CHAPTER 16

HYDROCARBONS

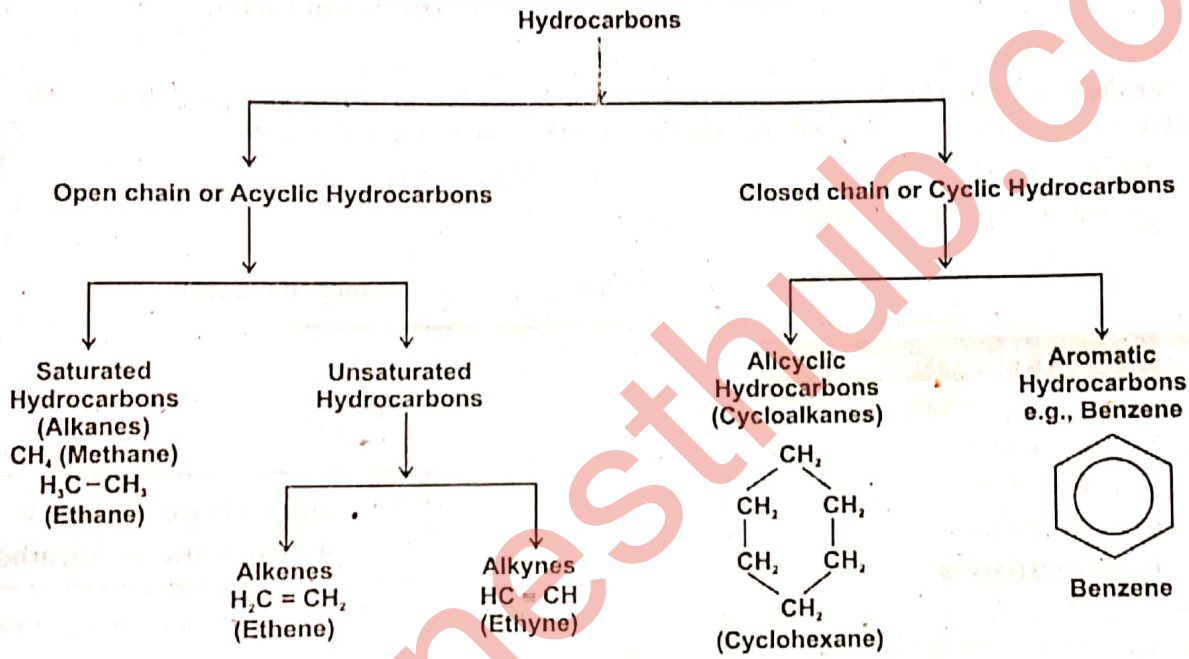
Hydrocarbons

"Organic compounds which contain carbon and hydrogen only are called hydrocarbons." e.g, Methane (CH_4), Acetylene (C_2H_2), Benzene (C_6H_6) etc.

- The ability of carbon atoms to attach with each other to form a chain or ring is called Catenation.

Types of hydrocarbons

Hydrocarbons have been divided into various classes on the basis of their structures as shown below:



(A) Open Chain Hydrocarbons

The hydrocarbons in which carbon atoms attached with each other to form open chains are called open chain hydrocarbons. They are further classified into two types:

1. Saturated hydrocarbons: (Alkanes or Paraffins)
2. Unsaturated hydrocarbons: (Alkenes or Olefins) and (Alkynes or Acetylenes)

Q. Differentiate between saturated and unsaturated hydrocarbons

1. Saturated Hydrocarbons

- These are the hydrocarbons in which carbon atoms are attached with each other through single bonds.
- Each carbon atom is sp^3 hybridized.
- No further atoms or group of atoms can be attached to the carbon atoms of such hydrocarbons. This is why they are known as saturated hydrocarbons.
- These may have straight chain or branched chain.

Examples:

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
Pentane (Straight Chain)

$CH_3 - CH(CH_3) - CH_2 - CH_3$
2- Methylbutane (Branched Chain)

2. Unsaturated Hydrocarbons

- These are the hydrocarbons in which at least two carbon atoms are attached through double or triple bonds. Each carbon is sp^2 or sp hybridized.
- They are called unsaturated because all the four valencies of carbon are not fully utilized. More atoms or groups can be attached to the carbon.

For examples: alkenes and alkynes.

(i) Alkenes or Olefins

These are the unsaturated hydrocarbons in which at least two carbon atoms are sp^2 hybridized, which cause to form a double bond between these carbon atoms. Alkenes may be straight chain or branched chain.

$CH_2 = CH - CH_2 - CH_3$
1-Butene **(Straight Chain)**

$CH_2 = CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$
3-Methyl-1-butene **(Branched Chain)**

(ii) Alkynes or acetylenes

These are the unsaturated hydrocarbons in which at least two carbon atoms are sp hybridized, which cause to form a triple bond between these carbon atoms. Alkynes may be straight chain or branched chain.

$CH \equiv C - CH_2 - CH_2 - CH_3$
1-Pentyne **(Straight Chain)**

$CH \equiv C - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$
3-Methyl-1-butyne **(Branched Chain)**

(B) Closed Chain Hydrocarbons

These are the hydrocarbons in which carbon atoms attach with each other to form rings.

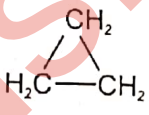
Types: These hydrocarbons are of following two types:

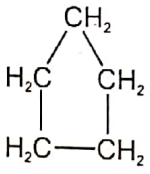
1. Alicyclic Hydrocarbons
2. Aromatic Hydrocarbons

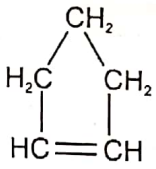
Q. Differentiate between alicyclic and aromatic hydrocarbons.

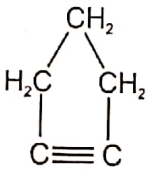
(1) Alicyclic Hydrocarbons:

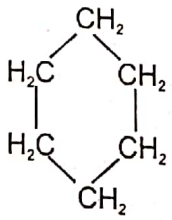
Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons. Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons.


Cyclopropane


Cyclopentane

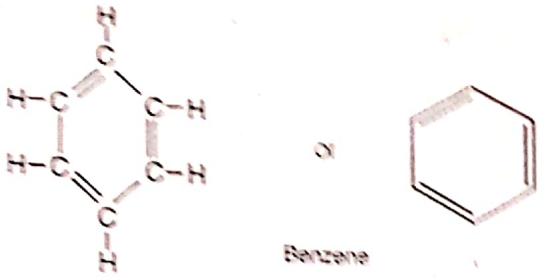

Cyclopentene


Cyclopentyne

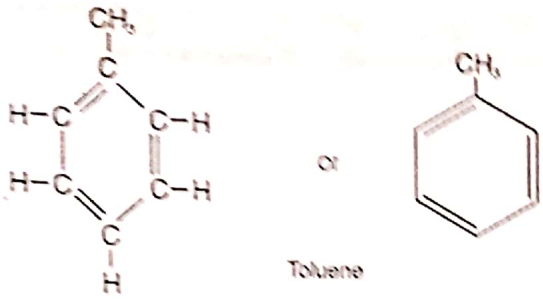

Cyclohexane

(2) Aromatic Hydrocarbons:

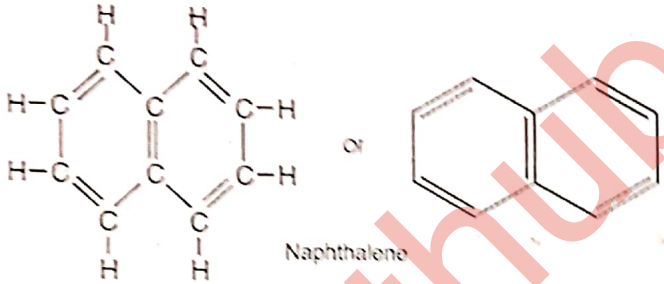
Benzenoid cyclic hydrocarbons are known as aromatic hydrocarbons. In these compounds, all the carbon atoms present in the ring are sp^2 hybridized. Benzene, which is the simplest aromatic hydrocarbon, has a regular hexagonal structure with alternate single or double bonds between carbon atoms.



Benzene



Toluene



Naphthalene

QUICK QUIZ

1. What is catenation?

Ans. Catenation:

"The self linking property of an element is called catenation".

Carbon shows maximum catenation property due to high C – C bond energy. Carbon is a unique element and it is essential element of organic compounds. A large number of organic compounds is due to catenation property of carbon.

2. What are hydrocarbons?

Ans. Hydrocarbons are organic compounds which contain carbon and hydrogen only, e.g. methane (CH_4), benzene (C_6H_6) etc.

3. Why saturated hydrocarbons are called paraffins?

Ans. Saturated hydrocarbons (alkanes) are called paraffins (Latin : parum = little, affins = affinity) due to their least reactivity (inertness) towards acids, bases etc. under ordinary conditions. It is due to their non-polar nature and inertness of σ-bond.

4. Why unsaturated hydrocarbons are called olefins?

Ans. The word olefins is derived from Latin word "olefiant" meaning oil forming. Actually the lower members of alkenes (unsaturated hydrocarbons) form oily product on treatment with chlorine or bromine.

5. What is hybridization?

Ans. Hybridization:

"The process in which mixing of atomic orbitals having different shapes and energies to form hybrid orbitals with same shape and energy but different orientation is called hybridization."

- According to this, the atomic orbitals differing in shapes and energies intermix to form new orbitals which are

called **hybrid orbitals.**

- They differ with the parent atomic orbitals in shape and possess specific geometry.

6. Why benzene is called aromatic hydrocarbons?

Ans. Benzene (C_6H_6) shows aromaticity and follows Huckel rule. Therefore benzene is aromatic hydrocarbon.

7. What is hexagonal structure?

Ans. Hexagonal structure has six sides of equal lengths and angle between any two sides is of 120°. Benzene has hexagonal structure.

ALKANES AND CYCLOALKANES

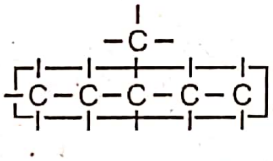
Alkanes

Simplest organic molecules with only C and H atoms having single bond between any two carbon atoms. Commercially important as fuels and oils.

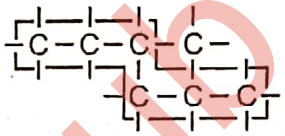
Nomenclature

The IUPAC rules of naming alkanes are as:-

1. Locate the largest continuous chain of carbon atoms independent of direction of the chain. It is called main chain, stem, principal chain or parent chain.

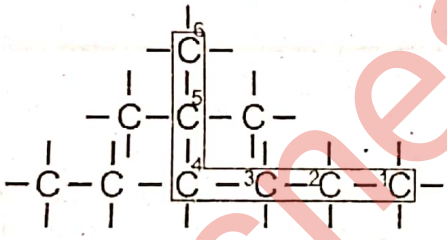


Longest chain (Horizontal)

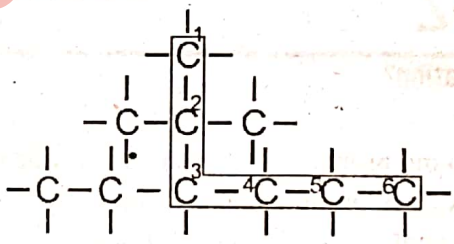


Longest chain (zig-zag)

2. If there are two or more chains of equal lengths, the chain with larger number of branches is selected as main chain.
3. Number the main chain starting from the end nearest to the substituent.



(Incorrect)

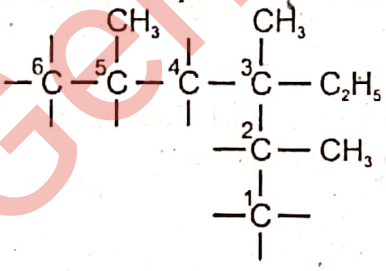


(correct)

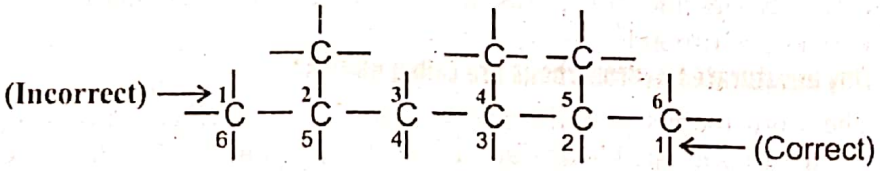
4. When two identical substituents are present at equal distance from either end, number the chain starting with end which gives their minimum sum.

   Since the sum of number 2 + 3 + 5 = 10, is less than 2 + 4 + 5 = 11, the correct numbering starts from the right.
5. The position of substituent is indicated by the number of carbon atom to which it is attached.

   The number is prefixed to the name of group separated by hyphen.

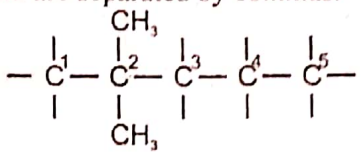


3-Ethyl-2,3,5-trimethylhexane



6. Names of alkyl groups are written before the name of parent hydrocarbon in alphabetical order or in order of increasing size, separated by hyphen.
7. When two or more like groups are present, their numbers are indicated by prefixes di, tri-,tetra-, etc.

Their numbers are grouped together and are separated by commas.

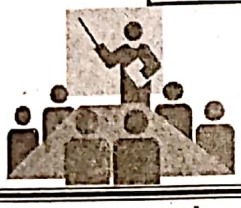


2, 2-Dimethylpentane

8. If two identical groups appear at the same C-atom, the number is repeated twice, separated by commas.
9. The longest chain of the substituent is numbered starting with the carbon attached directly to the main chain. Parenthesis are used to separate the numbering of the substituent and the main chain.

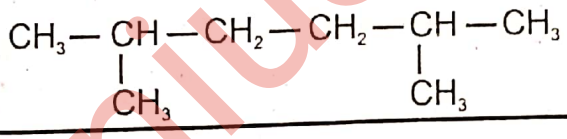
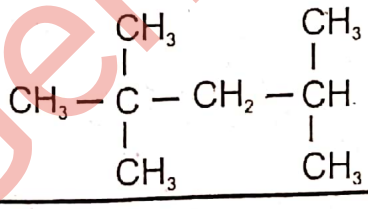
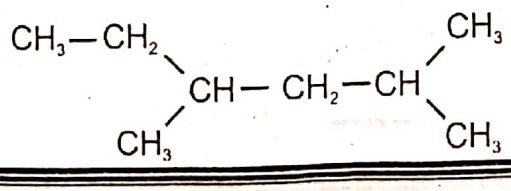
The structural formulae and names for the simple alkanes are shown in the following table.

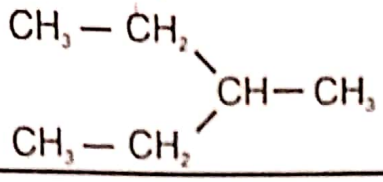
Number of C-atoms	Molecular Formula	Condensed Formula	Line Drawing	Alkane Name
1	CH_4	-	-	methane
2	C_2H_6	CH_3-CH_3		ethane
3	C_3H_8	$CH_3CH_2CH_3$		propane
4	C_4H_{10}	$CH_3(CH_2)_2CH_3$		butane
5	C_5H_{12}	$CH_3(CH_2)_3CH_3$		pentane
6	C_6H_{14}	$CH_3(CH_2)_4CH_3$		hexane
7	C_7H_{16}	$CH_3(CH_2)_5CH_3$		heptane
8	C_8H_{18}	$CH_3(CH_2)_6CH_3$		octane
9	C_9H_{20}	$CH_3(CH_2)_7CH_3$		Nonane
10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$		Decane



Activity

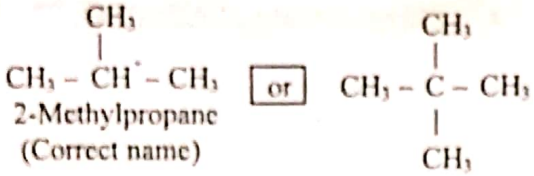
1: Name each of the following compounds according to IUPAC System.

Structure	IUPAC Name
(a) 	2, 5-Dimethylhexane
(b) 	2, 2, 4-Trimethylpentane
(c) 	2, 4-Dimethylhexane

(d) 	3-Methylpentane

2: Indicate what is wrong with each of the following names. Give the correct IUPAC name if possible.

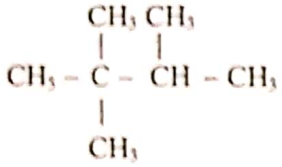
(a) 2-Dimethyl Propane (wrong name)



2, 2-Dimethylpropane (Correct name)

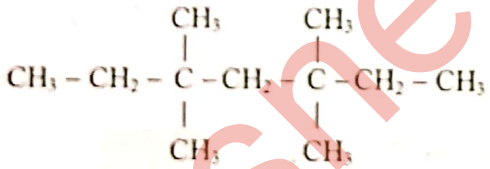
(b) 2,2,3-Methyl Butane (wrong name)

Reason: If there are three alike substituents (methyl), the prefix tri- is used with methyl.



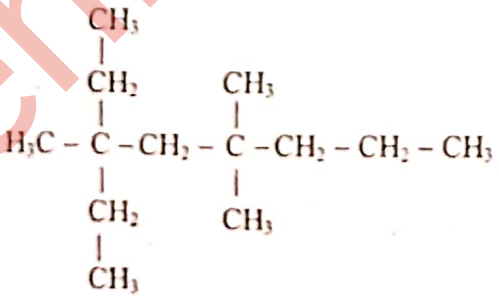
2,2, 3-Trimethylbutane (correct name)

(c) 3,3-Dimethyl-5,5-Dimethyl Heptane (wrong name)



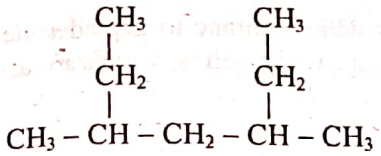
3, 3, 5, 5-Tetramethylheptane (correct name)

(d) 2,2-Diethyl-4,4-Dimethyl Pentane (wrong name)



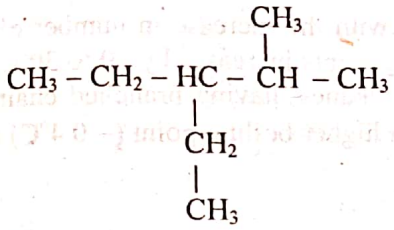
3-Ethyl-3,5,5-trimethyloctane (correct name)

(e) 2,4-Diethyl Pentane (wrong name)



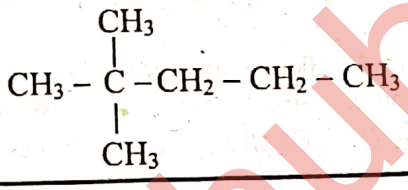
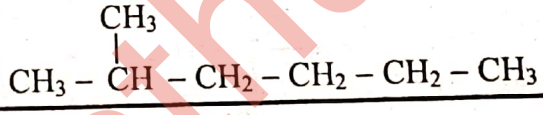
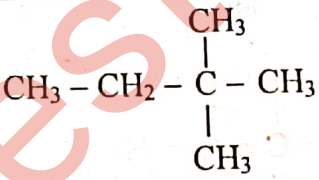
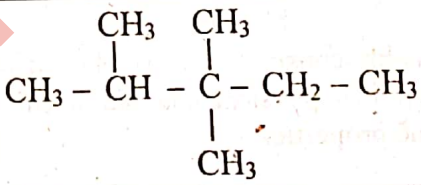
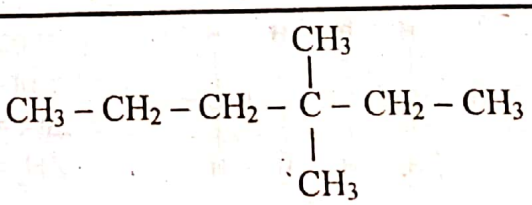
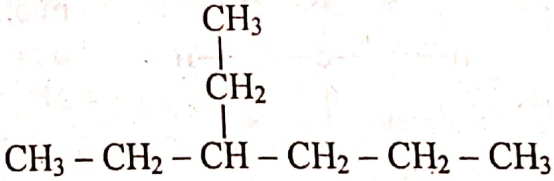
3, 5-Dimethylheptane

(f) 3-Ethyl-4-Methyl Pentane (wrong name)



3-Ethyl-2-methyl pentane (correct name)

3: Write the structures of the following compounds.

Name	Structure
(a) Neo heptane	
(b) Iso-Heptane	
(c) Trimethylethyl Methane	
(d) Dimethyl Ethyl Isopropyl Methane	
(e) Dimethyl Propyl Ethyl Methane	
(f) 3-Ethyl Hexane	

Physical Properties

(a) Physical State:

Methane to butane (C_1 to C_4) are colorless, odorless gases while pentane to heptadecane (C_5 to C_{17}) are colorless, odorless liquids. The higher members from C_{18} onwards are waxy solids, which are also colorless and odorless.

(b) Solubility:

Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, ether, carbon tetrachloride etc.

(c) Melting point & Boiling point:

Their boiling points, melting points, density etc increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in mass. The boiling points increases by 20 to 30°C for addition of each CH_2 group to the molecule. However the boiling points of alkanes, having branched chain structures are lower than their isomeric normal chain alkanes, e.g. n-butane has a higher boiling point (– 0.4°C) than iso-butane (–10.2°C).

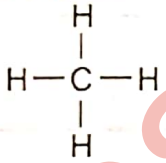
Structure

- Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by single bond.
- They have a generic formula of C_nH_{2n+2} (a relationship that also defines the maximum number of hydrogen atoms that can be present for a given number of C atoms).

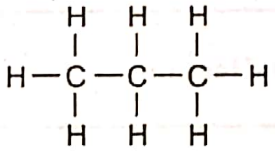
Isomeric Alkanes

- Structures of the simple C_1 to C_4 alkanes are shown below in a variety of representations. As the number of C atoms increases then other isomeric structures are also possible.
- The molecular formula for the C_1 to C_3 alkanes lead to single, unique structures.

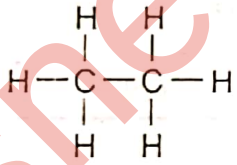
Methane
CH_4
(b.pt. = – 160°C)



Propane
C_3H_8
(b.pt. = –42°C)

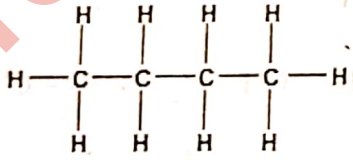


Ethane
C_2H_6
(b.pt. = – 89°C)



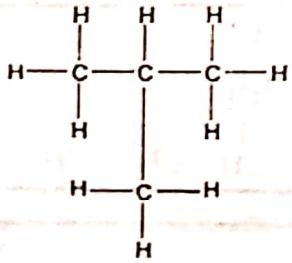
- **Butane, C_4H_{10}** has two possible constitutional isomers. It is important to be able to recognize isomers because they can have different chemical, physical and biological properties. The constitutional isomers of C_4H_{10} are shown below along with some properties:

n-butane



m.pt. = –139°C
b.pt. = –0.4°C
ΔH_f = –125.6 kJ/mol = –30.0 kcal/mol
ΔH_c = –2877 kJ/mol = –687 kcal/mol

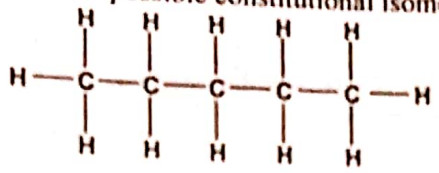
isobutane



m.pt. = –161°C
b.pt. = –10.2°C
ΔH_f = –135.6 kJ/mol = –32.4 kcal/mol
ΔH_c = –2868 kJ/mol = –685 kcal/mol

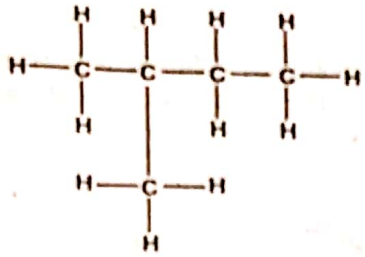
- **Pentane, C_5H_{12}**, has three possible constitutional isomers:

n-pentane



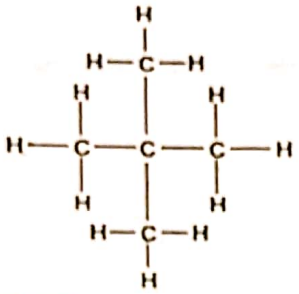
b.pt. = 36.1°C
ΔH_f = –147 kJ/mol = –35.1 kcal/mol
ΔH_c = –3509 kJ/mol = –839 kcal/mol

iso-pentane



b.pt. = 30°C
ΔH_f = –154.1 kJ/mol = –36.8 kcal/mol
ΔH_c = –3502 kJ/mol = –837 kcal/mol

neo-pentane



b.pt. = 9.5°C
ΔH_f = –168.0 kJ/mol = –40.1 kcal/mol
ΔH_c = –3493 kJ/mol = –835 kcal/mol

Relative Stability of Alkanes

Branched alkanes are more stable than linear alkanes, e.g. 2-Methylpropane is more stable than n-butane.

Reactivity

The Alkanes or Paraffins are inert towards acids, alkalies, oxidizing and reducing agents under normal conditions.

Explanation:

The unreactivity of alkanes can be explained on the following basis:

(i) Inertness of σ bond

In a σ bond, the electrons are very tightly held between the nuclei. A lot of energy is required to break it. Moreover, the electrons present in a σ bond can neither attack on any electrophile nor a nucleophile can attack on them. Hence Alkanes are less reactive.

(ii) Non-polar bonds

The electronegativity of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C – H and C – C are equally shared making them almost nonpolar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc find no sites in the alkane molecules to which they could be attached.

However, under suitable conditions, Alkanes give two types of reactions:

(i) Thermal and catalytic reactions

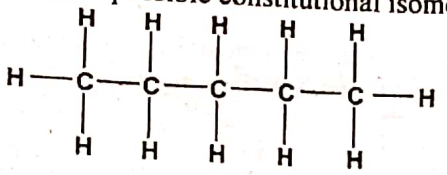
(ii) Substitution Reactions: These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

CYCLOALKANES

Another type of molecules containing only sp^3 hybridized C and H atoms connected by single bonds are possible with a ring of 3 or more C atoms. These are the **cycloalkanes** which are fairly common in the world of organic chemistry both man-made and natural.

- **Pentane, C_5H_{12}**, has three possible constitutional isomers:

n-pentane



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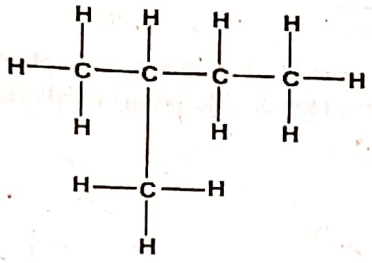
iso-pentane



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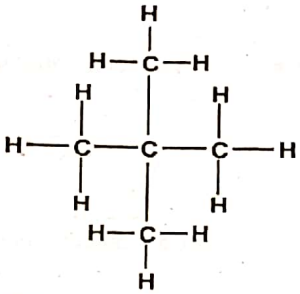
neo-pentane



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CYCLOALKANES

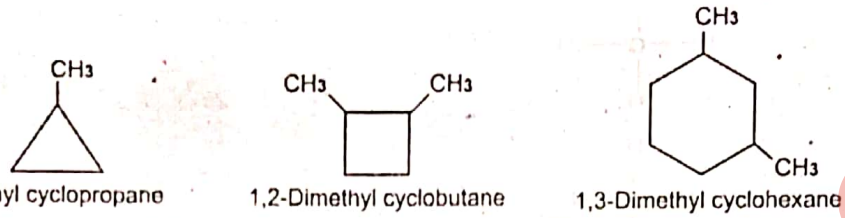
Another type of molecules containing only sp^3 hybridized C and H atoms connected by single bonds are possible with a ring of 3 or more C atoms. These are the **cycloalkanes** which are fairly common in the world of organic chemistry both man-made and natural.

1. Nomenclature

- According to IUPAC system, cycloalkanes with one ring are named by prefixing cyclo to the name of the corresponding alkanes having the same number of carbon atoms as the ring. e.g.

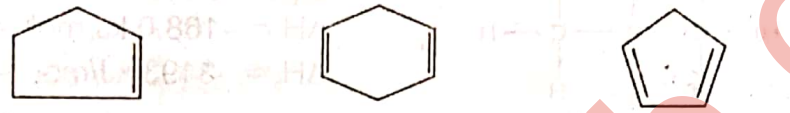
Cyclo propane Cyclo butane Cyclo pentane

- The substituents are numbered in such a way that the sum of numbers is kept minimum. e.g. If the alicyclic hydrocarbon is unsaturated, the rules applied to alkenes (for double bond) or alkynes (for triple bond), are used, e.g,



Methyl cyclopropane 1,2-Dimethyl cyclobutane 1,3-Dimethyl cyclohexane

Multiple bonds are given the lowest possible number.



Cyclo pentene Cyclo 1, 4-hexadiene Cyclo 1, 3-pentadiene

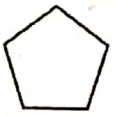
2. Physical Properties

Like alkanes, the low polarity of all the bonds in cycloalkanes means that the only intermolecular forces in cycloalkanes are the very weak induced dipole - induced dipole forces, also known as **London forces** which are easily overcome. Like alkanes, cycloalkanes also have low melting and boiling points.

3. Structure

They have a generic formula of C_nH_{2n}, (note: there are 2 less H atoms compared to the analogous alkane).

The C_3 to C_6 cycloalkanes are shown below in a variety of representations.

Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	

4. Reactivity

Very similar reactivity to the closely related alkanes which have the same type of bonds. Since C and H atoms have very similar electronegativities, both the C – H and C – C bonds are non-polar. As a result, cycloalkanes, like alkanes, are not a very reactive functional group.

QUICK QUIZ

. What are polar, non polar and weakly polar compounds?

Ans. Polar compounds

The compounds containing polar bonds (Bonds in which electronegativity difference between bonded atoms

is more than 0.4) are called polar compounds. e.g. $^{\delta+}H - C\ell^{\delta-}$, $H^{\delta+} - O^{\delta-} - H^{\delta+}$

Non-polar compounds

The compounds having non-polar bonds (Bonds in which electronegativity difference between bonded atoms is less than 0.4) are called non-polar compounds. e.g. Methane (CH_4), benzene (C_6H_6) etc.

Weakly polar compounds

The compounds having weakly polar bonds are called weakly polar compounds. e.g. ethene, ethyne etc.

2. What are isomers?

Ans. "Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism."

- The structural formula of a compound shows the arrangement of atoms and bonds present in it.
- The isomers have different physical properties.

3. What are inert compounds?

Ans. Inert compounds

Those compounds which are least reactive or inert are called inert compounds.

e.g. alkanes, ethers etc.

4. What is sigma bond?

Ans. Sigma bond

A bond which is formed by linear (head to head) overlapping of partially filled orbitals is called sigma (σ) bond.

- It is stable so less reactive.
- First bond between two atoms is always σ-bond.

e.g. $H \overset{\sigma}{-} C\ell$, $H - \underset{H}{\overset{H}{C}} \overset{\sigma}{-} H$ etc.

5. What are intramolecular and intermolecular forces?

Intramolecular forces	Intermolecular forces
• Those forces which are present within the molecules between atoms are called intramolecular forces.	• Those forces which are present between two molecules are called intermolecular forces.
• Nature of substance is determined by intramolecular forces.	• State of a substance (solid, liquid and gas) is determined by intermolecular forces.
Examples: Covalent bond, ionic bond, coordinate covalent bond etc.	**Examples:** van der Waal's forces (dipole-dipole forces, dipole induced dipole forces, London dispersion forces), Hydrogen bonding etc.

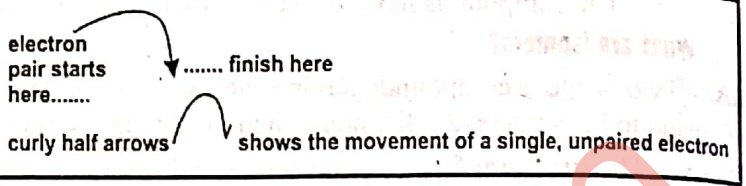
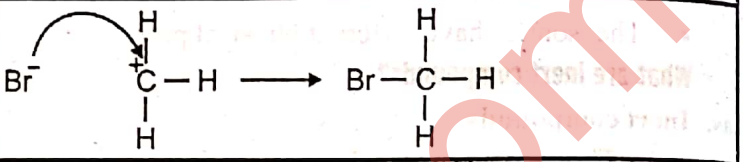
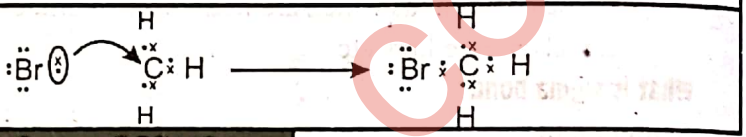
RADICAL SUBSTITUTION REACTIONS (Halogenation of alkanes)

Overview

- Substitution of R-H (alkane) by X provides the alkyl halide, (R-X) and HX.
- Alkane R-H relative reactivity order: 3° > 2° > 1° > methyl.
- Halogen reactivity $F_2 > C\ell_2 > Br_2 > I_2$.
- Only chlorination and bromination are useful in the laboratory.
- Reaction proceeds via a radical chain mechanism

Reaction Mechanism

Interesting information:

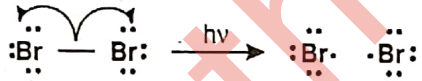
• When reaction mechanisms are being described, a 'curly arrow' is sometimes used to show the movement of a pair of electrons.	
• The beginning of the arrow shows where the electron pair starts from and the arrow head shows where the pair ends up. • A half-arrow is used to show the movement of a single electron in reactions involving free radicals.	
• Figure shows a pair of electrons moving from the Br^- ion to the region between the bromine and the carbon, where it forms a covalent bond between the atoms.	
• The same reaction is shown again below, with all the bonding electrons indicated.	

Free radical Mechanism for the Bromination of Methane

Halogenation (bromination) of alkanes is believed to proceed through free radical mechanism. It involves the following three steps.

Step 1 (Initiation)

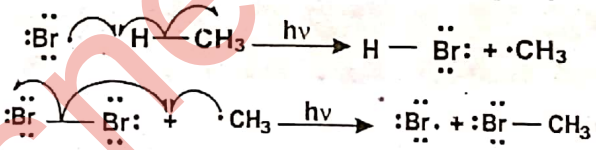
Heat or UV light causes the weak halogen bond to undergo homolytic cleavage to generate two bromine free radicals and starting the chain process.



Step 2 (Propagation)

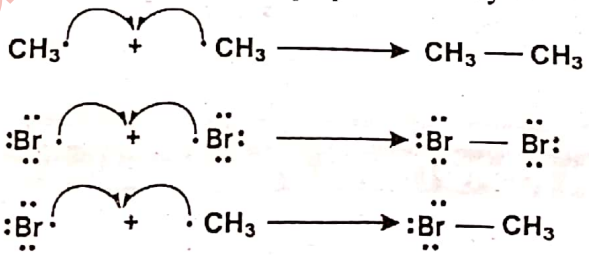
(a) A bromine free radical abstracts a hydrogen atom from methane to form HBr and a methyl radical.

(b) The methyl radical abstracts a bromine atom from another molecule of Br_2 to form the methyl bromide product and another bromine radical, which can then itself undergoes reaction creating a cycle that can repeat.



Step 3 (Termination)

Various reactions between the possible pairs of radicals allow for the formation of ethane, Br_2 or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle.



The mechanism for chlorination of higher alkanes is the same.

OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

Loss of e^- = Oxidation
Gain of e^- = Reduction

Oxidation [O] and reduction [R] are opposite and both must occur simultaneously, hence **redox reactions.**

Organic chemists will normally describe a reaction as either oxidation or reduction depending on the fate of the major organic component.

Oxidation	Reduction
• more C–O bonds (or other atoms more electronegative than C)	• less C–O bonds (or other atoms more electronegative than C)
• less C–H bonds	• more C–H bonds
• loss of electrons	• gain of electrons
• increased oxidation state. e.g. +1 to +3	• decreased oxidation state. e.g. +1 to -1

ALKENES

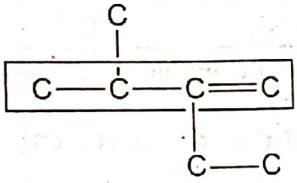
Nomenclature

IUPAC system for naming alkenes is as follow:

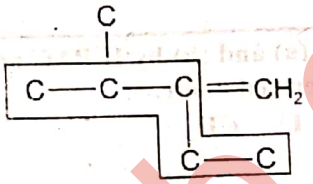
(1) The longest continuous chain containing double bond is selected as parent chain.

(2) The ending 'ane' is replaced by 'ene'.

(3) The chain is numbered in such a manner as to give minimum number to the doubly bonded C-atoms.

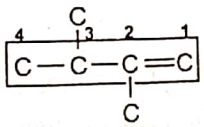


The parent chain containing double bond (correct)

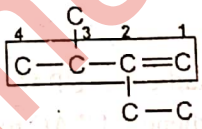


Longest chain with no double bond (incorrect)

(4) The position of double bond is indicated by the lower number of C-atom.



2-ene (incorrect)

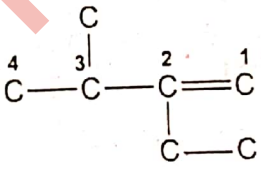


1-ene (correct)

(5) The lower number of C-atom is placed before the name of parent alkene.

(6) The presence of more than one double bonds is indicated by the suffix -diene for two double bonds, -triene for three double bonds and so on.

(7) Alkyl groups are indicated by the methods mentioned in alkane.



2-Ethyl-3-methyl-1-butene (correct)

Activity

1. Name the following Olefins by the IUPAC Systems

No.	Olefin (Alkene)	IUPAC Name
(a)	Ethene	$CH_2 = CH_2$
(b)	Propene	$CH_3 - CH = CH_2$

(c)	3-Hexene	$CH_3 - CH_2 - HC = CH - CH_2 - CH_3$
(d)	Methyl propene	$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2$
(e)	1, 3-Pentadiene	$CH_2 = CH - CH = CH - CH_3$
(f)	1, 2, 3-Hexatriene	$CH_2 = C = C = CH - CH_2 - CH_3$
(g)	2, 3-Dimethyl-2-butene	$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}} = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - CH_3$
(h)	2, 2, 5, 5-Tetramethyl-3-hexene	$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}} - CH = CH - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}} - CH_3$

2. Name the compounds (a) and (b) by IUPAC nomenclature and compounds (c) and (d) by their trivial/commo names and (e) by its derived name.

(a) $CH_2 = C = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - CH_3$

(b) $H_2C = \underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}} - CH = CH_2$

(c) $CH_2 = \underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{\overset{\displaystyle \alpha}{C}}} - CH = CH_2$

(d) $\overset{\alpha}{CH_3} - \overset{\beta}{CH_2} - \overset{\gamma}{CH} = CH - CH_2 - CH_2 - CH_3$

(e) $CH_2 = CH - CH_3$

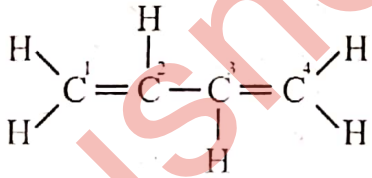
Ans. (a) 3-Methyl-1, 2-butadiene (1UPAC name) (b) 2-Ethyl-1, 3-butadiene (1UPAC name)

(c) 2-Ethyl-1, 3-butadiene (1UPAC name) (d) 3-Heptene (γ-Heptene)

(e) Propene

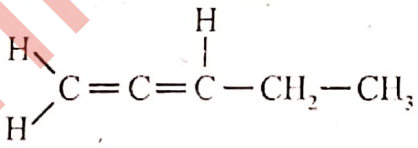
3. Write structural formulas for the following compounds and discuss the geometric isomerism in each case.

(a) 1,3-Butadiene



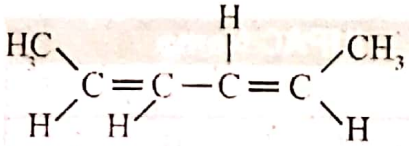
- It does not exhibit geometric isomerism.

(b) 1,2- Pentadiene



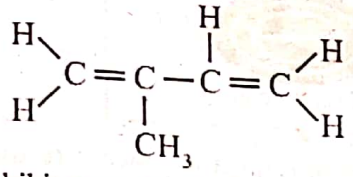
- It does not exhibit geometric isomerism.

(c) 2,4 -Hexadiene



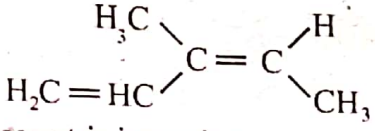
- It shows geometric isomerism.

(d) 2-Methyl-1,3-butadiene



- It does not exhibit geometric isomerism.

(e) 3-Methyl-1,3-pentadiene



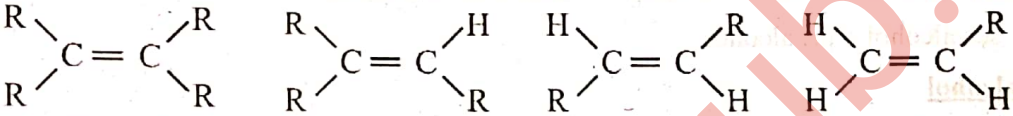
- It will show geometric isomerism.

Relative Stability of Alkenes

There are 3 factors that influence alkene stability:

1. Degree of substitution: More highly alkylated alkenes are more stable, so stability of alkenes decreases in the following order: **tetra > tri > di > mono-substituted**

e.g.



2. Stereochemistry: Trans alkenes are more stable than cis alkenes due to reduced stearic interactions when R groups are on opposite sides of the double bond.

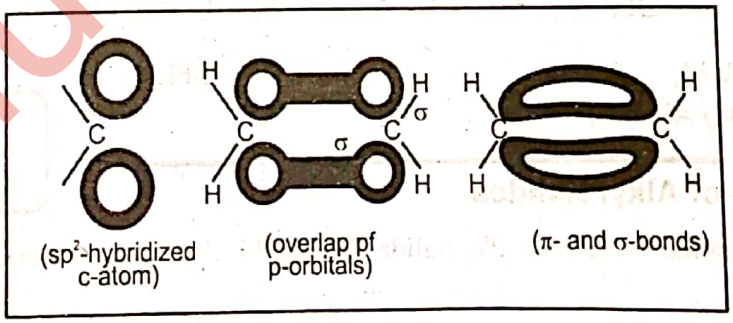
Trans alkene (more stable) Cis alkene (less stable)

3. Conjugated alkenes are more stable than isolated alkenes.

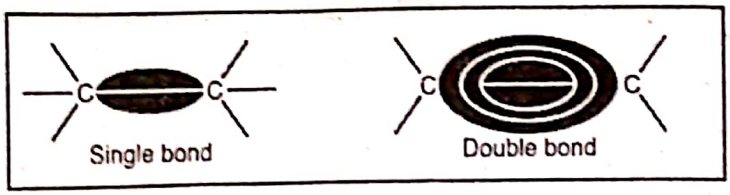
e.g.
- $H_2C = CH - HC = CH - CH_3$ 1, 3-Pentadiene (conjugated and more stable)
- $H_2C = CH - CH_2 - CH = CH_2$ 1, 4-Pentadiene (less stable but more reactive)

Structure of Alkenes

- The carbon atoms linked through π-bond are sp^2 hybridized. Therefore, each C-atom carries three sp^2-hybrid orbitals and one p-orbital. The p-orbitals overlap to form π-bond and hybrid orbitals form σ-bond due to linear overlapping.



- The carbon-carbon distance in ethene is shorter (1.34 Å) than the C – C bond distance of ethane (1.54 Å). It is due to increased electron density between carbon atoms which draws atoms very close to each other.



- Carbon atoms are coplanar, and the rotation of one C-atom with respect to other is restricted due to π electrons. As a result alkenes exhibit cis-trans isomerism.

Preparation of Alkenes

1. Dehydration of Alcohols

Removal of water molecule is called dehydration.

Example:

When vapours of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.

$$\underset{\text{Alcohol}}{R-CH_2-\underset{OH}{\underset{|}{CH_2}}} \xrightarrow[340\text{-}450^\circ C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

P_4O_{10}, H_2SO_4, H_3PO_4 are also used for dehydration. The ease of dehydration of various alcohols is in the order.

Ter.alcohol > sec.alcohol > pri.alcohol

For primary alcohol

$$\underset{\text{Primary Alcohol}}{R-CH_2-\underset{OH}{\underset{|}{CH_2}}} \xrightarrow[140\text{-}170^\circ C]{75\%\ H_2SO_4} R-CH=CH_2 + H_2O$$

For secondary alcohol

$$\underset{\text{Secondary Alcohol}}{R-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3} \xrightarrow[100^\circ C]{60\%\ H_2SO_4} R-CH=CH-CH_3 + H_2O$$

For tertiary alcohol

$$\underset{\text{Tertiary Alcohol}}{R-\underset{CH_3}{\underset{|}{C}}-OH} \xrightarrow[85^\circ C]{20\%\ H_2SO_4} R-\underset{CH_3}{\underset{|}{C}}=CH_2 + H_2O$$

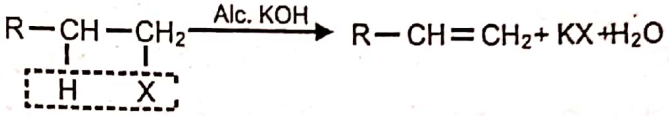
De – Hydro-halogen-action
↓ ↓ ↓ ↓
Removal H X process

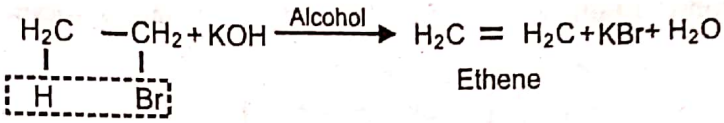
2. Dehydrohalogenation of Alkyl Halides

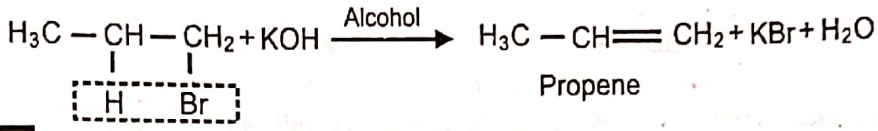
Removal of hydrogen halide (HX) from alky halides is called Dehydrohalogenation"

Example:

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation to form alkenes.







Reactivity of Alkenes

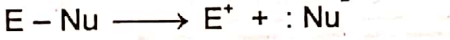
There is a relatively diffuse region of high electron density in alkenes as compared to alkanes. This is due to π-bonds in alkenes. Since in alkenes, π-bond is weaker than σ-bond, it requires less energy to break a π-bond. Hence the reactions of alkenes involve weaker π-bond and electrophilic addition occurs. It involves the change of a π-bond to sigma bond through addition reactions.

Reactions of Alkenes

Mechanism of Electrophilic Addition Reactions of Alkenes

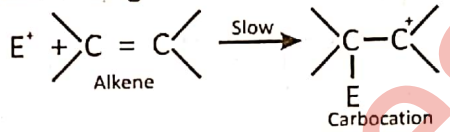
It involves the following steps:

The reagent E – Nu ionizes to give an electrophile and nucleophile.



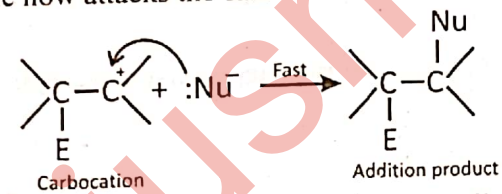
Step 1:

The electrophile attacks the carbon – carbon double bond and forms a covalent bond with one carbon and other carbon bears positive charge. As a result a carbocation is formed.



Step 2:

The nucleophile now attacks the carbocation to form an addition product.



Since the reaction is initiated by addition of electrophile, so it is called electrophilic addition reaction.

(1) Hydrogenation

A process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5atm) to give a saturated compound is known as catalytic hydrogenation.

Explanation:

It is a highly exothermic process and the amount of heat evolved when one mole of an alkene is hydrogenated is called **Heat of Hydrogenation**. The heat of hydrogenation of most alkene is about 120kJ $mole^{-1}$ for each double bond present in a molecule. The catalysts employed are Pt, Pd and Raney Nickel.

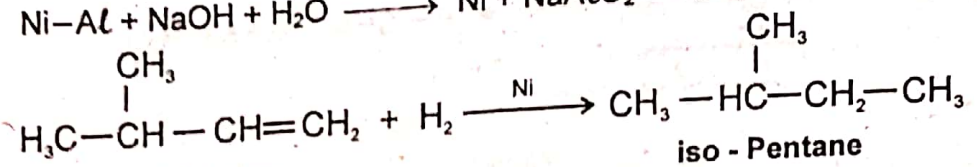
Raney Nickel:

Raney nickel is a spongy form of nickel. It has porous surface.

Preparation:

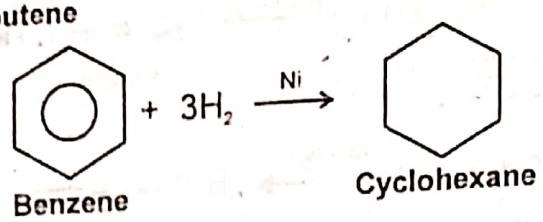
It is prepared by treating a Ni – Aℓ alloy with caustic soda.

$$Ni\text{–}A\ell + NaOH + H_2O \longrightarrow Ni + NaA\ell O_2 + 3/2H_2$$



3-Methyl-1-butene

iso - Pentane



Benzene

Cyclohexane

Applications:

Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry.

- In industry, it is used for the manufacture of vegetable ghee from vegetable oils.
- In the laboratory, it is used as a synthetic method as well as an analytical tool as the reaction is generally quantitative.

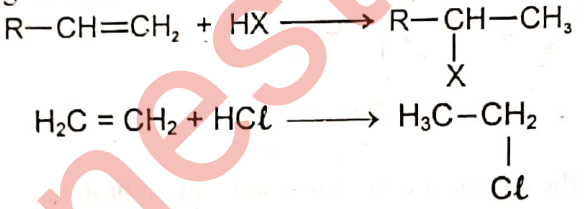
SHORT QUESTIONS

- Define catalytic hydrogenation & heat of hydrogenation.
- What is Raney nickel? How it is produced?
- Write down applications of hydrogenation.
- State Markownikov's Rule. Give suitable example.

(2) Hydrohalogenation

Alkenes react with aqueous solution of halogen acid to form alkyl halides.

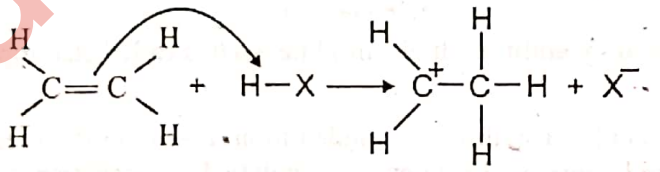
The order of reactivity of halogen acids is HI > HBr > HCℓ



Mechanism

The addition of a hydrogen halide to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation.

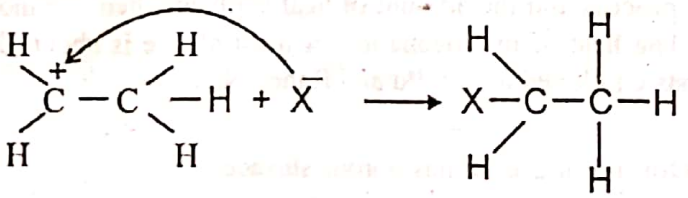
(i) Formation of carbocation



(Carbocation)

(ii) Attack of nucleophile

The carbocation then reacts with the halide ion.

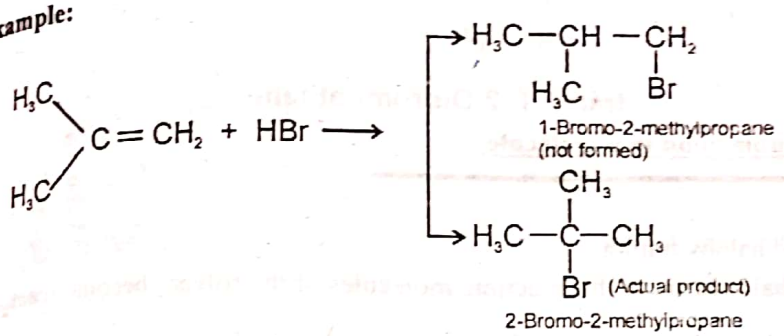


Markownikov's Rule

The addition of hydrogen halide over an unsymmetrical alkene is according to Markownikov's Rule. It states that

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms".

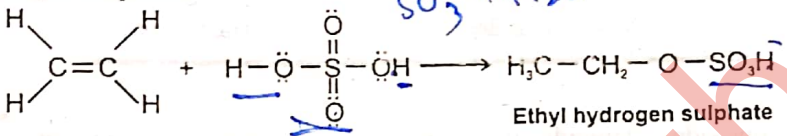
Example:



MCQ: Which of the following product is obtained when propene is treated with HBr in the presence of peroxide.
(a) 1-Bromopropane (b) 2-Bromopropane
(c) 1-Bromopropene (d) 1,2-Dibromopropane
HINT:
Kharasch method (anti Markownikov's rule)

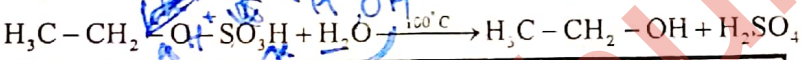
(3) Hydration

Addition of water is called hydration. Some reactive alkenes react with water in the presence of suitable substances as acid etc. to form alcohol. It is possible as alkenes are soluble in cold concentrated sulphuric acid. They react by addition to form alkyl hydrogen sulphate.



Ethyl hydrogen sulphate

The alkyl hydrogen sulphate on boiling with water decomposes to give corresponding alcohol.

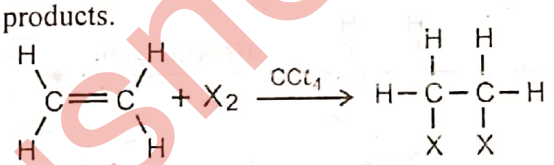


SHORT QUESTIONS

Q. How would you convert:
(i) ethene to ethyl alcohol.
(ii) propene to propyl alcohol.

(4) Halogenation

The alkenes react with halogen in an inert solvent like carbon tetrachloride (CCl_4) at room temperature to give vicinal dihalides or 1,2 dihalogenated products.

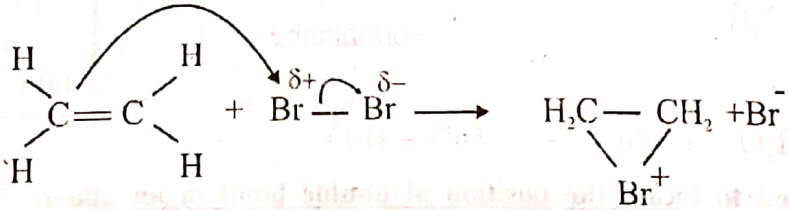


Vicinal dihalide

- Br_2 and Cl_2 are effective electrophilic reagents.
- Fluorine is too reactive to control the reaction..
- Iodine does not react.

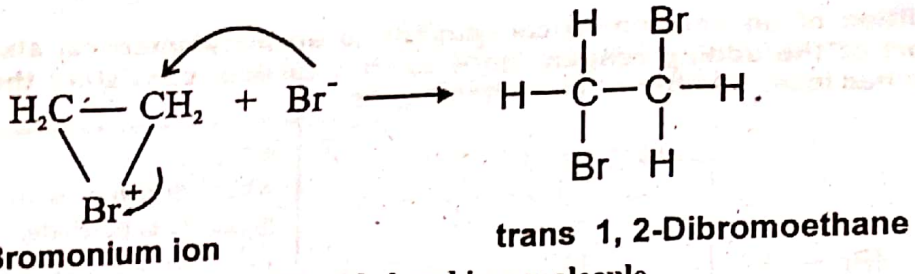
Mechanism:

(a) A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.



Bromonium ion

(b) The nucleophilic bromide ion then attacks on the carbon of the bromonium ions to form vicinal dibromide and the color of bromine is discharged.



Bromonium ion

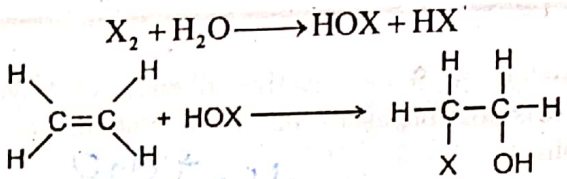
trans 1, 2-Dibromoethane

This test is applied for the detection of double bond in a molecule.

(5) Halohydration

Addition of hypohalous acid (HOX) is called halohydration.

Alkenes react with hypohalous acid to give halohydrin. In this reaction, molecules of the solvent become reactants too.

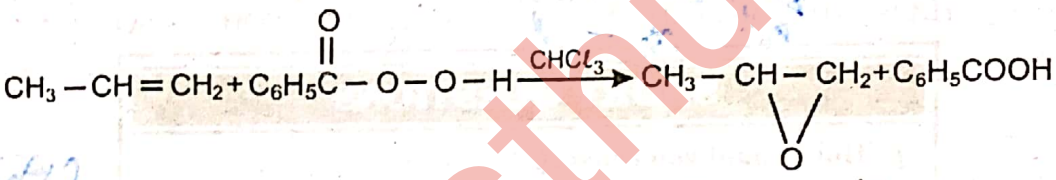


$X_2 = Cl_2$ or Br_2

Halohydrin

(6) Epoxidation

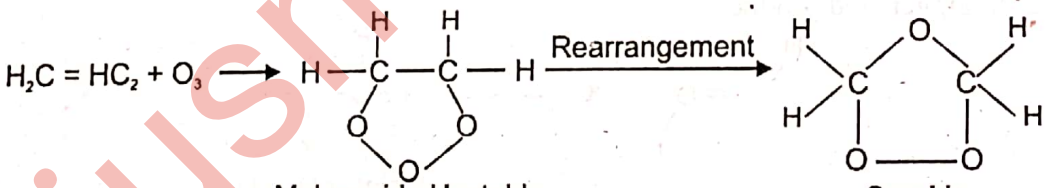
It is the formation of epoxides. Peracids such as per oxyacetic acid or peroxy benzoic acid react with alkenes to form epoxides.



(Epoxy propane)

(7) Ozonolysis

Ozone (O_3) reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.

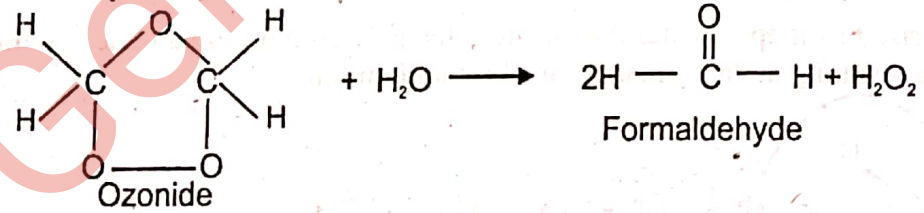


Molozonide Unstable

Ozonide

Reduction of Ozonide

Ozonides are unstable compounds and are reduced directly on treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones).



Ozonide

Formaldehyde

$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Ozonolysis is used to locate the position of double bond in an alkene. The C-atom of double bond changed to carbonyl group.

MCQ's

What will be the position of double bond when in alkene acetaldehyde and propanone are formed on ozonolysis?

(a) C_1 (b) C_2 (c) C_3 (d) C_4

MCQ'S

Q. Which carbonyl compounds are formed by the ozonolysis of:

(i) Ethane (ii) Propene (iii) 2-Butene (iv) 1-Butene

(8) Polymerization

The process in which small organic molecules (monomers) combine together to form a larger molecule (polymer) is called polymerization.

Example: Ethene polymerizes to polythene at 400°C at a pressure of 100 atm.

$$n\ CH_2 = CH_2 \xrightarrow[\text{100 atm pressure}\ \text{traces of } O_2\ (0.1\%)]{400^\circ C} \left[CH_2 - CH_2\right]_n$$

Polyethylene

A good quality polythene is obtained when ethene is polymerized in the presence of aluminium triethyl $Al(C_2H_5)_3$ and titanium tetrachloride ($TiCl_4$).

Interesting Information

Examples of natural and synthetic polymers

	Polymer	Monomer	Where you found it
Natural	Protein	Amino acids	Wool, silk, muscle etc
	Starch	α-D Glucose	Potato, wheat, barley, rice, maize etc
	Cellulose	β-D Glucose	Paper, wood, dietary fibre etc.
	DNA	Nucleotides	Genes, chromosomes etc.
Synthetic	Polythene	Ethene	Bags, washing-up bowls, etc
	Polychloroethene (PVC)	Chloroethene (vinyl chloride)	Fabric coatings, electrical insulation, toys etc.
	Poly (phenylethene) (polystyrene)	Phenylethene (styrene)	food containers, cosmetic bottles, toys, packing materials, etc.
	Polyester	Ethane-2-diol and benzene-1,2-dicarboxylic acid	Skirts, shirts, trousers, water tank etc.

Conjugation

The word "**conjugation**" is derived from a Latin word that means "to link together". In organic chemistry, it is used to describe the situation that occurs when p systems are "linked together".

- An "**isolated**" p system exists only between a single pair of adjacent atoms (e.g. **C = C**)
- An "**extended**" p system exists over a longer series of atoms (e.g. **C = C – C = C** or **C = C – C = O** etc.
- An extended p system results in an extension of the chemical reactivity.

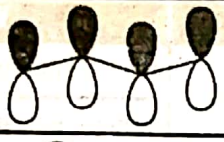
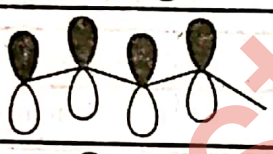
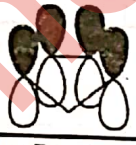
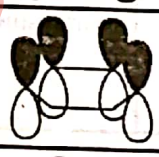
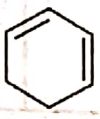
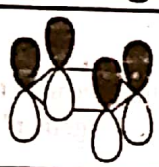
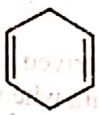
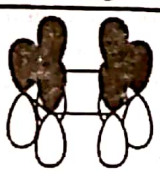
Requirements for Conjugation

The fundamental requirement for the existence of a conjugated system is revealed if one considers the orbital involved in the bonding within the system:

- A conjugated system requires that there is a continuous array of "p" orbitals that can align to produce a bonding overlap along the whole system.
- If a position in the chain does not provide a "p" orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point.

Examples:

We can investigate these differences by studying the following examples, pay particular attention to the "p" orbitals:

System	p system	Structural formula	Type
Ethene		$H_2C = CH_2$	isolated
Propene		$CH_3 - HC = CH_2$	isolated
1,2-Propadiene (allene)		$H_2C = C = CH_2$	cumulated
1,3-Butadiene		$H_2C = CH - HC = CH_2$	conjugated
1,3-Pentadiene		$H_2C = CH - HC = CH - CH_3$	conjugated
1,4-Pentadiene		$H_2C = CH - H_2C - HC = CH_2$	isolated
1,3-Cyclopentadiene			conjugated
1,3-Cyclohexadiene			conjugated
1,4-Cyclohexadiene			isolated
Benzene			conjugated

Stability of System

The result of conjugation is that there is extra p bonding interactions between the adjacent p systems that results in an overall stabilization of the system.

QUICK QUIZ

1. What is conjugation?

Ans. The word "conjugation" is derived from a Latin word that means "to link together". In organic chemistry terms, it is used to describe the situation that occurs when π systems (double bonds) are "linked together".

2. What are conjugated alkenes?

Ans. Those alkenes which have a continuous array of p-orbitals that can align to produce a bonding overlap along the whole system are called conjugated alkenes.

e.g. 1, 3-Butadiene $H_2C = CH - HC = CH - CH_3$

3. What is pi bond?

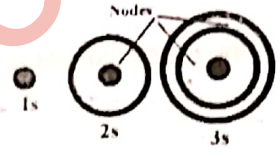
Ans. A bond which is formed by parallel or side to side overlap of atomic orbitals is called pi (π) bond.

- Electronic charge density is present above and below bond axis of two nuclei.
- Charge density of π bond is more diffused due to lesser nuclear attraction.
- π-bond is comparatively reactive.
- e.g. $H_2C = CH_2$

4. What are s and p orbitals?

Ans. **s-Orbitals**

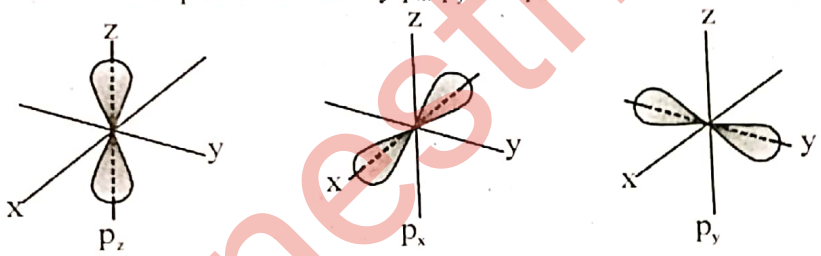
s-orbital has a spherical shape and is usually represented by a circle, which in turn, represents a cut of sphere. The probability for finding the electron is zero between two orbitals. This place is called **nodal plane or nodal surface.**



Shapes of s-orbitals with increasing principal quantum number

p-Orbitals

p-subshell has three values of magnetic quantum number. So p-subshell has three orientations in space i.e., along x, y and z axes. All the three p-orbitals namely p_x, p_y and p_z have dumb-bell shapes.



Shapes of p-orbitals

5. What is dehydration?

Ans. The removal of water from a substance is called dehydration. Usually $A\ell_2O_3$, P_4O_{10}, H_2SO_4, H_3PO_4 are used for dehydration.

$$\underset{\text{Alcohol}}{R-CH_2-\underset{OH}{\underset{|}{CH_2}}} \xrightarrow[340\text{-}450^\circ C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

6. What is dehydrohalogenation?

Ans. Removal of hydrogen halide (HX) from alky halides is called dehydrohalogenation"

Example:

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation to form alkenes.

$$H_3C-CH_2-CH_2-Br + KOH \xrightarrow{\text{Alcohol}} H_3C-CH=CH_2 + KBr + H_2O$$

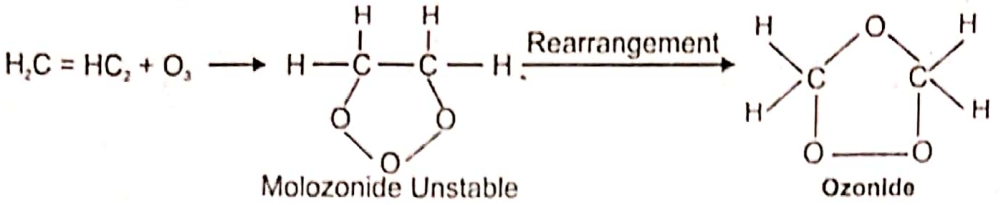
7. What is hydrogenation?

Ans. Addition of hydrogen (H_2) to an unsaturated substance is called hydrogenation. During this process cleavage of π bond occurs. Catalytic hydrogenation involves Ni, Pt or Pd as catalysts.

$$CH_2 = CH_2 + H_2 \xrightarrow[200-300\ ^\circ C]{Ni} CH_3 - CH_3$$

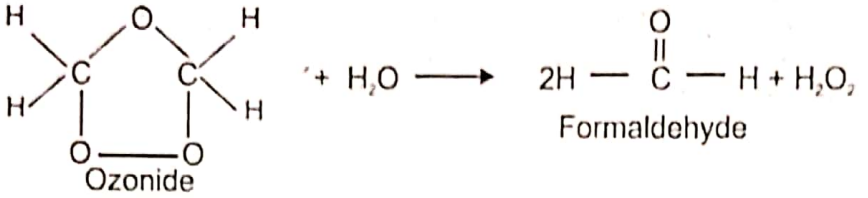
8. What is ozonolysis?

Ans. Ozonolysis is a method of oxidatively cleaving alkenes or alkynes using ozone (O_3), a reactive allotrope of oxygen. The process allows for carbon-carbon double or triple bonds to be replaced by double bonds with oxygen. This reaction is often used to identify the structure of unknown alkenes, by breaking them down into respective carbonyl compounds. e.g.



Molozonide Unstable

Ozonide



Ozonide

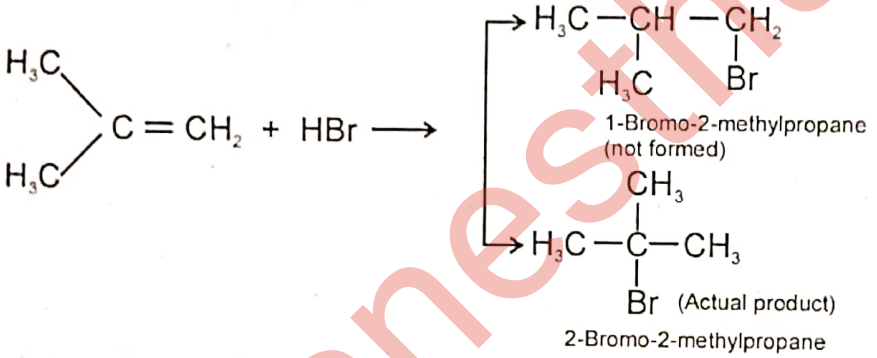
Formaldehyde

9. What is Markownikov's rule?

Ans. Markownikov's Rule

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms."

Example:



2-Bromo-2-methylpropane

10. What is electrophilic reagents?

Ans. Electrophilic Reagent:

- Positively charged ions (cations) are electrophiles. e.g. H^+, $C\ell^+$, Br^+, NH_4^+ etc.
- Neutral molecules in which central atom is electron deficient. e.g. BH_3, BF_3, $BeC\ell_2$, $A\ell C\ell_3$, $ZnC\ell_2$, $FeC\ell_3$ etc.
- Lewis acids are usually electrophiles.
- Neutral molecules in which central atom contains partial positive charge act as electrophiles. e.g. SO_3, $PC\ell_5$, CO_2 etc.

11. What is nucleophilic reagents?

Ans. Nucleophilic Reagent:

- Negatively charged ions (anions) are nucleophiles. e.g. H^-, $C\ell^-$, Br^-, SO_4^{-2} etc.
- Neutral molecules in which central atom have lone pairs of electrons. e.g. $PC\ell_3$, PH_3, SO_2, NH_3, H_2O etc.
- Lewis bases are usually nucleophiles.
- The molecules which contain pi electrons in their structures act as nucleophiles. e.g. ethene, benzene etc.

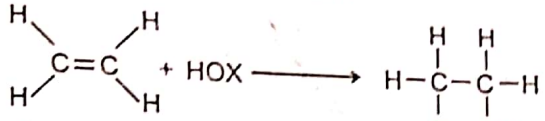
12. What is halohydration?

Ans. Halohydration

Addition of hypohalous acid (HOX) is called halohydration.

Alkenes react with hypohalous acid to give halohydrin. In this reaction, molecules of the solvent become reactant too.

$$X_2 + H_2O \longrightarrow HOX + HX$$



$X_2 = C\ell_2$ or Br_2

Halohydrin

13. What is polymerization?

Ans. Polymerization

The process in which small organic molecules (monomers) combine together to form a larger molecule (polymer) is called polymerization.

Example: Ethene polymerizes to polythene at 400°C at a pressure of 100 atm.

$$n\ CH_2 = CH_2 \xrightarrow[\text{100 atm pressure}\ \text{traces of } O_2\ (0.1\%)]{400^\circ C} +CH_2-CH_2+_n$$

Polyethylene

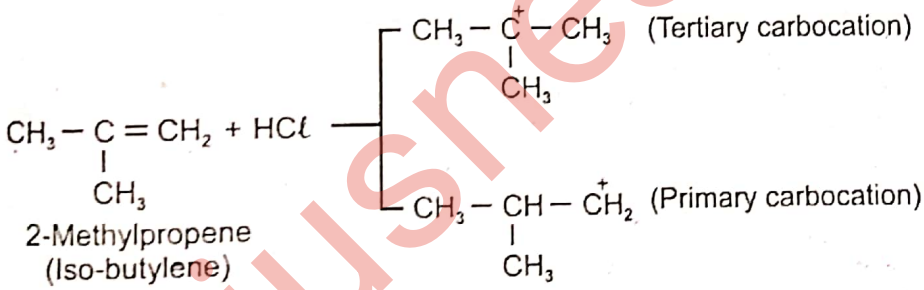
14. When 2-Methyl propene reacts with HCℓ:

What are the structures of the two possible intermediate carbocations?

(i) Which of the two Ions is the more stable?

(ii) What will be the major product of the reaction between 2-Methyl propene and HCℓ?

Ans. In the addition of HCℓ to 2-Methylpropene, two intermediate carbocations are formed as follow:



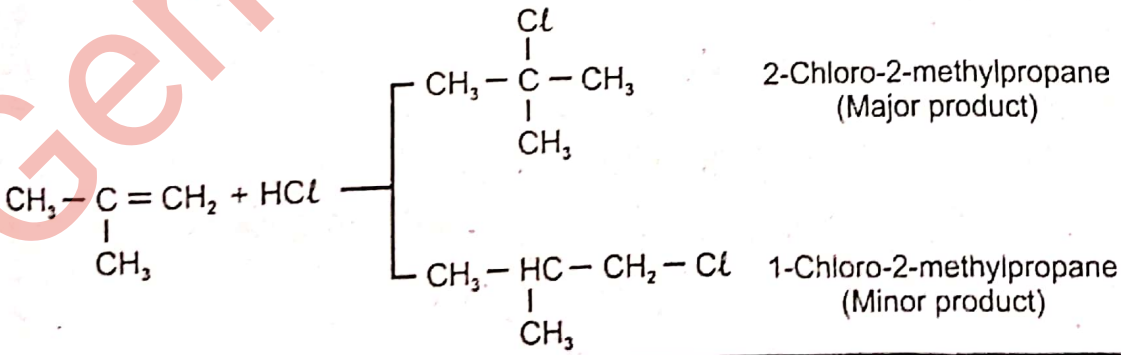
2-Methylpropene
(Iso-butylene)

(Tertiary carbocation)

(Primary carbocation)

(i) Tertiary carbocation is more stable than primary carbocation, as it has nine (9) hyperconjugation structures.

(ii)



2-Chloro-2-methylpropane
(Major product)

1-Chloro-2-methylpropane
(Minor product)

Exercise: Q.3(1) What is isomerism? Explain different types of isomerism?

ISOMERISM

"Compounds that have the same molecular formula but different chemical structures are called isomers and the phenomenon is called isomerism."

Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule.

Types of Isomerism

There are two main types of isomerism:

(A) Structural Isomerism (B) Stereoisomerism

(A) Structural Isomerism

"When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called Structural Isomerism".

- In other words, structural isomers are compounds that have the same molecular formula but different structural formulas.

Structural isomerism is of following five types:

(1) Chain Isomerism

Chain isomers have the same molecular formula but differ in order in which the carbon atoms are bonded to each other.

Example:

C_5H_{12}:

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
(n-pentane)

$CH_3 - CH(CH_3) - CH_2 - CH_3$
2-Methylbutane (Iso-pentane)

$CH_3 - C(CH_3)_2 - CH_3$
2, 2-Dimethylpropane (Neo-pentane)

(2) Position Isomerism

Position isomers have the same molecular formula but different in the position of the same functional group on the carbon chain.

Examples:

(i) C_3H_7Cl:

$CH_3 - CH_2 - CH_2 - Cl$
1 – Chloropropane

$CH_3 - CH(Cl) - CH_3$
2 – Chloropropane

(ii) C_4H_8: $CH_3 - CH_2 - CH = CH_2$
1 – Butene

$CH_3 - CH = CH - CH_3$
2 – Butene

(3) Functional group Isomerism

Functional isomers have the same molecular formula but different functional groups.

Examples:

(i) C_2H_6O: $CH_3 - O - CH_3$
Dimethyl ether

$CH_3 - CH_2 - OH$
Ethyl alcohol

(ii) C_3H_6O:

$CH_3 - CH_2 - C(=O) - H$
Propanaldehyde

$CH_3 - C(=O) - CH_3$
Propanone

Formula	Functional Isomers
(i) C_nH_{2n}	Alkene and cycloalkane
(ii) C_nH_{2n-2}	Alkadiene and alkyne; cycloalkene
(iii) $C_nH_{2n+2}O$	Alcohol, ether
(iv) $C_nH_{2n}O$	Aldehyde, ketone
(v) $C_nH_{2n}O_2$	Acid, ester, hydroxy aldehyde and hydroxy ketone

(4) Metamerism

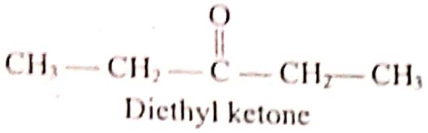
This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group.

- Metamers belong to the same homologous series.
- It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom. i.e., – O –, – S –, – NH –, – CO –.

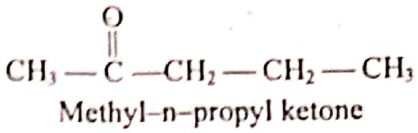
Examples:

(i) $C_4H_{10}O$: $CH_3 - CH_2 - O - CH_2 - CH_3$ Diethyl ether; $CH_3 - O - CH_2 - CH_2 - CH_3$ Methyl–n–propyl ether

(ii) $C_5H_{10}O$:



Diethyl ketone



Methyl–n–propyl ketone

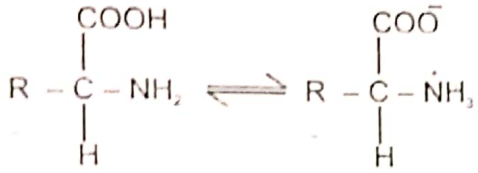
(5) Tautomerism

This type of isomerism arises due to shifting of proton (H^+) from one atom to other in the same molecule.

It involves the shifting of position of proton (H^+). This type of hydrogen atom is known as "mobile" hydrogen.

Examples:

(i)



Amino acid Zwitter ion

(ii)

Keto-Form Enol-Form

(B) Stereoisomerism

"When isomerism is caused by the different arrangements / orientation of atoms or groups in space, the phenomenon is called Stereoisomerism."

- The stereoisomers have the same structural formulas but differ in arrangement of atoms in space.
- In other words stereoisomerism is exhibited by such compounds which have the same structural formula but differ in configuration. (The term configuration refers to the three-dimensional arrangement of atoms that characterizes a particular compound).

Stereoisomerism is of two types:

(1) Optical Isomerism

(2) Geometrical or Cis-Trans Isomerism

Chiral Center

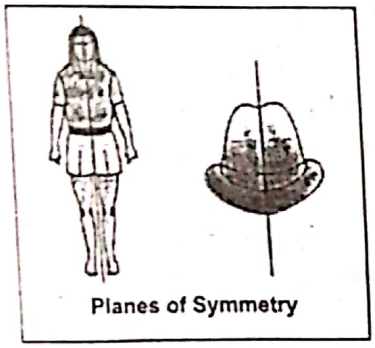
First, we will discuss plane of symmetry which helps us to understand this topic.

Plane of Symmetry

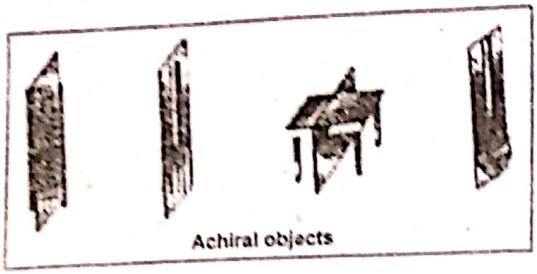
"A plane which divides an object into two symmetrical halves, is said to be plane of symmetry."

- A symmetric object is referred to as Achiral.
- Achiral molecule has at least one asymmetric center and does not have a plane of symmetry.
- An achiral molecule has a plane of symmetry

Example: A person or a hat has a plane of symmetry.



Planes of Symmetry



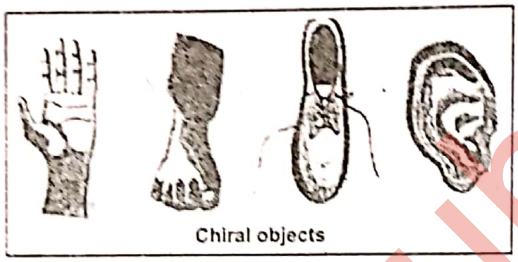
Achiral objects

Dissymmetric or Chiral Object

"An object lacking a plane of symmetry is called dissymmetric or Chiral (pronounced as Ki-ral)."

Examples: A person's hand or gloves lack plane of symmetry.

- A dissymmetric object cannot be superimposed on its mirror image. A left hand for example does not possess a plane of symmetry, and its mirror image is not another left hand but a right hand.
- The two are not identical because they cannot be superimposed if we were to lay one hand on top of the other, the fingers and the thumb would clash.



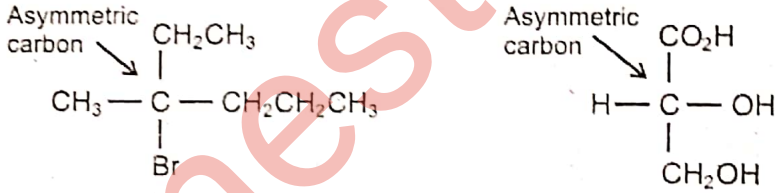
Chiral objects

The mirror image relationship of the left hands. Notice that right hand is the mirror image of the left hand.

Carbon-Based Chiral Centers

"A carbon atom which is bonded to four different groups is called an asymmetric carbon atom."

Examples:



- The term asymmetric carbon atom is rather misleading. It only means that a carbon atom is bonded to four different groups and that a molecule of this type lacks plane of symmetry. Such a molecule is called asymmetric (Latin a = without), that is, without symmetry.
- Presently the term dissymmetric or chiral molecules are often for asymmetric molecules.

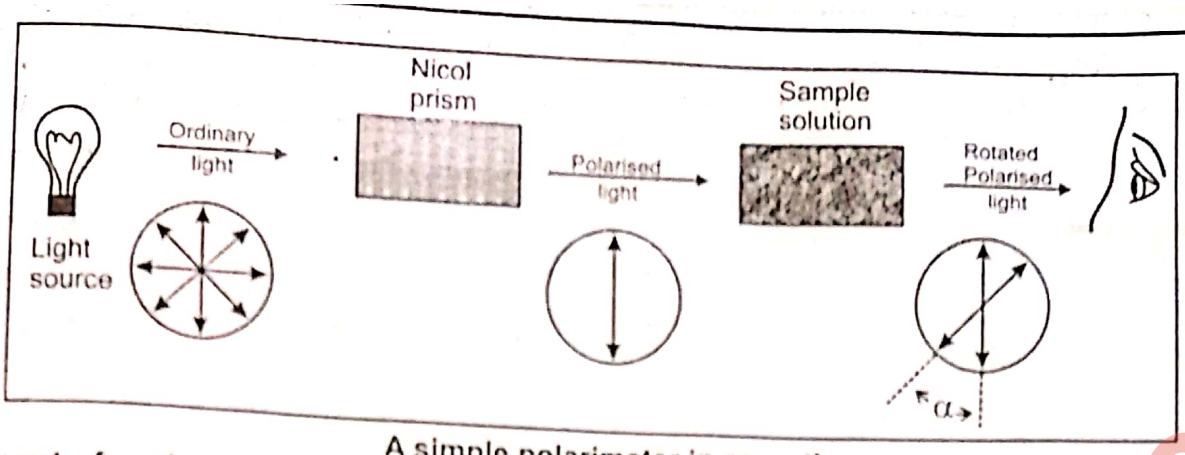
Optical Activity

"The property of a compound to rotate the plane of polarized light is called optical activity"

Explanation:

Light from ordinary electric lamp is composed of waves vibrating in many different planes. When it is passed through Nicol prism (made of calcite, $CaCO_3$) or polaroid lens, light is found to vibrate in only one plane, and is said to be plane-polarized or simply polarized.

The diagrams illustrate the vibrations of ordinary and polarized light from a beam propagated perpendicularly to the plane of paper. Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be Optically Active. This property of a compound is called Optical Activity.



A simple polarimeter in operation

Measurement of optical activity

Optical activity in a compound is detected and measured by means of a Polarimeter. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarized light is rotated through a certain number of degrees, either to the right (clockwise) or to the left (anti-clockwise).

Dextrorotatory: The compound which rotates the plane of polarized light to the right (clockwise) is said to be dextrorotatory. It is indicated by the sign (+).

Laevorotatory: The compound which rotates the plane of polarized light to the left (anticlockwise) is said to laevorotatory. It is indicated by the sign (−).

The magnitude of rotation in degrees is referred to as observed rotation, alpha (α).

(1) Optical isomerism

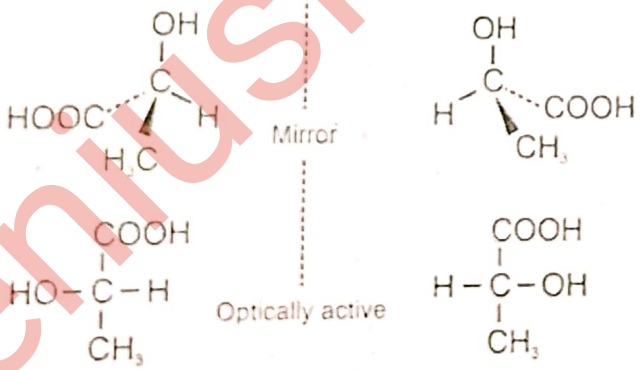
"An optically active compound can exist in two isomeric forms which rotate the plane of polarized light in opposite directions. These are called optical Isomers and the phenomenon is known as optical isomerism."

- The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as **Dextrorotatory Isomer** or (+) isomer.
- The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the **Laevorotatory Isomer** or (−) isomer.

Examples:

(i) Optical Isomerism of Lactic Acid

Lactic acid (2-Hydroxypropanoic acid) shows optical isomerism. It contains one asymmetric carbon atom. Two three dimensional structures are possible for lactic acid.



(+)-Acid
mp = 26°C

(−)-Acid
mp = 26°C

Equimolar mixture of (+) and (−) forms racemic mixture
mp = 18°C

These structures are not identical because they cannot be superimposed on each other.

On the mirror image of the other, such non superimposable mirror image forms are optical isomers and called enantiomers. Thus, three forms of lactic acid are known. Two are optically active and one is optically inactive.

(+) Lactic Acid: It rotates the plane of polarized light to the right (clockwise direction) and is called dextrorotatory.

(–) Lactic Acid: It rotates the plane of polarized light to the left (anticlockwise direction) and is called laevorotatory. It is the mirror image of (+) lactic acid and vice versa.

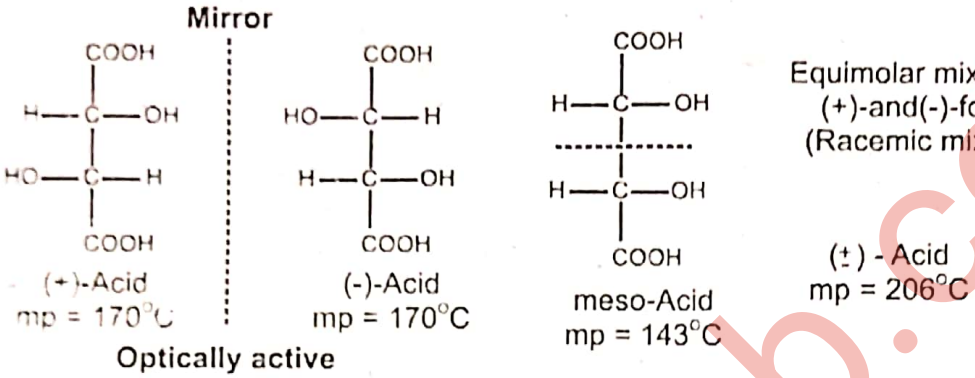
(±) Lactic Acid: It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (–) forms (racemic mixture).

(ii) Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two asymmetric carbon atoms.

Four forms of tartaric acid are known. Two of them are optically active and two are optically inactive. The optically active forms are related to each other as an object to its mirror image. That is, they are enantiomers.

Isomers of Tartaric Acid



Optically active

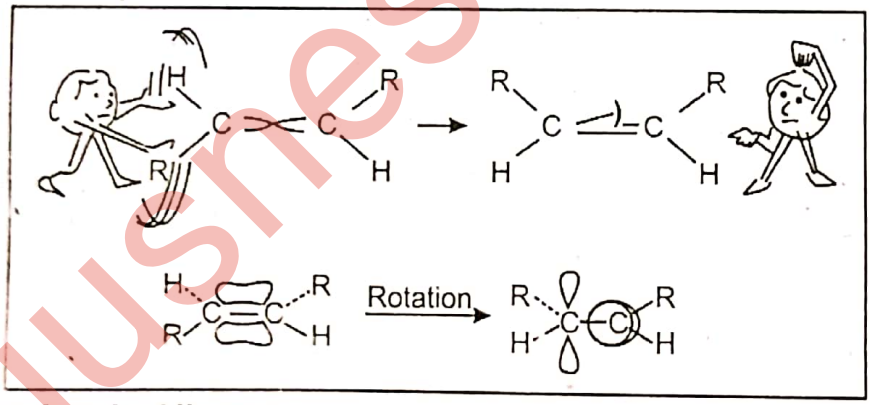
(+)Tartaric Acid: It rotates the plane of polarized light to the right (clockwise direction) and is called dextrorotatory.

(–) Tartaric Acid: It rotates the plane of polarized light to the left (anticlockwise direction) and is called levorotatory.

(±)Tartaric Acid: It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

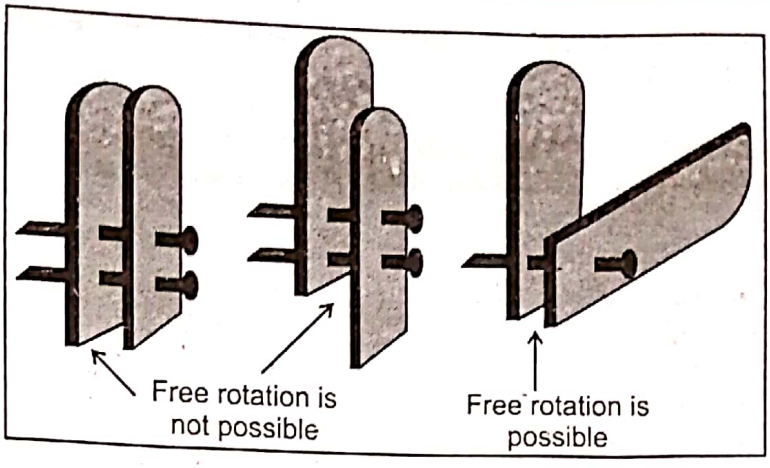
(2) Geometric or Cis-trans Isomerism

Geometrical isomerism (also called cis trans isomerism) results from a restriction in rotation about double bonds, or about single bonds in cyclic compounds.



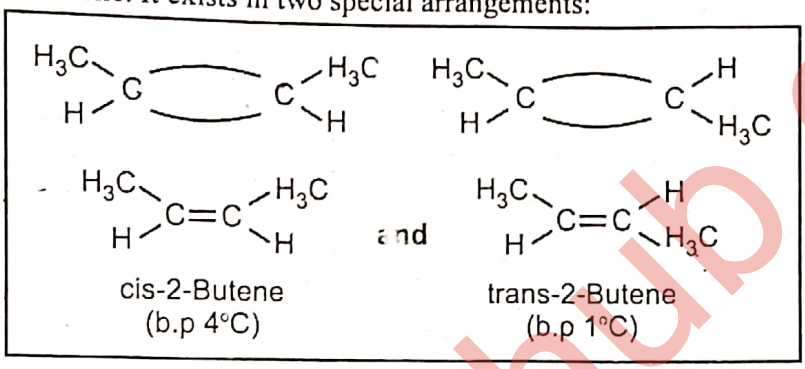
(A) Geometrical Isomerism in Alkenes

- The carbon atoms of the carbon-carbon double bond are sp^2 hybridized.
- The carbon-carbon double bond consists of a sigma bond and a pi bond. The sigma bond is formed by the overlap of sp^2 hybrid orbitals. The pi bond is formed by the overlap of p orbitals.
- The presence of the pi bond locks each molecule in one position.
- The two carbon atoms of the C = C bond and the four atoms that are attached to them lie in one plane and their positions in space are fixed.
- Rotation around the C = C bond is not possible because rotation would break the pi bond.
- This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes.
- A popular analogy for this situation is based upon two boards and two nails. Driving one nail through two boards will not prevent free rotation of the two boards. But once a second nail used, the boards cannot be freely rotated.



Example:

Consider the case of 2-Butene. It exists in two special arrangements:



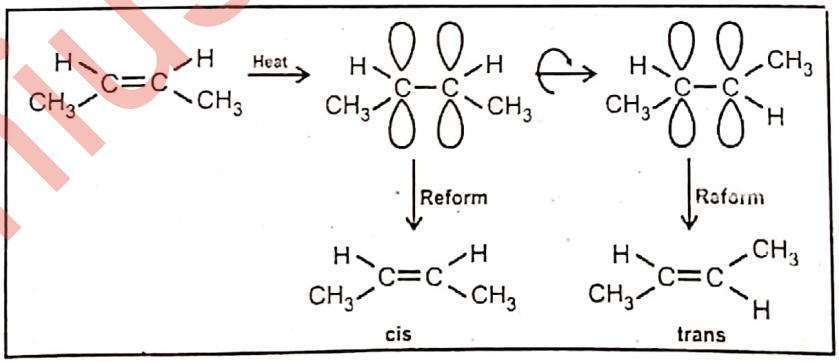
These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms cis and trans.

- **The cis isomer** is one in which two similar groups are on the same side of the double bond.
- **The trans isomer** is that in which two similar groups are on the opposite sides of the double bond.

Consequently, these types of isomers are often called cis-trans isomers. These are stereoisomers because they have the same structural formula but different special arrangement of atoms.

Interconversion of Cis-Trans isomers

The conversion of cis-isomer into trans-isomer or vice versa is possible only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62 Kcal/mole) to break the pi (π) bond so that rotation about sigma bond becomes possible. Upon cooling, the reformation of the pi bond can take place in two ways giving mixture of trans-2-Butene and cis-2-Butene.



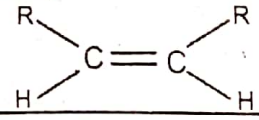
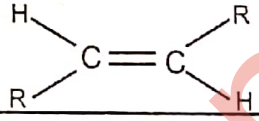
Stability of geometric Isomers

The trans isomers are more stable than the corresponding cis isomers. This is because, in cis isomers, the bulky groups are on the same side of the double bond. The stearic repulsion of groups makes the cis isomers less stable than the trans isomer in which the bulky groups are far (they are on the opposite sides of the double bond).

The geometrical isomers have different physical and chemical properties. They can be separated by conventional physical techniques like fractional distillation, gas chromatography etc.

Q. Differentiate between cis and trans isomers.

Ans.

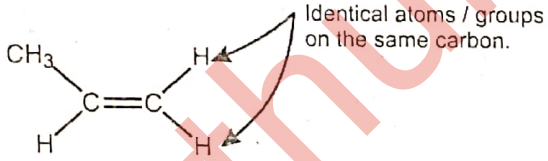
Cis - isomer	Trans - isomer
1. The geometric isomer in which the two bulky group are present on the same side of the double bond is called cis isomer.	1. The geometric isomer in which the two bulky groups are present on the opposite side of the double bond is called trans isomer.
2. Cis isomer is given by 	2. Trans isomer is given by 
3. Generally cis form of a compound is unstable due to stearic repulsion of bulky groups.	3. The trans form of a compound is stable due to opposite presence of bulky groups.

Conditions for geometric isomerism

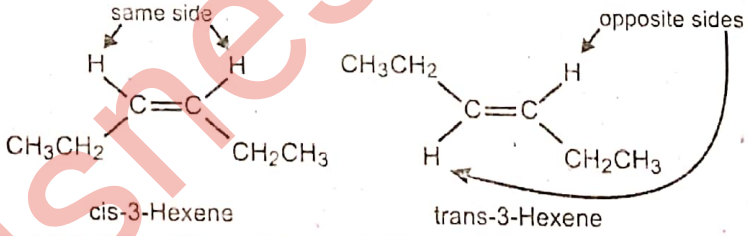
All alkenes do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded carbon atom is attached to two different atoms or groups.

Examples:

(i) **Propene ($CH_3CH = CH_2$):** No geometrical isomers are possible for propene. This is because one of double bonded carbons has two identical groups (H atoms) attached to it.



(ii) **3-Hexene ($CH_3CH_2CH = CHCH_2CH_3$):** It shows cis trans isomerism. This is because each double bonded carbon atom is attached to two different groups (CH_3CH_2 and H). The cis and trans isomers of 3-hexene are shown below:



cis-3-Hexene trans-3-Hexene

(iii) **Butenedioic acid ($HOOC - CH = CH - COOH$):** Geometrical isomers are possible because each double bonded carbon atom has two different groups attached to it (H and COOH).

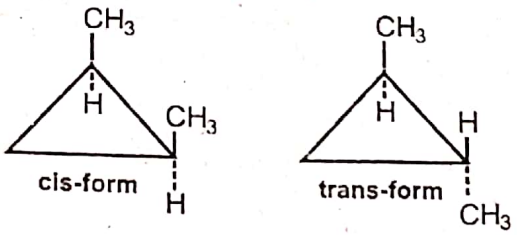
trans-butenedioic acid
(Fumaric acid)
m.p 130°C

cis - butenedioic acid
(Maleic acid)
m.p 288°C

(B) Geometrical Isomerism in Cyclic Compounds

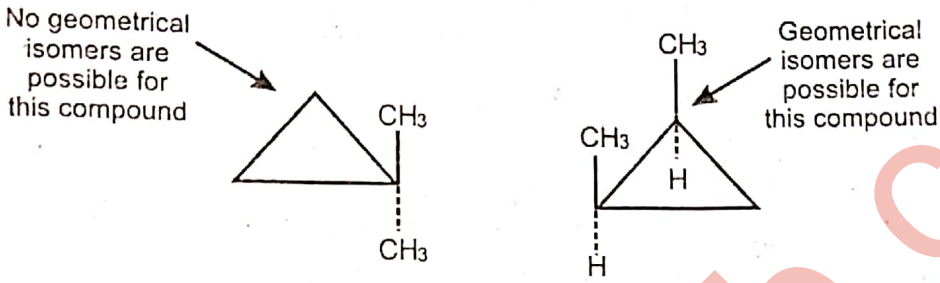
Geometrical isomerism is also possible in cyclic compounds. There can be no rotation about carbon-carbon single bond forming a ring because rotation would break the bonds and break ring. A requirement for geometrical isomerism in cyclic compounds is that there must be at least two other groups beside hydrogen on the ring and these must be on different ring carbon atoms.

Example: 1,2-dimethylcyclopropane exists in two isomeric forms.



- In cis-1,2-dimethylcyclopropane, the two methyl groups are on the same side of ring.
- In trans 1, 2-dimethylcyclopropane, they are on opposite sides.

Note: No geometrical isomers are possible for 1,1-dimethylcyclopropane.



QUICK QUIZ

1. Define or explain the following terms:
(a) Structural isomerism (b) Stereoisomerisms (c) Geometrical isomerism (d) Optical isomerism
(e) Asymmetric carbon (f) Chiral molecule

Ans. (a) **Structural isomerism**

When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called Structural Isomerism.

(b) **Stereoisomerisms**

When isomerism is caused by the different arrangements / orientation of atoms or groups in space, the phenomenon is called Stereoisomerism.

(c) **Geometrical isomerism**

Those compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as cis-trans or geometric isomerism.

(d) **Optical isomerism**

An optically active compound can exist in two isomeric forms which rotate the plane of polarized light in opposite directions. These are called optical isomers and the phenomenon is known as optical isomerism.

(e) **Asymmetric carbon**

A carbon atom which is bonded to four different groups is called asymmetric carbon atom.

(f) **Chiral molecule**

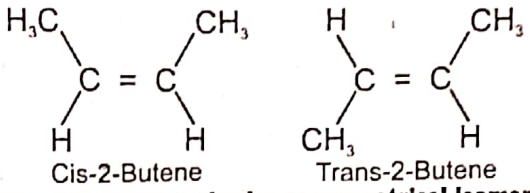
A chiral molecule is a molecule that is not superimposable on its mirror image.

2. State the necessary condition for a compound to show geometrical isomerism. Illustrate your answer with examples.

Ans. The necessary and sufficient condition for a compound to exhibit geometric isomerism is that the two groups attached to the each double bonded carbon must be different.

Example:

C_4H_8:

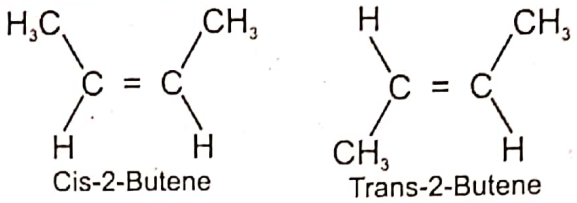


3. Which of the following compounds shows geometrical isomerism?

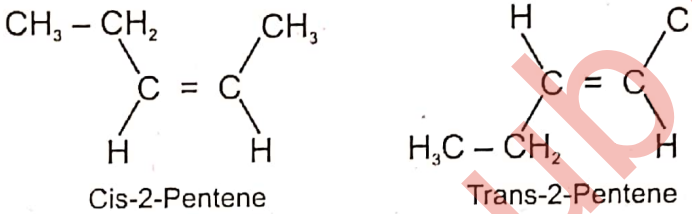
(a) 2-Butene (b) 2-Methylbutene (c) 2-Pentene (d) 1,2-Dichloropropane

Ans. • **Following compounds show geometrical isomerism:**

2-Butene:

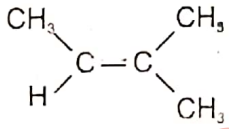


2-Pentene:

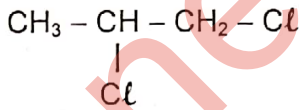


• **Following compounds do not show geometrical isomerism:**

2-Methylbutene:



1,2-Dichloropropane:



4. Which of the following compounds show geometrical isomerism:

(a) $CH_3 - CH = CH_2$

(b) $CH_3CH_2CH_2CH = CHCH_3$

Ans. 2-Hexene ($CH_3CH_2CH_2CH = CHCH_3$) exhibits geometrical isomerism because groups attached to doubly bonded carbon atom are different. On the other hand propene ($CH_3 - CH = CH_2$) does not exhibit cis-trans isomerism.

5. What is optical activity: How is it measured?

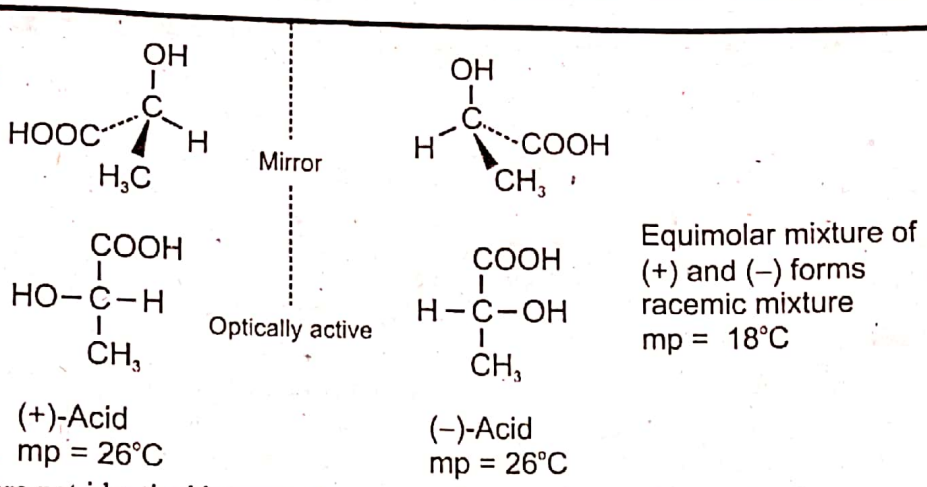
Ans. • The property of a compound to rotate the plane of polarized light is called optical activity.

• It is measured by polarimeter.

6. Write a note on optical isomerism of lactic acid

Ans. Optical Isomerism of Lactic Acid

Lactic acid (2-Hydroxypropanoic acid) shows optical isomerism. It contains one asymmetric carbon atom. Two three dimensional structures are possible for lactic acid.



These structures are not identical because they cannot be superimposed on each other.

On the mirror image of the other, such non superimposable mirror image forms are optical isomers and called enantiomers. Thus, three forms of lactic acid are known. Two are optically active and one is optically inactive.

(+) Lactic Acid: It rotates the plane of polarized light to the right (clockwise direction) and is called dextrorotatory.

(–) Lactic Acid: It rotates the plane of polarized light to the left (anticlockwise direction) and is called laevorotatory.

(–) Lactic acid: is the mirror image of (+) lactic acid and vice versa.

(±) Lactic Acid: it does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (–) forms (racemic mixture).

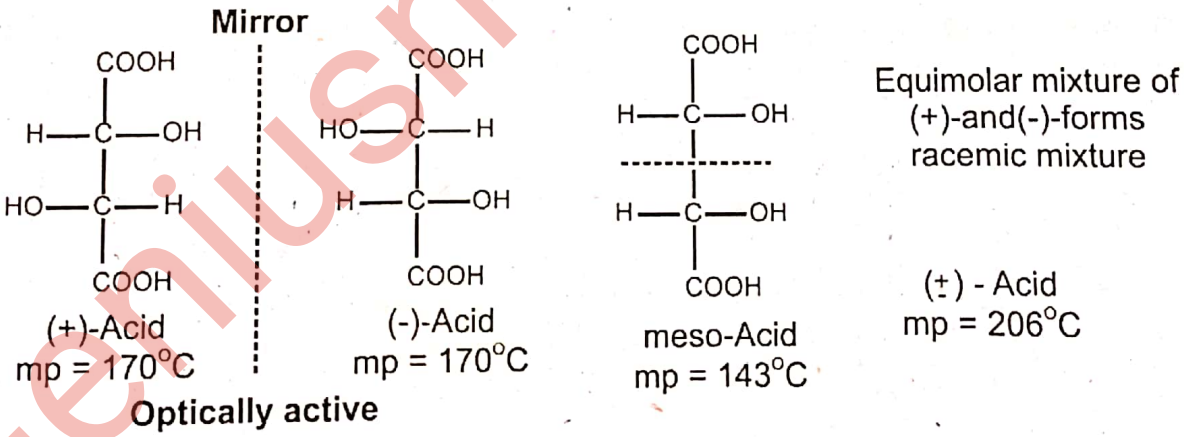
7. Write a note on optical isomerism of tartaric acid

Ans. Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two asymmetric carbon atoms.

Four forms of tartaric acid are known. Two of them are optically active and two are optically inactive. The optically active forms are related to each other as an object to its mirror image. That is, they are enantiomers.

Isomers of Tartaric Acid



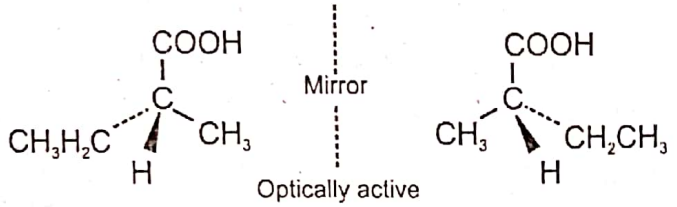
(+)Tartaric Acid: It rotates the plane of polarized light to the right (clockwise direction) and is called dextrorotatory.

(–) Tartaric Acid: It rotates the plane of polarized light to the left (anticlockwise direction) and is called levorotatory.

(±)Tartaric Acid: It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimola mixture of (+) and (-) forms (racemic mixture).

8. An acid of formula $C_5H_{10}O_2$ is optically active. What is its structure?

Ans.



Optically active

9. How does cis-isomer convert into trans-isomer?

Ans. The conversion of cis-isomer into trans-isomer is possible only if it is heated to a high temperature or absorbs light. The heat supplies the energy (about 62 kcal.mol^{-1}) to break the pi (π) bond so that rotation about sigma bond becomes possible. Upon cooling, the reformation of the pi (π) bond can take place in two ways giving mixture of trans and cis isomers.

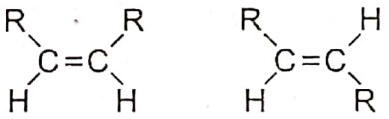
10. The trans – isomer is more stable. Why?

Ans. Stability of cis – trans isomers:

Cis-form of a compound is generally unstable because two bulky groups are on the same side of double bond. These groups cause stearic repulsion making cis-isomer unstable.

In trans-form bulky groups are on the opposite side of the double bond. Due to absence of stearic repulsion trans-isomer is more stable.

Example:



cis - alkene trans - alkene

ALKYNES

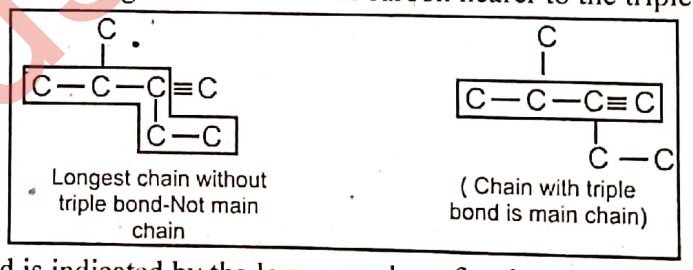
Nomenclature

IUPAC System:

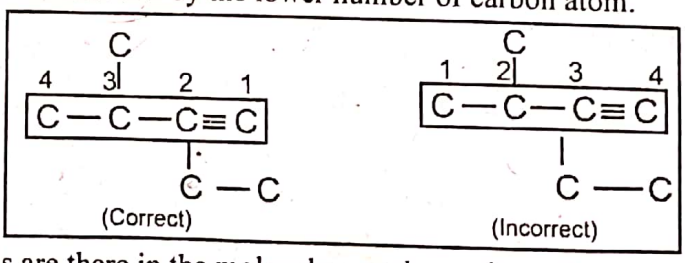
(1) The parent hydrocarbon is the continuous chain containing triple bond.

(2) The ending 'ane' of the alkane is changed by - yne.

(3) The main chain is numbered starting from the terminal carbon nearer to the triple bond.



(4) The position of triple bond is indicated by the lower number of carbon atom.



(5) If two or more triple bonds are there in the molecule, use the prefixes di-, tri-, etc.

(6) Alkyl groups are indicated by the methods described while naming alkanes.

Naming of molecules containing both the double and triple bonds

(1) The suffix 'ene' is used to denote the presence of double bond and the suffix -yne to denote the presence of triple bond.

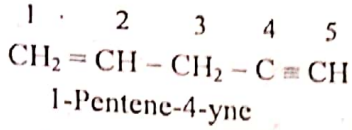
(2) The suffix -'ene' always precedes -'yne' in the name of compound, even when the double bond is assigned the large number.

(3) The position number for the double bond is placed before the name of parent hydrocarbon.

(4) The position number of triple bond is placed between -'ene' and -'yne'.

(5) If same number would result from each terminal, the double bond is given the lower possible number.

e.g.



1-Pentene-4-yne

Activity

Give the IUPAC names of the following:

No.	Alkyne	IUPAC Name
(a)	$CH_3 - CH_2 - C \equiv CH$	1-Butyne
(b)	$HC \equiv C - C \equiv CH$	1, 3-Butadiyne
(c)	$CH_2 = CH - C \equiv CH$	1-Buten-3-yne
(d)	$CH \equiv C - C \equiv C - CH = CH - CH_3$	5-Hepten-1,3-diyne
(e)	$CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$	3-Hexyne

Relative Stability of Alkynes

Alkynes are more stable as compared to alkenes due to the presence of extra pi-bond. That is why alkynes are less reactive than alkenes. This can be supported if we compare thermodynamic data of alkynes and alkenes, which is:

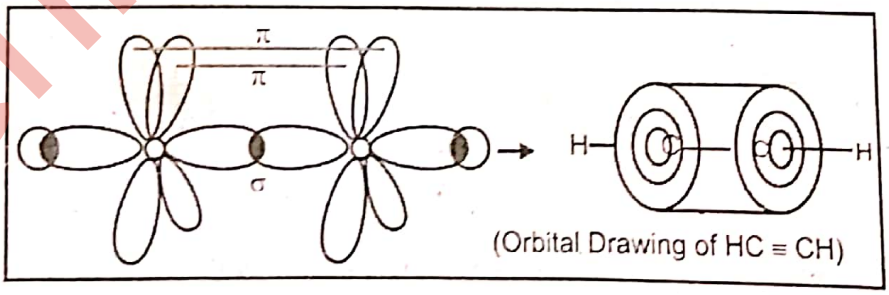
ΔH of 1-Hexyne = – 290 kJ mol^{-1}

ΔH of 1-Hexene = – 126 kJ mol^{-1}

Structure of Alkynes

The two carbons of acetylene (alkyne) are sp-hybridized. They are linked by a sigma (σ) bond due to sp-sp orbitals overlap. The two unhybridized p-orbitals on one carbon overlap with two p-orbitals on other carbon to form two pi (π) bonds. The cloud of pi-electrons is present cylindrically symmetrical about the carbon-carbon sigma (σ) bond.

Rotation about carbon-carbon sigma bond does not cause any change in energy and electron density. It is a linear molecule, and hence geometrical isomer is not observed in it.



(Orbital Drawing of HC ≡ CH)

Physical Properties

1. In general, alkynes are non-polar and are insoluble in water but soluble in non-polar organic solvents.
2. They are colourless, odourless except acetylene (C_2H_2) which has a garlic like odour.
3. The melting points, boiling points and densities increase gradually with the increase in molecular masses.

4. The first three members (ethyne, propyne & butyne) are gases. The next eight members ($C_5 - C_{12}$) are liquids and higher members are solids at room temperature.

Methods of preparation of alkynes

Alkynes can be prepared by the following methods:

(i) Elimination reaction

(ii) Alkylation of sodium acetylide

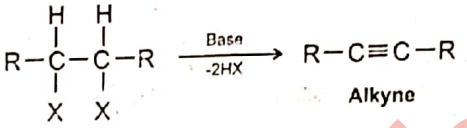
(i) Elimination of Hydrogen Halide

Alkynes can be prepared by dehydrohalogenation of vicinal and geminal dihalides in the presence of some alkaline reagents.

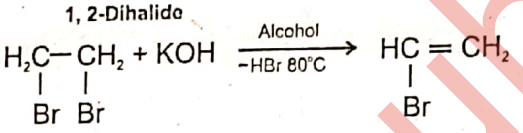
(a) From Vicinal Dihalide

A vicinal dihalide contains two halogen atoms on adjacent carbon atoms. On elimination of two molecules of hydrogen halides from two adjacent carbons, it gives an alkyne.

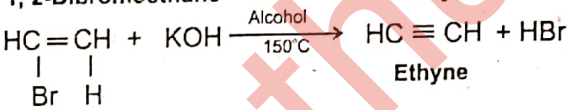
Higher alkynes are also formed in the presence of alcoholic KOH. e.g.



1, 2-Dihalide

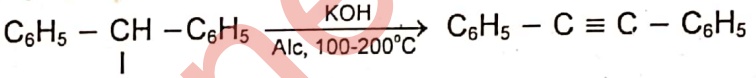


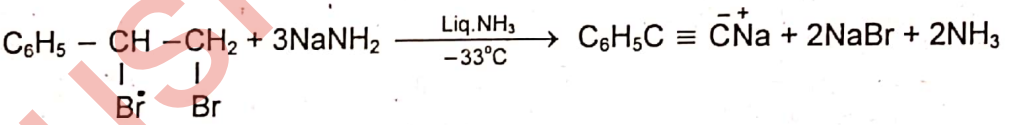
1, 2-Dibromoethane — Vinyl bromide

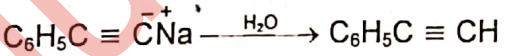


Vinyl bromide

- In the presence of strong base such as KOH and at high temperature, triple bond at terminal C-atom migrates to give more disubstituted alkynes. Therefore, alcoholic KOH is useful when rearrangement is not possible.
- 1-Alkynes can be prepared from vicinal dihalides with sodium amide in liquid ammonia.

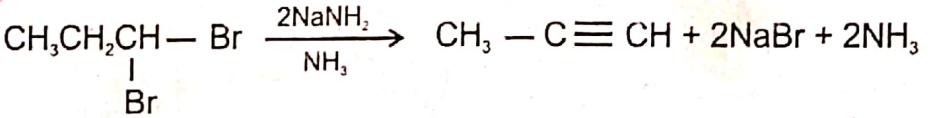






(b) From Geminal Dihalide:

A geminal dihalide contains two halogen atoms linked with the same carbon atom. On treatment with strong base it gives alkyne, e.g.



Reactivity of alkyne

Acetylene (alkyne) is an unsaturated hydrocarbon and shows addition reactions. It also undergoes substitution reactions due to easy cleavage of C – H bond. The pi-electrons are present cylindrically symmetrical about carbon-carbon sigma bond and the removal of terminal hydrogen is possible without disturbing carbon–carbon bonding. Therefore electrophilic substitution reactions are possible in 1-Alkynes.

$$H - C \equiv C^{\delta-} - H^{\delta+}$$

$$R - C \equiv C - H \xrightarrow{B:^-} R - C \equiv C:^- + B - H$$

Q. Why alkynes are more reactive than alkenes in electrophilic addition reaction?

Acidity of Terminal Alkynes

- In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atom with sp-s overlap. As sp hybrid orbital has 50% s-character in it and renders the carbon atoms more electronegative.
- As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.
- This $H^{\delta+}$ can be substituted with metal. The substitution reaction occurs due to $H^{\delta+}$ and is called electrophilic substitution reaction.

Examples:

(i) When 1-Alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.

$$R - C \equiv CH + 2NaNH_2 \xrightarrow{\text{liq } NH_3} R - C \equiv C^- Na^+ + NH_3$$

$$HC \equiv CH + 2Na \longrightarrow Na^+ C^- \equiv C^- Na^+ + H_2$$

Disodium acetylide

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

(ii) Acetylides of copper and silver are obtained by passing acetylene through the ammoniacal solution of cuprous chloride and silver nitrate respectively.

$$HC \equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC \equiv CAg + 2NH_4NO_3 + 2H_2O$$

Disilver acetylide or silver Ethynide (white ppt.)

$$HC \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC \equiv CCu + 2NH_4Cl + 2H_2O$$

Dicopper acetylide or copper Ethynide (Reddish brown ppt)

Q. Distinguish between ethene and ethyne.

Regeneration of alkynes:

Silver and copper acetylides react with acids to regenerate alkynes.

$$AgC \equiv CAg + H_2SO_{4(dil.)} \longrightarrow CH \equiv CH + Ag_2SO_4$$

$$AgC \equiv CAg + HNO_{3(dil.)} \longrightarrow HC \equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification, separation and identification of alkynes.

Addition Reactions of Alkynes

- Alkynes undergo addition reactions in an analogous fashion to those of alkenes. The high electron density of the pi bonds makes them nucleophile.
- Two factors influence the relative reactivity of alkynes compared to alkenes:

(i) increased nucleophilicity of the starting pi system

(ii) stability of any intermediates (for example carbocations)

(1) Hydrogenation

Alkynes react with hydrogen gas in the presence of suitable catalysts like finely divided Ni, Pt or Pd. In the first step alkenes are formed which then take up another molecule of hydrogen to form an alkane.

$$HC \equiv CH + H_2 \xrightarrow[\text{Heat}]{Ni} H_2C = CH_2$$

Ethyne Ethene

$$CH_2 = CH_2 + H_2 \xrightarrow[\text{Heat}]{Ni} H_3C - CH_3$$

Ethene Ethane

Partial hydrogenation to trans alkene:

Alkynes can be reduced to **trans-alkenes** using Na in liquid NH_3. This reaction is **stereospecific** giving only the **trans-alkene** via an **anti** addition.

$$R-C\equiv C-R + 2[H] \xrightarrow[-33^\circ C]{Na/\text{liquid } NH_3} \underset{R}{\overset{H}{}}C=C\underset{H}{\overset{R}{}}$$

Trans-Alkene

Note that the stereochemistry of this reaction complements that of catalytic hydrogenation. The reaction proceeds via single electron transfer from the Na with H coming from the NH_3. These reaction conditions do not reduce alkenes; hence the product is the alkene.

(2) Hydrohalogenation

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkenes.

$$HC\equiv CH + H-Br \longrightarrow H_2C=\underset{Br}{CH}$$

Ethyne — Vinyl bromide

Second addition is according to Markownikov's Rule.

$$H_2C=\underset{Br}{CH} + H-Br \xrightarrow[\text{addition}]{\text{Markownikov's}} H_3C-\overset{Br}{\underset{Br}{CH}}$$

1, 1 - Dibromoethane

(3) Hydration

Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C.

$$HC\equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} H_2C=\underset{}{\overset{OH}{CH}} \quad \text{(Vinyl alcohol)}$$

Rearrangement of alcohol:

Vinyl alcohol is an unstable. It has the hydroxyl group attached to a doubly bonded carbon atom and isomerizes to acetaldehyde.

$$H_2C=\underset{}{\overset{OH}{CH}} \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-H \quad \text{(Acetaldehyde)}$$

Except acetylene all others alkynes give ketones.

$$CH_3-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} H_3C-\underset{O=H}{\overset{}{C}}=CH_2 \rightleftharpoons H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

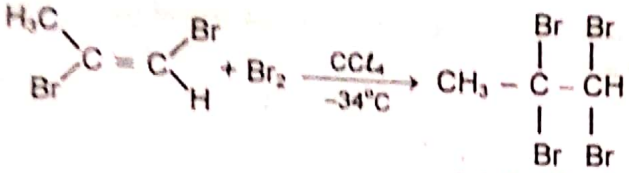
Acetone (Ketone)

This reaction is industrially important because aldehydes can be prepared by this method.

(4) Bromination

Chlorine and bromine add to the acetylenic triple bond in the presence of Lewis acid as catalyst. The halogenation may be stopped at the dihaloalkene stage because the double bond of dihaloalkene is less nucleophilic than even triple bond itself.

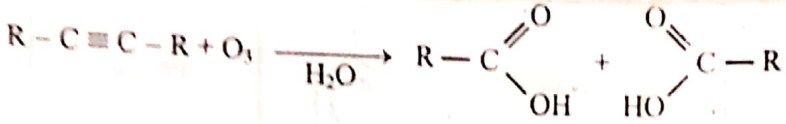
$$CH_3-C\equiv CH + Br_2 \xrightarrow[-34^\circ C]{CCl_4} \underset{Br}{\overset{H_3C}{}}C=C\underset{H}{\overset{Br}{}}$$



1, 1, 2, 2-Tetrabromopropane

(5) Ozonolysis

When ozone reacts with alkyne followed by aqueous work up, we get $2RCO_2H$.



QUICK QUIZ

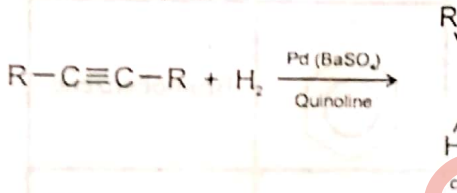
Q. What are reducing agent? Would you use to convert an alkyne to a (i) Cis-alkene (ii) Trans alkene?

Ans. Reducing Agent:

A substance which reduces other but oxidizes itself is called reducing agent. e.g. Metals (Na, Zn, Cu etc), $FeSO_4$, Oxalic acid etc.

(i) Formation of Cis-alkene

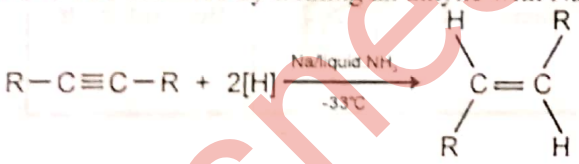
Controlled hydrogenation of alkynes with hydrogen gas in an equimolar ratio over heated catalysts, gives alkenes. The catalyst is finely divided palladium supported on $BaSO_4$ and poisoned by treatment with quinoline (Lindlar's catalyst).



cis - Alkene

(ii) Formation of Trans-alkene

A trans alkene can be obtained by treating an alkyne with Na in liquid NH_3 at -33°C.



trans - Alkene

BENZENE AND SUBSTITUTED BENZENES

Discovered by = Michael Faraday
Isolated by = Hoffmann, isolated it from coal tar.
Molecular formula = C_6H_6
Molecular weight = 78
Special Features = (i) Resonance (ii) Electrophilic substitution reactions (iii) Aromaticity

- Michael Faraday discovered benzene in 1825, in the gas produced by destructive distillation of vegetable oil.

As a functional group, benzene and substituted benzenes are called arenes.

Nomenclature

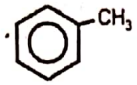
Mono Substituted Benzenes

Common system of naming:

The following procedures are adopted for naming mono substituted benzenes:

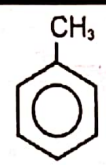
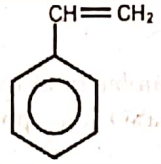
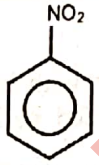
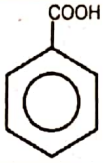
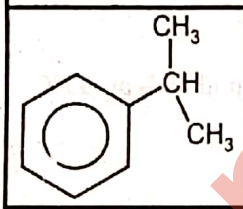
(1) Parent name is benzene and the substituent is indicated by a prefix, e.g., methyl, ethyl, chloro, nitro etc.

(2) The substituent and the benzene ring taken together may form a new parent name. The largest parent name is preferred e.g., $C_6H_5CH_3$ may be named as:

(i) Methyl benzene 

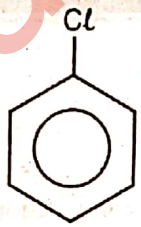
(ii) Phenyl methane.

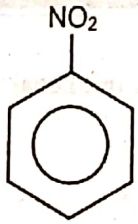
According to "the largest rule" methyl benzene is preferred. The common name of some compunds are:

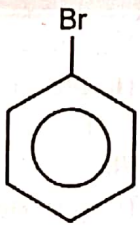
Structure	Names	Structure	Names
	Toluene		Phenol
	Aniline		Anisole
	Styrene		Nitrobenzene
	Benzoic acid		Bromobenzene
	Cumene		Benzaldehyde

IUPAC System of Naming:

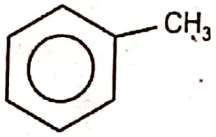
(i) Monosubstituted derivatives of benzene are named by prefixing the name of substituted to the word 'benzene'. e.g.,

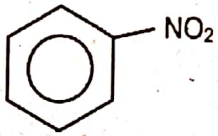

Chlorobenzene

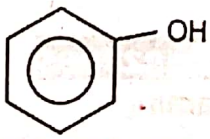

Nitrobenzene


Bromobenzene

(ii) Many aromatic compounds have been known by their common or trivial names, which are still in use. IUPAC system retains these names: A few are given below:

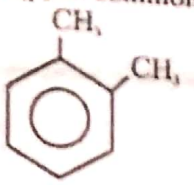

Toluene


Nitrobenzene

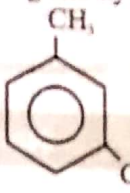

Phenol

Disubstituted Benzenes

(1) When there are two substituents on benzene ring, their relative positions are indicated by prefixes *ortho*(o), meta(m) and para(p) in common system of naming and by numerals while naming according to IUPAC system.



1,2 – Dimethylbenzene
(o-Xylene)



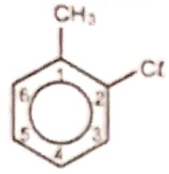
1,3 – Dimethylbenzene
(m-Xylene)

1,4 – Dimethylbenzene
(p-Xylene)

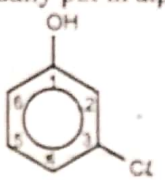
(2) If the substituents are different and one of them is an alkyl group, the numbering is started from the ring carbon which is linked to the alkyl group and the second substituent gets the lowest possible number.

(3) When a common name is used, the substituent which is responsible for name, e.g., – CH_3 in toluene, and – OH in phenol, is considered to be on carbon -1, i.e., numbering is started from the carbon of ring bearing that group such a disubstituted compound.

(4) When two substituents are different, they are usually put in alphabetical order.



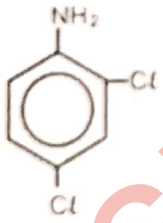
o-chlorotoulene
2-Chlorotoulene (IUPAC)



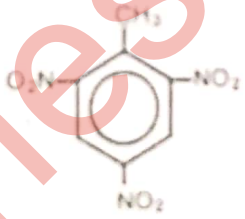
m-chlorophenol
3-Chlorophenol (IUPAC)

p-bromophenol
4-Bromophenol (IUPAC)

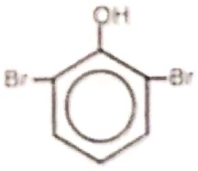
(5) Poly substituted benzenes are named by numbering the substituent to ring so as to give the substituents lowest possible numbers. The last named substituent is assumed to be at position number 1. This number is not indicated in the name.



2,4-Dichloroaniline

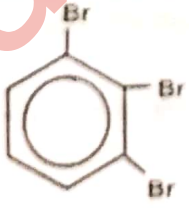


2,4,6 -Trinitrotoluene

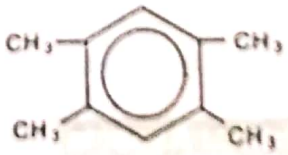


2,6-Dibromophenol

(6) If the substituents are all alike, their positions are indicated by numbering the substituents in a manner so as to give the lowest number to the substituents.

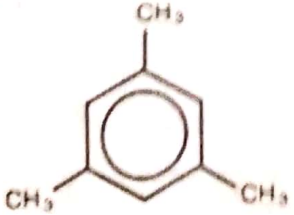


1,2,3-Tribromobenzene

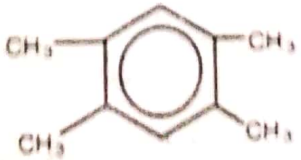


1,2,4,5-Tetramethylbenzene

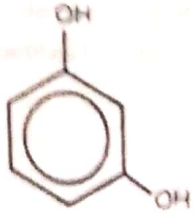
(7) Some polysubstituted benzenes are still known by their common name.



Mesitylene



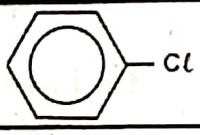
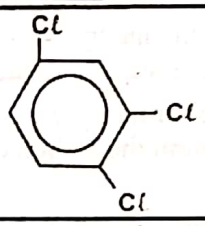
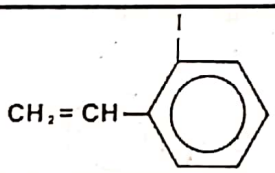
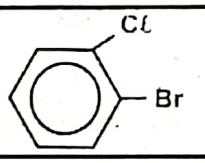
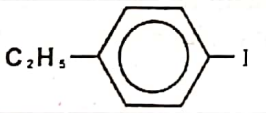
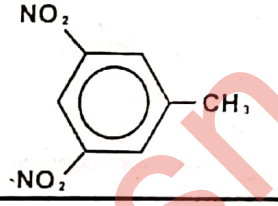
Durene



Resorcinol

Activity

1. Give the suitable names to each of following:

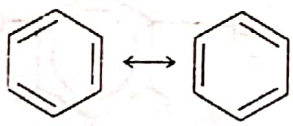
No.	Structure	Name
(a)		Chlorobenzene
(b)		1, 2, 4-Trichlorobenzene
(c)		2-Iodostyrene
(d)		2-Bromochlorobenzene
(e)		4-Iodoethylbenzene
(f)		3, 5-Dinitrotoluene
(g)		4-Iodotoluene or p-Iodotoluene

Physical Properties

In the absence of polar substituents, arenes are typical hydrocarbons having low melting points, boiling points and low solubility in polar solvents.

Structure (Molecular Orbital Aspects)

- Benzene has a planar, cyclic, conjugated structure.
- All 12 atoms in benzene, C_6H_6, lie in the same plane.
- If one draws benzene as alternating C = C and C – C then the two different Kekule structures are obtained. These are two equally valid resonance contributors.



Kekule structures

- Alternatively, these two forms can be combined in the resonance hybrid and the conjugated system represented by a circle as in the Robinson structure.

Robinson Structure

Note that all of the C – C bonds are 1.4 Å (between typical C = C and C – C distances).

Q. Which representation structure of benzene the best?

Ans. In benzene all the C – C bonds are known to be of equal length so there are no C = C (double bond) and C – C (single bond). This is best represented by the resonance hybrid in the Robinson form.

Robinson Structure

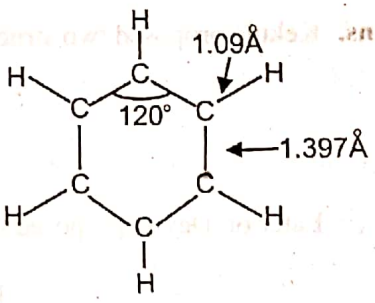
Q. Why we use Kekule structures?

Ans. The key to organic chemistry is being able to understand mechanisms and drawing curved arrows to account for the positions of the electrons. The Kekule structures give a more precise description of the electrons positions that can avoid confusion. Therefore, it is a good idea to use a Kekule representation.

Limitation of Kekule's Structures

Kekule's structure failed to explain:

1. Why benzene is less reactive?
2. It shows dual character, i.e., it shows addition as well as substitution reactions.
3. It has less heat of formation, and
4. It has equal C – C bonds.



X-rays analysis of Benzene Structure

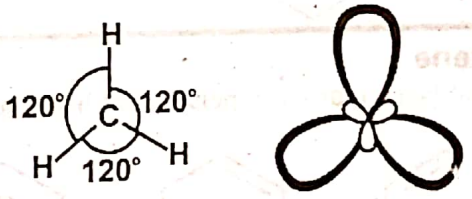
Spectroscopic studies and X-rays analysis have shown that:

- Benzene is a regular, flat planar hexagon.
- All six hydrogen atoms are co-planar with six carbon atoms.
- The bond angles are: (i) C – $\hat{C}$ – C = 120°, and (ii) C – $\hat{C}$ – H = 120°

Exercise: Q.3(b) Explain the structure of benzene according to atomic orbital structure.

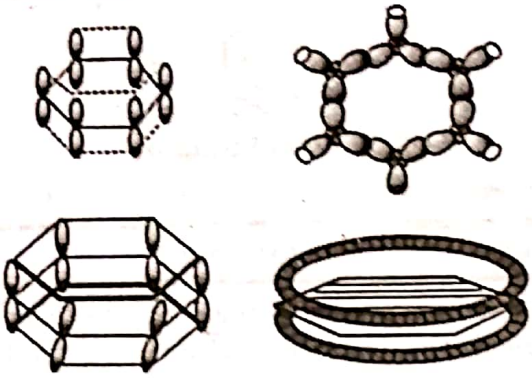
Molecular orbital treatment of benzene

- In benzene each C-atom is in a state of sp^2 hybridization because each C-atom is attached to three atoms.
- Combination of such six structures and overlap of six hydrogen atoms (1s) produces the following sigma framework of benzene.



- Six atomic p-orbitals one on each C-atom, are present perpendicular to this sigma bonding. Each p-orbital is in a position to overlap in parallel manners with neighbouring p-orbitals to give a continuous sheath of negative charges.
- It results in extensive delocalized pi-bonding which spreads over all the carbon nuclei of benzene.

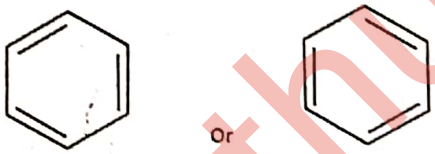
- Delocalization of p-orbitals over the entire ring produces sandwich like structure of benzene and decreases the energy of molecule. Consequently, the molecule becomes more stable and less reactive.



- According to this molecular orbital picture, each carbon-carbon bond in benzene consists of one full sigma bond and half a pi-bond. Because of this reason, the carbon-carbon bond length is equal and benzene shows substitution as well as addition reactions.

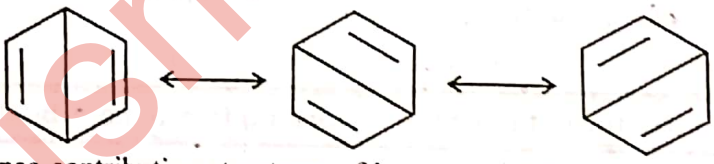
QUICK QUIZ

Q. Criticize the following statement:
"Benzene is a mixture of molecules most of which have the structure."

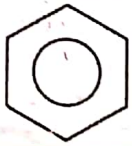


Ans. Kekule proposed two structures for benzene.

Later on Dewar proposed three more structures.

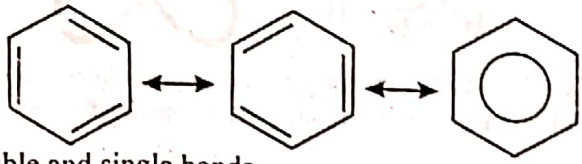


Actually these are resonance contributing structures of benzene which show various positions of electrons during delocalization. The actual structure of benzene is its hybrid structure.



Modern Representation of Benzene

With the help of molecular orbital behaviour we conclude that benzene has a regular hexagonal structure with an inscribed circle.



A hexagon with alternate double and single bonds.

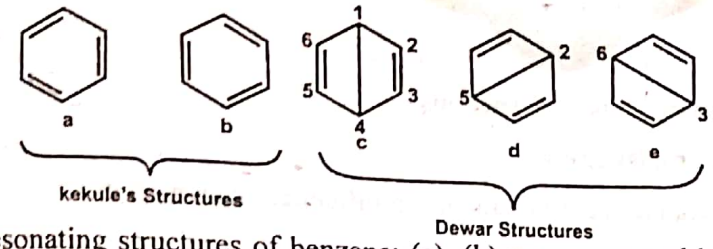
Resonance, Resonance energy and stabilization

Resonance

"The possibility of different pairing schemes of valence electrons of atom is called resonance" and the different structures thus arranged are called "Resonance Structures".

Explanation:

- The resonance is represented by a double-headed arrow (↔).
- The following different pairing schemes of the fourth valence (the p-electrons) of carbon atoms are possible in benzene.



- The resonating structures of benzene: (a), (b) were proposed by Kekule and c, d, e were proposed by Dewar.
- The stability of a molecule increases with increase in the number of its resonance structures.

Thus molecule of benzene is chemically quite stable.

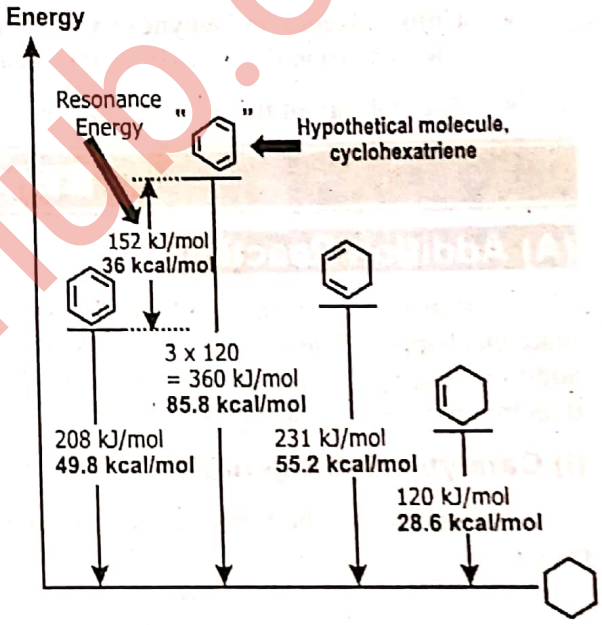
In alkanes the C – C bond length is 154pm.
In alkenes the C = C bond length is 134pm.
In alkynes the C ≡ C bond length is 120pm.
In benzene the C–C bond length is 139.7 pm.

Resonance Hybrid

In fact the structure of benzene is a resonance hybrid of all five structures, (a), (b), (c), (d) and (e) in which the Kekule's structure (a) and (b) have the larger contribution (80%) and Dewar's structures (c), (d) and (e) contribute a little (20%). Therefore, benzene molecule can be represented by either of the two Kekule's structures.

The three alternate single and double bonds in the above structure are called conjugate bonds or resonating bonds.

Since the structure of benzene is a resonance hybrid, therefore all the C – C bond lengths are equal but different from those in alkanes, alkenes and alkynes. It is intermediate between those in alkanes and alkenes.



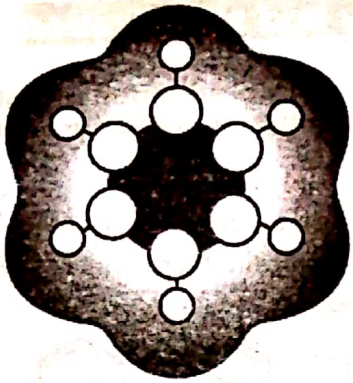
Resonance Energy

"The difference in potential energy between the actual molecular entity and the contributing structure of lowest potential energy is called resonance energy."

- The **resonance energy** of a compound is a measure of the extra stability of the conjugated system compared to the corresponding number of isolated double bonds. This can be calculated from experimental measurements.
- The diagram shows the experimental heats of hydrogenation, ΔH_h, for three molecules, which are benzene, 1,3-cyclohexadiene and cyclohexene. These are related in such a way (under appropriate conditions) that they can all be reduced to the same product, cyclohexane.
- The ΔH_h for "cyclohexatriene", a hypothetical molecule in which the double bonds are assumed to be isolated from each other, is calculated to be 3 times the value for cyclohexene. This value reflects the energy we could expect to be released from 3 isolated C = C.
- By comparing this value with the experimental value for benzene, we can conclude that benzene is 152 kJ or 36 kcal / mol **more stable** than the hypothetical system. This is the resonance energy for benzene.

Reactivity and Reactions

The image shows the electrostatic potential for benzene. The inner area has high electron density and the outer area has low electron density. Note the nucleophilic character of the aromatic p system.



The reactivity issues can be separated into two types of reactions:

(i) Reactions of electrophiles directly on the aromatic ring.

(ii) Reactions of the substituents (since the neighboring aromatic group influences its reactivity).

For reactions directly on the aromatic ring:

- The cyclic array of p-bonds is a region of high electron density so arenes are typically nucleophiles (like alkenes and alkynes).
- Unlike alkenes and alkynes (which undergo addition reactions), arenes typically undergo substitution reactions in which a group (usually -H) is replaced and the aromatic system is retained.
- The stability of the aromatic system favours substitution over addition which would destroy the aromatic system.

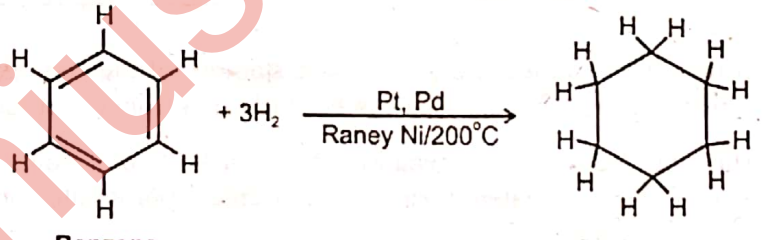
REACTIONS OF BENZENE

(A) Addition Reactions

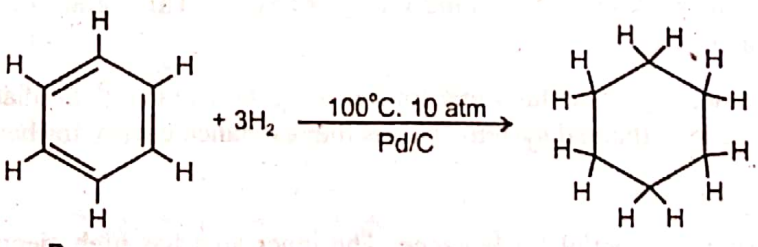
Benzene is highly unsaturated compound. Although it has three double bonds but it does not undergo addition reactions happily. The reason is that it shows resonance. The delocalization of six pi (π) electrons makes it extra stable. In addition reactions, benzene loses its extra stability. So for addition reaction benzene requires more vigorous conditions than that of alkenes and alkynes.

(i) Catalytic Hydrogenation

Benzene can be hydrogenated in the presence of a catalyst as Pt, Pd, or Raney Ni only at higher temperature and pressures.



Benzene Cyclohexane

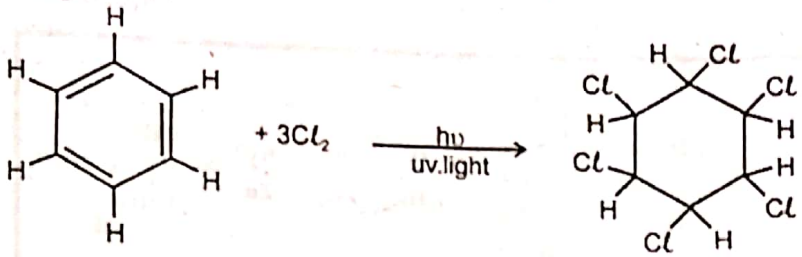


Benzene Cyclohexane

If we use the metals like Ru, Rh, supported at carbon then hydrogenation becomes easier.

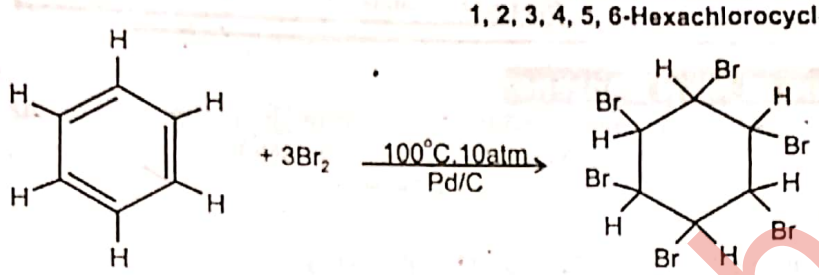
(ii) Addition of Halogens

Benzene can add three molecules of chlorine or bromine under the influence of sunlight. The benzene ring becomes saturated, and we get benzene hexachloride and benzene hexabromide. This reaction shows that benzene has three double bonds in the ring.



Benzene

Benzene hexachloride or
1, 2, 3, 4, 5, 6-Hexachlorocyclohexane



Benzene

Benzene hexabromide or
1, 2, 3, 4, 5, 6-Hexabromocyclohexane

Note: The reaction of F_2 with benzene is very vigorous, while with I_2 it is very slow.

Conclusion:

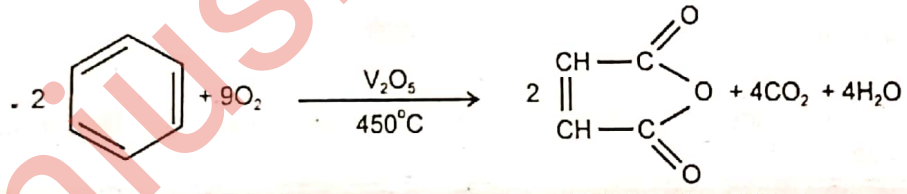
The addition reactions of hydrogen and halogens (Cl_2, Br_2) with benzene show that benzene is unsaturated hydrocarbon and has three double bonds in it.

(B) Oxidation Reactions

Benzene is stable towards general oxidizing agents. However, it can be oxidized under certain conditions:

(i) Catalytic oxidation

When benzene is oxidized with air in the presence of V_2O_5 at 450°C, then we get maleic anhydride



Benzene

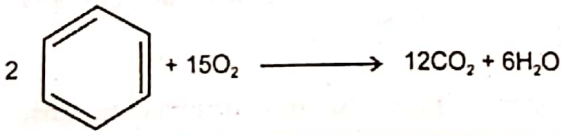
Maleic anhydride

This is commercial method for the preparation of maleic anhydride.

- Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$.

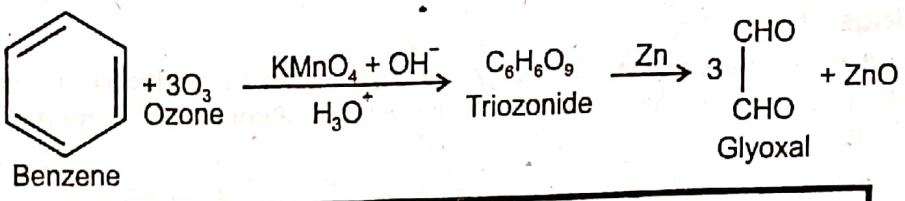
(ii) Combustion:

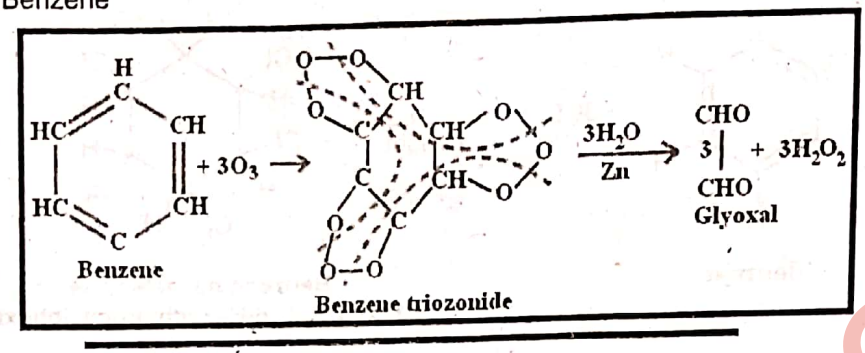
When benzene is burnt in the presence of air or oxygen, CO_2 and H_2O are produced, just like other aliphatic hydrocarbons



(iii) Ozonolysis:

Benzene reacts with ozone and gives glyoxal. First of all triozonide is produced as an intermediate.

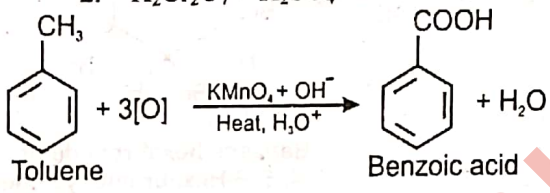


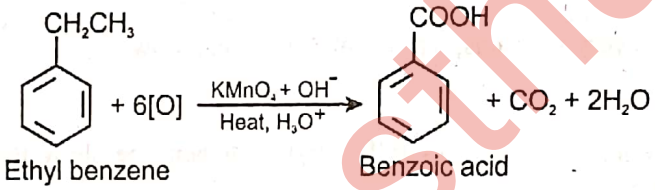


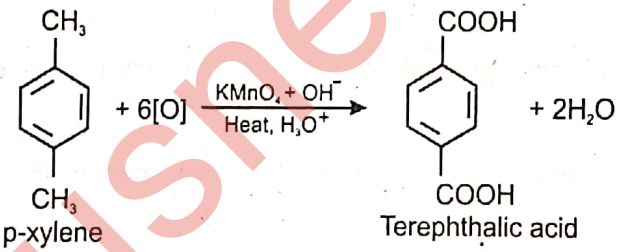
(iv) Side Chain Reactions of Alkyl Benzene:

Alkyl groups present in the benzene ring are oxidized into carboxylic groups. The oxidizing agents are:

1. $KMnO_4 + H_2SO_4$ 2. $K_2Cr_2O_7 + H_2SO_4$ 3. dil. HNO_3







Conclusion:

When both methyl groups are oxidized and benzene ring remains unaffected, then it means that benzene ring is stable towards oxidizing agents.

ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

General Introduction

The pi-electrons of benzene are highly stabilized due to resonance. They are not readily available for the electrophilic attack like the electrons of alkenes. They do not assist in the attack of weak electrophiles. Hence more powerful electrophiles are required for a successful attack to penetrate and break the continuous sheath of electron cloud in benzene.

Explanation:

Substitution of halogen in benzene requires iron or corresponding ferric halide as catalyst. It reacts with halogen molecule to produce a powerful electrophile:

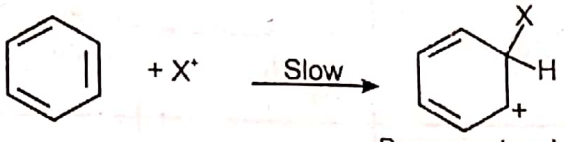
Formation of a strong electrophile (X^+)

$$2Fe + 3X_2 \longrightarrow 2FeX_3$$

$$FeX_3 + X_2 \longrightarrow \underset{\text{Tetra haloferrate ion (III)}}{FeX_4^-} + X^+ \text{ (Halogenonium ion)}$$

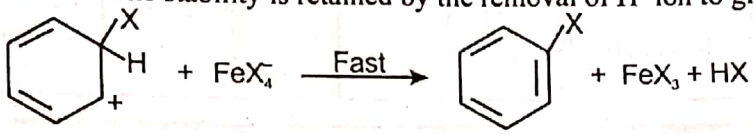
Attack of electrophile at pi-bond

The halogenonium ion thus produced attacks as a powerful electrophile on the electrons of benzene ring.



Benzenonium ion

It makes benzene unstable. The stability is retained by the removal of H^+ ion to give substitution product.

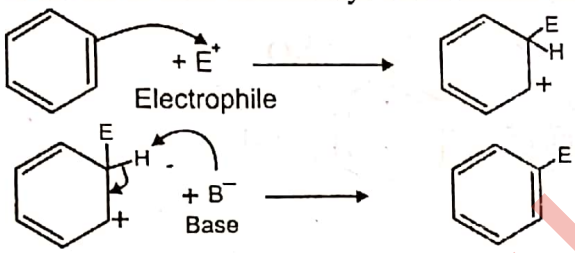


Benzenonium ion

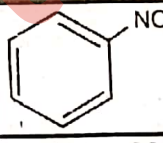
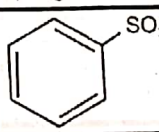
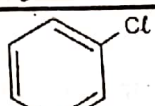
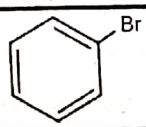
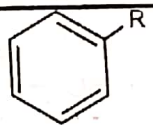
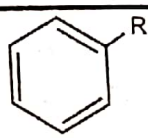
Q. Write down general mechanism of electrophilic substitution reactions of benzene?

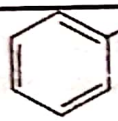
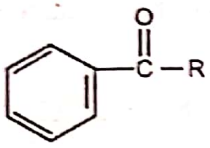
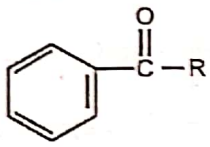
General pattern of substitution

The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.



Substitution is preferred over addition in order to preserve the stable aromatic character.

Reaction	Reagents	Electrophile	Product	Comments
Nitration	HNO_3 / H_2SO_4	NO_2^+		E^+ formed by loss of water from nitric acid
Sulphonation	H_2SO_4 or SO_3 / H_2SO_4	SO_3		Reversible
Halogenation	Cl_2 / Fe or $FeCl_3$	Cl^+		E^+ formed by Lewis acid removing Cl^-
	Br_2 / Fe or $FeBr_3$	Br^+		E^+ formed by Lewis acid removing Br^-
Alkylation	R – Cl / $AlCl_3$	R^+		E^+ formed by Lewis acid removing Cl^-
	R – OH / H^+	R^+		E^+ formed by loss of water from alcohol

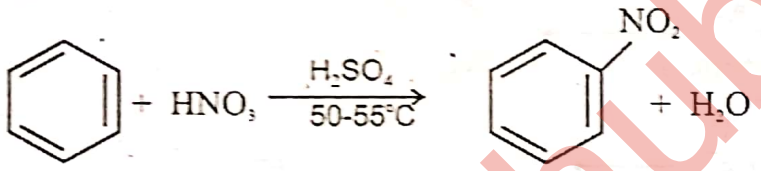
	$RC=CR/H^+$	R^+		E^+ formed by protonation of alkene
Acylation	$R-\overset{O}{\overset{\|\|}{C}}-Cl/AlCl_3$	RCO^+		E^+ formed by Lewis acid removing Cl^-
	$R-\overset{O}{\overset{\|\|}{C}}-O-\overset{O}{\overset{\|\|}{C}}-R/AlCl_3$	RCO^+		E^+ formed by Lewis acid removing RCO_2^-

Q.3(6) Explain the following electrophilic substitution reactions of benzene with mechanism.
(i) Nitration (ii) Sulphonation (iii) Halogenation

(i) Nitration

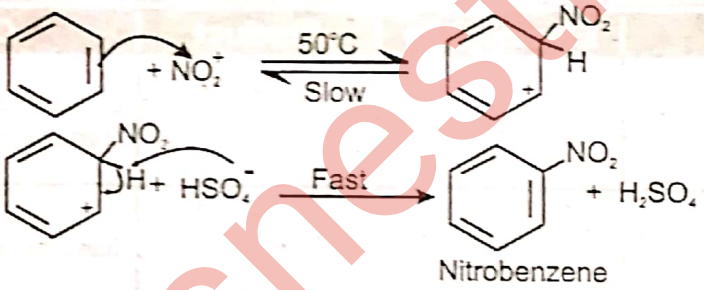
$HONO_2 + HSO_4^- \rightarrow SO_4^- + NO_2 + H_2O$

"The introduction of nitro group (– NO_2) in benzene by substituting hydrogen of benzene ring is called nitration".



Mechanism

Sulphuric acid reacts with nitric acid to generate nitronium ion.



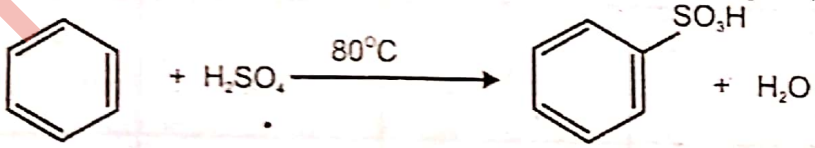
Nitrobenzene

(ii) Sulphonation

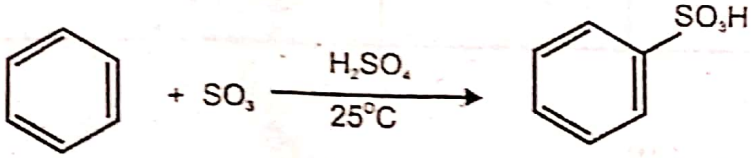
$H_2SO_4 + H_2SO_4 \rightarrow H_3O^+ + SO_3 + HSO_4^-$

"The introduction of sulphonic acid group (– SO_3H) in benzene by substituting hydrogen of benzene ring is called sulphonation."

- When benzene is heated with fuming H_2SO_4 or concentrated H_2SO_4 it yields benzene sulphonic acid.
- Fuming H_2SO_4 has free sulphur trioxide which is electron deficient (electrophile) and causes substitution.



Benzenesulphonic acid

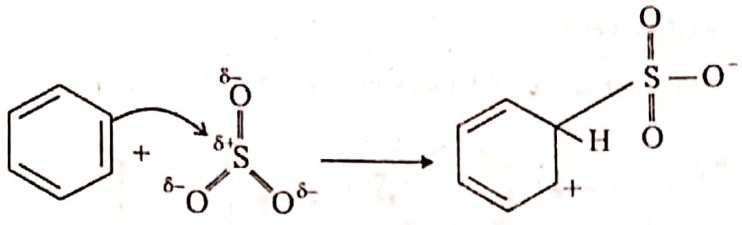


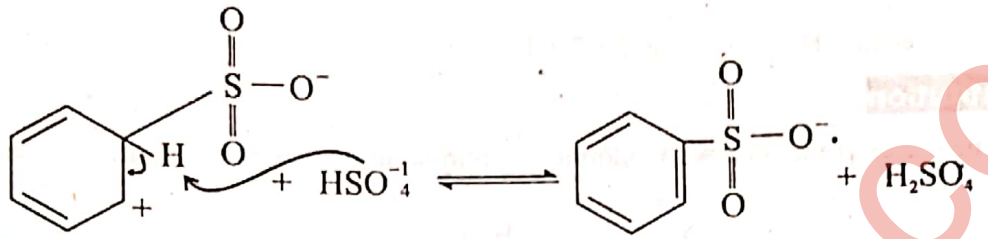
- Reaction conditions show that fuming H_2SO_4 is more reactive than concentrated H_2SO_4.

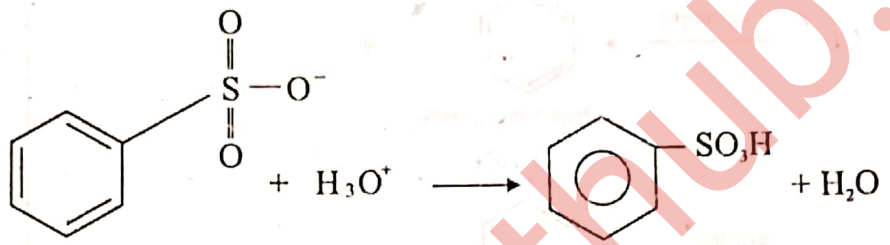
Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3.

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO_4^-$$

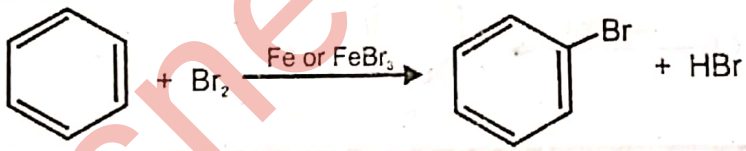






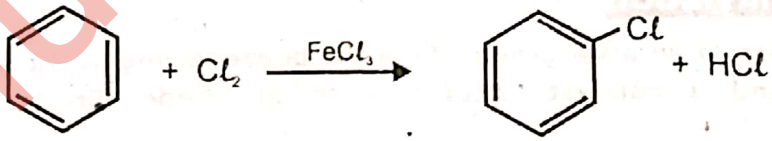
(iii) Halogenation

"The introduction of halogen (x) in benzene by substituting hydrogen of benzene ring is called halogenation."



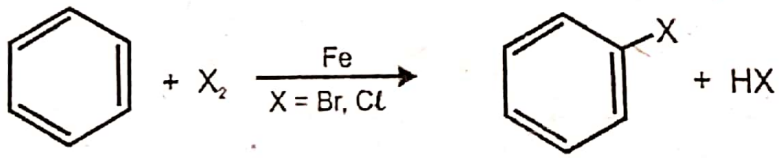
Bromobenzene

Similarly,



Chlorobenzene

Generally,



Halogenation of benzene occurs with halogens (X_2) in the presence of a catalyst FeX_3.

- Chlorination and bromination are normal reactions.
- Fluorination is too vigorous to control.
- Iodination gives poor yield.

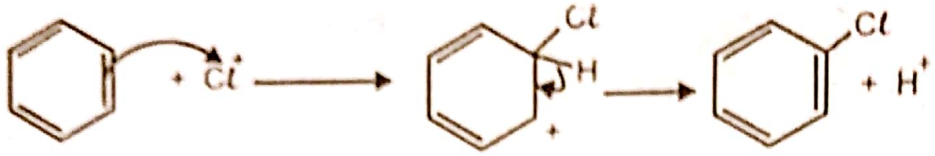
Mechanism:

The actual halogenation agent is X^+ that is formed by the following mechanism.

$$X_2 + FeX_3 \longrightarrow X^+ + FeX_4^-$$

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

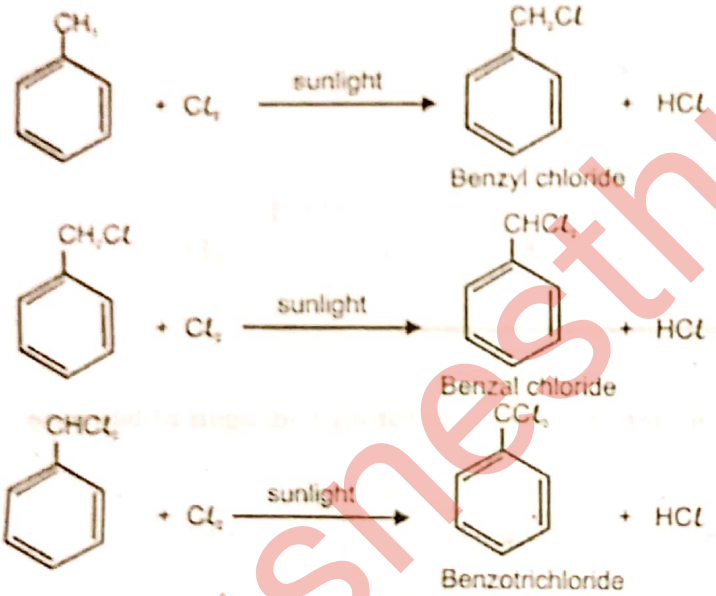
Cl^+ being a strong electrophile is ready for successful attack on benzene.

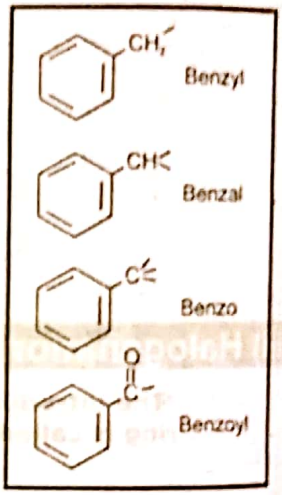


$$FeCl_4^- + H^+ \longrightarrow HCl + FeCl_3$$

Side chain substitution

When alkyl benzenes are treated with chlorine or bromine in the presence of sunlight, only the alkyl groups are substituted.



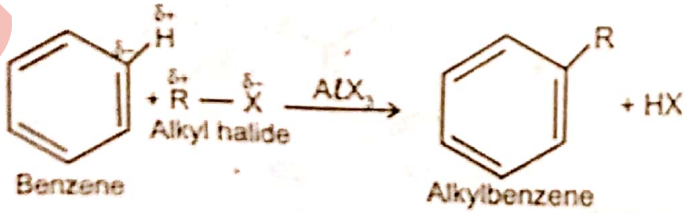


Exercise Q.3(5) Explain Friedel Craft acylation and alkylation with complete mechanism.

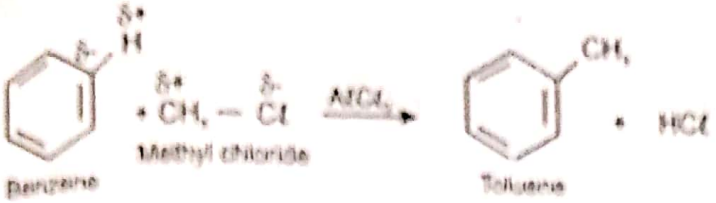
(iv) Friedel-Crafts Alkylation

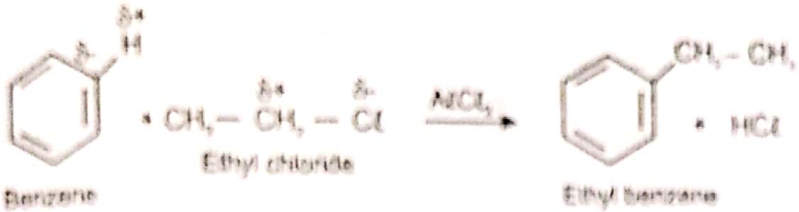
"The introduction of an alkyl group (R) in the benzene ring in the presence of an alkyl halide and a catalyst ($AlCl_3$) is called Friedel Crafts alkylation or Alkylation."

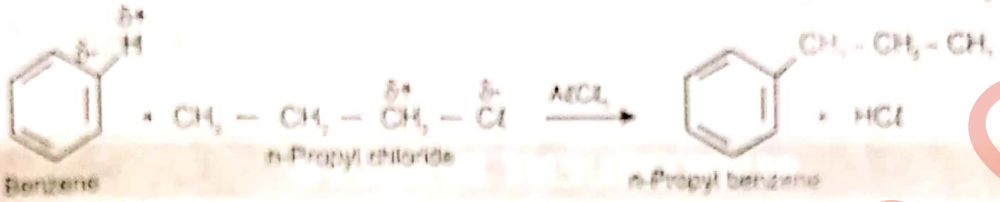
Overall reaction:



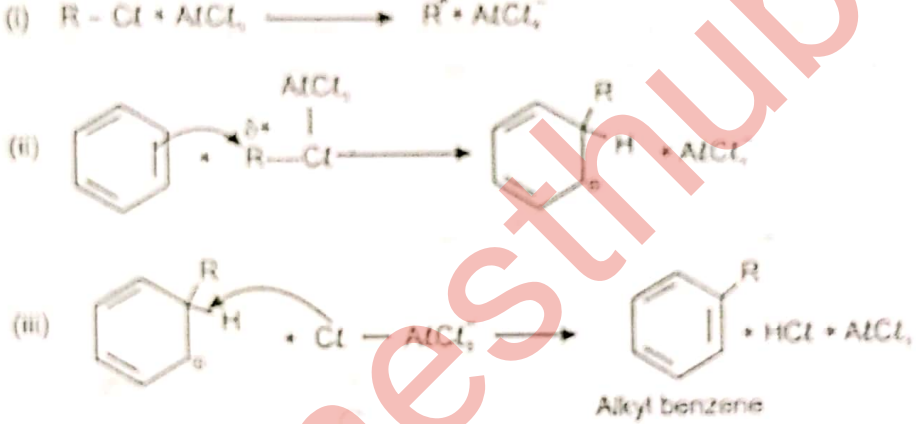
Examples:







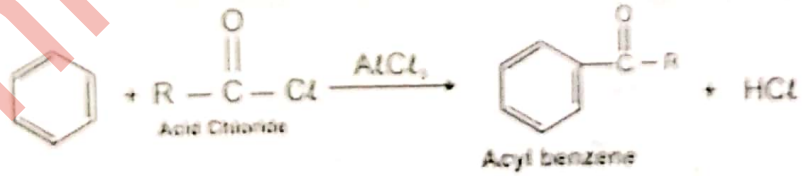
Mechanism:



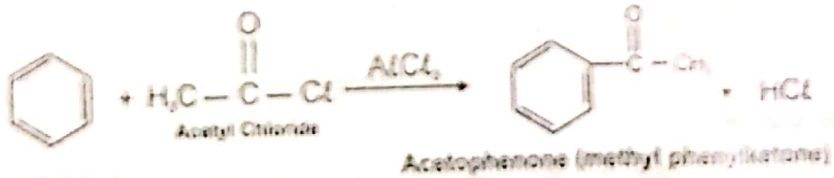
(v) Friedel-Crafts Acylation

"The introduction of an acyl group ($R-\overset{O}{\overset{\|}{C}}-$) in the benzene by substituting hydrogen of benzene ring in the presence of an acyl halide and a catalyst ($AlCl_3$) is called Friedel Crafts Acylation or Acylation."

Overall reaction:

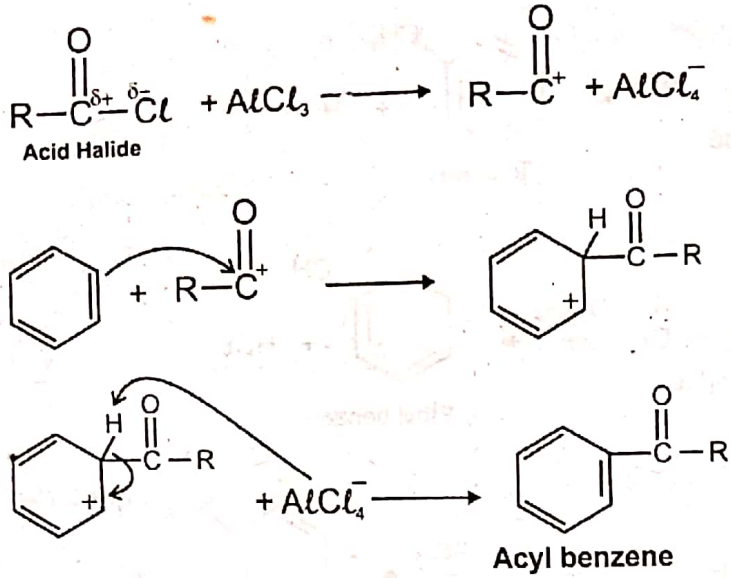


Example:



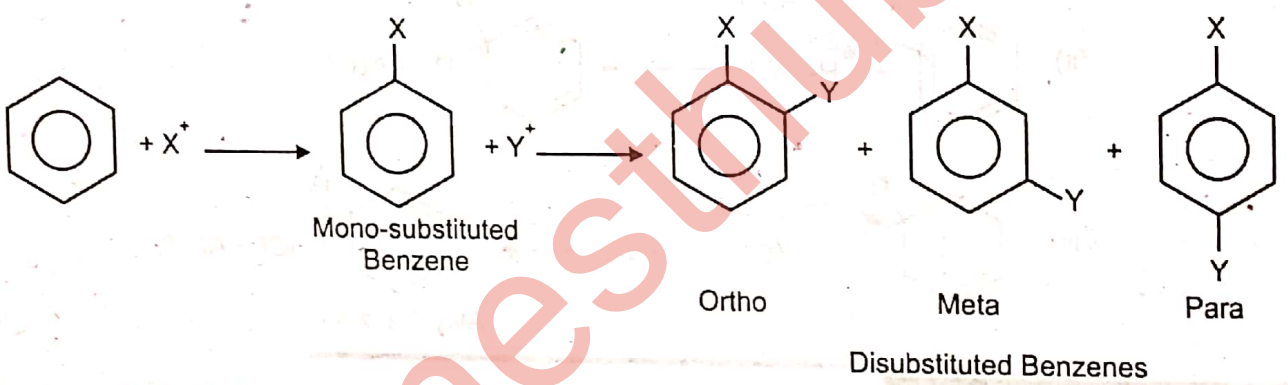
Acetophenone (methyl phenyl ketone)

Mechanism:



SUBSTITUENT EFFECTS

When an electorphilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent. However, the position of a second group into the ring depends on the nature of the first group. The second substituted may enter at ortho, para or meta position.

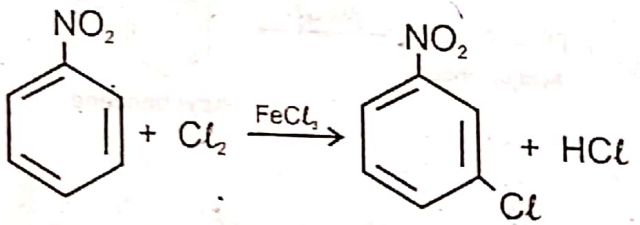


On chance basis 40% ortho, 40% meta and 20% para disubstituted products are expected. However the results do not agree with chance substitution ratio.

Examples:

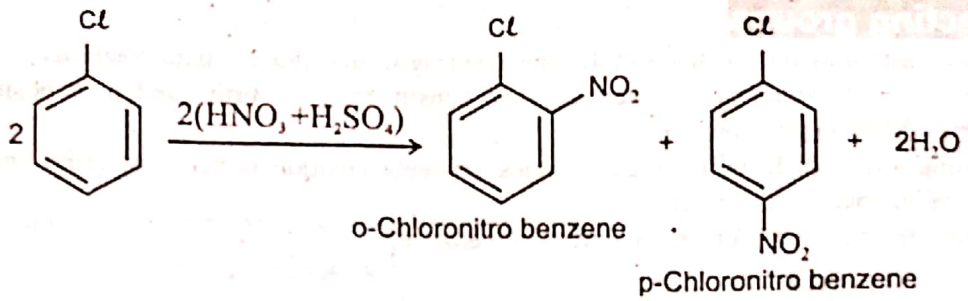
(i) Chlorination of nitrobenzene

m–Chloronitro benzene is the main product of the following halogenation reaction.



(ii) Nitration of chlorobenzene

A mixture of o-Chloronitrobenzne and p-Chloronitrobenzene is obtained from the nitration of chlorobenzene.



o-Chloronitro benzene

p-Chloronitro benzene

It means that the groups already present in the benzene ring directs the second entrant and thus determines the position, which may be taken up by it. There are two types of groups:

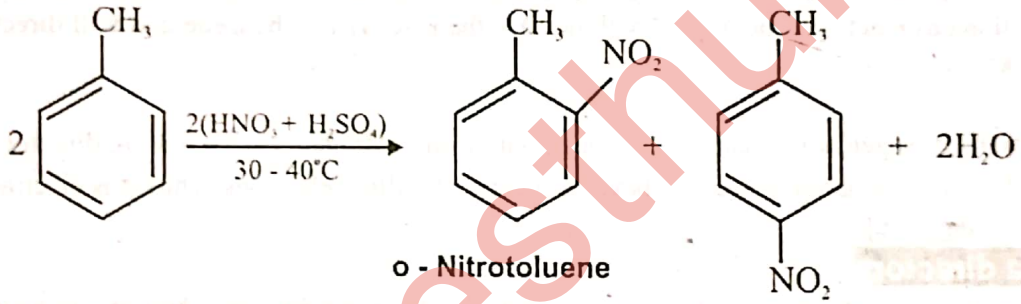
(a) Ortho- and para- directing groups

(b) Meta- directing groups

(1) Ortho and para directing groups

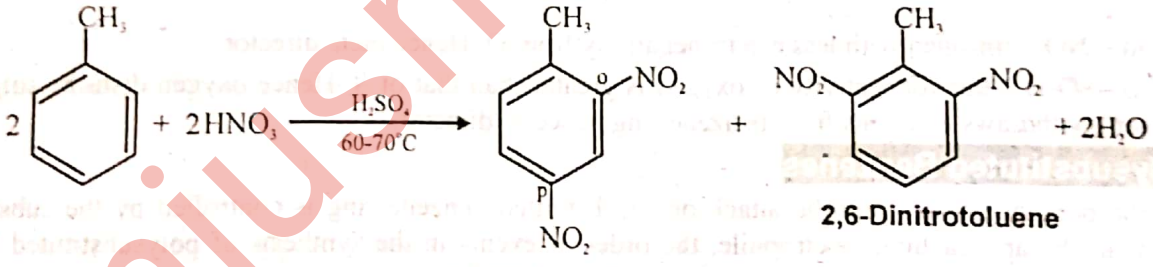
- These groups release electrons towards the benzene ring, at ortho and para positions. Because these position are richer in electron for attack of an electrophile.
- The second group is substituted at ortho and para positions.
- They also enhance the reactivity of benzene ring.

Example: Nitration of toluene: The electron releasing effect of methyl groups is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.



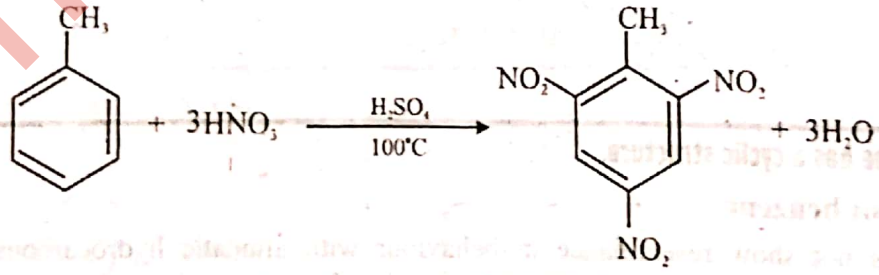
o - Nitrotoluene

p - Nitrotoluene



2,4-Dinitrotoluene

2,6-Dinitrotoluene



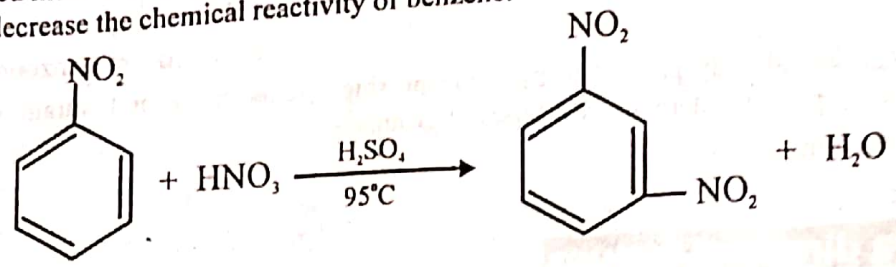
2,4,6-Trinitrotoluene (TNT)

Other examples of ortho and para directing groups are:

$-N(CH_3)_2$, NHR, $-NH_2$, –OH, – OR ($-OCH_3$), – SH, – OCOR, – X (–Cl, –Br, –I) etc.

(2) Meta-directing groups

- These groups withdraw the electrons of the benzene ring from ortho and para positions.
- Due to the electron withdrawing effect of such substituents, the ortho and para position are more electron deficient than the meta position.
- The incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups are called meta-directing groups.
- These groups decrease the chemical reactivity of benzene.



m - dinitrobenzene

The substitution of third nitro groups is not possible because nitro group has deactivated the ring.

Other examples of meta directing groups are:

$-N^+R_3$, $-C \equiv N$, $-COOH$, $-CHO$, $-COR$ etc.

Rules

Predicting ortho and Para directors

If the electronegativity of the atom of the group attached to the benzene ring is greater than any atom of the group, the whole group will act as electron repelling. It will increase the reactivity of benzene and will direct the new entrant to ortho, para positions.

Examples:

(i) In $-NH_2$, nitrogen with greater electronegativity from hydrogen. Hence o & p-, director.

(ii) $C\ell$ – has no other atom hence will have no danger of pulling electrons. Thus it is electron repelling and o & p- directing group.

Predicting meta directors

If the electronegativity of the atom of the group attached to the benzene ring is less, it will be under constraint and it will withdraw electrons form the ring making it less reactive and directing the new entrant to meta position.

Examples:

(i) In $-NO_2$, nitrogen with less electronegativity from O. Hence meta director.

(ii) In $-SO_3H$, electronegativity of oxygen is greater than that of S. Hence oxygen disturbs sulphur, which in turn withdraws electrons from benzene ring hence m-director.

Making Polysubstituted Benzenes

Since the position of electrophilic attack on a substituted benzene ring is controlled by the substituent already present rather than the approaching electrophile, the order of events in the synthesis of polysubstituted benzenes need careful planning to ensure success.

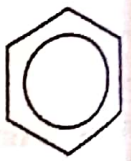
QUICK QUIZ

1. (b) Prove that benzene has a cyclic structure.

Ans. Cyclic Structure of benzene

(i) Benzene does not show resemblance in behaviour with aliphatic hydrocarbons (alkanes, alkenes and alkynes). So, its straight chain structure is ruled out.

(ii) **Kekule** proposed cyclic structure for benzene having three double bonds alternating with three single bonds. **Dewar** also suggested three resonance contributing cyclic structures for benzene.



Benzene

(iii) **X-ray** studies show regular hexagonal planar structure of benzene.

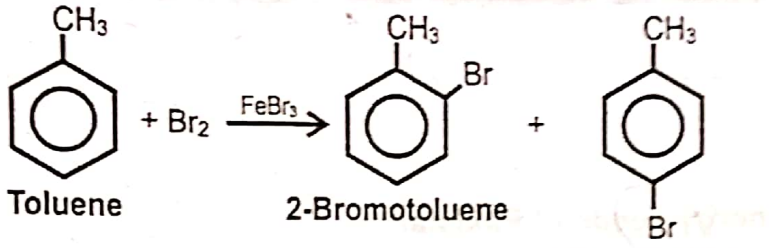
(iv) **Atomic orbital treatment** of benzene structure shows that π - electrons are delocalized and all six carbon atoms are equivalent.

(v) Since the structure of benzene is a **resonance hybrid**, therefore all the C – C bond lengths are equal. So, benzene is given a cyclic structure.

2. **Predict the major products of bromination of the following compounds**

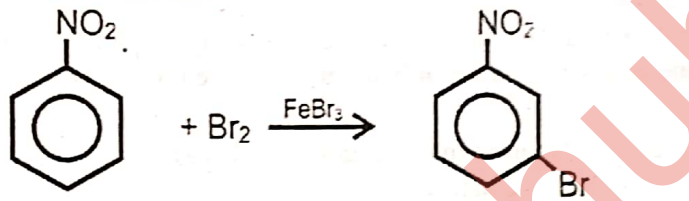
(a) Toluene (b) Nitrobenzene (c) Bromobenzene (d) Benzoic acid (e) Benzaldehyde (f) Phenol

Ans. **(a) Bromination of Toluene:**



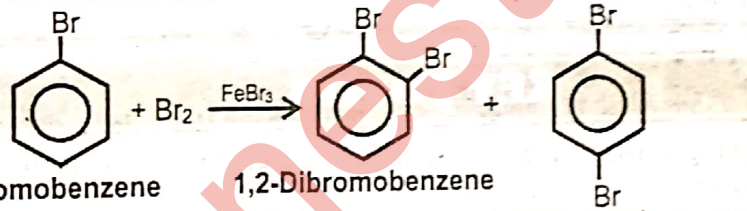
Toluene — 2-Bromotoluene — 4-Bromotoluene

(b) Bromination of Nitrobenzene:



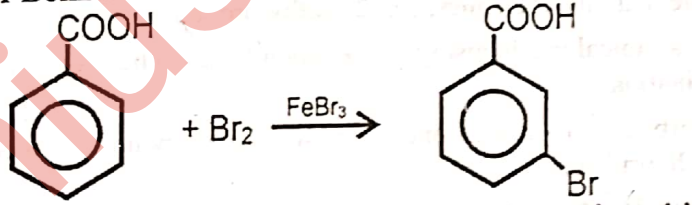
Nitrobenzene — 3-Nitrobromobenzene

(c) Bromination of Bromobenzene:



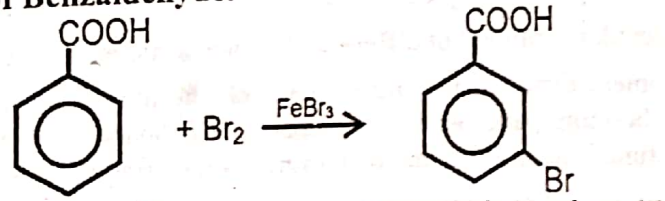
Bromobenzene — 1,2-Dibromobenzene — 1,4-Dibromobenzene

(d) Bromination of Benzoic acid:



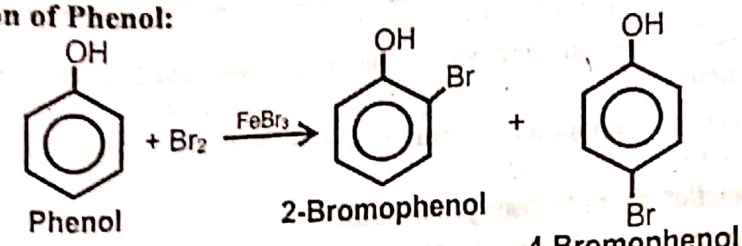
Benzoic acid — 3-Bromobenzoic acid

(e) Bromination of Benzaldehyde:



Benzoic acid — 3-Bromobenzoic acid

(f) Bromination of Phenol:



Hydrocarbons

Important as fuel for future energy needs of Pakistan

- Ethanol, Natural Gas, Propane
- Biodiesel - an alternative fuel based on vegetable oils or animal fats
- Methanol - also known as wood alcohol

P-Series fuels - a blend of ethanol, natural gas liquids and methyltetrahydrofuran (MeTHF). P-Series fuels can be used alone or mixed with gasoline in any ratio by simply adding it to the tank.

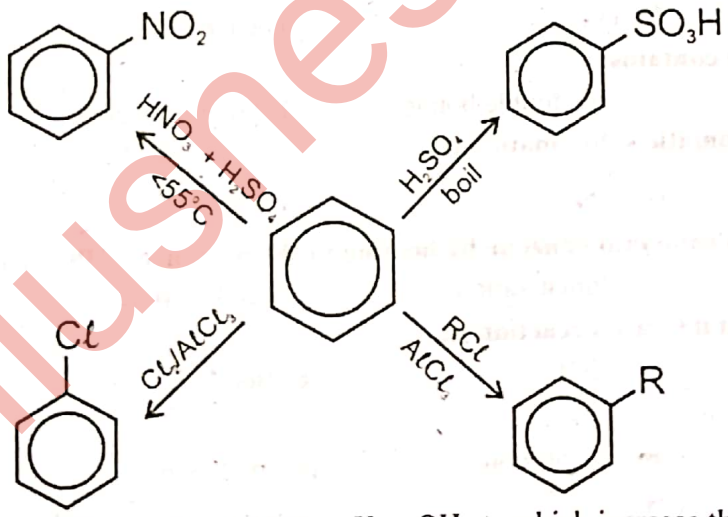
Uses of Hydrocarbons

1. Butane is used as a fuel in lighter and is also used in some camping stoves.
3. Coal is used for the manufacturing of synthetic petrol.
4. Ethylene is the hormone that causes tomatoes and apples to ripen.
5. Oxyacetylene torch is used for cutting of metals.
6. Methane is used to manufacture urea fertilizer.

KEY POINTS

- Compared to other functional groups, alkanes tend to have low melting and boiling points and very low solubility in polar solvents such as water.
- Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by sigma bonds. They have a general formula of C_nH_{2n+2}.
- Branched alkanes are more stable than linear alkanes, e.g. 2-methylpropane is more stable than n-butane.
- Alkanes react with halogens by a radical mechanism to give haloalkanes. The mechanism consists of three steps, initiation, propagation and termination.
- Alkenes are unsaturated hydrocarbons with at least one C = C the double bond is composed of a σ and a π bond. Carbon atoms in alkenes are sp^2 hybridized.
- Alkenes are very reactive compounds. They undergo electrophilic reactions very easily.
- Addition of unsymmetrical reagent to an unsymmetrical alkene takes place in accordance with the Markownikov's Rule.
- Compounds that have the same molecular formula but different chemical structures are called isomers.
- **Constitutional** (or structural) isomers differ in the order in which the atoms are connected so they contain different functional groups and / or bonding patterns: e.g. 1-Propanol, 2-Propanol and ethyl methyl ether (C_3H_8O) **Stereoisomers** contain the same functional groups and differ only in the arrangement of atoms in space.
- **Conformational** isomers (or conformers or rotamers) are stereoisomers produced by rotation about sigma bonds.

- **Configurational** isomers are stereoisomers that do not readily interconvert at room temperature and can (in principle at least) be separated.
- **Geometric** isomers are configurational isomers that differ in the spatial position around a bond with restricted rotation (e.g. a double bond).
- **Optical** isomers are configurational isomers that differ in the 3D relationship of the substituents about one or more atoms.
- **Enantiomers** are optical isomers that are non-superimposable mirror images.
- **Diastereomers** are optical isomers that are not enantiomers.
- Hydrocarbons containing a triple bond are known as alkynes or acetylenes.
- Alkynes undergo addition reactions and two molecules of a reagent are added in it.
- The decreasing reactivity order of alkanes, alkenes and alkynes are as follows: Alkenes > Alkynes > Alkanes
- Aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.
- Aromatic hydrocarbons containing one benzene ring in their molecules are called monocyclic aromatic hydrocarbons.
- Aromatic hydrocarbons containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons.
- The electrons in benzene are loosely held and the ring acts as a source of electrons.
- Hence benzene is readily attacked by electrophiles in the presence of a catalyst.
- Since electrophilic substitutions reaction lead to resonance stabilized benzene derivatives so substitution are the main reaction of benzene.
- Resonance energy of benzene is 152kJ/mole.
- Structure of benzene is the resonance hybrid of two Kekule's structures and three Dewar's structures.
- The C_6H_5 – group is called phenyl.
- The characteristic reactions of benzene is electrophilic substitution. Some important substitution reactions are shown on the following diagram.



- Groups like $-NH_2$, NHR, – OR, – SH, – OCOR, – X, – OH etc which increase the electron density in the nucleus and facilitate further electrophilic substitutions are known as ortho and para- directing groups.
- Groups like CN, –CHO, NH_3, NR_3, CCl_3, which decrease the reactivity of Benzene nucleus and direct the incoming group at m- position.

EXERCISE

Q1. Multiple Choice Questions. Encircle the correct answer:

- Read the question carefully.
- Try to answer the question yourself before reading the answer choices.
- Guess only if you can eliminate one or more answer choices.
- Drawing a picture can help.
- Don't spend too much time on any one question.
- In-depth calculations are not necessary; approximate the answer by rounding.

(i) **The molecule of ethane possesses which hybridization;**
(a) sp^3 (b) sp^2 (c) sp (d) sp^2d

(ii) **The sp^2 hybrid orbitals are oriented in space at one angle;**
(a) 109.5° (b) 180° (c) 100° (d) 120°

(iii) **The geometry of acetylene is,**
(a) angular (b) bent (c) trigonal (d) linear

(iv) **Which reaction is used as test for the presence of alkene;**
(a) reaction of cold diluted alkaline $KMnO_4$ (b) combustion
(c) polymerization (d) catalytic hydrogenation

(v) **The general formula of alkane is;**
(a) C_nH_{2n+2} (b) C_nH_n (c) C_nH_{2n} (d) C_nH_{2n-2}

(vi) **Sodalime is;**
(a) NaOH (b) KOH
(c) mixture of Na and Ca hydroxide (d) CaO and NaOH

(vii) **The marsh gas is**
(a) ethane (b) methane (c) propane (d) butane

(viii) **Acidic hydrogen is present in**
(a) acetylene (b) ethane (c) benzene (d) ethene

(ix) **The benzene molecule contains:**
(a) three double bonds (b) two double bonds (c) one double bond (d) none of these

(x) **The electrophile in aromatic sulphonation is;**
(a) H_2SO_4 (b) HSO_4^- (c) SO_3 (d) SO_4^{-2}

(xi) **The conversion of n-hexane into benzene by heating in the presence of Pt is called;**
(a) isomerization (b) aromatization (c) dealkylation (d) rearrangement

(xii) **Catalyst used for Friedal Craft's reaction is;**
(a) HNO_3 (b) $AlCl_3$ (c) $BeCl_3$ (d) $FeCl_3$

(xiii) **Benzene cannot undergo**
(a) elimination (b) substitution (c) oxidation (d) addition

(xiv) **Shape of benzene molecule is**
(a) pyramidal (b) linear planar (c) trigonal (d) hexagonal planar

(xv) **In which one of the following compounds, the benzene ring is isolated;**
(a) naphthalene (b) anthracene (c) phenanthrene (d) diphenyl ethane

(xvi) **Two compounds have the same composition and also have the same atoms attached to the same atoms although with different orientations in space. These compounds are**
(a) identical (b) position isomers (c) structural isomers (d) stereoisomerism

(xvii) **The isomers of a substance must have**
(a) same chemical properties (b) same molecular weight

(c) same structural formula (d) same functional groups

(xviii) **Ethanol and dimethyl ether are best considered:**
(a) structural isomers (b) stereoisomers (c) enantiomers (d) diasteromers

(xix) **Alkenes show geometrical isomers due to**
(a) asymmetry (b) rotation around a single bond
(c) resonance (d) restricted rotation around a double bond

(xx) **Geometrical isomerism is shown by**
(a) lactic acid (b) maleic acid (c) 1-Butene (d) 1,1-Dichloroethylene

(xxi) **A molecule is said to be chiral**
(a) if it contains plane of symmetry (b) if it contains center of symmetry
(c) if it cannot be superimposed to its mirror image (d) if it can be superimposed on its mirror image

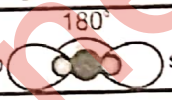
(xxii) **Which of the statements is false regarding chiral compounds**
(a) rotate the plane of polarized light (b) have cis and tans isomers
(c) exist as enantiomers (d) can be detected with a polarimeter

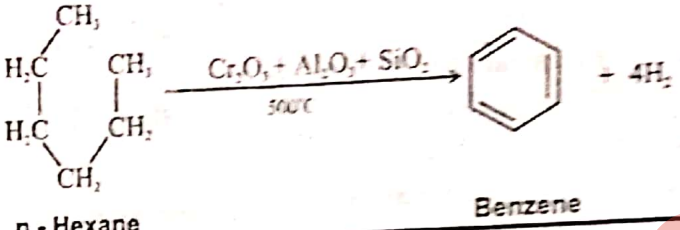
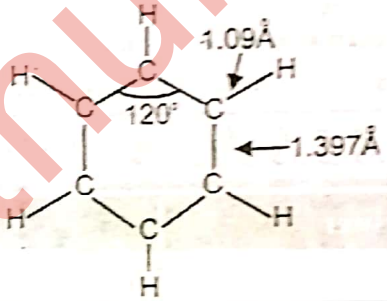
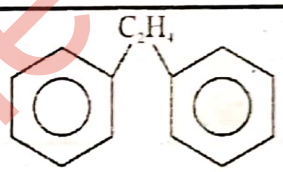
(xxiii) **An optically active compound**
(a) must contain at least four carbons (b) when in solution rotate the plane of polarized light
(c) must always contain an asymmetric carbon atom
(d) in solution always give a negative reading in polarimeter

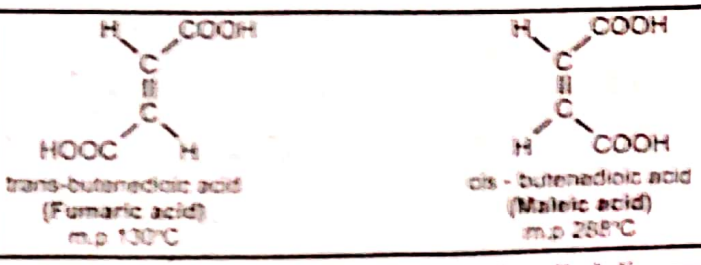
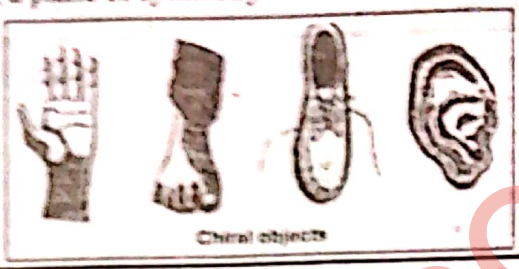
(xxiv) **Plane polarized light is affected by**
(a) identical molecules (b) all polymers (c) chiral molecules (d) all biomolecules

(xxv) **It is possible to distinguish between optical isomers**
(a) by using chemical tests (b) by mass spectrometry (c) by IR spectroscopy (d) by polarimetry

SOLVED EXERCISE MCQs

Q.No	Answer	Reason
(i)	(a) sp^3	In ethane, there is C – C so each carbon is sp^3 hybridized.
(ii)	(d) 120°	Angle b/w each orbital is 120°.
(iii)	(d) linear	
(iv)	(a) reaction of cold diluted alkaline $KMnO_4$	When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline $KMnO_4$ solution (Baeyer's Reagent) at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ solution is discharged during the reaction.
(v)	(a) C_nH_{2n+2}	The general formula of alkane is C_nH_{2n+2}.
(vi)	(d) CaO and NaOH	Soda-lime is prepared by soaking quick lime (CaO) with caustic soda solution and drying the product.
(vii)	(b) methane	The name marsh gas was given to methane because it was found in marshy places.
(viii)	(a) acetylene	In acetylene, the hydrogen atom is bonded to the carbon atom with sp-s overlap. The sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic. $H^{\delta+}—C^{\delta-} \equiv C^{\delta-}—H^{\delta+}$
(ix)	(d) none of these	In benzene molecule, the six p-orbitals of six carbon atoms overlap with each other to form a continuous delocalized p-electron cloud sheath, so, actually,

		three double bonds are not present.
(x)	(c) SO_3	During sulphonation of aromatic compounds, SO3 acts as an electrophile and it is generated by: $H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO_4^-$
(xi)	(b) aromatization	The conversion of Aliphatic compounds into aromatic compounds is aromatization.  n - Hexane Benzene
(xii)	(b) $AlCl_3$	The introduction of an alkyl group (R) in the benzene ring in the presence of an alkyl halide and a catalyst ($AlCl_3$) is called Friedel Crafts alkylation or Alkylation.
(xiii)	(a) elimination	Benzene gives substitution reactions, oxidation reactions as well as addition reactions. As it is very stable so elimination is not possible.
(xiv)	(d) hexagonal planar	The X-ray studies of benzene have confirmed that benzene has regular hexagonal structure 
(xv)	(d) diphenyl ethane	 Diphenylethane
(xvi)	(d) stereoisomerism	When isomerism is caused by the different arrangements / orientation of atoms or groups in space, the phenomenon is called Stereoisomerism.
(xvii)	(b) same molecular weight	Since isomers have same molecular formula therefore they most have same molecular weight.
(xviii)	(a) structural isomers	Functional isomers have the same molecular formula but different functional groups. **C_2H_6O:** $CH_3 - O - CH_3$ Dimethyl ether; $CH_3 - CH_2 - OH$ Ethyl alcohol. Functional group isomers is a kind of structural isomers.
(xix)	(d) restricted rotation around a double bond	When two carbon atoms are joined by a double bond, they cannot rotate freely. As a result, the relative positions of the various groups attached to these carbon atoms get fixed and gives rise to cis- trans isomers.

(xx)	(b) maleic acid	 trans-butenedioic acid (Fumaric acid) m.p 130°C; cis - butenedioic acid (Maleic acid) m.p 288°C
(xxi)	(c)if it cannot be superimposed to its mirror image	An object lacking a plane of symmetry is called dissymmetric or Chiral.  Chiral objects
(xxii)	(b) have cis and tans isomers	Cis- and trans-isomerism is geometrical isomerism. It is not related to the chiral nature of molecule.
(xxiii)	(b) when in solution rotate the plane of polarized light	An optically active compound can exist in two isomeric forms which rotate the plane of polarized light in opposite directions. These are called optical Isomers and the phenomenon is known as optical isomerism
(xxiv)	(c) chiral molecules	Plane polarized light is affected by chiral molecules.
(xxv)	(d) by polarimetry	Optically isomers can rotate the pane polarized light in different directions. Thus they can be identified by polarimetry.

SHORT ANSWERS QUESTIONS

2. Give brief answers to the following questions.

(i) Why carbon is sp^3 hybridized in the compounds?

Ans. When a carbon atom is linked to 4 other atoms and those atoms are arranged in space at the corners of a tetrahedron (bond angle 109.5°), then the hybridization is sp^3. In this hybridization carbon intermixes one s-orbital and three p-orbitals, which produces four sp^3 hybrid orbitals.

(ii) How is pi-bond formed in alkenes and alkynes?

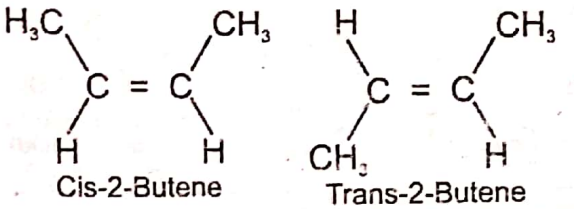
Ans.
- In alkenes, three sp^2 orbitals of each carbon atom overlap separately with other orbitals of atoms to form three σ-bonds. This gives rise to what is called the σ-frame work. The unhybridized orbitals of each carbon atom will then overlap in a parallel fashion to form a π-bond.
- In alkynes, two sp hybridized orbitals overlap to form a σ-bond. The other sp orbital is utilized to form a σ-bond with other orbital of the neighbouring atom. The two unhybridized p orbitals on a carbon atom will overlap separately with the p orbitals of the other carbon atom to give two π-bonds both perpendicular to the σ-framework.

(iii) What is cis-trans isomerism?

Ans. Those compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as the cis-trans or geometric isomerism.

Example:

C_4H_8:



(iv) Why alkanes are relatively chemically inert?

Ans. Alkanes are least reactive compounds due to following two reasons:

(i) Non – polar nature:

The eletronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C – H and C – C are equally shared making them almost non-polar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc find no reaction site in the alkane molecules to which they could be attached.

(ii) Inertness of σ-bond:

In a σ-bond the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover, the electrons present in a σ-bond can neither attack on any electrophile nor a nucleophile can attack on them. Both these facts make alkanes less reactive.

(v) Alkenes usually undergo addition reactions while alkanes do not why?

Ans. Alkenes are unsaturated hydrocarbons due to the presence of double bond. As a result the characteristic reactions of alkenes are electrophilic addition reactions. On the other hand, alkanes are saturated hydrocarbons. Therefore they usually undergo substitution reactions.

(vi) What is stereoisomerism?

Ans. Stereoisomerism:

When isomerism is caused by the different arrangements / orientation of atoms or groups in space, the phenomenon is called Stereoisomerism.

- The stereoisomers have the same structural formulas but differ in arrangement of atoms in space.

Stereoisomerism is of two types:

(1) Optical Isomerism (2) Geometrical or Cis-Trans Isomerism

(vii) How optical isomers arise?

Ans. Optical isomers arise when a carbon atom is bonded to four different groups. These can be attached in two different ways, one of which is the mirror image of the other. This type of isomerism is called optical isomerism, because the two isomers affect plane-polarized light differently.

- The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as **Dextrorotatory Isomer** or (+) isomer.
- The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the **Laevorotatory Isomer** or (–) isomer.

(viii) What are conjugated bonds formed?

Ans. Conjugated bonds are formed when there is alternation between double and single bonds. These enables the electrons to be delocalized over the whole system and so be shared by many atoms. This means that the delocalized electrons may move around the whole system.

e.g. One of the simplest conjugated molecules is 1,3-butadiene ($H_2C = CH – HC = CH_2$).

(ix) Why alkenes are more reactive than alkynes?

Ans. A π–bond in alkenes is not only weak but its electrons are more exposed to an attack by an electrophilic reagent. Both these facts make the alkenes a very reactive class of compounds. Alkynes although contain two π–bonds are less reactive than alkenes towards electrophilic regents. This is because the bond distance between the two triple bonded carbon atoms is very short and hence the π–electrons are not available to be attacked by electrophilic reagents.

(x) Justify the given order of reactivity? Alkenes > Alkynes > Alkanes

Ans. The general decreasing reactivity order of alkanes, alkenes and alkynes is as follows:

Alkenes > Alkynes > Alkanes

It has already been explained that a π–bond in alkenes is not only weak but its electrons are more exposed to an attack by an electrophilic reagent. Both these facts make the alkenes a very reactive class of compounds. Alkynes although contain two π–bonds are less reactive than alkenes towards electrophilic regents. This is because the bond distance between the two triple bonded carbon atoms is very short and hence the π–electrons are not available to be attacked by electrophilic reagents. **Alkynes are, however, more reactive than alkenes towards nucleophilic reagents.**

(xi) What is meant by dehydration of alcohols?

Ans. **Dehydration of Alcohols**

Removal of water molecule from an alcohol is called dehydration of alcohol.

Example:

When vapours of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.

$$\underset{\text{Alcohol}}{R-CH_2-\underset{OH}{\underset{|}{CH_2}}} \xrightarrow[340\text{-}450\,^{\circ}C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

(xii) What are polymerization reactions?

Ans. **Polymerization**

The process in which small organic molecules (monomers) combine together to form a larger molecule (polymer) is called polymerization.

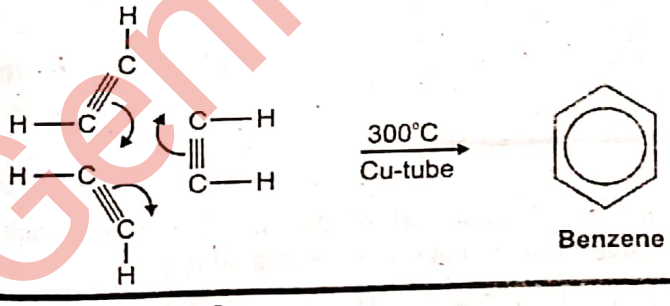
Example: Ethene polymerizes to polythene at 400°C at a pressure of 100 atm.

$$n\ CH_2 = CH_2 \xrightarrow[\text{100 atm pressure}\ \text{traces of } O_2\ (0.1\%)]{400^{\circ}C} \underset{\text{Polyethylene}}{+CH_2-CH_2+_n}$$

(xiii) How will you convert acetylene into benzene?

Ans. **Conversion of Acetylene to Benzene**

When acetylene is passed through a copper tube at 300°C, it polymerizes to benzene.



Benzene

(xiv) What is resonance?

Ans. **Resonance:**

The possibility of different pairing schemes of an valence electrons of atom is called resonance" and the different structures thus arranged are called "Resonance Structures.

(xv) What is resonance energy?

Ans. Resonance energy:

The difference in potential energy between the actual molecular entity and the contributing structure of lowest potential energy is called resonance energy.

e.g. The resonance energy for benzene is 152 kJ or 36 kcal / mol.

Q.3. Give detailed answers for the following questions

2. (a) How will you prepare 1-butene from?

(i) an alkyl halide (ii) Alcohols (iii) Electrolysis of salt (iv) Vic-dihalides.

Ans. (i) an alkyl halide

When 1-bromobutane is heated with alcoholic potassium hydroxide, it undergoes dehydrohalogenation to form 1-butene.

$$\underset{\text{1-Bromobutane}}{CH_3 - CH_2 - \underset{H}{\overset{}{CH}} - \underset{Br}{\overset{}{CH}}} + KOH \xrightarrow{\text{alcohol}} \underset{\text{1-Butene}}{CH_3 - CH_2 - CH = CH_2} + KBr + H_2O$$

(ii) Alcohols

When vapors of 1-butanol is treated with H_2SO_4 at 140-170°C, dehydration takes place with the formation of 1-butene.

$$\underset{\text{1-Butanol}}{CH_3 - CH_2 - \underset{H}{\overset{}{CH}} - \underset{OH}{\overset{}{CH_2}}} \xrightarrow[140\text{-}170^\circ C]{H_2SO_4} \underset{\text{1-Butene}}{CH_3 - CH_2 - CH = CH_2} + H_2O$$

(iii) Electrolysis of salt

When aqueous solution of potassium salt of ethyl succinic acid is electrolyzed, then 1-butene is produced. This reaction is called Kolbe's electrolysis.

$$\begin{array}{l} CH_2 - COOK \\ | \\ CH - COOK \\ | \\ CH_2 \end{array} + 2H_2O \xrightarrow{\text{electrolysis}} \underset{\text{1-Butene}}{\begin{array}{l} CH_2 \\ | \\ CH \\ || \\ CH_2 \end{array}} + 2CO_2 + 2KOH + H_2$$

(iv) Vic-dihalides.

Vicinal dihalides have two halogen atoms on adjacent carbon atoms. 1,2-dibromobuane is a vicinal dihalide. When it is treated with Zn in anhydrous solvent e.g. methanol or acetic acid, it gives 1-butene.

$$\underset{\text{1,2-Dibromob6utane}}{CH_3 - CH_2 - \underset{Br}{\overset{}{CH}} - \underset{Br}{\overset{}{CH_2}}} + Zn \xrightarrow{CH_3OH} \underset{\text{1-Butene}}{CH_3 - CH_2 - CH = CH_2} + ZnBr_2$$

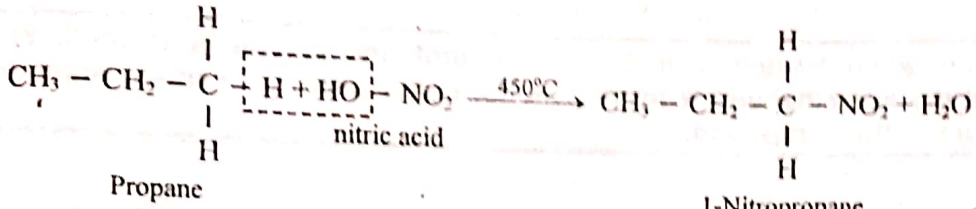
(b) What products is formed when n-propane undergo following reactions?
(i) Combustion (ii) Nitration

Ans. (i) Combustion

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O + \text{heat}$$

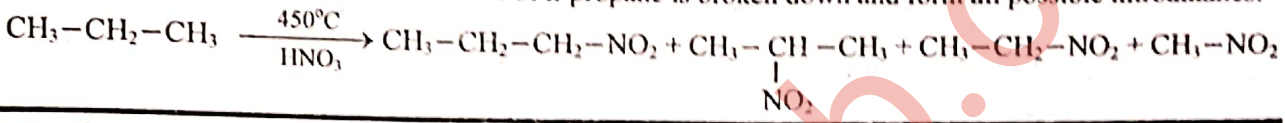
(ii) Nitration

n-Propane reacts with nitric acid in vapour-phase under drastic conditions (at 400-500°C) to give nitropropane.



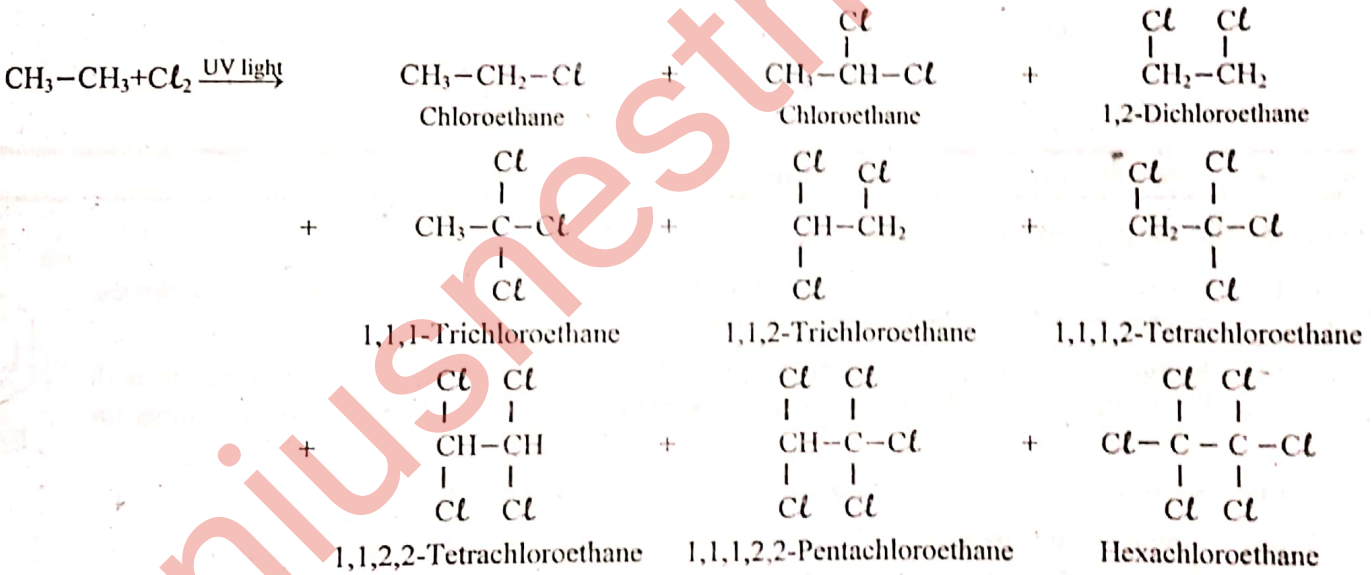
Propane — nitric acid — 1-Nitropropane

However, under drastic conditions, the molecule of n-propane is broken down and form all possible nitroalkanes.



3. (a) When ethane reacts with Cl_2 in UV light the mixture of products is formed Give the detail of reaction with mechanism and all types of products.

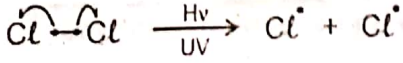
Ans: Ethane reacts with Cl_2 in UV light to give a mixture of products. The reaction occurs by free radical mechanism. This reaction is called radical substitution reaction. the products of the reactions are:



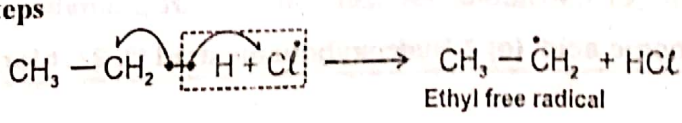
Mechanism: Free Radical Substitution

Initiation step

Step-1

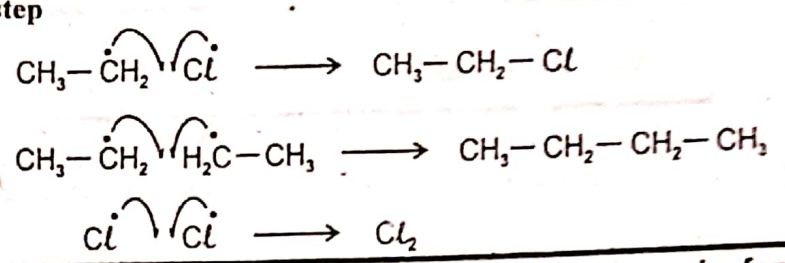


Propagation steps



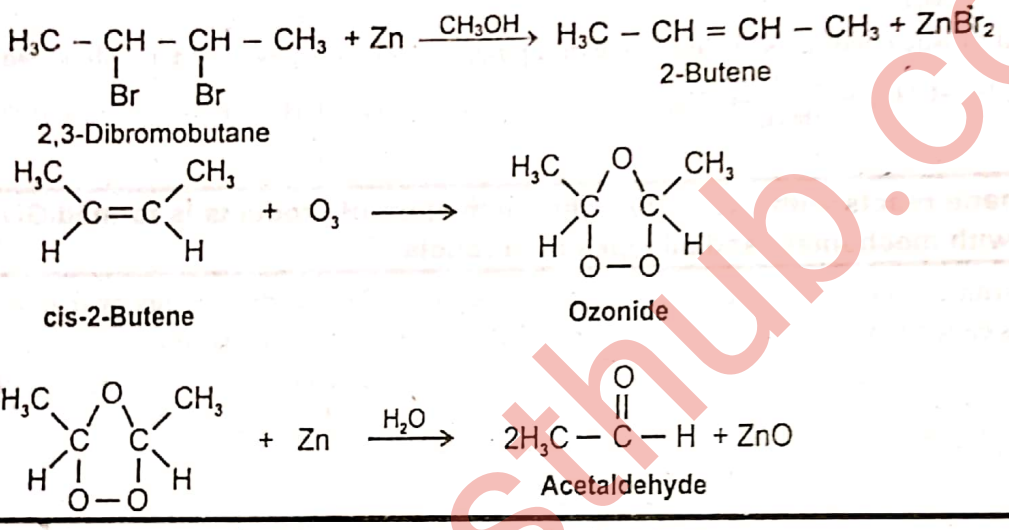
- These two steps are repeated over and over again. Thus, all hydrogens of ethane are replaced by chlorine atoms. The hydrogen atoms are replaced one by one.

Termination step



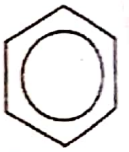
(b) A compound when treated with Zn in methanol, the alkene is formed. When alkene is ozonolysed the acetaldehyde is formed as the major product. Explain reactions; give name and structure of the compound.

Ans.



4. (a) How will you prove that benzene has cyclic structure.

Ans. Cyclic Structure of benzene


Benzene

(i) Benzene does not show resemblance in behaviour with aliphatic hydrocarbons (alkanes, alkenes and alkynes). So, its straight chain structure is ruled out.

(ii) **Kekule** proposed cyclic structure for benzene having three double bonds alternating with three single bonds. **Dewar** also suggested three resonance contributing cyclic structures for benzene.

(iii) **X-ray** studies show regular hexagonal planar structure of benzene.

(iv) **Atomic orbital treatment** of benzene structure shows that π-electrons are delocalized and all six carbon atoms are equivalent.

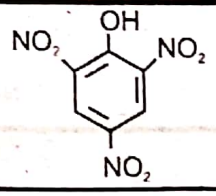
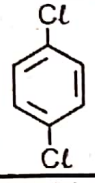
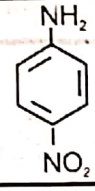
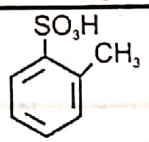
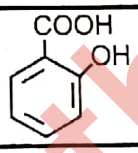
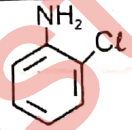
(v) Since the structure of benzene is a **resonance hybrid**, therefore all the C-C bond lengths are equal. So, benzene is given a cyclic structure.

7. Write the structural formulas for the following benzene derivatives:

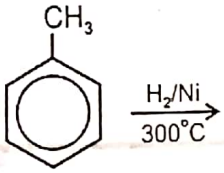
(a) 2, 4, 6-Trinitrophenol (b) 1,4-Dichlorobenzene (c) 4-Nitrophenylamine

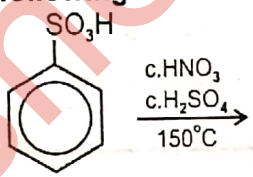
(d) 2-Methlbenznesulphonic acid (e) 2-Hydroxybenzoic acid (f) 2-Chlorophenylamine

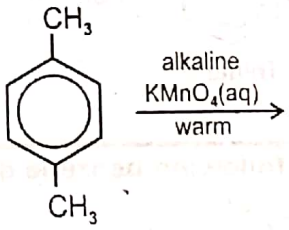
Ans.

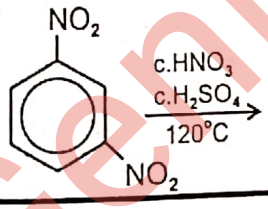
No.	Benzene derivative	Structural Formula
(a)	2,4,6-Trinitrophenol	
(b)	1,4-Dichlorobenzene	
(c)	4-Nitrophenylamine	
(d)	2-Methlbenznesulphonic acid	
(e)	2-Hydroxybenzoic acid	
(f)	2-Chlorophenylamine	

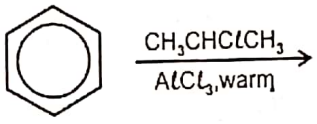
8. Predict the major products of the following reactions:

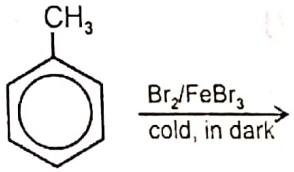
(a) 

(b) 

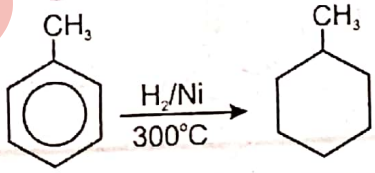
(c) 

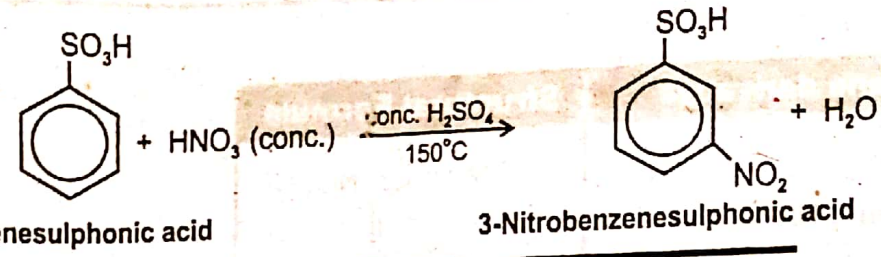
(d) 

(e) 

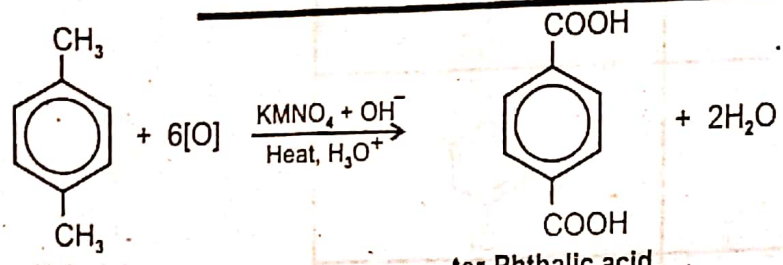
(f) 

Ans.

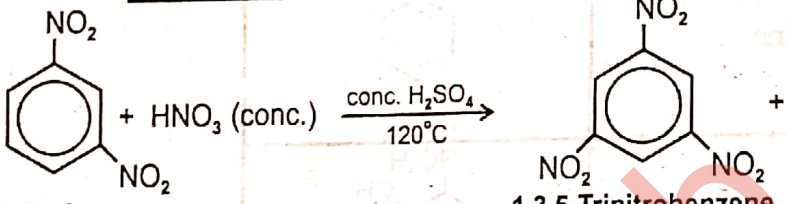
(a) 

(b) 

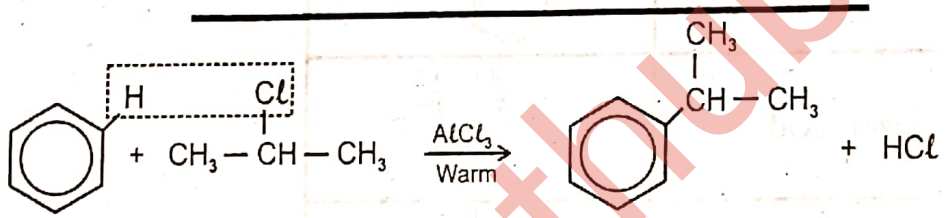
Benzenesulphonic acid — 3-Nitrobenzenesulphonic acid

(c) 

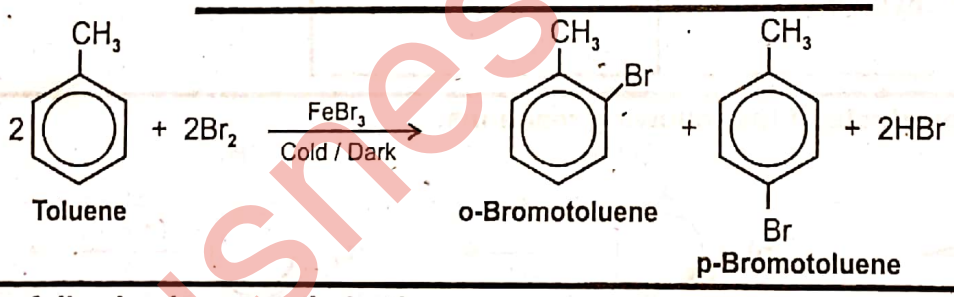
p-Xylene — ter-Phthalic acid

(d) 

1,3-Dinitrobenzene — 1,3,5-Trinitrobenzene

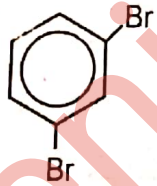
(e) 

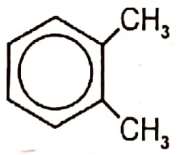
Benzene — Isopropylbenzene

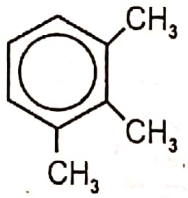
(f) 

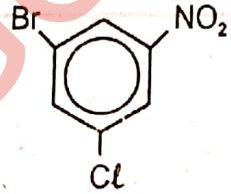
Toluene — o-Bromotoluene — p-Bromotoluene

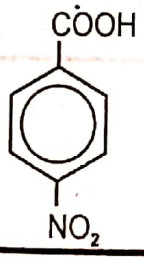
9. Name the following benzene derivatives:

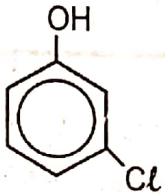
(a) 

(b) 

(c) 

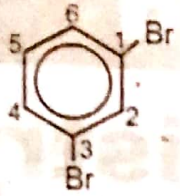
(d) 

(e) 

(f) 

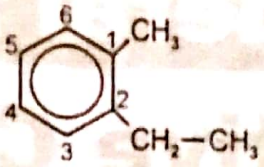
Ans.

(a)



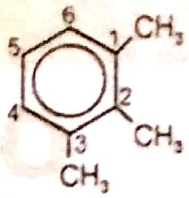
1, 3-Dibromobenzene

(b)



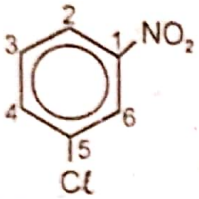
2-Ethyltoluene

(c)



1,2,3-Trimethylbenzene

(d)

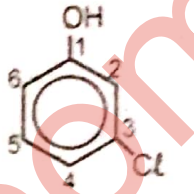


3-Bromo-5-chloronitrobenzene

(e)

4-Nitrobenzoic acid

(f)



3-Chlorophenol

Skill Activity

Take small quantity of alkali metals and alkaline earth metals salts like NaCℓ, KNO_3, $CaCO_3$, $SrCℓ_2$, $Ba(CH_3COO)_2$ etc. and make paste with conc. HCℓ and note the colour of the flame on the burner.