ii) Controlled oxidation

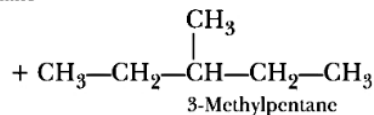
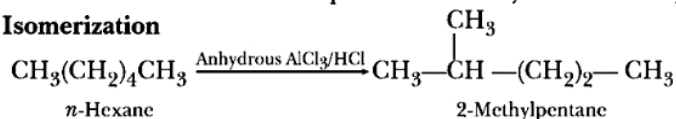


(iii) Reaction with steam

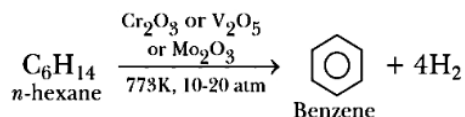


This reaction is an industrial process for the synthesis of dihydrogen gas.

(iv) Isomerization



(v) Aromatisation



4. ALKENES: Alkenes are unsaturated hydrocarbons containing carbon-carbon double bond (C=C) in their molecules. Carbon-carbon double bond is made of a σ (sigma) and a π (pi) bond. Alkenes are represented by the general formula C_nH_{2n} . Alkenes are also known as olefins (derived from Greek word **olefiant** meaning oil forming) because lower members of this series form oily products when treated with chlorine.

(a) Structure of Double bond: Alkenes are unsaturated hydrocarbons containing carbon-carbon double bond (C=C) in their molecule. Carbon-carbon double bond is made up of one strong σ -bond (bond dissociation enthalpy 397 kJ mol^{-1}) and a weak π -bond (bond dissociation enthalpy 284 kJ mol^{-1}). The orbital diagrams of ethene molecule are shown below in the Fig. 6.5 and Fig. 6.6.

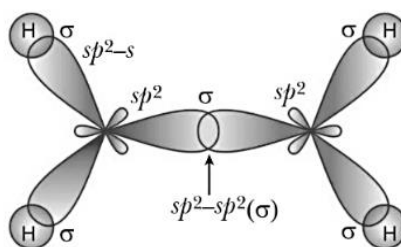


Fig. 6.5 Orbital picture of ethene depicting σ bonds only

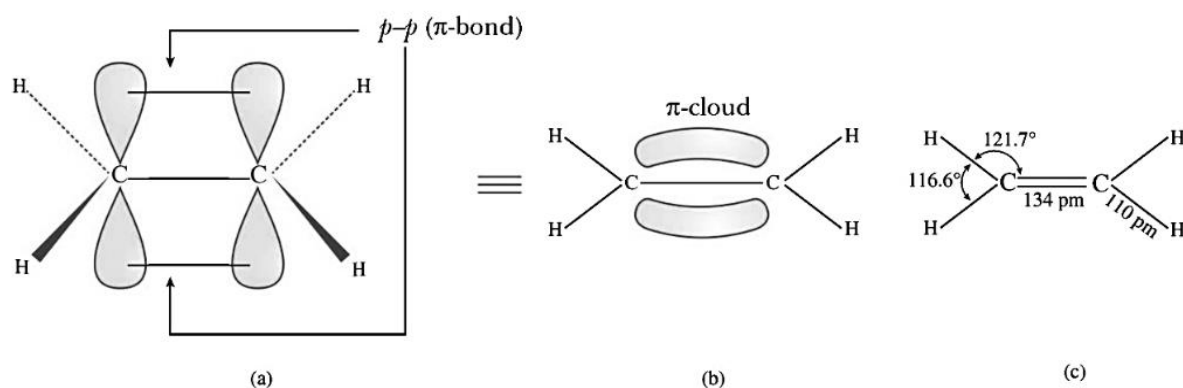


Fig. 6.6 Orbital picture of ethene showing formation of (a) π -bond, (b) π -cloud and (c) bond angles and bond lengths

(b) **Nomenclature of Alkenes:** In IUPAC system, they are named as alkenes. The name of the alkenes is obtained by replacing terminal 'ane' of the corresponding alkane by the suffix 'ene'.

IUPAC names of some alkenes are tabulated below:

Table 6.2: Nomenclature of some Alkenes

Formula	Structure	Common name	IUPAC Name
C_2H_4	$CH_2=CH_2$	Ethylene	Ethene
C_3H_6	$CH_3-CH=CH_2$	Propylene	Propene
C_4H_8	$CH_3-CH_2-CH=CH_2$	α -butylene	Butene or But-1-ene
	$CH_3-CH=CH-CH_3$	β -butylene	But-2-ene
	$\begin{array}{c} CH_3 \\ \\ CH_2=C-CH_3 \end{array}$	Isobutylene	2-methylpropene
C_5H_{10}	$CH_3-CH_2-CH_2-CH=CH_2$	α -pentylene	Pentene
	$CH_3-CH_2-CH=CH-CH_3$	β -pentylene	Pent-2-ene
	$\begin{array}{c} CH_2=CH-CH-CH_3 \\ \\ CH_3 \end{array}$		3-methylbut-1-ene
C_6H_{12}	$CH_3-CH_2-CH_2-CH_2-CH=CH_2$	α -hexylene	Hexene
	$CH_3-CH_2-CH_2-CH=CH-CH_3$	β -hexylene	Hex-2-ene

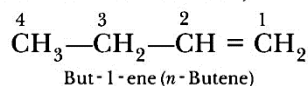
(c) **Isomerism in Alkenes**

Alkenes exhibit the following types of isomerism:

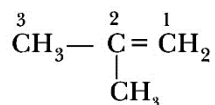
(i) **Structural isomerism:** When the isomers differ only in the arrangement of atoms or groups within the molecule, without any reference to space, these are known as **structural isomers**, and the phenomenon as **structural isomerism**.

Alkenes show following types of structural isomerism.

1. Chain isomerism: This type of isomerism is due to the nature of carbon chains—straight or branched chain. The simplest acyclic alkene which can exhibit chain isomerism is butene,



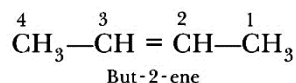
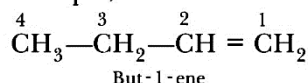
Straight carbon chain



2-Methylpropene (Isobutene)

Branched carbon chain

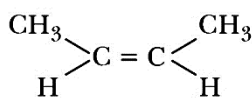
2. Position isomerism: Position isomers differ in the position of the double bond. For example,



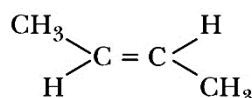
(ii) **Geometrical Isomerism:** The stereoisomerism exhibited by alkenes due to the difference in the spatial arrangement of atoms or groups about the double bonded carbon atoms is called **geometrical isomerism**. Ethene exhibits geometrical isomerism.

Cause of Geometrical Isomerism: In alkene the carbon-carbon double bond consists of σ -bond and π -bond. A π -bond prevents free rotation of carbon atoms of the double bond to each other. Due to this restricted or hindered rotation, the relative positions of atoms or groups attached to the carbon atoms of the double bond get fixed. Therefore, two different arrangements are possible when each of the two doubly bonded carbon atoms has two different atoms or groups.

But-2-ene exists in the following two geometrical isomeric forms.



(A)

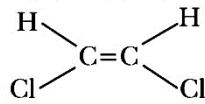


(B)

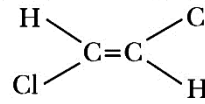
The isomer (A), in which the similar atoms or groups lie on the same side of the double bond, is called the **cis-isomer** while the isomer (B) in which the similar atoms or groups lie on the opposite side of the double bond, is called **trans-isomer**.

Distinction between cis-and trans-isomers: Geometrical isomers possess different physical properties. Their chemical properties are similar but not identical. Hence, geometrical isomers can be distinguished on the basis of their physical properties.

1. The *cis*-isomer is more polar than *trans*-isomer. For example, the dipole moment of *cis*-dichloroethene is 0.33 D while that of *trans* isomer is almost zero.



cis-Dichloroethene
 $\mu = 0.33 \text{ D}$



trans-Dichloroethene
 $\mu \approx 0 \text{ D}$

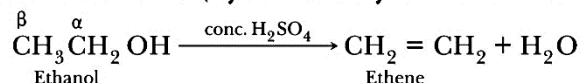
2. The *cis*-isomer has higher boiling point than the *trans*-isomer. For example, the boiling point of *cis*-but-2-ene is 277 K while that of *trans*-isomer is 274 K.

3. The *cis*-isomer has lower melting point than the *trans*-isomer.

4. *cis*-isomer is less stable than the *trans*-isomer.

(d) Preparation of Alkenes

(i) **From Alcohols (By acidic dehydration of alcohols)**

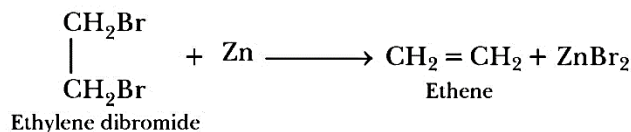


(ii) **From alkyl halides:** Alkenes can be prepared by **dehydrohalogenation** (*i.e.*, removal of HX) of alkyl halides.

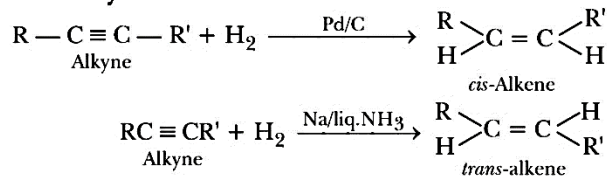


Saytzeff rule: Depending upon the structure, alkyl halides may give one or more isomeric alkenes. According to this rule, whenever two alkenes are theoretically possible during a dehydrohalogenation reaction, it is always the more highly substituted alkene (*i.e.*, having lesser number of hydrogen atoms on the double bond) which predominates.

(iii) From dihalogen derivatives (Vicinal dihalides)



(iv) From alkynes

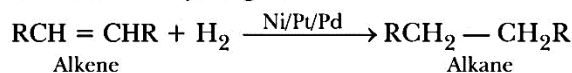


(e) Physical Properties

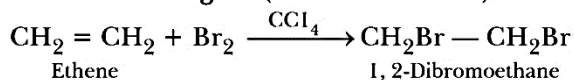
- (i) Physical state:** The first three alkenes (ethene, propene and butene) are colourless gases at room temperature; the next eleven members containing 5 to 18 carbon atoms ($\text{C}_5 - \text{C}_{18}$) are liquids while the higher members are solids. Ethene has a pleasant smell but all other alkenes are odourless.
- (ii) Melting points:** The melting point of alkenes is quite low and usually increases with the increasing molecular mass.
- (iii) Boiling points:** The boiling point of alkenes is also low and increases regularly with increase in molecular mass. The branched chain alkenes, however, have lower boiling point than the corresponding straight chain alkenes.
- (iv) Solubility:** Alkenes are non-polar compounds. They are, therefore, insoluble in water but readily dissolve in organic solvents like alcohol, benzene, ether, carbon tetrachloride, etc.
- (v) Density:** Alkenes are lighter than water.
- (vi) Dipole moments:** Since the π -electrons of alkenes are easily polarised, they are weakly polar and have dipole moments higher than the non-polar alkanes.

(f) Chemical Properties

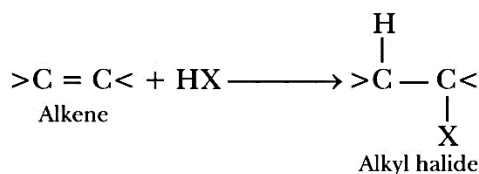
(i) Addition of dihydrogen



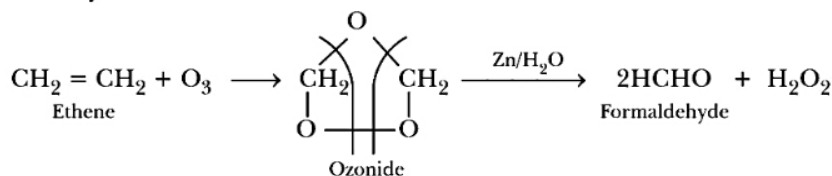
(ii) Addition of halogens (Unsaturation test)



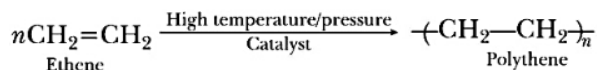
- (iii) Addition of halogen halides:** Alkenes react with halogen halides ($\text{HX} = \text{HCl, HBr, HI}$) to form alkyl halides.



(vii) **Ozonolysis**



(viii) **Polymerization**



5. **ALKYNES:** Alkynes are unsaturated hydrocarbons containing carbon-carbon triple bond ($\text{C}\equiv\text{C}$) in their molecules. The simplest alkyne is ethyne or acetylene, C_2H_2 or $\text{HC}\equiv\text{CH}$. Alkynes can be represented by the general formula $\text{C}_n\text{H}_{2n-2}$.

(a) **Structure of Alkynes:** In alkynes ($\text{RC}\equiv\text{CR}$), the two carbon atoms are linked by a triple bond consisting of one and two π -bonds. The carbon atoms forming a triple bond ($\text{C}\equiv\text{C}$) are sp hybridized; sp hybridized orbitals of the two carbon atoms overlap head on (*i.e.*, linear overlap) forming a σ bond and the unhybridized orbitals of carbon atoms overlap side ways (lateral overlap) forming two π bonds. This portion of the molecule in all alkynes is linear in nature. In acetylene (*i.e.*, ethyne) the $\text{H}-\text{C}-\text{C}$ bond angle is 180° and ($\text{C}\equiv\text{C}$) bond distance is 120 pm (1.20 \AA) and the $\text{C}\equiv\text{C}$ bond strength is 823 kJ mol^{-1} which is stronger than ethene ($\text{C}=\text{C}$; 681 kJ mol^{-1}) and ethane ($\text{C}-\text{C}$; 348 kJ mol^{-1}).

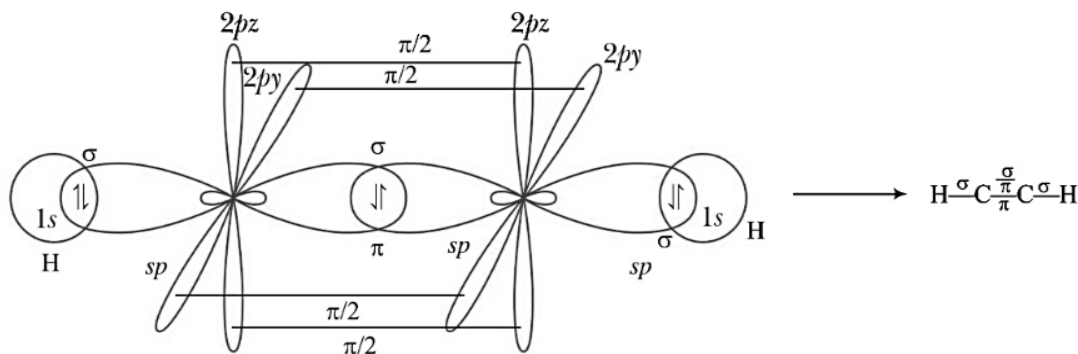


Fig. 6.7 Orbital diagram of acetylene

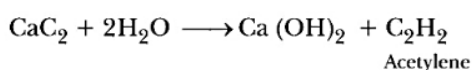
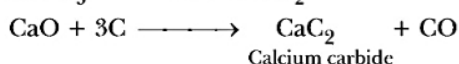
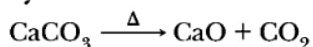
(b) **Nomenclature:** The IUPAC names of some alkynes are given in the table below:

Table 6.3: Nomenclature of some Alkynes

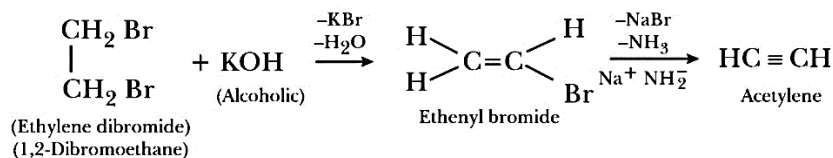
Formula	Structure	Common name	IUPAC Name
C_2H_2	$\text{CH}\equiv\text{CH}$	Acetylene	Ethyne
C_3H_4	$\text{CH}_3-\text{C}\equiv\text{CH}$	Methyl acetylene	Propyne
C_4H_6	$\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$	Ethyl acetylene	Butyne
	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$	Dimethyl acetylene	But-2-yne

(c) **Preparation of Alkynes**

(i) **By the action of water on calcium carbide**



(ii) By Dehydrohalogenation of vicinal dihalides



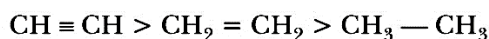
(d) Physical Properties

- (i) **Physical State:** The first three members of alkynes series *viz.* ethyne (C_2H_2), propyne (C_3H_4) and butyne (C_4H_6) are gases at room temperature, while those containing five to thirteen carbon atoms ($\text{C}_5 - \text{C}_{13}$) are liquids and the higher alkynes are solids. All alkynes are odourless but acetylene, due to the presence of phosphine as impurity, smells like garlic.
- (ii) **Melting and Boiling Points:** The melting and boiling point of alkynes is slightly higher than the corresponding alkanes and alkenes. This is due to the more close packing of the linear molecules of alkynes than the corresponding alkanes and alkenes. The melting and boiling point of alkynes increases regularly with the increase in molecular mass.
- (iii) **Solubility:** Alkynes are non-polar compounds. They are, therefore, insoluble in water but readily dissolve in organic solvents such as benzene, carbon tetrachloride, petroleum, ether, etc.
- (iv) **Density:** Alkynes are lighter than water; their densities lie in the range $0.69 - 0.77 \text{ g/cm}^3$. Densities of alkynes increase as the molecular size increases.

(e) Chemical Properties

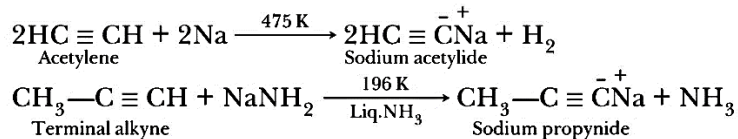
- (i) **Acidic character of acetylene:** Unlike alkanes and alkenes, alkynes behave as strong acids.

In alkynes, sp -hybrid orbital has more s -character than sp^2 and sp^3 hybrid orbitals and thus more electronegative. Consequently, the electron pair of $\text{C}-\text{H}$ bond is displaced more towards carbon atom than hydrogen atom and helps in the release of H^+ ion by a strong base. Thus, they behave as acid. The acidic character of different hydrocarbons is as follows:

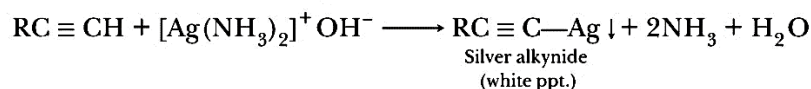


The acidic character of alkynes are shown by the following reactions:

1. Reaction with Na or NaNH_2 in liq. NH_3

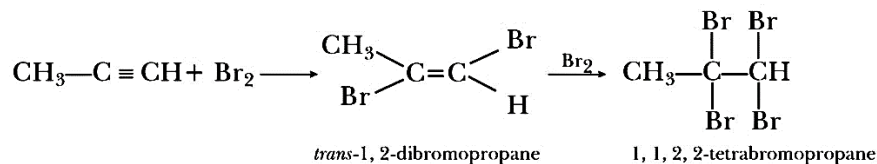


2. Reaction with Tollen's reagent



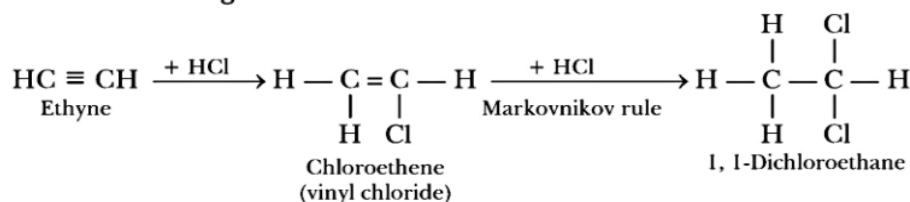
- (ii) **Addition Reactions:** Alkynes undergo electrophilic addition reactions.

1. Addition of Halogens

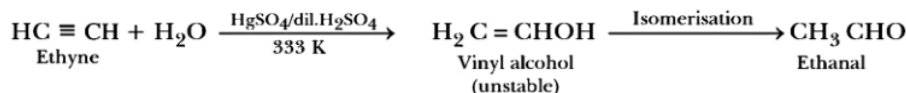


This reaction is used for unsaturation test (*i.e.*, for double and triple bonds).

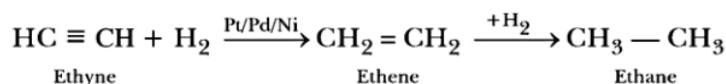
2. Addition of Halogens Halides



3. Addition of Water: Hydration of alkynes



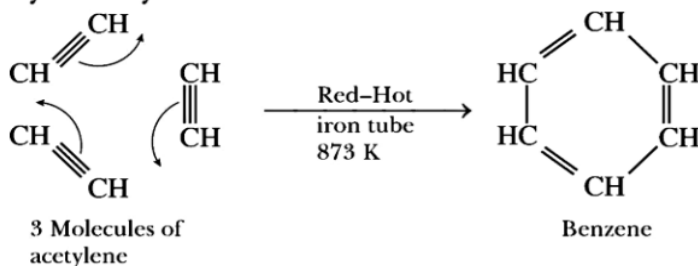
4. Addition of dihydrogen (Hydrogenation)



(iii) Polymerisation

1. Linear Polymerisation: Under suitable conditions, polymerisation of ethyne molecule produces a high molecular weight conjugated polyene known as polyacetylene $[-\text{CH}=\text{CH}-\text{CH}=\text{CH}-]_n$. It conducts electricity under special conditions.


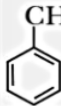
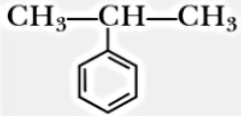
2. Cyclic Polymerisation

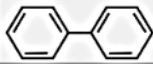
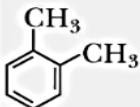
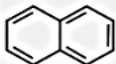


6. Aromatic Hydrocarbons or Arenes: Aromatic hydrocarbons are the compounds of carbon and hydrogen which contain one or more benzene rings. They are also as called arenes. Benzene (C_6H_6) is the parent member of the arenes or aromatic hydrocarbons. Aromatic hydrocarbons containing a benzene ring is called benzenoids and those not containing a benzene ring are known as non-benzenoids.

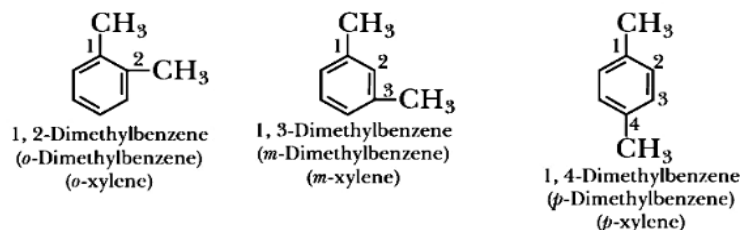
(a) Nomenclature of Arenes: The arenes can be represented by the general formula $\text{C}_n\text{H}_{2n-6m}$ where n is the number of carbon atoms and m is the number of rings. Some of the examples of arenes are given below in the table 6.4.

Table 6.4: Nomenclature of Some Arenes

Structural formula	IUPAC Name
	Benzene
	Methylbenzene (Common name: Toluene)
	Isopropylbenzene (Common name: Cumene)

	Diphenyl
	1, 2-Dimethylbenzene
	Naphthalene

(b) **Isomerism in Arenes:** Arenes exhibit position isomerism. Because of the symmetrical structure of benzene, replacement of one hydrogen atom of benzene by any substituent produces only a single product. Thus, monosubstitution products of benzene do not show position isomerism. However, when two hydrogen atoms are replaced from benzene by two substituents, then three isomers are obtained which differ in the position of substituents. For example, when two hydrogen atoms of benzene are replaced by methyl groups, three isomers of alkyl benzene are obtained. These are

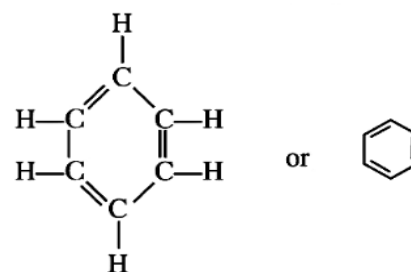


Thus, *disubstitution products of benzene show position isomerism.*

(c) **Structure of Benzene:** From its chemical composition and molecular weight, the benzene was known to contain six carbon atoms and six hydrogen atoms which indicates that it is unsaturated as it contains eight hydrogen atoms less than the corresponding parent saturated hydrocarbon hexane, C_6H_{14} .

The unsaturation and saturation of benzene molecule is supported by the observations given below:

- (i) With O_3 , benzene forms a triozonide which indicates the presence of three double bonds.
- (ii) In presence of sunlight, it forms monosubstituted derivative which indicates that all the six carbon and hydrogen atom are identical.

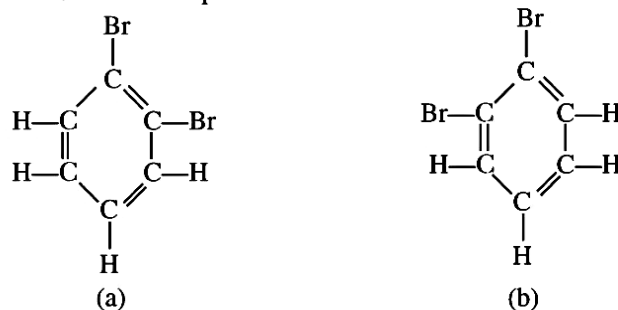


The first insight into the structure of benzene was given by **August Kekule** on the basis of the above observations. He proposed the cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom as shown below.

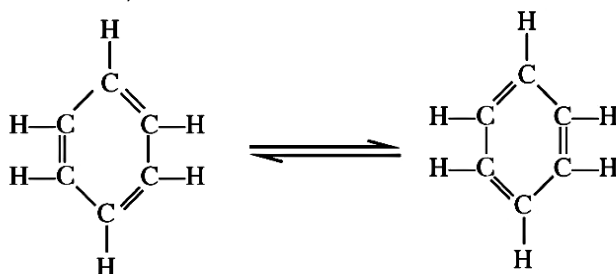
Drawbacks of the Kekule Structure: There are three drawbacks of the Kekule structure.

- (i) Because of the presence of three double bonds, the benzene molecule should be highly reactive towards addition reactions. But contrary to this, benzene behaves as a saturated hydrocarbon and readily undergoes substitution reactions.
- (ii) Kekule structure of benzene contains two kinds of bonds *i.e.*, single and double bonds, between carbon atoms. But X-ray studies have shown that the structure of benzene is a regular hexagon with an angle of 120° and all carbon-carbon bond lengths are equal 1.39 \AA (139 pm) which lie between C—C single bond length of 1.54 \AA (154 pm) and double bond length of 1.34 \AA (134 pm).

(iii) According to Kekule structure, two 1, 2-disubstituted benzene (a and b) (e.g., 1, 2-dibromobenzene), differing in the position of bromine relative to the double bond, should be possible.



In structure (a) there is a double bond between two carbon atoms carrying a bromine atom and in structure (b) there is a single bond between carbon atoms carrying a bromine atom. But only one 1, 2-dibromobenzene is known. To account for this, Kekule visualised the benzene molecule as a dynamic thing, and described it in terms of two structures (given below) between which the benzene molecule alternates.



As a consequence, the two dibromobenzenes would be in rapid equilibrium.

Resonance Structure of Benzene: Structure of benzene can be explained on the basis of resonance; the structure that differ only in the arrangement of electrons. Benzene is a resonance hybrid of the following two structures (A and B) which have the same arrangement of atoms but differ only in arrangement of electrons.

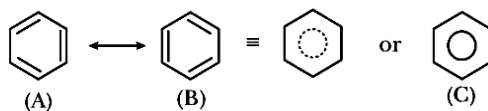


Fig 6.8: Resonating structures of Benzene

Orbital Structure of Benzene: The orbital structure of benzene can be explained with the help of molecular orbital theory. According to this theory, each carbon atom in benzene is sp^2 hybridized; this means that each carbon atom possesses three sp^2 hybrid orbitals inclined at an angle of 120° and the fourth p_z orbital disposed perpendicularly to the plane of sp^2 hybrid orbitals. Out of three sp^2 hybrid orbitals, of each carbon atom, two overlap axially with the two sp^2 hybrid orbitals of the two adjacent carbon atoms forming C—C sigma bonds. The third sp^2 hybridized orbital of each carbon atom overlaps with the half filled s orbital of hydrogen atom to form C—H sigma bond.

The unhybridized $2p_z$ orbital on each carbon atom overlaps sideways with similar orbital of the carbon atom on either side to form two sets of π -bonds. The resultant orbital cloud is spread over all the six carbon atoms forming two continuous ring like electron clouds, one lying above and the other below the plane of carbon atoms. Thus, the six electrons of the p_z orbitals cover all the six carbon atoms; this is said to be *delocalized*. This delocalization of π -electrons results in stronger bonds and more stable molecule.

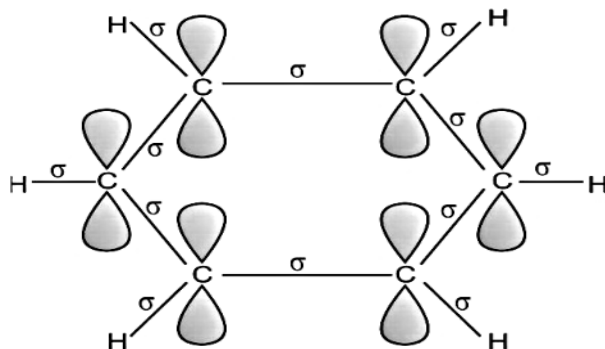


Fig 6.9: Each sp^2 hybridized carbon of benzene forming two C—C sigma bonds and one C—H sigma bond and containing p_z orbital with one electron.

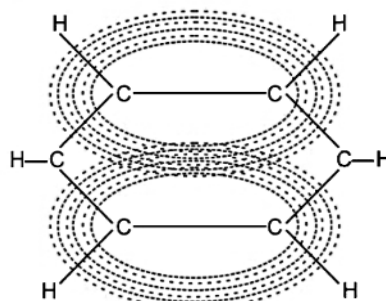
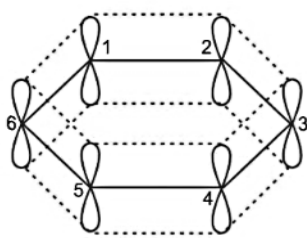


Fig 6.10: Orbital picture of benzene showing ring like π -electron clouds, one lying above and the other below the plane of carbon atoms.

(d) **Aromaticity:** The characteristic properties exhibited by aromatic compounds are called as aromaticity.

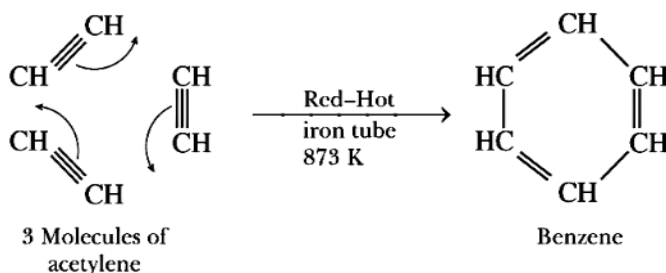
Huckel's rule—Aromaticity: According to this rule, an organic compound having cyclic planar structure with conjugated bond system is said to be aromatic if it contains $(4n + 2)$ number of π -electrons in it where $n = 1, 2, 3, 4, \dots$

Antiaromatic: If an organic compound having cyclic, planar structure with conjugated π -bond system contains $4n$ electrons instead of $(4n + 2)$ number of π -electrons, it is said to be antiaromatic.

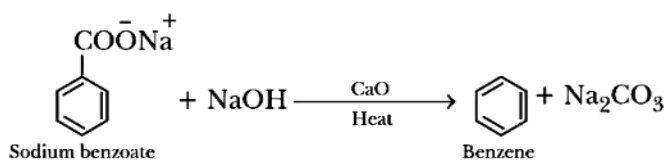
Non-aromatic: If an organic compound is not planar, lacks conjugation and is acyclic, then the compound is said to be non-aromatic.

(e) **Preparation of Aromatic hydrocarbons**

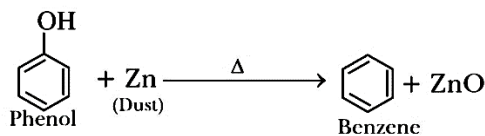
(i) **From Alkynes:**



(ii) **By Decarboxylation of aromatic acids:**



(iii) From phenol:



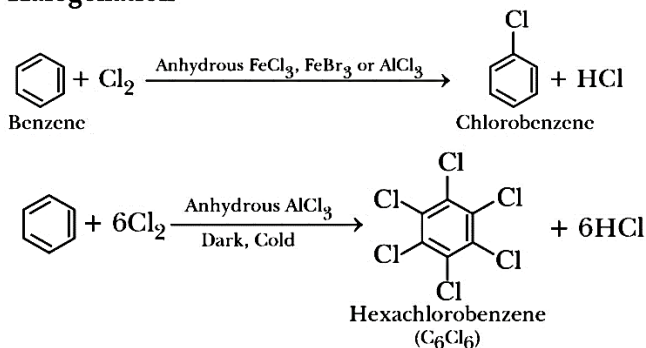
(f) Physical Properties

- (i) Aromatic hydrocarbons containing upto eight carbon atoms are colourless liquids while the higher ones are solid with characteristic smell.
- (ii) Aromatic hydrocarbons are insoluble in water but are soluble in organic solvents.
- (iii) They are highly inflammable and burn with a sooty flame.

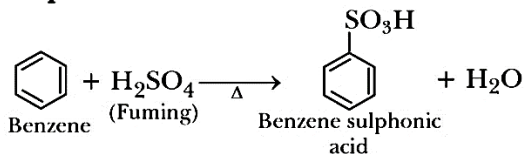
(g) Chemical Properties

(i) **Substitution Reactions:** Arenes undergo electrophilic substitution reactions.

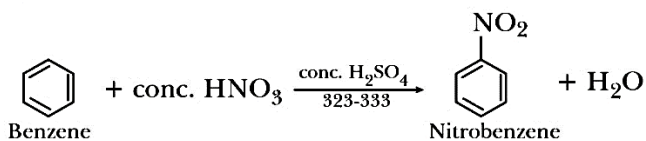
1. Halogenation



2. Sulphonation

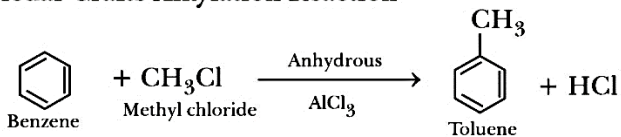


3. Nitration

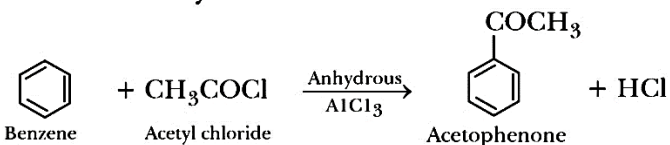


4. Friedal-Crafts Reaction: It is of two types:

• Friedal-Crafts Alkylation Reaction

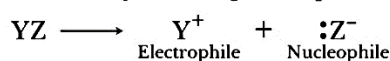


• Friedel Crafts Acylation Reaction

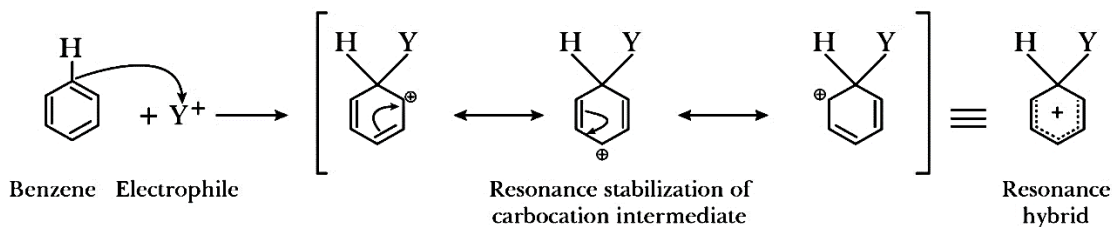


Mechanism of Electrophilic Substitution Reactions

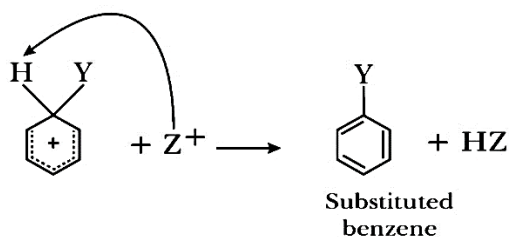
Step 1. Generation of attacking electrophile



Step 2. Formation of carbocation intermediate

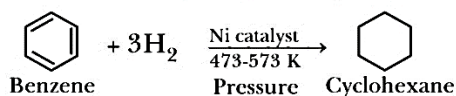


Step 3. Loss of a proton from the carbocation.

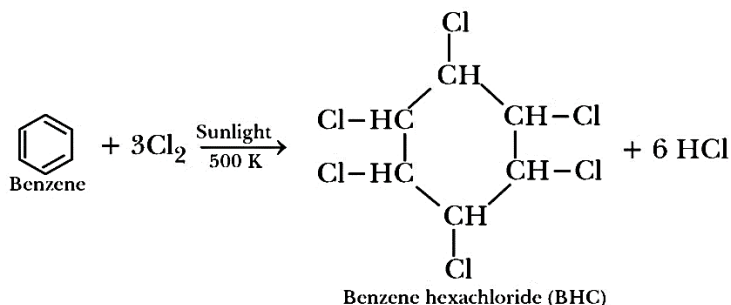


(ii) **Addition Reactions:** Two important addition reactions are as follow:

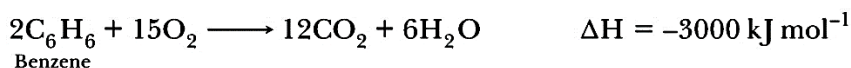
1. Addition of hydrogen: Hydrogenation



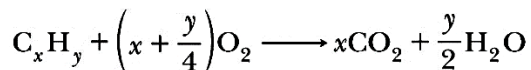
2. Addition of halogen



(iii) **Combustion Reactions**



The general chemical equation is



(h) **Directive Influence of Substituents:** The ability of a group already present in the benzene ring to direct the incoming group to a particular position on the benzene ring is called the **directive influence of the group**.

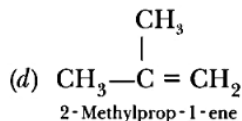
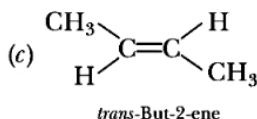
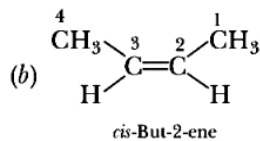
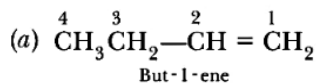
Ortho and Para Directing Substituents: The substituents or groups which direct the incoming group to ortho and para positions are called ortho-para directing groups. These groups release electrons (*i.e.*, electron donating) and activate the benzene ring. The common examples are $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NH}_2$, etc.

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

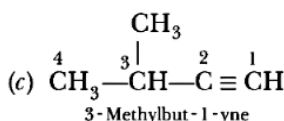
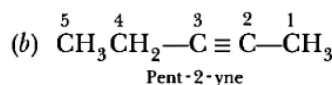
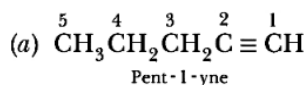
(i) C_4H_8 (one double bond)

(ii) C_5H_8 (one triple bond)

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

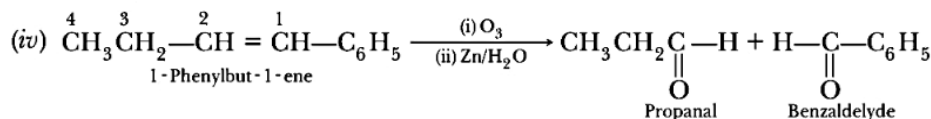
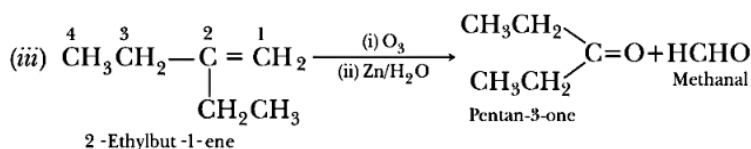
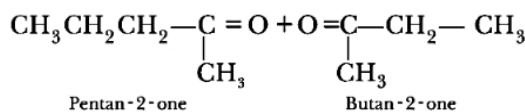
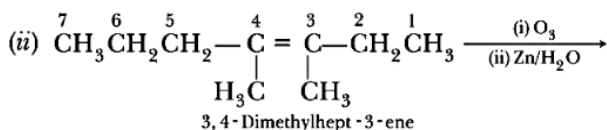
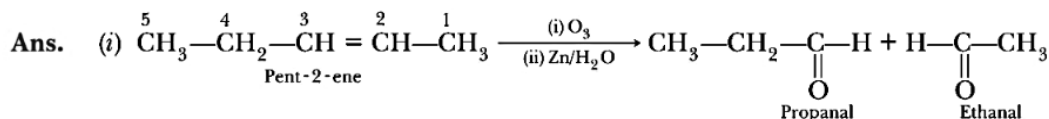


(ii) Isomers of C_5H_8 having one triple bond is

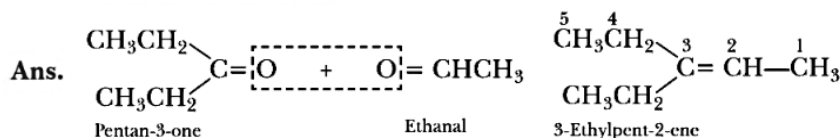


3. Write IUPAC names of the products obtained by the ozonolysis of the following compounds:

(i) Pent-2-ene (ii) 3,4-Dimethylhept-3-ene (iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene



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



5. 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_3CHO).

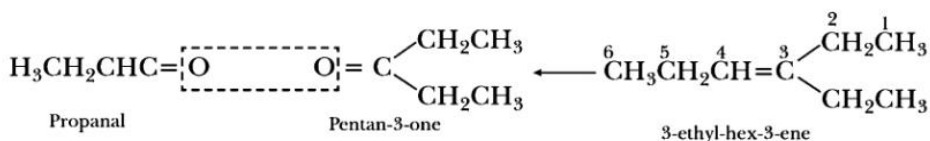
(ii) Write two moles of ethanal side by side with their oxygen atoms pointing towards each other. Remove the oxygen atoms and join them by a double bond to obtain the structure of alkene 'A'.



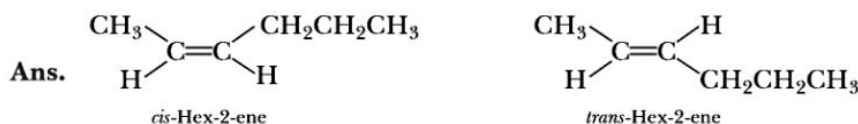
But-2-ene has three C—C, eight C—H σ -bonds and one C—C π -bond.

6. Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?

Ans. Write the structures of propanal and pentan-3-one with their oxygen atoms facing each other. Remove oxygen atoms and join the two fragments by a double bond to obtain the structure of the alkene.



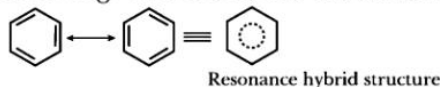
7. Draw the *cis* and *trans* structures for hex-2-ene. Which isomer will have higher b.p and why?



cis-Hex-2-ene have higher boiling point than *trans*-Hex-2-ene because of the presence of stronger dipole-dipole interactions in *cis*-Hex-2-ene than *trans*-Hex-2-ene (almost non-polar).

8. Why is benzene extraordinarily stable though it contains three double bonds?

Ans. Resonance or delocalization of electrons usually leads to stability. Since, in benzene all the six π -electrons of the three double bonds are completely delocalized between the six carbon atoms of the benzene ring. Therefore, it is extraordinarily stable.

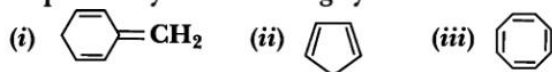


9. What are the necessary conditions for any system to be aromatic?

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

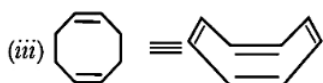
- (i) It should be cyclic and planar.
- (ii) It should contain Huckel number of electrons. *i.e.*, $(4n + 2) \pi$ -electrons where $n = 0, 1, 2, 3, \dots$ etc.

10. Explain why the following systems are not aromatic?



Ans. (i) sp^3 -hybridized carbon. Since the presence of a sp^3 -hybridized carbon, therefore the system is not planar. It contains six π -electrons but the system is not fully conjugated as all the six π -electrons do not form a single cyclic electron cloud which surrounds all the atoms of the ring. Hence, it is not an aromatic compound.

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



Cyclooctatetraene is not planar and contains 8π -electrons. Therefore, the system is not aromatic since it does not contain a planar cyclic cloud having $(4n+2)\pi$ electrons.

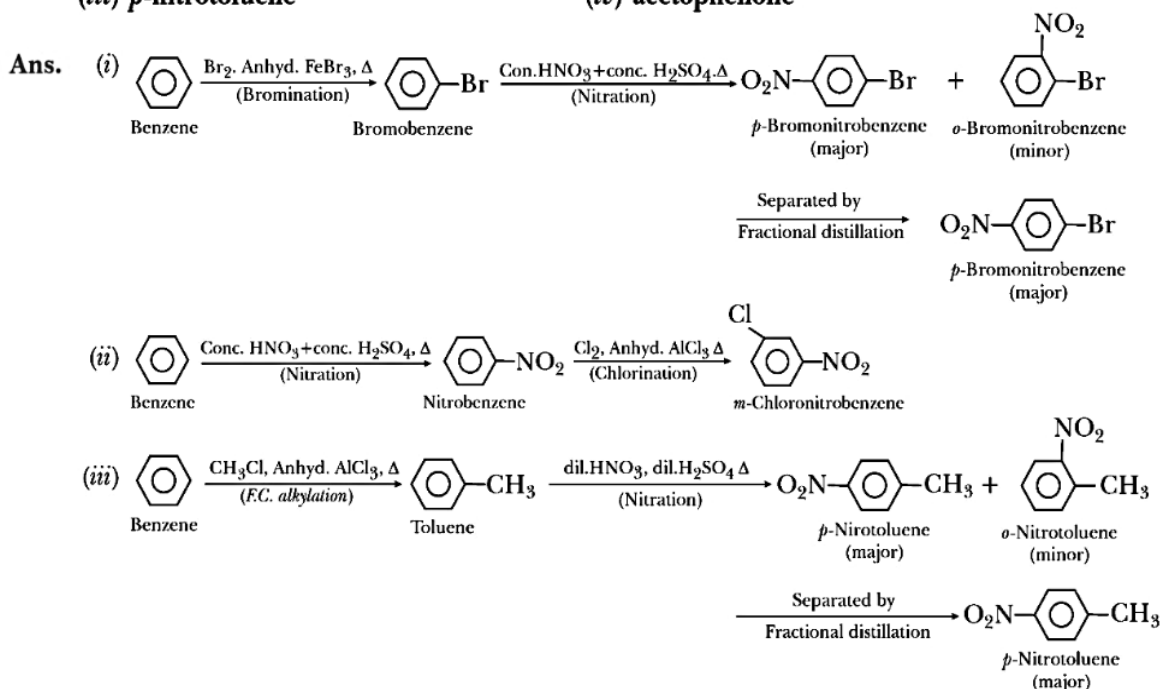
11. How will you convert benzene into

(i) *p*-nitrobromobenzene

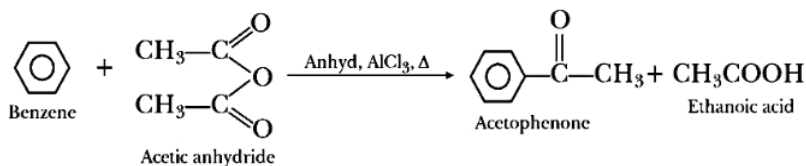
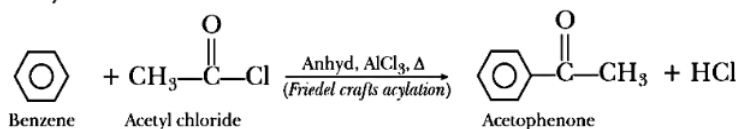
(ii) *m*-nitrochlorobenzene

(iii) *p*-nitrotoluene

(iv) acetophenone

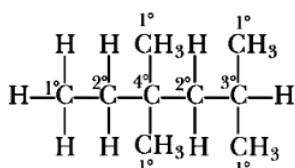


(iv) Acetophenone can be prepared by F.C. acylation using either acetyl chloride or acetic anhydride.



12. In the alkane, $\text{CH}_3\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}(\text{CH}_3)_2$, identify 1° , 2° , 3° carbon atoms and give the number of H-atoms bonded to each one of these.

Ans. The structural formula of the given compound is



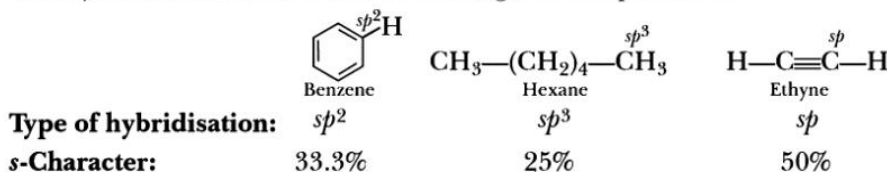
15 H bonded to five 1° carbon
4 H bonded to two 2° carbon
1 H bonded to one 3° carbon

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

Ans. As the branching increases, the surface area of an alkane decreases. Therefore, van der Waals forces of attraction are minimum and hence the boiling point of the alkane decreases with branching.

16. 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 the given compounds is



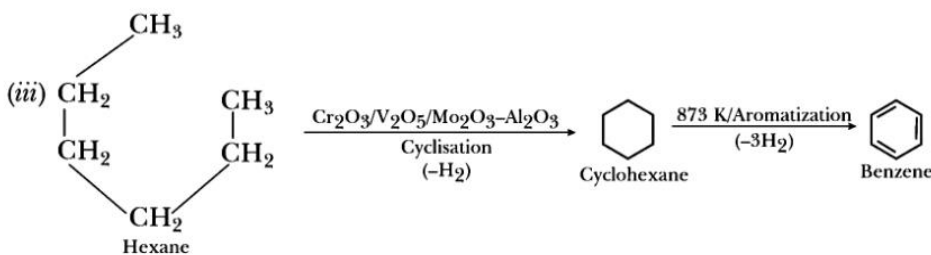
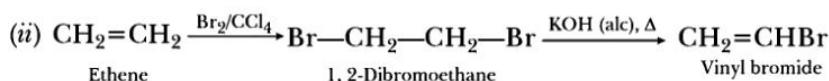
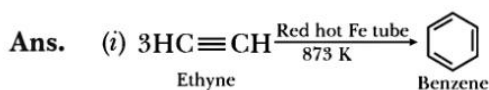
The partial +ve charge on the H-atom increases and hence the acidic character increases as the *s*-character of the orbital increases. Thus, the acidic character decreases in the order: Ethyne > Benzene > Hexane.

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

Ans. Benzene contains three π bonds in conjugation. Due to the presence of π electron cloud lying above and below the plane of the aromatic ring, it is a rich source of electrons. Therefore, it attracts the electrophiles (*i.e.*, electron seeking reagents) towards itself and repels nucleophiles (electron-rich reagents). As a result, benzene undergoes electrophilic reaction easily and nucleophilic with difficulty.

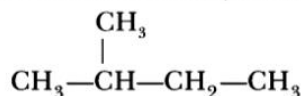
18. How would you convert the following compounds into benzene?

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

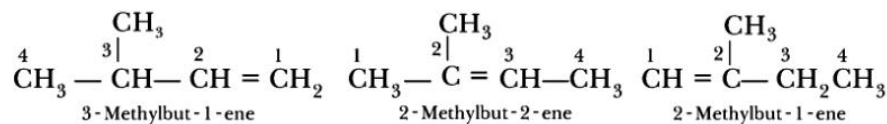


19. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

Ans. The structural formula of 2-methylbutane is



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



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

(i) Chlorobenzene, 2, 4-dinitrochlorobenzene, *p*-nitrochlorobenzene.

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

Ans. (i) Higher the electron density on the benzene ring, more reactive is the compound towards electrophilic substitution reactions. Since, NO_2 is a more electron-withdrawing group than Cl, therefore, more the number of nitro groups, less reactive is the compound. Hence, the overall reactivity decreases in the order:

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

(ii) 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. Hence, the overall reactivity decreases in the order:

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

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

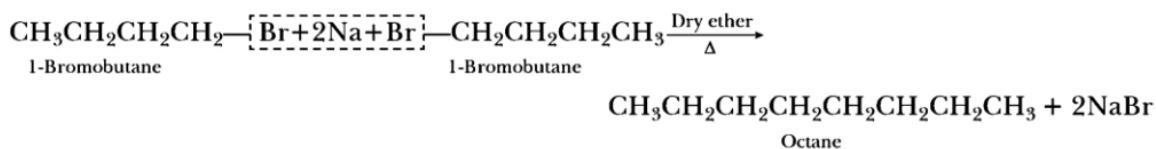
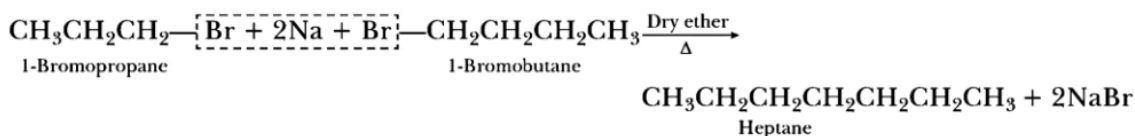
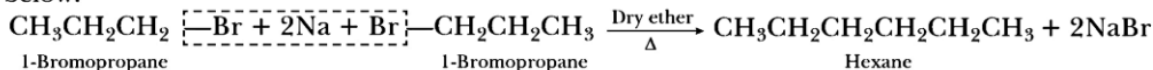
Ans. CH_3 group is electron-donating while $-NO_2$ group is electron-withdrawing. Therefore, maximum electron density will be in toluene, followed by benzene and least in *m*-dinitrobenzene. Hence nitration decreases in the order: toluene > benzene > *m*-dinitrobenzene.

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

Ans. The Lewis acid catalysts other than anhydrous $AlCl_3$ used during ethylation of benzene (Friedel crafts alkylation) is $FeCl_3$, BF_3 , $SnCl_4$ etc.

23. Why is Wurtz reaction not preferred for the 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 are taken. Since, two alkyl halides can react in three different ways, therefore, a mixture of three alkanes 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:



CASE-BASED QUESTIONS

1. Influence of the Nanotube Type on the Conformational Behaviour of Encapsulated Ethane Molecule.

It is well known that the nanotubes may significantly alter the physicochemical properties of the encapsulated molecules [1–3]. In particular, it has been shown recently that the eclipsed conformation is the most favourable in the case of ethane molecule inside a single-wall carbon nanotube, in contrast to the free ethane molecule with the potential energy minimum

If the total of the group numbers (in the periodic table) of the constituent atoms of the existing group is 1, 7, or 13, the group will have ortho-para directing influence, in all other cases meta. The group number of an alkyl radical is to be taken as 1.

The following examples illustrate the above rule. CH_2CO group: Adding the group numbers of the alkyl radical and the various atoms we get $(1 + 4 + 6) = 11$. Its influence will thus be meta directive.

Existing group	Sum	Predicted influence	Observed influence
R, Na, K	1	Ortho-para	Ortho-para
Cl, Br, I, OH, OR, NH_3 , NHR, NH_2 , HR_2	7	Ortho-para	Ortho-para
CH_2Cl , CH_5NH_2	13	Ortho-para	Ortho-para
CCl_3 , SO_3H	25	Meta	Meta
NO_2 , COOH , COOR , CONH_2	17	Meta	Meta
CH_3CO , CHO , COR	11	Meta	Meta
CN	9	Meta	Meta
COCO_2H	27	Meta	Meta
CH_2NO_2	23	Meta	Meta
NH_3Cl , NR_4Cl	15	Meta	Meta

NH_2 group: Adding the group numbers of the various atoms we get $(5 + 2) = 7$. By the above rule its influence will be ortho-para directive. The table shows the predicted and experimentally observed influences.

The rule does not apply to the exceptional cases like $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$, etc., pointed out by Holleman⁴ and therefore suffers from the usual drawbacks.

[Source: *J. Chem. Educ.* 1953,30,9,465]

Based on the above information, answer the following questions:

- What type of reagents affects characteristic benzene substitution?
- Classify $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$ and $\text{—CH}_2\text{OH}$ substituent groups by their orientation and reactivity.
- Compare the activating effects of the following *o*, *p*-directors and explain your order.
 $\text{—}\ddot{\text{N}}\text{H}_2$ and $\text{—}\ddot{\text{N}}\text{H—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$
- Why all meta-directing groups are deactivating groups?
- How can we identify the ortho and para-directing groups?

Answers

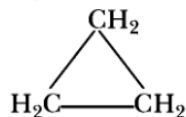
- Electrophilic reagents affects characteristic benzene substitution.
- $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$ is deactivating and *m*-directing substituent while $\text{—CH}_2\text{OH}$ is activating and *o*,*p*-directing group.
- The order is $\text{—NH}_2 > \text{—NH—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$ because of conjugation in the amide.
- All meta-directing groups are deactivating groups because the presence of these groups decreases the electron density on benzene ring and decreases the reactivity towards electrophilic substitution reaction.
- If the atom of a group which is directly bonded to benzene ring is electron rich, either due to negative charge or lone pair of electrons or both, then the group will be ortho, para-directing group.

SHORT ANSWER QUESTIONS-I

(2 marks)

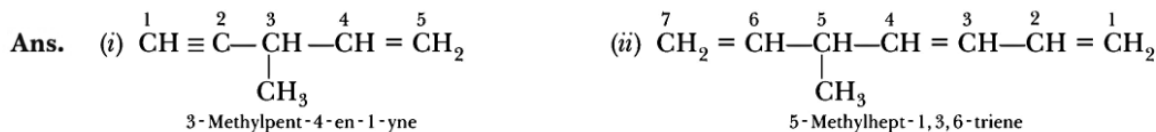
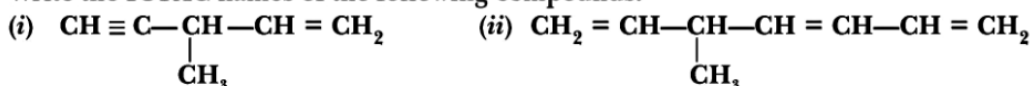
1. (i) Which is the simplest cycloalkane?
(ii) 2,3-Dichlorobut-2-ene exhibits geometrical isomerism. Which of the two isomers will have higher boiling point?

Ans. (i) Cyclopropane is the simplest cycloalkane.



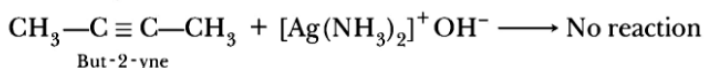
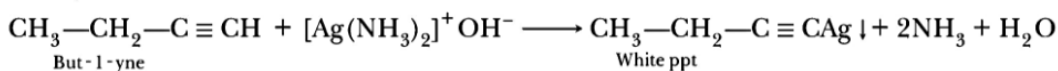
(ii) *cis*-isomer will have higher boiling point than *trans*-isomer due to stronger dipole-dipole interactions present in the *cis*-isomer.

2. Write the IUPAC names of the following compounds.



3. How would you distinguish between but-1-yne and but-2-yne?

Ans. With ammonical silver nitrate solution, but-1-yne would give a white precipitate whereas but-2-yne does not react.

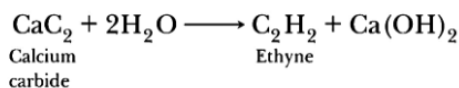


4. (i) Name the product obtained when ethyne reacts with dilute H_2SO_4 and dilute HCl in presence of Hg^{2+} ion.

(ii) How does calcium carbide react with water?

Ans. (i) With dilute H_2SO_4 in presence of Hg^{2+} ion, ethyne gives acetaldehyde (CH_3CHO) but with dilute HCl under similar conditions, vinyl chloride ($\text{CH}_2 = \text{CHCl}$) is formed.

(ii) Calcium carbide reacts with water to form acetylene.



5. (i) By which process you would locate the position of triple bond in a compound?

(ii) Which of the following compounds is most acidic?

Propane, Butane, But-1-yne, But-1-ene, But-2-yne

Ans. (i) Ozonolysis

(ii) But-1-yne is most acidic.

6. (i) What is meant by Huckel rule?

(ii) Select the meta directing groups from the following.

—Cl, —OH, —NH₂, —NO₂, —CHO, —SO₃H

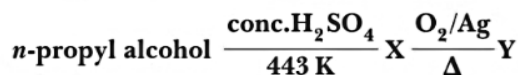
Ans. (i) According to this rule, a cyclic, planar, conjugated system containing a total of $(4n + 2)\pi$ electrons behave as aromatic compounds.

(ii) Meta-directing groups are —NO₂, —SO₃H and —CHO.

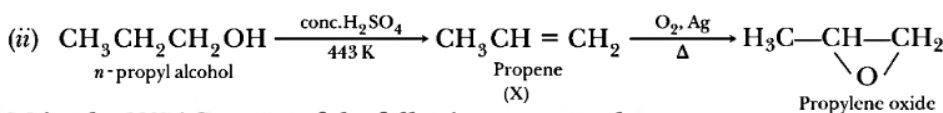
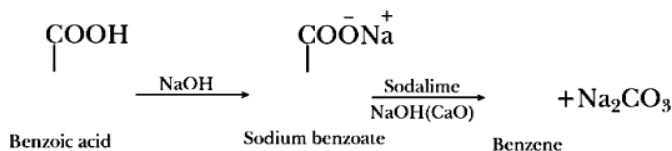
7. (i) How would you bring about the following conversion?

Benzoic acid to benzene

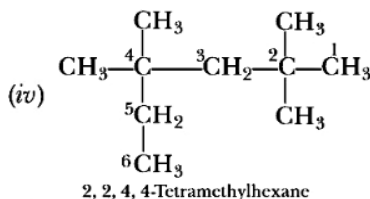
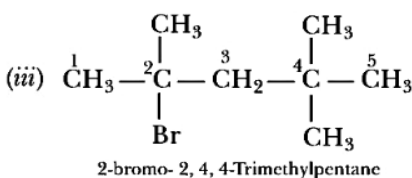
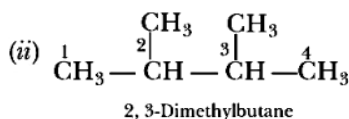
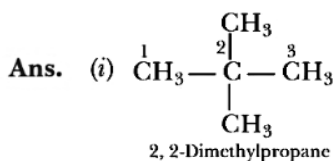
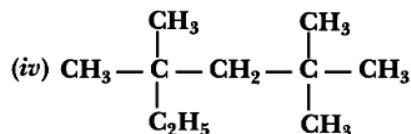
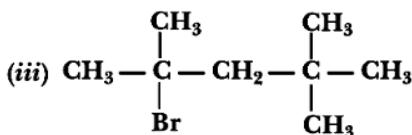
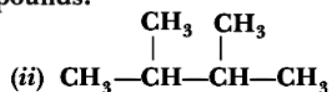
(ii) Complete the following reaction



Ans. (i) Benzoic acid to benzene



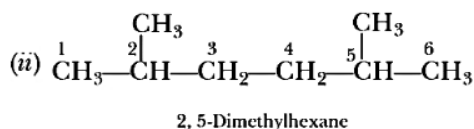
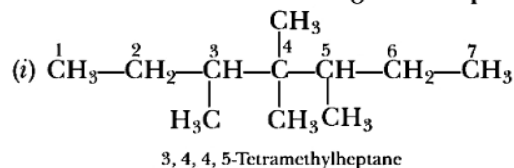
8. Write the IUPAC names of the following compounds:



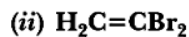
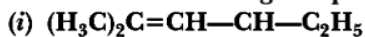
9. Write structural formulas of the following compounds.



Ans. The structural formula of the given compounds are as follow.



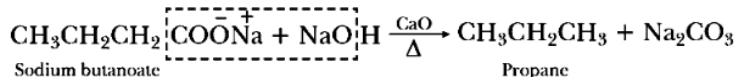
10. Which of the following compounds will show cis-trans isomerism?



Ans. Alkenes (i) and (ii) have identical atoms or groups on one of the carbon atoms of the double bond and therefore do not show geometrical isomerism. On the other hand, alkenes (iii) and (iv) have different atoms or groups on each carbon atom of the double bond and hence exhibit geometrical isomerism.

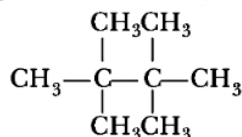
11. Sodium salt of which acid will be needed for preparation of propane? Write chemical equation for the reaction.

Ans. Since one carbon atom is lost as CO_2 during decarboxylation. Thus, the acid needed must contain one carbon atom more than propane, *i.e.*, butanoic acid.

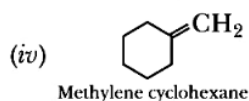
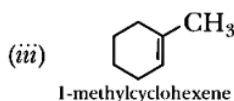
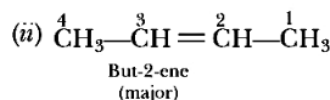
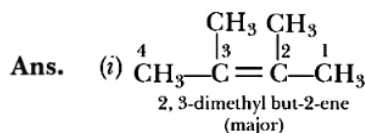
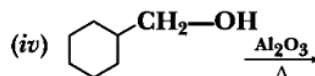
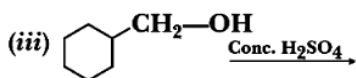
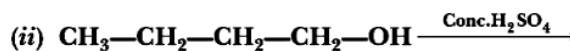
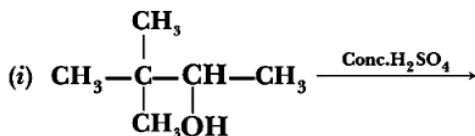


12. An organic compound C_6H_{18} on monochlorination gives a single monochloride. Write the structure of the hydrocarbon.

Ans. Since, the hydrocarbon (C_6H_{18}) on monochlorination gives a single monochloride, therefore, all the 18 H-atoms are equivalent. The only such hydrocarbon is 2, 2, 3, 3-tetramethylbutane, *i.e.*,

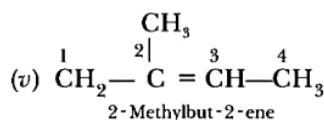
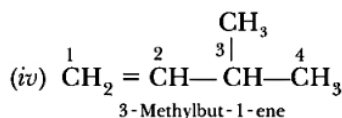
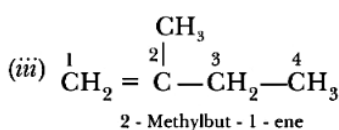
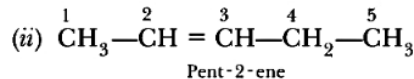
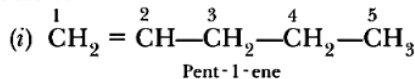


13. Give the major product in the following reactions:



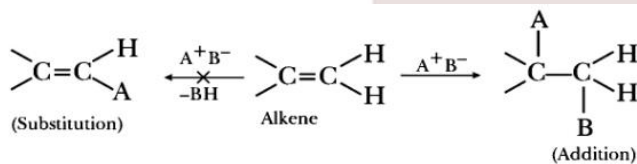
14. Write the structures and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10} .

Ans. The structural isomers and their IUPAC names of alkenes corresponding to C_5H_{10} are given below:

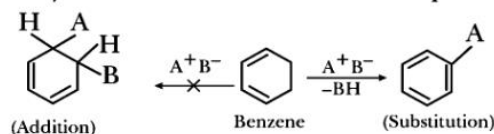


15. Why do alkenes prefer to undergo electrophilic addition reactions while arenes prefer electrophilic substitution reactions? Explain. [NCERT Exemplar]

Ans. Alkenes undergo electrophilic addition reaction rather than electrophilic substitution reaction because electrophilic addition reaction of alkenes are accompanied by the large energy changes and thus are energetically favourable.



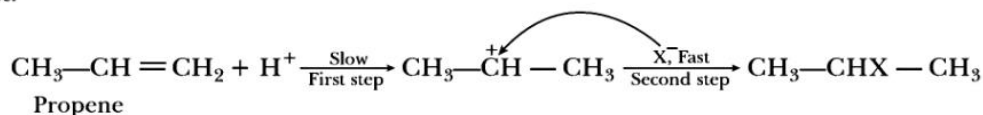
On the other hand, during electrophilic addition reaction of arenes, the aromatic character of benzene is destroyed, *i.e.*, the resonance energy of the benzene is lost while during electrophilic substitution, it remains intact. Therefore, electrophilic addition reactions of arenes is less energetically favourable than that of electrophilic substitution reactions.



16. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is $430.5 \text{ kJ mol}^{-1}$, $363.7 \text{ kJ mol}^{-1}$ and $296.8 \text{ kJ mol}^{-1}$ respectively. What will be the order of reactivity of these halogen acids?

[HOTS] [NCERT Exemplar]

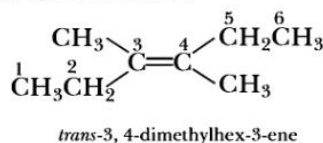
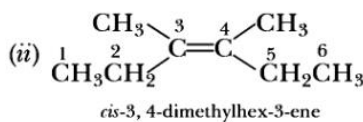
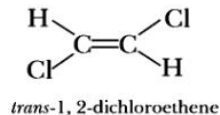
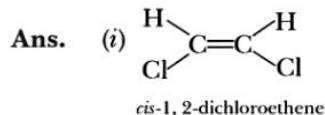
Ans. In the reaction of propene with HCl, HBr or HI, first a H^+ adds to give the same carbocation intermediate which then undergoes nucleophilic attack by the halide ion (X^-) to give the addition product.



Since the bond dissociation energy decreases in the order:

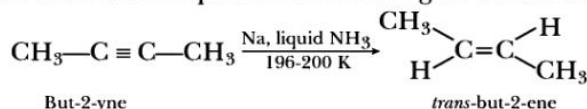
$\text{HCl} (430.5 \text{ kJ mol}^{-1}) > \text{HBr} (363.7 \text{ kJ mol}^{-1}) > \text{HI} (296.8 \text{ kJ mol}^{-1})$ and therefore, the reactivity of the halogen acids decreases in the reverse order: $\text{HI} > \text{HBr} > \text{HCl}$.

17. Draw the structures of *cis*- and *trans*-isomers of the following compounds. Also write their IUPAC names. (i) $\text{CHCl}=\text{CHCl}$ (ii) $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$



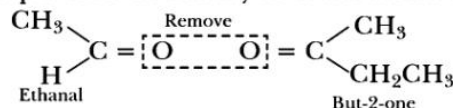
18. Alkynes on reduction with sodium in liquid ammonia form *trans* alkenes. Will the butene thus formed on reduction of but-2-yne shows the geometrical isomerism? [NCERT Exemplar]

Ans. Since but-2-ene is capable of exhibiting geometrical isomerism, therefore, reduction of but-2-yne with Na in liquid ammonia will give *trans* but-2-ene.

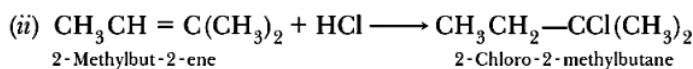
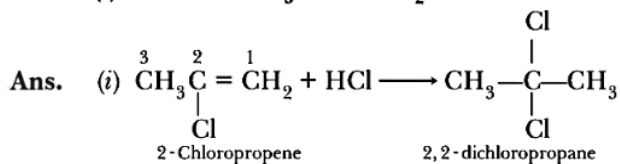
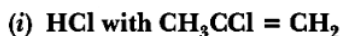


19. An alkene with molecular formula C_6H_{12} gives ethanal and but-2-one on ozonolysis. Give the structure and IUPAC name of the alkene.

Ans. The products of ozonolysis of the alkene are



23. Use Markownikov's rule to predict the product of the reaction

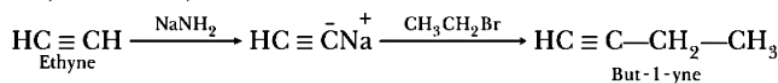


24. How would you convert

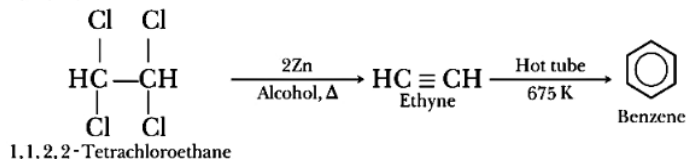
(i) Ethyne into *n*-butyne

(ii) 1, 1, 2, 2-Tetrachloroethane to benzene

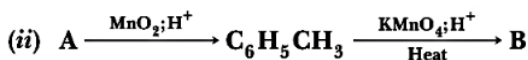
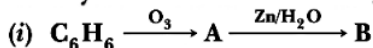
Ans. (i) Ethyne to *n*-butyne



(ii) 1, 1, 2, 2-Tetrachloroethane to benzene



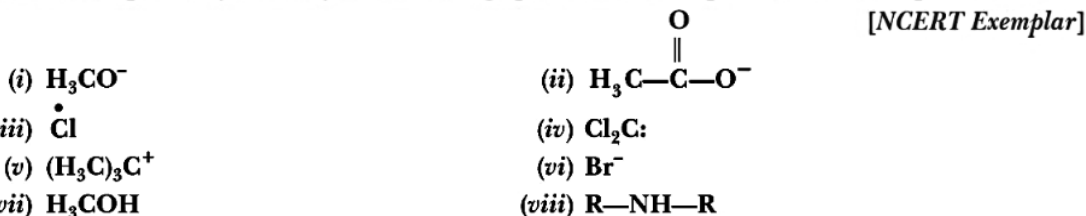
25. Identity A and B in the following reactions.



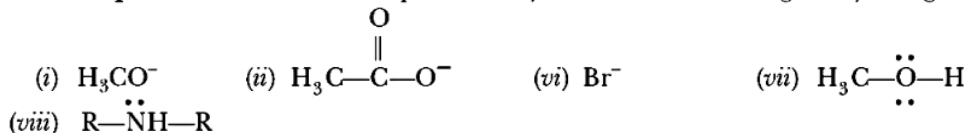
Ans. (i) A = Benzene triozone; B = glyoxal

(ii) A = $\text{C}_6\text{H}_5\text{CHO}$; B = $\text{C}_6\text{H}_5\text{COOH}$

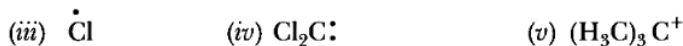
26. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.



Ans. Nucleophiles are electron-rich species. They can be neutral or negatively charged, *i.e.*,

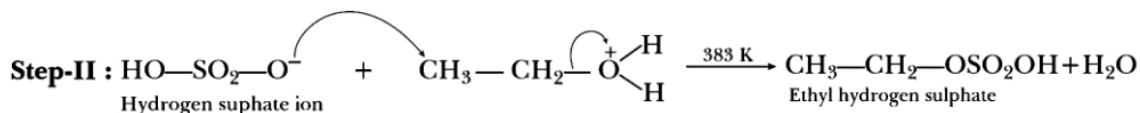
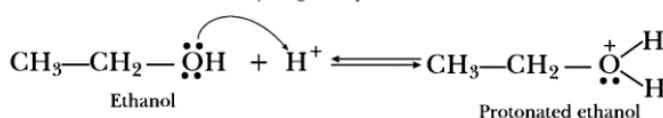
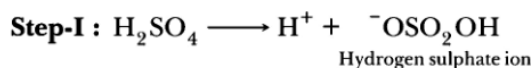


Electrophiles are electron-deficient species. They can be neutral or positively charged, *i.e.*,



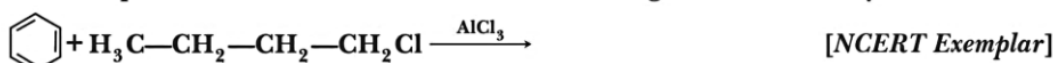
27. Suggest a route to prepare ethyl hydrogen sulphate ($\text{CH}_3-\text{CH}_2-\text{OSO}_2-\text{OH}$) starting from ethane ($\text{C}_2\text{H}_5\text{OH}$). [HOTS]

Ans. When ethanol is heated with conc. H_2SO_4 at 383 K (*i.e.*, 110° C), ethyl hydrogen sulphate is formed.

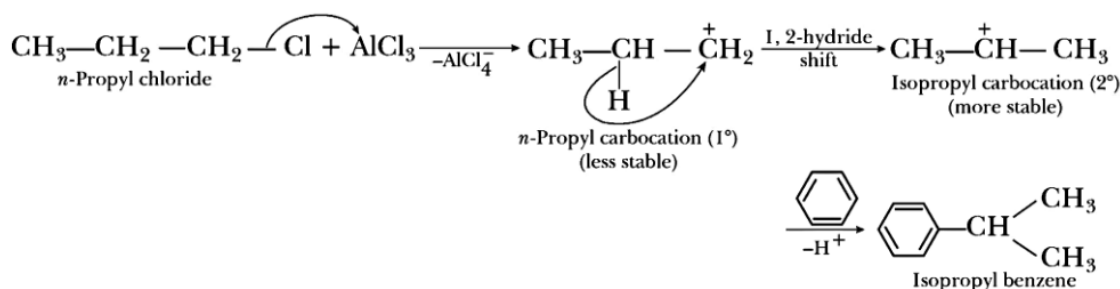


Temperature should not be allowed to rise above 383 K, as diethyl ether will be obtained at 413 K or ethene at 433–443 K.

28. What will be the product obtained as a result of the following reaction and why?



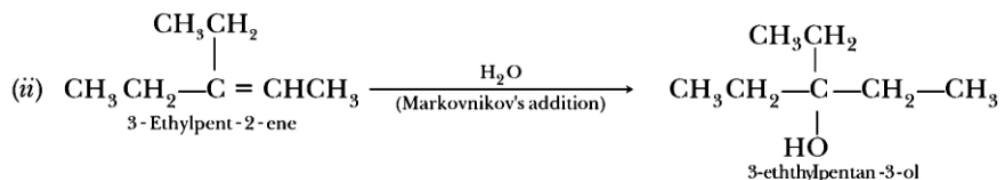
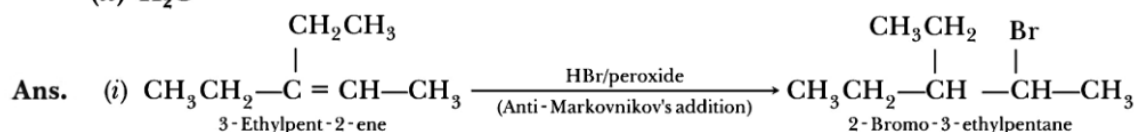
Ans. During Friedal craft's reactions, carbocations are the intermediates. Therefore, AlCl_3 first reacts with *n*-propyl chloride to form *n*-propyl cation. This being 1° is less stable and rearranges to the more stable 2° carbocation by an hydride shift. The isopropyl carbocation then reacts with benzene to form isopropylbenzene.



29. Give the structures of the major products from 3-ethylpent-2-ene under each of the following reaction conditions.

(i) HBr in the presence of peroxide

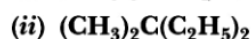
(ii) H_2O



SHORT ANSWER QUESTIONS–II

(3 marks)

1. Write IUPAC names of the following compounds

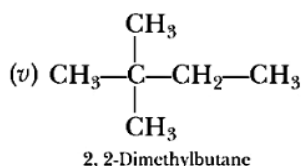
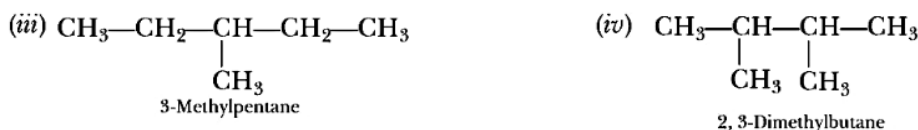
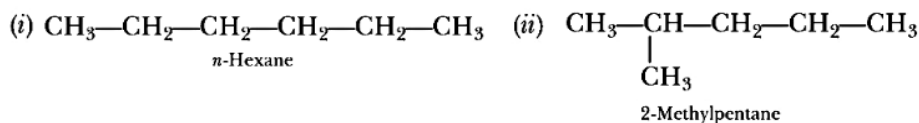


(iii) Tetra-tert-butylmethane

Ans. The IUPAC names of the given alkanes are:

4. Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14} . Also write their IUPAC names.

Ans. The different isomers of alkanes with molecular formula C_6H_{14} is:



5. Rotation around carbon-carbon single bond of ethane is not completely free. Justify statement.

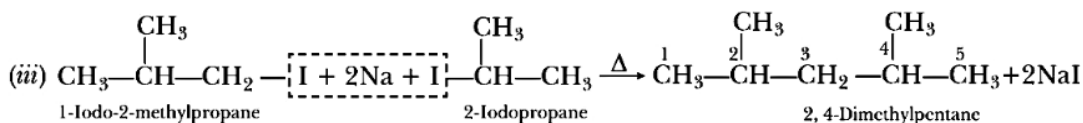
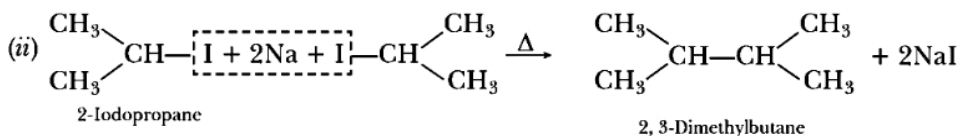
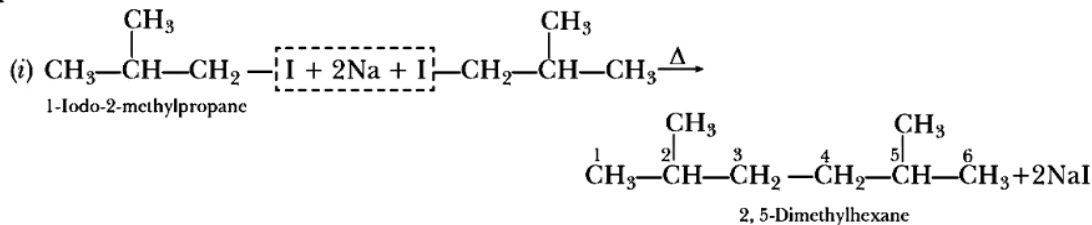
[NCERT Exemplar]

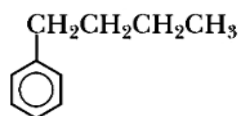
Ans. Rotation about C—C single bond is restricted due to repulsions between the electron clouds of the C—H bonds on adjacent carbon atoms. As a result of these repulsions, ethane exists in infinite number of conformations, out of which, two extreme conformations *i.e.*, staggered and eclipsed are important.

Out of staggered and eclipsed conformations, staggered structures are highly stable as the atoms or groups of front back carbon atoms are 60° apart from each other and in eclipsed form, the bond pairs of electrons come very close to each other and strongly repel each other which makes the molecule very unstable. The energy difference of $12.55 \text{ kJ mol}^{-1}$ is the energy barrier to rotation about C—C single bond in ethane. However, this energy barrier is not large enough to prevent rotation. Thus, the two conformations are readily inter convertible and as a result it is not possible to separate the two conformers of ethane.

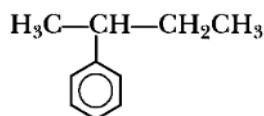
6. Write the structures and names of products obtained in the reaction of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane. [NCERT Exemplar]

Ans. Wurtz reaction between 1-iodo-2-methylpropane and 2-iodopropane gives the following three products:

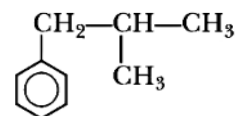




n-Butylbenzene



sec-Butylbenzene



2-methylpropylbenzene

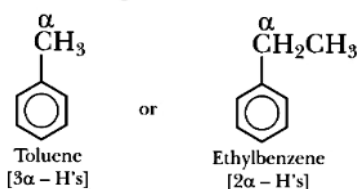
All these isomers are easily oxidised to benzoic acid.

13. Give reasons for the following:

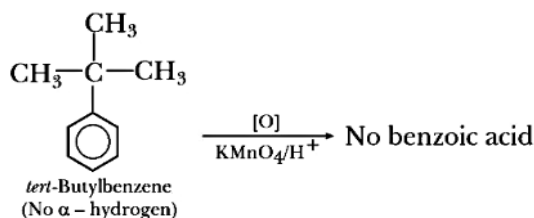
(i) **tert-Butylbenzene does not give benzoic acid on oxidation with acidic KMnO_4**

(ii) **$\text{CH}_2 = \text{CH}^-$ is more basic than $\text{HC} \equiv \text{C}^-$.**

Ans. (i) Alkylbenzenes in which the alkyl groups contain one or more α -hydrogen or benzylic hydrogen on vigorous oxidation with acidic KMnO_4 ultimately give the corresponding benzoic acids irrespective of the length of the carbon chain. For example,

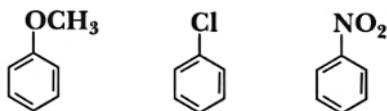


tert-Butylbenzene, on the other hand, does not contain any α -hydrogen or benzylic hydrogen and hence does not undergo oxidation to give benzoic acid.



(ii) $\text{CH}_2 = \text{CH}^-$ is the conjugate base of the acid $\text{H}_2\text{C} = \text{CH}_2$ and $\text{HC} \equiv \text{C}^-$ is the conjugate base of the acid $\text{HC} \equiv \text{CH}$. We know that stronger the acid, weaker is the conjugate base. Since, $\text{HC} \equiv \text{CH}$ is stronger acid than $\text{CH}_2 = \text{CH}_2$, therefore, $\text{CH}_2 = \text{CH}^-$ is a stronger base than $\text{HC} \equiv \text{C}^-$.

14. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. Give reason. [NCERT Exemplar]



Ans. The reactivity of arenes towards electrophiles depends upon their relative electron density in the benzene ring. Higher the electron density, more reactive is the arene.

Since $-\text{OCH}_3$ group in anisole is strongly electron donating due to its +R-effect. As a result, it increases the electron density in the ring and hence makes anisole more reactive than benzene towards electrophiles.

On the other hand, $-\text{NO}_2$ group in nitrobenzene and Cl atom in chlorobenzene, both are electron-withdrawing and hence decreases the electron density in the ring. As a result, both nitrobenzene and chlorobenzene are less reactive than benzene towards electrophiles. Moreover, electron density in chlorobenzene is more than nitrobenzene and hence chlorobenzene is more reactive than nitrobenzene towards electrophiles.

Thus, the overall reactivity of these three compounds towards electrophiles decreases in the order:

Anisole > chlorobenzene > nitrobenzene.

LONG ANSWER QUESTIONS

(5 marks)

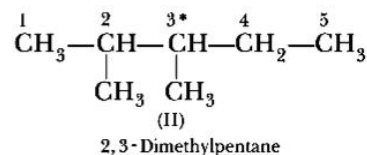
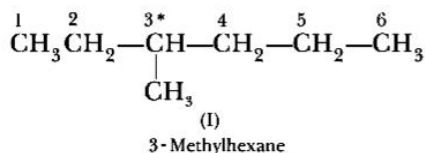
1. Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11} . Write IUPAC names of alcohols obtained by attachment of $-OH$ groups at different carbons of the chain.

Ans.

	Structure of $-C_5H_{11}$ alkyl group	Corresponding alcohols	IUPAC Name of alcohols
1.	$CH_3-CH_2-CH_2-CH_2-CH_2-$	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	Pentan-1-ol
2.	$CH_3-\underset{ }{CH}-CH_2-CH_2-CH_3$	$CH_3-\underset{ }{CH}-CH_2-CH_2-CH_3$ OH	Pentan-2-ol
3.	$CH_3-CH_2-\underset{ }{CH}-CH_2-CH_3$	$CH_3-CH_2-\underset{ }{CH}-CH_2-CH_3$ OH	Pentan-3-ol
4.	$\begin{array}{c} CH_3 \\ \\ CH_3-CH-CH_2-CH_2- \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-CH-CH_2-CH_2-OH \end{array}$	3-Methylbutan-1-ol
5.	$\begin{array}{c} CH_3 \\ \\ CH_3-CH_2-CH-CH_2- \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-CH_2-CH-CH_2-OH \end{array}$	2-Methylbutan-1-ol
6.	$\begin{array}{c} CH_3 \\ \\ CH_3-C-CH_2-CH_3 \\ \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-C-CH_2-CH_3 \\ \\ OH \end{array}$	2-Methylbutan-2-ol
7.	$\begin{array}{c} CH_3 \\ \\ CH_3-C-CH_2- \\ \\ CH_3 \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-C-CH_2OH \\ \\ CH_3 \end{array}$	2,2-Dimethylpropan-1-ol
8.	$\begin{array}{c} CH_3 \\ \\ CH_3-CH-CH-CH_3 \\ \end{array}$	$\begin{array}{c} CH_3 \quad OH \\ \quad \\ CH_3-CH-CH-CH_3 \end{array}$	3-Methylbutan-2-ol

2. There are six different alkenes (A), (B), (C), (D), (E) and (F). Each on addition of one mole of hydrogen gives (G) which is the lowest molecular weight hydrocarbon containing only one asymmetric carbon atom. None of the above alkenes give acetone as a product on ozonolysis. Give the structures of (A), (B), (C), (D), (E) and (F). Identify the alkene which is likely to give a ketone containing more than five carbon atoms on treatment of a warm concentrated solution of alkaline $KMnO_4$. [HOTS]

Ans. The lowest molecular weight hydrocarbon (G) with one asymmetric carbon atom obtained by adding one mole of H_2 to alkenes can have two structures (I and II).



All the six alkenes (A), (B), (C), (D), (E) and (F) would give only (I) on adding one mole of hydrogen. These alkenes are

Ans.

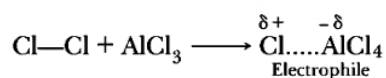
Compound	Aromatic/Non-aromatic
(A)	Contains planar ring with conjugated π -bonds and follows $(4n + 2)\pi$ electrons rule, i.e., $6\pi e^-$ and therefore aromatic.
(B)	The ring is not planar and has incomplete delocalisation of πe^- s. Moreover does not have $(4n + 2)\pi e^-$ s. Therefore non-aromatic.
(C)	Contains planar ring with six delocalised π -electrons and follows $(4n + 2)\pi$ electrons rule. Therefore, aromatic.
(D)	Contains planar ring with only 4 delocalised π -electrons and does not follow Huckel rule. Therefore, antiaromatic.
(E)	Follows Huckel rule and contains planar ring with six delocalised π -electrons. It is aromatic.
(F)	Follows Huckel rule and ring is planar with 2 delocalised π electrons. Therefore, it is aromatic.
(G)	Follows Huckel rule and have planar ring but the delocalisation stops at sp^3 -hybridised CH_2 carbon. Therefore, non-aromatic.

6. Explain the mechanism of halogenation and nitration of benzene.

Ans. (i) Mechanism of Halogenation of Benzene

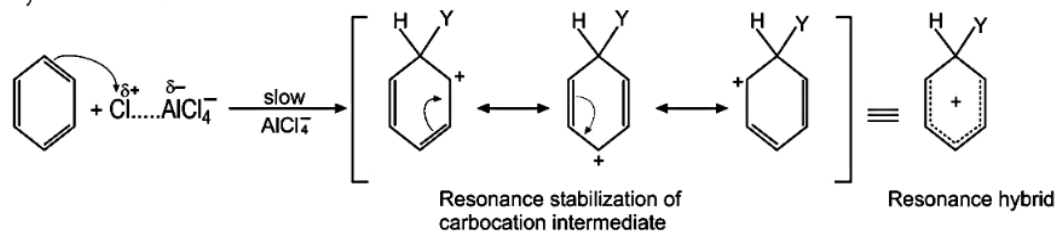
Halogenation of benzene is carried out by halogen at low temperature (310–320 K) and in the presence of Lewis acids such as ferric halide and aluminium halide in the absence of sunlight. The mechanism of halogenation of benzene is being illustrated with the help of chlorination of benzene. The chlorination of benzene involves the following steps.

Step 1. Generation of electrophile:



Step 2. Formation of carbocation or σ -complex:

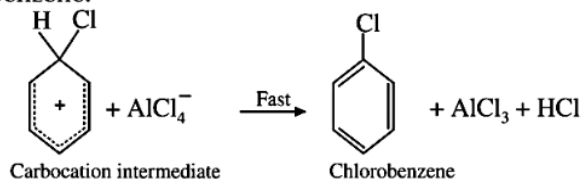
The electrophile attacks the benzene ring to form an intermediate carbocation which is stabilized by resonance.



This is the rate determining step.

Step 3. Loss of proton from carbocation intermediate:

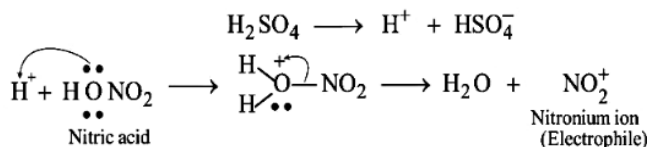
The carbocation intermediate loses a proton to AlCl_4^- ion and results in the formation of chlorobenzene.



(ii) Mechanism of Nitration

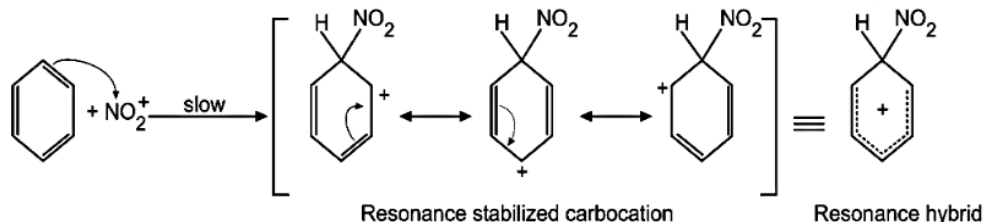
The nitration of benzene is carried out by treating benzene with a nitrating mixture (conc. HNO_3 and conc. H_2SO_4); sulphuric acid acts as a catalyst. The various steps involved are:

Step 1. Generation of nitronium (NO_2^+) electrophile:



Step 2. Formation of carbocation intermediate:

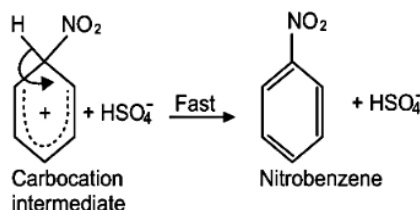
The electrophile attacks the benzene ring to form a carbocation which is stabilized by resonance.



This is a rate determining step.

Step 3. The loss of proton from the carbocation intermediate:

The carbocation intermediate loses a proton to the base (HSO_4^-) and results in the formation of nitrobenzene.

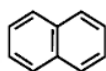


QUESTIONS FOR PRACTICE

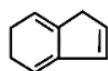
- (i) Which simplest alkene can exhibit geometrical isomerism?

(ii) Complete the reaction

$$\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{Alkaline KMnO}_4}$$
- Is it possible to isolate pure staggered ethane or pure eclipsed ethane at room temperature?
- IUPAC names of some alkanes are given below. Write their structures.
 - 2, 3, 5-Trimethylhexane
 - 3, 4, 8-Trimethyldecane
 - 2-Ethyl-3-methylpentane
 - 2, 3, 5-Trimethyl-4-propylheptane
- An alkene with molecular formula C_6H_{12} gives ethanal and butan-2-one on ozonolysis. Give the structure and IUPAC name of the alkene.
- How will you distinguish between 1, 3-butadiene and but-1-yne?
- Predict which one of the following is aromatic and why?



(i)



(ii)

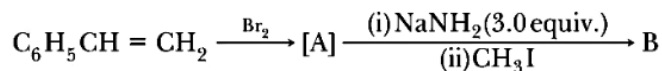


(iii)

- Bring out the following conversions:

- Carbon and hydrogen to benzene
- Ethyne to toluene
- Ethyl benzene to benzene

8. Complete the following reactions with appropriate structures of products:



9. An alkyl halide, X, of formula $\text{C}_6\text{H}_{13}\text{Cl}$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of X, Y and Z.
10. (i) Find the structure of a hydrocarbon that produces one mole each of ethanedial and butanedial on ozonolysis.
- (ii) Devise a scheme for the synthesis of *n*-butane using CH_3I as the only carbon source. Can you employ the reactions in your scheme to synthesise propane in fairly pure state? Explain.
- (iii) How many monochloro products would you expect when 2-methylbutane is chlorinated? Write their structures and IUPAC names.
- (iv) Which of the isomers in (iii) will not give one product only on dehydrohalogenation with alcoholic KOH?

III