Chemistry : Hydrocarbons

ALKANES

- **Alkanes** : The saturated aliphatic hydrocarbons containing C-C single bond is called alkanes.
- They are also called as paraffins due to their lew chemical reactivity.
- Its general formula is C_nH_{2n+2}

  Where n = No. of carbon atoms = 1, 2, 3, ... etc >- Alkanes containing only C-C and C-H single covalent bond,

e.g. i) n — 1, methane CH_4

ii) n = 2, ethane C2H6

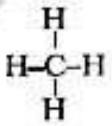
iii) n = 3, propane C3H8

- **Structural formula and electronic strucMHK**
- Every carbon atom in alkane are sp^3 **hybridised and** has a tetrahedral geometry with H-C-H, C- C-H and C-C-C bond,

i) **Methane CH_4**

- Methane contains one carbon atom and four hydrogen atoms.
- Carbon atom is tetravalent and hydrogen atom is monovalent. Therefore in methane one central carbon forms four single bonds with hydrogen atoms.

C-C = 154 Pm C -H = 112 Pm



- Bond strength in C-C = 200 Kcal/mole

- **Electronic structure**
- The exact arrangement of electrons around on atom in the formation of covalent bond is called as electronic structure,

i) **Methane : CH_4**

- Methane contains one C and four H atoms.
- Therefore four electrons in valence shell of carbon and there is one electron with hydrogen. Thus carbon in methane shares its four electrons with four different hydrogen atoms to form four single bonds.

- = electron of C x = electron of H

- **Classification of alkanes**
- Alkanes are straight chain and branched chain compounds.

i) **Straight chain compounds**

- The alkanes in which all carbon atoms are arrange in straight continuous chain are called as straight chain alkanes.
- In these carbon atom is linked to no more than two other carbon atoms. It is called as n-alkanes.

e.g. Methane = CH_4

Ethane = CH_3–CH_3

Propane = CH_3–CH_2–CH_3

n-butane = $CH_3 - CH_2 - CH_2 - CH_3$

ii) **Branched chain alkanes**

- The alkanes in which all carbon atoms are not in continuous chain but have side chain (branching) are called as branched chain alkanes.
- They are subdivided into two types.

a) **Iso-alkanes** - The alkanes which contain one carbon branch (methyl group) attached to the second carbon atom of normal chain are called iso- alkanes.

- The term 'iso' is used when one carbon atom is attached to three other carbon atoms.

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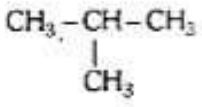
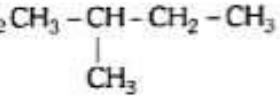
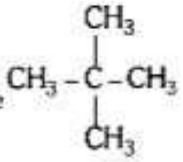
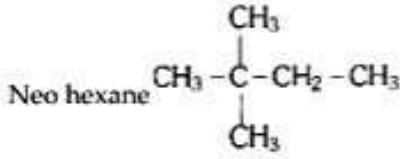
e.g. Isobutane 

Isopentane 

b) **Neo-alkanes** - The alkanes which contain two carbon branches attached to the second carbon atom of a normal chain are called neo alkanes.

❑ The term 'neo' is used when one carbon atom is attached to four other carbon atoms.

e.g. Neo pentane 

Neo hexane 

- **Types of carbon atoms in alkanes**

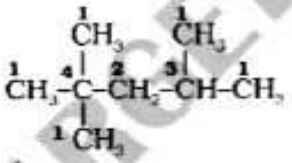
❑ Various carbon atoms present in alkane are classified in following manners.

i) **Primary carbon atom (1°)** - A carbon atom attached to only one other carbon atom.

ii) **Secondary carbon atom (2°)** - A carbon atom attached to two other carbon atoms.

iii) **Tertiary carbon atom (3°) -** A carbon atom attached to three other carbon atoms.

iv) **Quaternary carbon atom (4°) -** A carbon atom attached to four other carbon atoms.



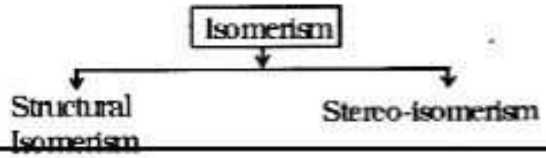
ISOMERISM

❑ The compound having same molecular formula but different structural formula are called as isomers and the phenomenon is called as isomerism.

❑ There are two types of isomerism.

A) Structural isomerism and

B) Stereoisomerism



1. Chain isomerisn 1. Optical isomerism
2. Position isomerism 2. Geometrical isomerian
3. Functional isomerian (cis-trans isomerian)
4. Metamerism
5. Tautomerism

A) Structural isomerism : The compounds having same molecular formula but different structural formulae are called as structural isomerism.

1) Chain isomerism - Difference in the arrangement of carbon atoms in a chain is called as chain isomerism.

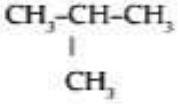
a) The first three members methane, ethane and propane are represented by only one structural formula they do not show isomerism because number of carbon atoms is less in their molecules.

b) As number of carbon atoms in alkane is increased four or more arrangements of atoms are possible.

e.g.

i) Butane (C_4H_{10}) have two isomers because it can have two types of arrangements of carbon atoms.

n-butane $CH_3 - CH_2 - CH_2 - CH_3$

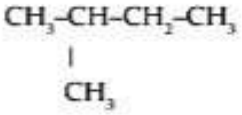
Isobutane 

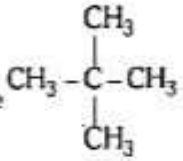
n-butane and iso-butane are chain isomers of each other.

ii) Pentane (C_5H_{12}) have three isomers can have three types of arrangement of carbon atoms,

n-pentane

$CH_3 - CH_2CH_2 - CH_2 - CH_3$

Isopentane 



n-pentane, isopentane, neo-pentane are chain isomers of each other,

c) As the number of carbon atoms increases, the number of possible isomers of alkanes also go on increasing, e.g. i) Butane (C_4H_{10}) has 2 chain isomers.

ii) Pentane (C_5H_{12}) has 3 chain isomers

iii) Hexane (C_6H_{14}) has 5 chain isomers

iv) Heptane (C_7H_{16}) has 9 chain isomers

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v) Octane (C_8H_{18}) has 18 chain isomers

vi) Nonane (C_9H_{20}) has 35 chain isomers

vii) Decane ($C_{10}H_{22}$) has 75 chain isomers

viii) Pentadecane ($C_{15}H_{32}$) has 4,347 chain isomers

Hexane = C_6H_{14}

i) n-hexane $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

ii) 2-methyl pentane $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

iii) 3-methyl pentane $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

iv) 2,3-dimethylbutane $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

v) 2,2-dimethyl butane $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_3$

Heptane (C_7H_{16})

i) n-heptane

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

ii) 2-methyl hexane

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

iii) 3-methyl hexane $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

iv) 2,2-dimethyl pentane: $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_2-CH_3$

v) 3,3-dimethyl pentane : $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_3$

vi) 2,3-dimethyl pentane $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{CH}}}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

vii) 2,4-dimethyl pentane: $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

viii) 2,2,3-trimethyl butane $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

ix) 2-ethyl pentane : $CH_3-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_3$

- **Conformation**
- **Alkyl radical group**

An alkane by the removal of one hydrogen atom is called as alkyl radical group.

- Its name is derived by changing the suffix '-ane' of alkane by'-yl'.
- An alkyl group possesses on unused valency and it is represented by a dash
- It is general formula C_nH_{2n+1}. e.g. Methyl is abrivated as Me, ethyl as Et, propyl as ft, butyl as Bu.

Alkane	Name of alkyl radical	Molecular formula of alkyl radical
Methane (CH_4)	Methyl	$-CH_3$
Ethane (CH_3-CH_3)	ethyl	$-CH_2-CH_3$ $-C_2H_5$
Propane ($CH_3CH_2CH_3$)	n-propyl iso-propyl	$-CH_2-CH_2-CH_3$ $CH_3-\underset{\displaystyle |}{CH}-CH_3$
n-butane $CH_3CH_2CH_2CH_3$	n-butyl sec.butyl	$CH_3-CH_2-CH_2-CH_3$ $CH_3-\underset{\displaystyle |}{CH}-CH_2-CH_3$
Isobutane	isobutyl ter.butyl	$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-$

1 Nomenclature

Alkanes are named by two systems.

(1) Common or trivial system

(2) IUPAC name system

(1) Common or trivial system

(trivial = insignificant = not important)

- In this system alkanes are named on the basis of their sources from which they are obtained.
- The first four members i.e. from methane to butane are named by their common names. But from fifth (pentane) and onwards are named by prefixing the

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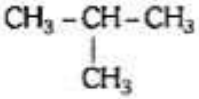
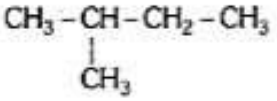
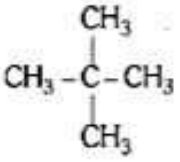
Greek numbers, like pent (5), hex (6), hept (7), are used before '-ane'

- Depending upon the nature of carbon chain prefix like n, iso, sec., neo are used to indicate isomers of an alkane. e.g. n-butane $CH_3–CH_2–CH_2–CH_3$

Isobutane 

n-pentane $CH_3–CH_2–CH_2–CH_2–CH_3$

isopentane 

neopentane 

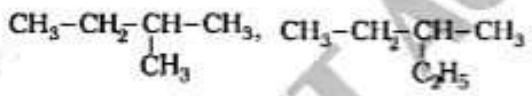
(2) **IUPAC system**

In this system the name given to an organic compounds consists of 3 parts, i.e. prefix + root name + suffix.

- Prefix = the nature of substituent group
- Root name %= the number of carbon atoms in the main chain
- Suffix = The nature of functional group.

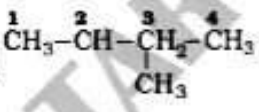
Rules :

1) The longest continuous carbon chain is selected as parent alkane.

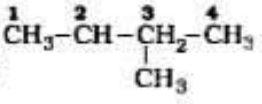
e.g. 

Parent alkane is butane.

2) The carbon chain is numbered from that end which is nearer to the side Chain.

e.g. 

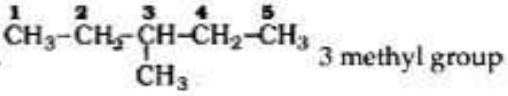
3) Any substituents attached to the longest chain are named and their positions are denoted by number of carbon atoms to which they are attached.

e.g. 

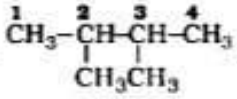
Substituent = methyl group

Position of methyl group = 2.

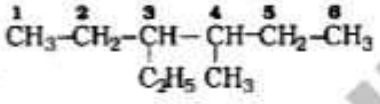
4) If branching is at equal distance then numbering can be started from any side (left side or right side)

e.g.  3 methyl group

5) If some substituent present two or more times, it is indicated by prefixing di, tri, tetra, etc.

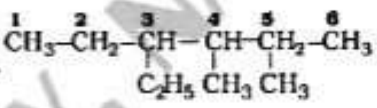
e.g.  2,3-dimethyl butane

6) When the different branches are at equal distance from the ends of the present chain, then the numbering and name started from alphabetical order.

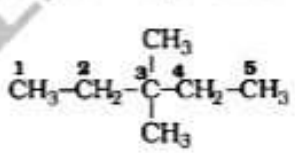
e.g. 

3-ethyl-4-methyl hexane

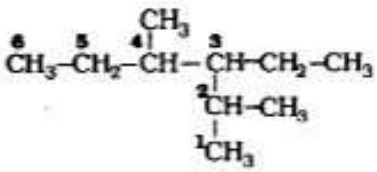
7) If different types of alkyl groups are attached to the parent chain they are named as alphabetically.

e.g. 

8) When two side chain present on the same carbon atom, the number of carbon atom is repeated for each side chain of parent chain.

e.g.  3,3-dimethyl pentane

9) When two or more same or different side chains of equal length are present then choose the one which has maximum number of substituents.



3-ethyl-2,4-dimethyl hexane

10) While writting the complete IUPAC name, a comma (,) is put to seperate a number from number and a hyphen (-) is put to separate a number from letter.

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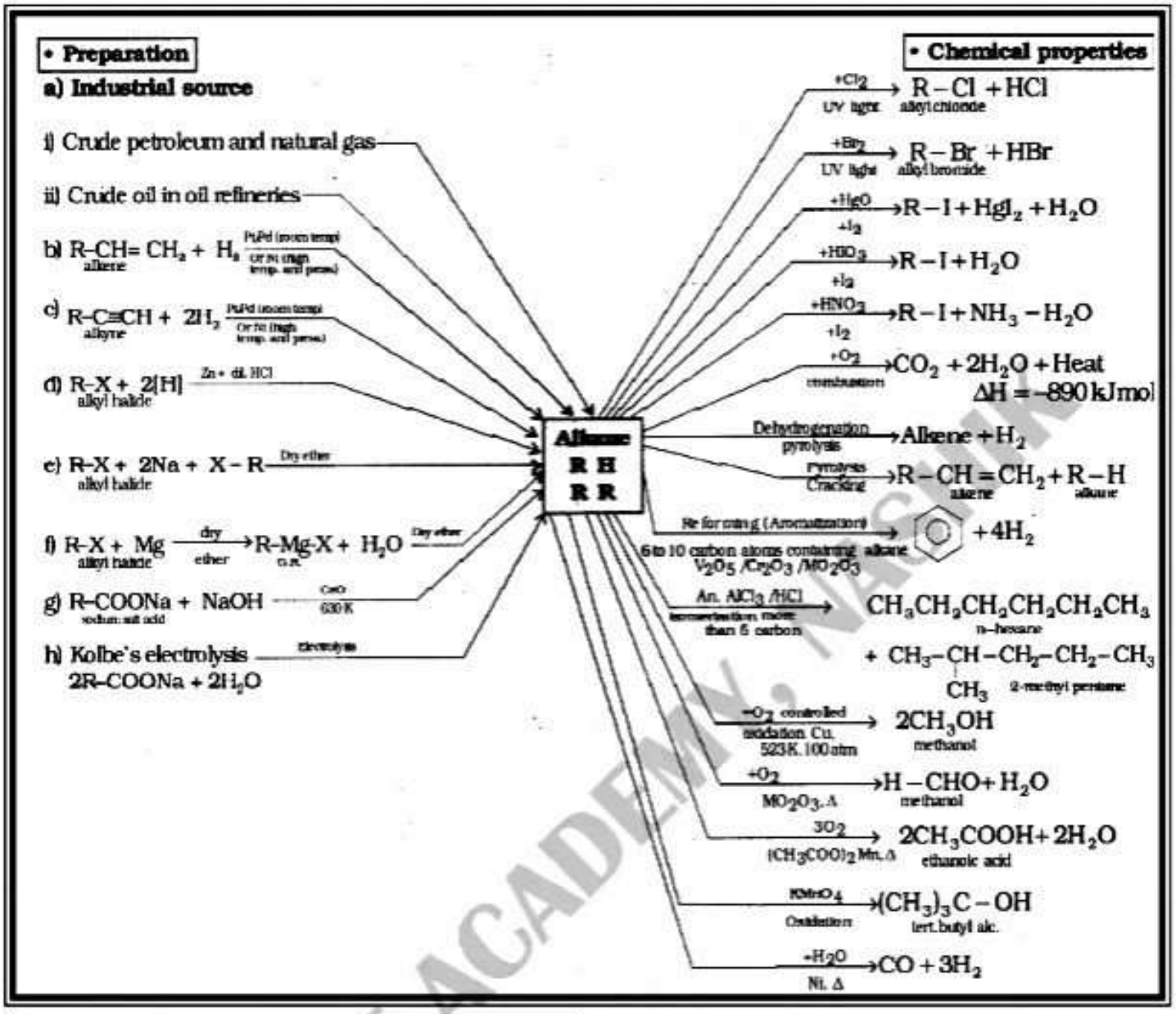
Preparation and chemical properties of alkanes :



MELTING POINT AND BOILING POINT OF ALKANES

Molecular formula	Name	Molecular mass/u	b.p. (K)	m.p. (K)
CH_4	Methane	16	111.0	90.5
C_7H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane.	58	.272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_6H_{12}	2,2-Dmethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5

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- **Physical properties of alkanes**

Polarity : The electronegativity of carbon and hydrogen is nearly the same.

- C-H and C-C bonds are non-polar covalent bonds and alkanes are, thus, nonpolar.
- The forces which hold non-polar molecules together are the van der Waals forces.
- Those are usually weak.
- Larger the surface area of molecules, stronger are such intermolecular van der Waals forces.
- The intermolecular forces are relatively stronger in straight chain alkanes than in branched alkanes Therefore straight chain alkanes have higher melting and boiling points.

- **Uses of alkanes**

i) Lower members of alkanes are used as fuels.

ii) Methane is used in manufacture of carbon black which is used in making paints, printing ink, boot polish, etc.

iii) Methane is used as illuminant.

iv) A mixture of n-butane and isobutane is used as cooking gas under the name of LPG.

v) Methanol, formaldehyde, methylene dichloride, CCl_4 etc. can be prepared from methane.

vi) Propane is used as refrigerant in the petroleum industry.

vii) Some higher alkanes (solid C20 - C30) are used in making candles, cosmetics, waterproof papers etc.

viii) Some higher alkanes (C17 - C20) are used as lubricants and insulators etc.

ix) Higher liquid alkanes are used as domestic or industrial fuels, such as kerosene and furnance oils.

ALKENES

- **Alkenes** : The unsaturated aliphatic hydrocarbons containing carbon carbon double are called as alkenes.

i) Its general formula is C_nH_{2n}.

ii) They are also called as olefins (Latin word - Ole = oil, fin = forming = making) oil forming because the lower members of the family.

iii) They contain two hydrogen atoms less than corresponding alkanes.

iv) The double bond in alkenes is knowing as ethylene/ olefinic bond. It consists of σ bond and one π bond.

v) Alkenes are more reactive than alkanes.

e.g. Ethylene = Ethene = n = 2, $CH_2 = CH_2$

Propylene = Propene = n = 3, $CH_3 - CH = CH_2$

- **Electronic structure and structural formula of ethene (Ethylene) a) Structural formula of ethene**

1) The two carbon and four hydrogen atoms lie in one plane and hence it is a trigonal planar molecule. Enthalpy of ethylene C = C ⇒ 681 kJ/mole

ii) Each carbon atom in ethylene is in sp^2 hybridisation state.

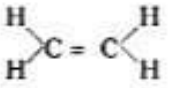
iii) The aliphatic unsaturated hydrocarbons containing two or three carbon-carbon double bonds are called as alkadienes and alkatrienes respectively.

iv) Ethene contain one π bond and five σ bonds.

v) Bond length C = C is 134 Pm = 1.34 Å

C– H is 110 Pm = 110 Å

vi) Bond angle H–C–H | H – C = C ⇒ 120°.



π bond enthalpy = 284 kj mol

σ bond enthalpy = 397 kj mol

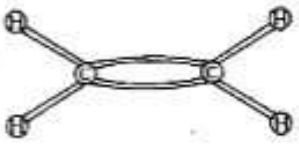
b) **Electronic structure :**

H • C : : C • H • = e^- of C

× = e – of H

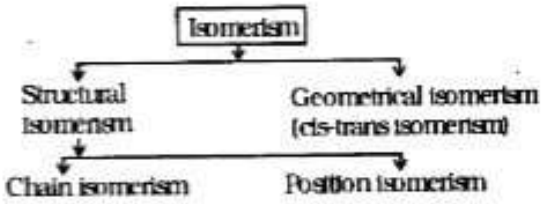
H H

c) **Ball and stick model of ethene**



- **Isomerism in alkenes**

- The compound having same molecular formula but different structural formulae are called as isomers and this property is called as isomerism.
- Alkenes exhibit the following isomerism.



i) **Chain isomerism**

- The isomerism in alkenes due to difference in arrangement of carbon atoms for the same position of double bond is used as chain isomerism.

The carbon chain may be straight or branched chain.

e.g. $CH_3 - CH_2 - CH = CH_2$

But-1-ene or n-butylene or a-butylene

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$CH_3-C=CH_2$
|
CH_3

isobutylene or 2-methyl propene or 2-methyl prop-1-ene

- a-butylene and isobutylene are chain isomers of each other.

ii) **Position isomerism**

- The isomerism in alkenes due to difference in the position of double bond for the similar carbon chain is called the position isomerism.

e.g. $CH_3-CH_2-CH=CH_2$ But-l-ene or a-butylene.

$CH_3-CH=CH-CH_3$ But-l-ene or/3-butylene.

- **Symmetrical alkenes** : It contains similar atoms or groups attached to the double bonded carbon atoms.

e.g. $CH_2=CH_2$ Ethene

$CH_3-CH=CH-CH_3$ But-2-ene

- **Unsymmetrical alkenes** : It contain different atoms or grops attached to the double bonded carbon atoms.

e.g. $CH_3-CH=CH_2$ Propene

$CH_3-CH_2-CH=CH_2$ But-l-ene

- **Geometrical isomerism** : (cis-trans isomerism) The difference in the spatial arrangement of the groups about the double bond is called as geometrical isomerism.

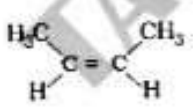
OR

- Isomers arising due to restricted rotation of atoms of groups about a double bond called cis-trans isomers and thus phenomenon is called as Geometrical isomerism.

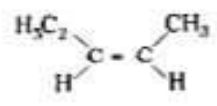
- The isomers are called as geometrical isomers, two types of geometrical isomers are possible,

a) **Cis-isomers** : The isomer in which similar atom or groups are present to the same side of the double bond is called as cis-isomers.

eg. $CH_3-CH=CH-CH_3$ $C_2H_5-CH=CH-CH_3$



cis-but-2-ene



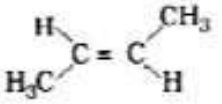
cis-pent-2-ene

[But its position isomers but-l-ene ($CH_3-CH_2-CH=CH_2$) does not show geometrical isomerism because the two same hydrogen atoms are attached to the double bonded carbon atom.]

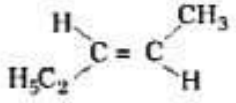
b) **Trans-isomers** : The isomers in which similar groups are present, to the opposite side of double bond is called as trans-isomers,

e.g. $CH_3-CH=CH-CH_3$

$C_2H_5-CH=CH-CH_3$



transrbut-2-ene



trans-pent-2-ene

- **Nomenclature**

I) **Common name system** : The common name of the first four members from C_2 to C_5 are derived from those of the corresponding alkanes by changing the suffix -ane to -ylene. The position of double bond is indicated by Greek letters like α, β, γ etc or sometimes numbers also.

e.g. i) $CH_2=CH_2$ ethylene

ii) $CH_3-CH=CH_2$ propylene

iii) $CH_3-CH_2-CH=CH_2$ α-butylene

iv) $CH_3-CH=CH-CH_3$ β-butylene

v) $CH_3-C(CH_3)=CH_2$ isobutylene

II) **IUPAC name system**

i) The longest continuous carbon chain containing C=C is selected as parent alkane.

e.g. $CH_3-CH_2-CH=CH_2$ Parent alkane is butane.

ii) The carbon chain is numbered from that end which is nearer to the double bond.

4 3 2 1

eg. $CH_3-CH_2-CH=CH_2$ Pent-l-ene

iii) The suffix '–ane' from corresponding alkane is replaced by'-ene'.

iv) Position of double bond is indicated by smallest possible number.

e.g. $CH_3-CH_2-CH=CH_2$ But-1-ene

Parent chain is butene Locant of double bond is 1

v) If side chain or alkyl groups are present on the parent chain, they are identified and their positions are indicated by proper number of carbon atoms.

e.g. $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{\displaystyle CH_3}{\overset{4}{CH}}-\overset{5}{CH_3}$

4-methyl pent-2-ene

vi) If double bond is present at equal distance from both ends and side chains are present, then numbering is such that the alkyl groups should get lowest number.

$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{2}{CH}}-\underset{\displaystyle CH_3}{\overset{3}{C}}=\overset{4}{CH}-\overset{5}{CH_2}-\overset{6}{CH_3}$

2,3-dimethyl hex-3-ene

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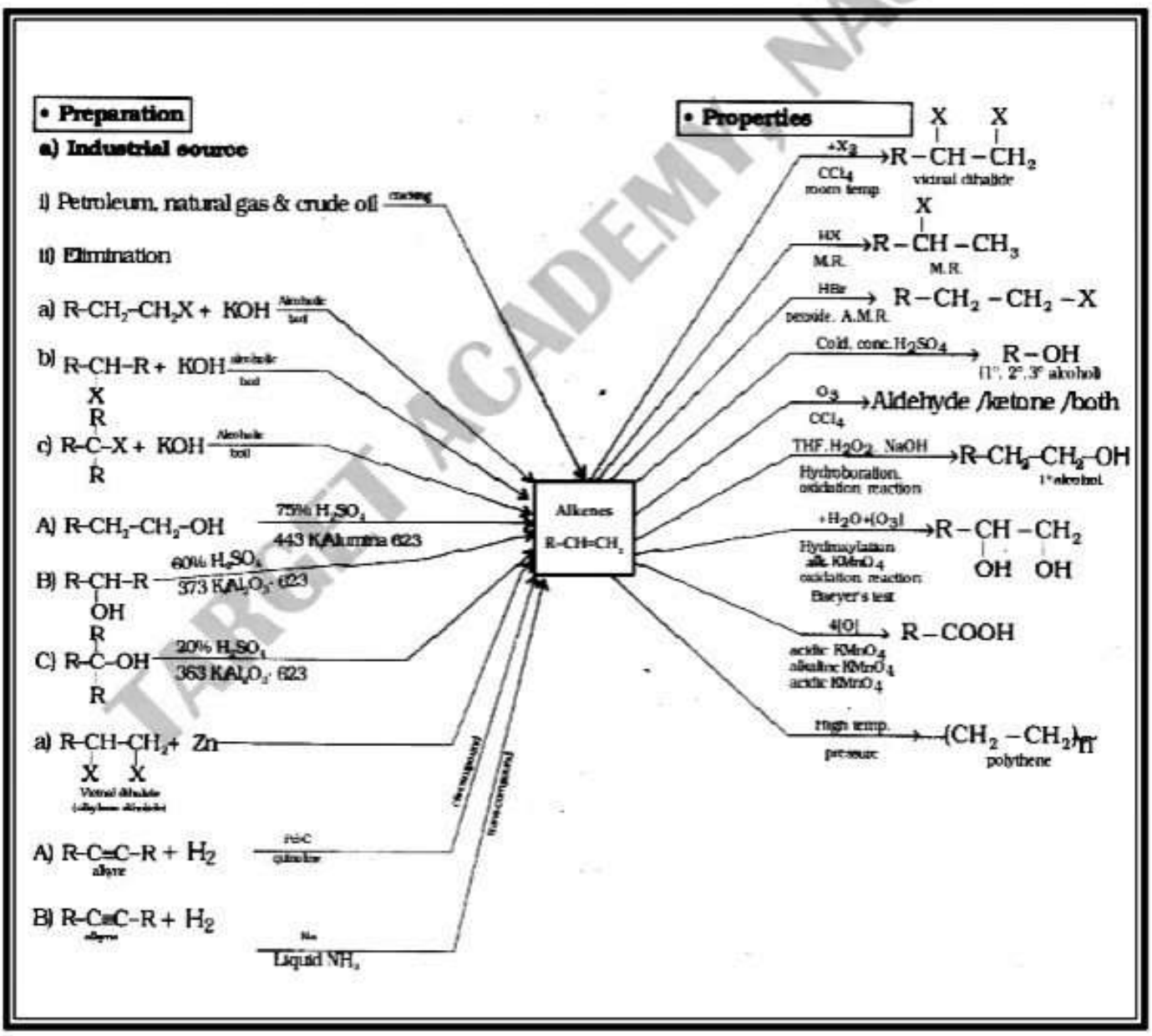
vii) If the double bond is equidistant from the two ends, number the carbon atoms from that end which is nearer to the first branching.

- **Physical properties of alkenes**
- Alkenes are nonpolar or weakly polar compounds those are insoluble in water, and soluble in nonpolar solvents like benzene, ether, chloroform.
- They are less dense than water.
- From Table, it is clear that the boiling point of alkane rises with increasing number of carbons.
- Branched alkenes have lower the boiling point than straight chain alkane.
- The boiling point of alkene is very nearly the same as that of alkane with the same carbon skeleton.

PREPARATION AND CHEMICAL PROPERTIES OF ALKANES



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MELTING POINT AND BOILING POINT OF ALKENES

Formula	Name	Molecular mass (u)	b.p. (K)	m.p. (K)
$CH_2=CH_2$	Ethene	28	171	104
$CH_2 = CHCH_3$	Propene	42	225	88
$CH_2 = CHCH_2CH_3$	But-l-ene	56	267	-
$CH_2 = CH(CH_2)_2CH_3$	Pent-l-ene	70	303	–
$CH_2=CH(CH_2)_3CH_3$	Hex-l-ene	84	337	135
cis $CH_3CH = CH\ CH_3$	cis-But-2-ene	56	277	134
trans $CH_3CH = CHCH_3$	trans-But-2-ene	56	274	167
$CH_2 = C(CH_3)_2$	Isobutylene	56	266	132

- **Uses of alkenes**

i) Ethene is used in artificial repining of fruits like banana, citrum, organges etc.

ii) Ethene is sometimes used as a general anaesthetic agent.

iii) Ethene is used in the preparation of poisonous gas called mustard gas.

iv) Ethene is used for oxy-ethene flame which is used for cutting and welding metals.

v) It is used for the manufacture of polyethene used in manufacture of plastic bags, table cloths, bottles, toys, pipes, etc.

vi) Ethene is used in the preparation of ethanol ethylene dichloride, diethyl ether, formaldehyde etc.

vii) Ethene is used as in the manufacture of ethylene glycol which is used as an antifreeze agent in automobiles of a collent for air craft engines.

viii) Propene is used as in the manufacture of isopropyl alcohol, acetone etc.

ALKYNES

- **Alkynes** : The aliphatic unsaturated hydrocarbons containing carbon-carbon triple bond in the molecule is called as alkynes.

i) Its general formula is C_nH_{2n-2}

(n = no. of carbon atoms where n = 2, 3, 4, 5, etc.)

ii) The C=C bond is also called acetylenic linkage and hence alkynes are commonly called as acetylenes.

iii) They contain four hydrogen atom less than corresponding alkanes.

e.g. $n = 2 \rightarrow C_2H_2$: HC = CH Ethyene/acetylene

$n = 3 \rightarrow C_3H_4$: CH_3– C = CH Propyne (allylene) methyl acetylene

$n = 4 \rightarrow C_4H_6$: CH_3–C = C–CH_3

But-2-yne (crotonylene) dimethyl acetylene

- **Structural formula of ethyne (acetylene)**

i) The molecular formula of ethyne is C_2H_2.

ii) It contains two carbon and two hydrogen atoms.

iii) Carbon contain four valence electrons and hydrogen contains one valence electron.

iv) In acetylene each carbon atom shares electrons to form a carbon carbon triple bond between them and remaining one electron of each carbon is shared by electron from hydrogen to form C–H single bond.

v) Acetylene is linear molecule, the bond angle is 180°.

vi) The bond length of C = C is 1.20 Å and C–H is 1.08 Å.

vii) The triple bond consists of one σ bond and two π bonds.

viii) Each carbon atom in a acetylene undergo sp hybridisation. H — C = C — H

C = C = 120 Pm C-H = 108 Pm.

- **Electronic structure of ethylene (acetylene)**

i) The electronic formula is also called as Lewis electron dot formula.

ii) In this way each carbon completes its octet and each hydrogen complete its duplet.

• = electron of C × = electron of H.

- **Ball and stick model of acetylene** : In this model, the atoms are shown by balls and bonds are represented by sticks.

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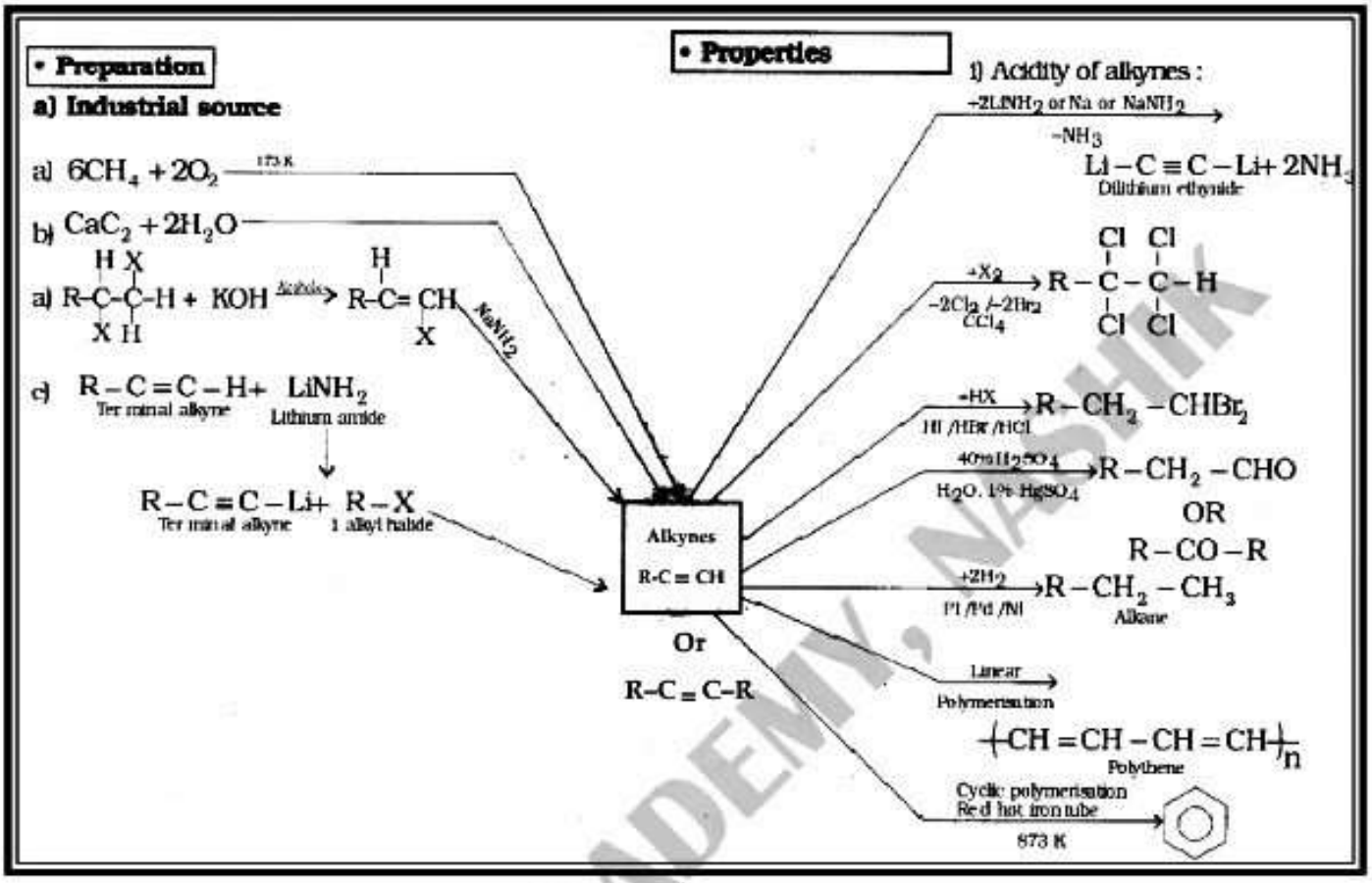
- **Nomenclature**

  Alkynes are named according to following two systems.

PREPARATION AND CHEMICAL PROPERTIES OF ALKYNES



1) **Common name / Trivial / Derived name system**: The first member of alkynes is commonly called acetylene and higher member of the series are considered as alkyl derivatives of acetylene. The system is also not much in use, useful for only lower members.

2) **IUPAC name system**

i) The longest continuous carbon chain containing C≡C is selected as parent chain.

ii) The carbon chain is numbered from that end which is nearer to the triple bond.

iii) The suffix '-ane' from corresponding alkanes is replaced by -yne'.

iv) The position of triple bond is indicated by lowest possible number.

v) If side chain are present their positions are indicated by proper number of carbon to which they are attached.

vi) The positional numbers of triple bond are placed immediately before the primay suffix '–yne'.

Structural formula	Common name	IUPAC name
HC ≡ CH	acetylene	ethyne
$CH_3-C\equiv CH$	methyl acetylene	propyne
$CH_3CH_2-C\equiv CH$	ethyl acetylene	But-l-yne
$CH_3C\equiv C-CH_3$	dimethyl acetylene	But-2-yne
$CH_3CH_2CH_2-C\equiv CH$	propyl acetylene	pent-l-yne
$CH_3CH_2C\equiv C-CH_3$	ethylmethyl acetylene	pent-2-yne
$CH_3-\underset{CH_3}{\overset{}{CH}}-C\equiv CH$	isopropyl acetylene	3-methyl but-l-yne
$CH_3-\underset{CH_3}{\overset{}{CH}}-C\equiv CH_3$	isopropyle methyl acetylene	4-methyl-pent--2-yne
$CH_2=CH-C=CH$	–	but-l-ene-3-yne

TARGET ACADEMY, NASHIK

- **Physical properties of acetylene**

i) The first three members (ethyne, propyne, butyne) in the homologous series are colourless and odourless gases, the next eight members (C_5 to C_{12}) colourless and odourless liquids. And the higher alkynes (F_{13} to onwards) are colourless and odourless solids.

ii) Ethyne has garlic odour because of impurity of phosphine (PH_3)

iii) Alkynes are slightly soluble in water but highly soluble in alcohol, acetone and benzene.

iv) Its boiling points and melting points and specific gravities show a regular increase with increase in their molecular weights.

v) Alkynes are more volatile than alkanes.

vi) Acetylene is lighter than air.

vii) Acetylene is poisonous.

viii) It burns in air with luminous flame.

- **Uses of acetylene :**

i. Ethyne (acetylene) is used in preparation of Ethanal (acetaldehyde), Propanone (acetone), ethanoic acid (acetic acid).

ii. It is used in the manufacture of polymers, synthetic rubber, synthetic fibre, plastic etc.

iii. For artificial ripening of fruits.

iv. In oxy-acetylene (mixture of oxygen and acetylene) flame for welding and cutting of metals.

AROMATIC COMPOUNDS

❑ **Aromatic compounds** : The cyclic carbon compounds which contain at least one benzene nucleus in their structure or which have benzenoid structure.

i) Organic compounds obtained from natural sources having pleasant and sweet odour were called as aromatic compounds.

(Greek word = Aroma - Fragrant smell)

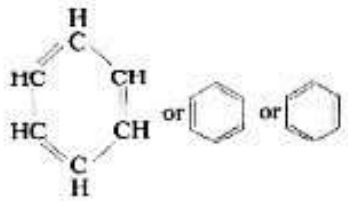
ii) Aromatic compounds contain a specific hexagonal ring structure of six carbon atoms called as benzene ring.

iii) The ring has alternate single and double bonds.

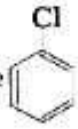
iv) Aromatic compounds are also regarded as benzene and its derivatives are also called arenes.

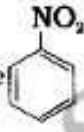
v) The main sources of benzene and other aromatic compounds are coal tar and petroleium.

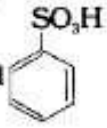
e.g. Benzene = C_6H_6 can be represented by Kekule structure of benzene.

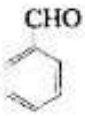


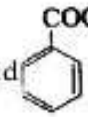
e.g. i) Naphthalene 

ii) Chlorobenzene 

iii) Nitrobenzene 

iv) Benzene sulphonic acid 

v) Benzaldehyde 

vi) Benzoic acid 

1 Characteristics of aromatic compounds

i) Aromatic compounds have high percentage of carbon and low percentage of H as compare to corresponding aliphatic compounds.

e.g. Benzene (C_6H_6) = C = 92.5%, H = 7.5%

Hexane (C_6H_{14}) = C = 83.77%, H = 16.3%

ii) Aromatic compounds are cyclic in nature. They possesses unusual stability due to resonating structure and have low heat of combustion.

iii) Aromatic compounds show high unsaturation. Some of them are having fragrant smell.

iv) They undergo substitution reactions more readily than addition reactions.

v) They are highly alkalies and other normal oxidising and reducing agents.

vi) They burn in air with sooty or smoky flame.

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Difference between aliphatic and aromatic compounds

Aromatic compounds	Aliphatic compounds
i) They contain higher % of carbon.	i) They contain lower % of carbon.
ii) They are closed chain compounds	ii) They are open chain compounds.
iii) They burn with sooty flame	iii) They burn with non- sooty flame.
iv) They are not attacked by normal oxidising and reducing agents	iv) Unsaturated aliphatic compounds are easily attacked by oxidising and reducing agents.
v) They are highly stable compounds.	v) They are less stable compounds.
vi) Aromatic hydroxy compounds are acidic.	vi) Aliphatic hydroxy compounds are neutral.
vii) They are mostlyobtained from coal tar	vii) They are mostly obtained from
viii) They preferably undergo substitution reaction.	viii) They undergosubstitution and and addition reaction.
ix) They do notdecolourise dil. aq. $KMnO_4$ and Br_2 inCCl_4	ix) Alkenes decolourise dil aq. $KMnO_4$ and Br_2 in CCl_4.

- **Structural and electronic structure of benzene**

i) **Structural formula of benzene**

- In 1865, Kekule assigned a structure of benzene. (Fredrich August Kekule)

a) Benzene contains 6 carbon and 6 hydrogen atoms. 6 carbon atoms are present at the corners of a regular hexagon to form a flat hexagonal ring.

b) Hydrogen atoms are present outside the hexagonal. Each carbon contains one hydrogen.

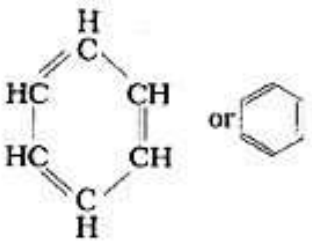
c) Tetravalency of carbon hexagonal ring contains alternate single and double bonds.

d) The bond angles C–C–H and C–C–C = 120°

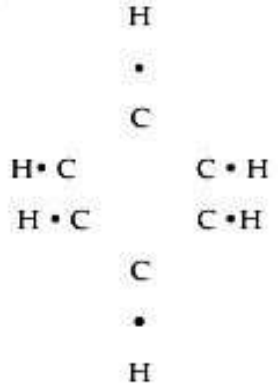
(cis sp^2 hybridized)

e) Benzene is a planar molecule and all the H and C atoms lie in one plane.

f) The carbon-carbon bond length in benzene is 139 Pm and 140 Pm which is intermediate between bond lengths for C–C = 1.54 A and C=C = 1.33Å and the value is the same for all the bonds.



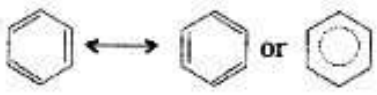
- **Electronic structure of benzene**



x = electron of C, • = electron of H.

i) The above structure is a single covalent bond represents a shaired pair of electrons and a double bond represents two pairs of shaired electrons.

ii) The unusual stability of benzene can be explained by resonance theory. The present structure of benzene is the resonance hybrid of two resonance structures.



Resonance structure Resonance hybrid

- **Physical properties of benzene**

i) Benzene is colourless liquid with a peculiar smell

ii) Its melting point is 278.5 K and boiling point is 353K.

iii) Its highly inflammable and burns with sooty flame.

TARGET ACADEMY, NASHIK

iv) It is insoluble in water but soluble in organic solvents like alcohol, chloroform, ethers, etc.

v) It is ligher than water its density (special gravity) is 0.898.

vi) Benzene is a good solvent for fats, oil, resin, etc.

vii) Benzene is toxic (poisonous) in nature.

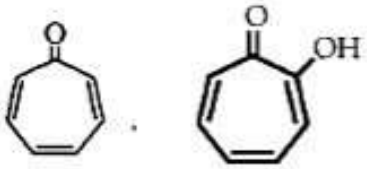
- **Types of aromatic compounds**

❑ Aromatic compounds are of two types.

1) **Benzenoid structure** : The compound contain one or more benzene rings in their structure is called as benzenoid structure.

e.g. benzene, benzaldehyde, benzoic acid, naphthalene, anthracene, etc.

2) **Non benzenoid structure** : The compound do not contain any benzene rings in their structure is called as non-benzenoid structure.

e.g. 

Tropone Tropolone

- **Aromaticcharacters (Huckel Rule)**

i) Aromatic compounds are cyclic, planar and conjugated compounds containing (4n + 2) π electrons.

ii) They undergo substitution and addition reactions. This property is known as aromaticity.

iii) Aromaticity due to delocalisation of π electrons of 2,6, 10, 14, etc.

e.g. Benzene (n = 1) has 6 π electrons.

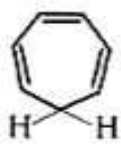
Naphthalene (n = 2) has 10 π electrons.

e.g.

i) 

Cyclobutadiene

Not. aromatic as number of π electrons is 4.

ii) 

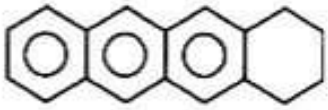
Tropylene cycloheptatriene

Not aromatic since it is non conjugated system.

iii) 

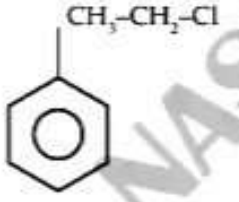
1,1-dimethyl cydopropene

Not aromatic as π electrons is 2 but is non-conjugated system.

iv) 

1,2-cyclohexyl anthracene

Not aromatic as it is non-conjugated.

v) 

1-chloro-2-phenyl ethane

❑ Benzene and arenes (aromatic hydrocarbon) are aromatic in nature.

❑ The most essential criteria for the aromatic character is that the compound most obey Huckel's rule.

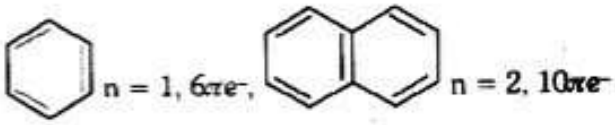
❑ According to the rule, 'A cyclic, planar and conjugated compound containing (4n + 2)π.

electrons.' Where n = 0, 1, 2, 3, 4, 5, , etc.

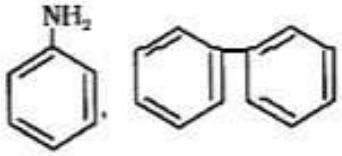
❑ Thus aromatic compound have delocalised electron cloud of π electrons of 2, 6, 10, 14 etc.

eg.

i) **Benzenotd aromatic compouds :**



Benzene Naphthalene



Aniline Diphenyl

because planar, conjugated, cyclic compounds,

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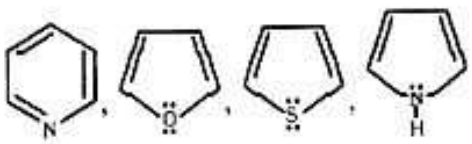
ii) **Non-benzenoid aromatic compounds**



Pyridine Furan Thiophane Pyrrole

because cyclic, planar, conjugated *6ti* electrons

iii) **Cyclic, planar, aromatic anion or carbon**

Cyclopenta dienyl anion, $6\pi e^-s$

Cycloheptatriene dianipn $10\pi e^-s$

Cyclopropenyl anion

Cycloheptatrienyl cation

tropylium cation

$6\pi e^-s$ spread over the entire ring

iv) **Cyclic, non-polar, non-aromatic compound**

Cyclopropenyl anion

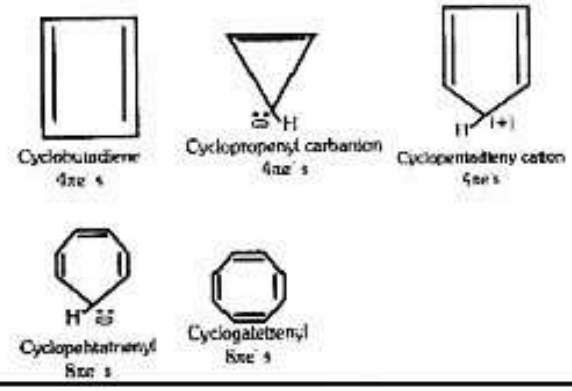
Cyclboctatetrine

$6\pi e^{-s}$ not spread over the entire ring.

v) Cyclic, planar, conjugated 4π and $6\pi e^-$ S in antiaromatic.

Hucle's rule : Monocyclic planar, completely conjugated polymers containing 4π e^- are destablished by resonance is called antiaromatic.

e.g. 1) Antiaromaticity ($4n\pi e^-s$ rule)



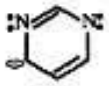
A = No. of π bonds + No. of lone pair + 1

A = Even value = compound is Aromatic.

A = Odd value = compound is Antiaromatic

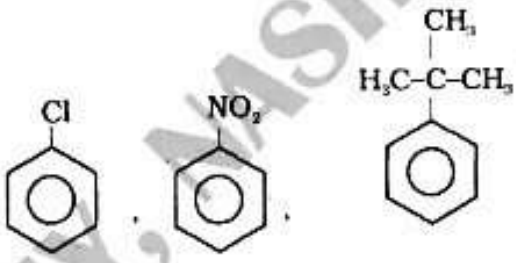
no conjugation non aromatic.

e.g.  A = 2 + 0 + I= 3 Antiaromatic

 A=2+I+I=4 Aromatic

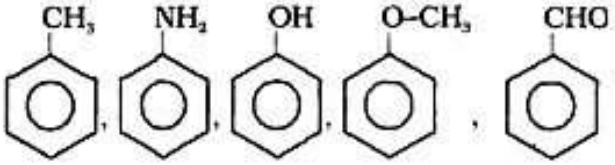
- **Nomenclature of benzene**

i) Monosubstituted benzene derivative is obtained by placing the name of substituent as a prefix to benzene.

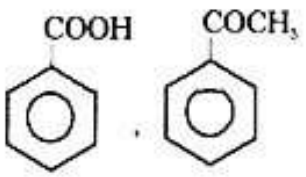
e.g. 

Chlorobenzene Nitrobenzene Tertbulyl benzene (2-methyl-2-phenyl propane)

ii) Many of monosubstituted benzene derivatives have common names and IUPAC names are same.

e.g. 

Toulene Aniline Phenol Anisole Benzaldetyde



Benzoic acid Acetophenone

iii) If the alkyl substituent is larger than benzene ring (seven or more C atoms). The compound is named as phenyl-substituted alkanes.

e.g. C_6H_5 = phenyl group, $C_6H_5–CH_2$ = benzyl group

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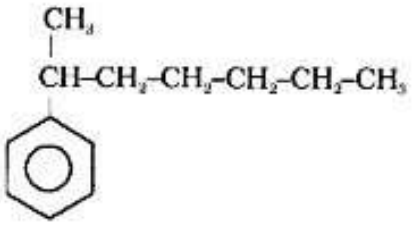
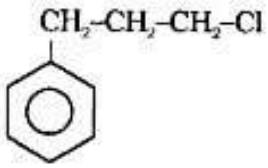
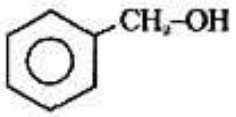


2-phenyl heptane



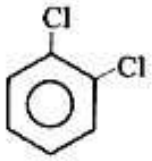


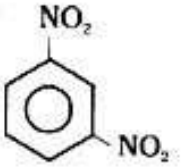
3-chloro-1-phenyl propane

benzyl alcohol

(phenyl methanol)

iv) The three possible isomers of disubstituted benzene derivatives are given common names by using one of the prefixes ortho (o = 1,2 position) meta (m = 1,3-position) or para (p = 1,4 position) If two substituents are different they are entered in alphabetical order.

e.g. 

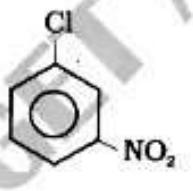


o-dichlorobenzene

(1,2-dichlorobenzene)

m-dinitrobenzene

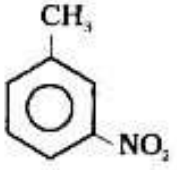
(1, 3-dinitrobenzene)



p-bromo-iodobenzene

(1, 4-bromoiodobenzene)

(1, 3-chloronitrobenzene)

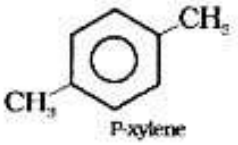


o-chloroaniline

(2-chloroaniline)

m-nitrotoulene

(3-nltrotoulene)

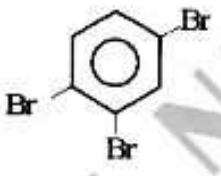


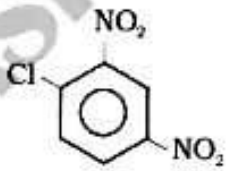
p-bromophenol

(4-bromophenol)

P-xylene (1, 4-dimethyl benzene)

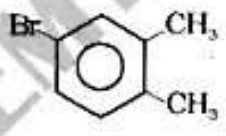
v) If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions. The direction of numbering should be such that it gives lowest combination of numbers. The names of substituents should be entered in alphabetical order.





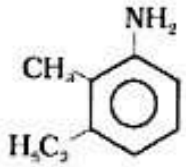
1,2,4-tribromobenzene

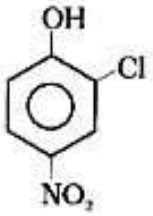
1-chloro -2,4-dirutrobenzene



4-hromo-1,2-dimethyl benzene

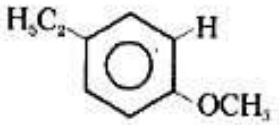
vi) If one of the groups, which gives a special name to the compound, is present then the special group is considered in position 1.

e.g. 



3-ethyl-2-methyl aniline

2-chloro-4-nitrophenol



4-ethyl-2-fluroanisole

II) Substitution reactions

(Electrophilic substitution reaction)

i) Benzene shows electrophilic substitution reactions.

ii) The replacement of one or more hydrogen atoms of benzene ring by halogens, $-NO_2$, $-SO_3H$ etc is called as substitution reaction.

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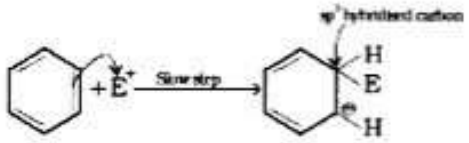
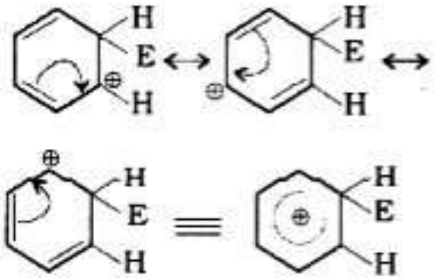
- **Mechanism of electrophilic substitution reactions**

i) **Formation of carbocation** : It is slow step reaction. Attack of electrophilic reagent on aromatic ring, results in the formation of σ-complex or arenium ion in which one of the carbon is sp^3 hybridised.



6 comptex or arenlum ion

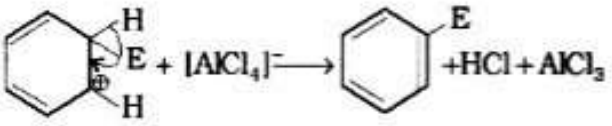
- Following three structures of arenium ion differ from each other only in position of double bonds and positive charge. The actual structure of arenium ion must be a resonance structure of these structures.
- The positive charge is not localised on one carbon atom but is distributed over the molecule. The arenium ion gets stabilised by resonance. Arenium ion loses its aromatic character because tHe delocalisation of π electrons steps at the sp^3 hybridisation carbon atom.

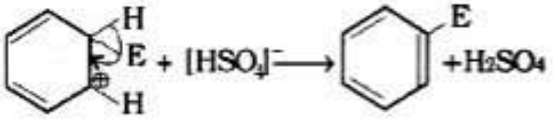


Removal of proton

- It is fast step reaction. It involves the abstraction of proton by a base (nucleophile- halogenation $[FeBr_4]^-$, alkylation $[AlCl_4]^-$, acylation, nitration $[HSO_4]^-$ from the sp^3 hybridised carbon atom. The aromatic character of the ring is restored.

e.g.

i) 

ii) 

- **Directive influence of functional group in monosubstituted benzene**

- When monosubstituted benzene is subjected to further substitution, three possible disubstituted products (ortho, meta, para) are not formed in equal proportions. Two types of behaviour are observed. Either ortho, para or meta products is formed. The nature of the substituent already present in the benzene ring determines the position of second substituent.

i) The substituent makes the ring more reactive than benzene is called as activating group.

ii) The substituent makes the ring less reactive than benzene is called as deactivating group.

iii) The group which direct the incoming group to ortho, para, meta positions are called ortho, para and meta directing groups.

iv) The reactivity of compound and orientation of substitution, inductive and resonance effect should be considered.

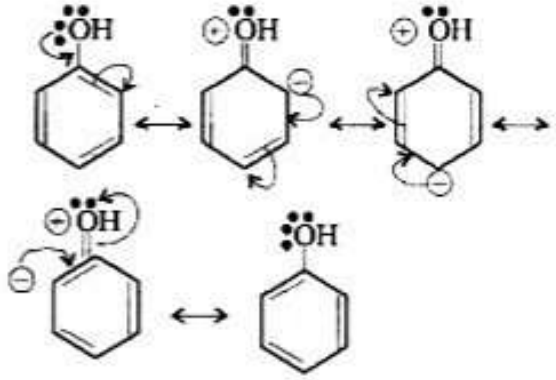
Substituents can be classified into three groups as below:

i) Activating and ortho, para directing groups.

Activating groups are,

e.g. $-NH_2$, NHR, $-NR_2$, –OH, –NHCOR, $-C_6H_5$, –R, –OR

- Let us discuss the directive influence of –OH group in benzene. Phenol is resonance hybrid of following structure.



- The electron density in benzene ring is slightly reduced due to weaker electron keeping withdrawing inductive effect of -OH group, the electron density at σ- and π- positions is increased due to stronger electron donating resonance effect.
- As a result, phenol is more reactive than benzene. Thus phenolic – OH group is activating and ortho, para directing group.

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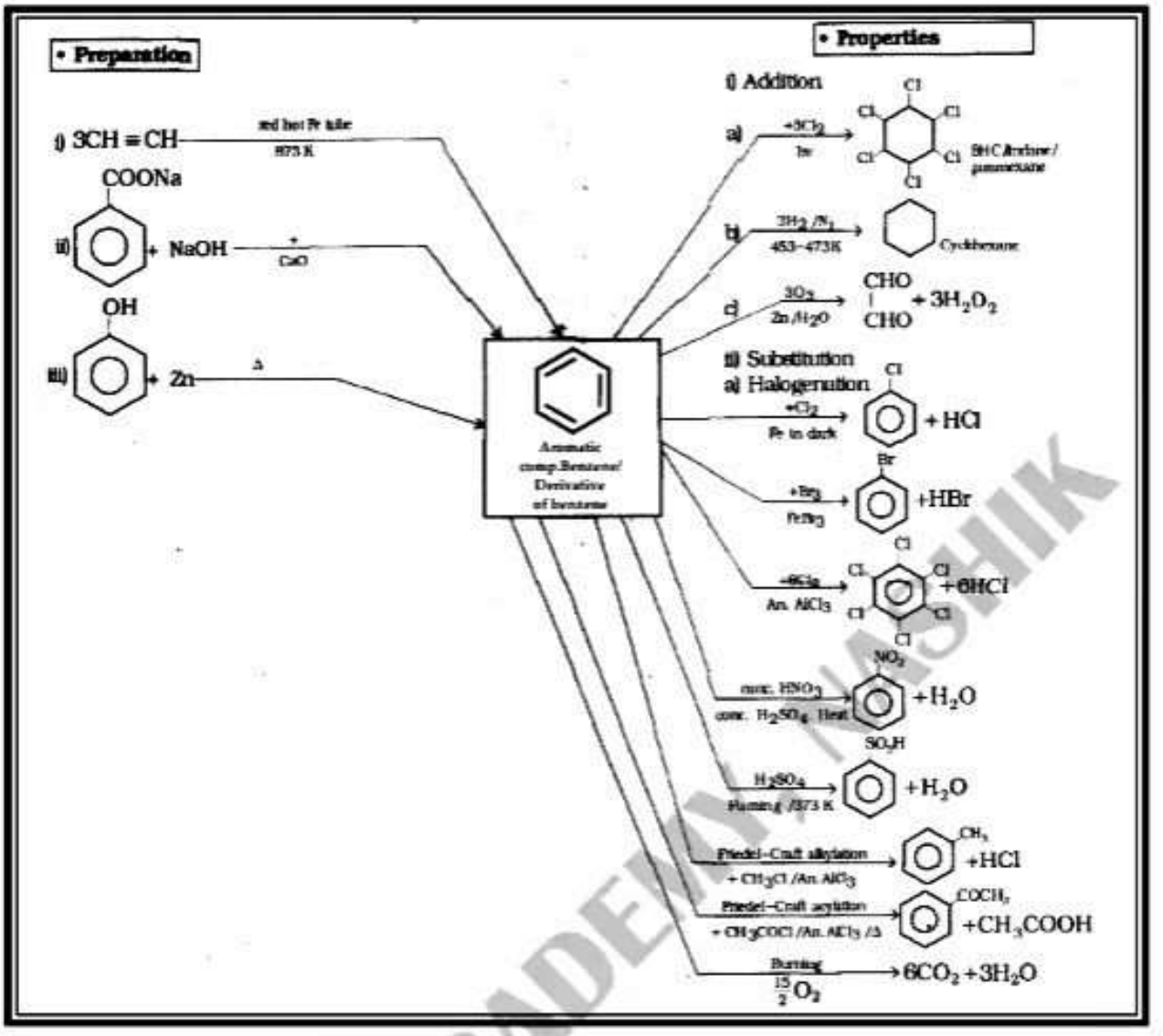


- **eactivating and ortho, para directing groups**

  e.g. –F; –Cl, –Br, –I.

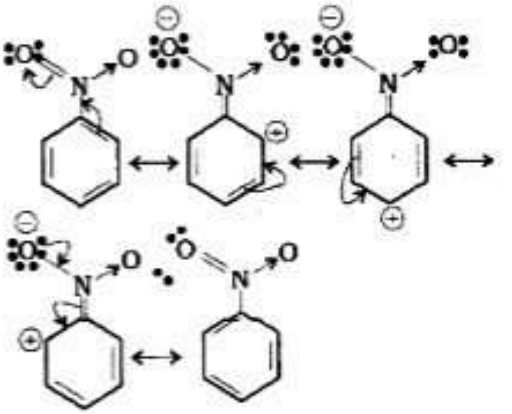
- In aryl halides, the halide atom has stronger electron withdrawing inductive effect and the electron donating resonance effect is weaker.
- As a result aryl halide is less reactive than benzene towards electrophilic attack.
- Thus halide atom is moderately deactivating. However, due to resonance effect, there is more electron density at o- and p-positions the halide group is also ortho, para directing groups.

- **Deactivating and meta directing groups**

  e.g. $-NO_2$, –CN, –COOH, –COOR, $-SO_3H$,

  –CHO, –COR $-\overset{+}{N}H_3$

- Nitrobenzene is resonance hybrid of following structure.



i) Due to strong electron withdrawing inductive effect, nitro group reduces the electron density in benzene ring.

ii) As a result, nitro group is deactivating group.

TARGET ACADEMY, NASHIK

iii) The resonating structures of benzene that the electron density is comparatively less at o- and p- positions than at m-position. This is due to strong electron withdrawing resonance effect.

iv) Thus electrophile attacks on comparatively electron-rich meta position. Hence, nitro group is meta directing.

- **Carcinogenicity and toxicity**

i) **Polycyclic aromatic hydrocarbon** : More than two benzene rings fused together are called as polycyclic aromatic hydrocarbons.

ii) Benzene and polynuclear aromatic hydrocarbons are toxic and said to possess cancer producing (carcinogenic) property.

iii) Such polycyclic aromatic hydrocarbons are produced by incomplete combustion of tobacco, coal and petroleum.

iv) They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer.

TARGET ACADEMY, NASHIK