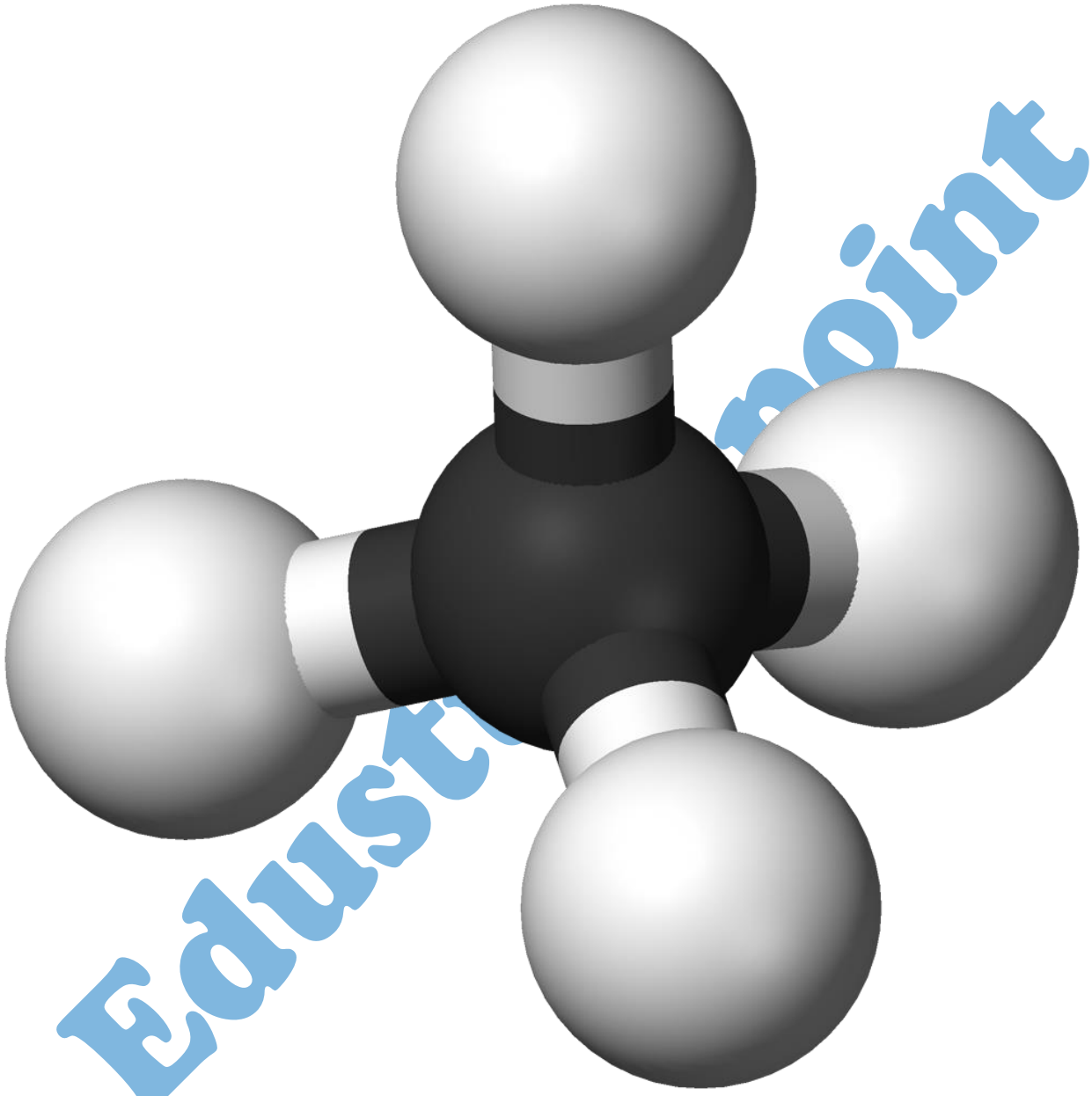
Hydrocarbons



DESIGNED

By

Edustudy point

Hydrocarbons: These are compounds of Hydrogen and carbon and we can derive other compounds by substituting Hydrogen with some other groups. They are generally called Fuel Compounds.

Alkanes: They are saturated Hydrocarbons with General Formula $C_n H_{2n+2}$

- These alkanes may be open chain like CH_4, C_2H_6, C_3H_8, C_4H_{10} , C_5H_{12}
- These can be cyclic alkanes with formula $C_n H_{2n}$ like Cyclopropane etc.
- In them there is Sp^3 hybridisation.

Nomenclature: While writing their IUPAC names the suffix used is "ane".

For example: CH_4 the suffix used is "ane" that is "methane".

Isomerism: They are the compounds with same molecular formula but different Structural formula.

- Alkanes show structural isomerism that is Chain isomerism is common in them.

Example: $CH_3 - CH_2 - CH_2 - CH_3$ (n- Butane)

$CH_3 - CH(CH_3) - CH_3$ (iso - Butane)

Alkanes can be classified as:

1. Primary alkane: Alkane in which a Carbon atom attached to one or none alkyl group is 1^0

   CH_3-CH_3 (ethane) 1^0

2. Secondary Alkane: In which a carbon is linked to two alkyl groups is 2^0

   CH_3-CH_2-CH_3 (propane) 2^0

3. Tertiary Alkane: Alkane in which a carbon atom is linked to three alkyl groups is 3^0

   $CH_3 - C(CH_3)_2 - CH_3$ (2-methyl propane) 3^0

Preparation of alkanes

(a) **From unsaturated Hydrocarbons**:-The method involved is by hydrogenation that is addition of H_2. It is also called as reduction reaction.

$CH_2 = CH_2 + H_2 \xrightarrow{\text{Raney Ni}} CH_3 - CH_3$

(ethene) (Ethane)

(b) From Alkyl halides (RX): These alkyl halides are formed by replacing Hydrogen by halogen (X).

Wurtz reaction: In this two molecules of alkyl halide react with sodium in presence of dry ether.

$CH_3Cl + 2Na + ClCH_3 \xrightarrow[\text{Ether}]{\text{Dry}} CH_3CH_3 + NaCl$

(c) Reduction of alkyl halides:

$CH_3CH_2Br + H_2 \rightarrow CH_3CH_3 + HBr$

(d) **From Carboxylic acids (RCOOH)**:

- **By Decarboxylation:** It is removal of of CO_2 In this first carboxylic acid, is made to react with sodium metal to form desired alkane.

$$CH_3COOH + Na \rightarrow CH_3COONa + H_2$$

- **Kolbe's electrolysis Reaction:** In this electric current is passed through metal carboxylic salt

$$CH_3CH_2COOH + HI \xrightarrow{\text{Red P}} CH_3CH_2CH_3 + H_2O + I_2$$

(ethanoic acid) (propane)

Physical Properties:

1. **Polarity of alkanes:** Alkanes are non-polar in nature because of same electro negatives of carbon atoms.
2. **Existence:** The force of attraction present in them is Vander wall forces due to which the lower members i.e. C_1 to C_4 exist as gases, C_5 – C_7 as liquid and higher ones are solid.
3. **Boiling point:** - Because of non-polar character they have low boiling point. The boiling points increase with increase in the number of carbon atoms.

   For example: $CH_3CH_2CH_2CH_3$ butane has more boiling point then 2 methyl propane
4. **Melting Point:** - Alkane with odd number of carbon atom has low melting point. And Alkane with even number of carbon atoms have high melting point
5. **Density:** It increases with increase number of C atoms.

Chemical properties of alkanes:

1) **Substitution reaction:** In this one or more Hydrogen's are replaced by other atoms.

   - Halogenations– In it the Substitution By halogen X (Cl, F, Br, I) occur

   Order of reactivity: F> Cl > Br > I

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl_2 + HCl$$
$$CH_3Cl + Cl_2 \xrightarrow{hv} CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \xrightarrow{hv} CHCl_3 + HCl$$

2) **Oxidation Reaction:** it is the Reaction with oxygen

$$CH_4 + O_2 \rightarrow CO_2 + H_2O + Heat$$

   - Incomplete combustion or oxidation :

$$CH_4 + O_2 \rightarrow CO + H_2O + Heat$$

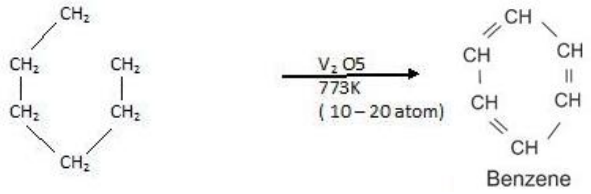
3) **Controlled oxidation:**

$$CH_4 + O_2 \xrightarrow{Cu} CH_3OH$$
$$CH_4 + O_2 \xrightarrow{MoO_3} HCHO + H_2O$$
$$C_2H_6 + O_2 \xrightarrow{Ag_2O} CH_3COOH$$

4) **Isomerisation:**

$$CH_3CH_2CH_2CH_3 \xrightarrow[AlCl_3]{\text{anhydrous}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

5) **Aromatization Reaction:** In this an Aromatic compounds are found are called (Cyclization)



6) **Thermal decomposition or pyrolysis**: In this breakdown of bigger alkane into lower alkanes occur and is called as thermal cracking.

$C_6H_{14} \rightarrow C_6H_{12} + H_2$

$C_6H_{14} \rightarrow C_4H_8 + C_2H_6$

$C_6H_{14} \rightarrow C_3H_6 + C_2H_4 + CH_4$

Alkenes: They are the hydrocarbons with C = C (double bond).

- Their General formula $C_n H_{2n}$

Nomenclature: Primary suffix + ene

For example: ($CH_2 = CH_2$) Ethene

Isomerism: There are two types of isomerism.

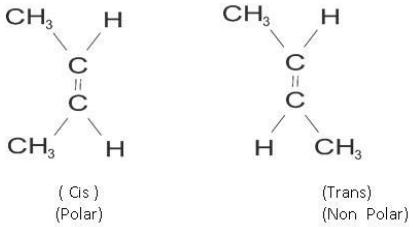
A. Structural isomerism: $CH_3\ CH_2\ CH_2\ CH = CH_2$ (pentene)

$CH_3 - C(CH_3) - CH = CH_2$ (3-methyl butene)

B. Stereoisomerism:

Geometrical Isomerism - The spatial arrangement of atoms is going to be different in it.

Ex: $CH_3\ CH = CH - CH_3$ (but-2 ene)



Preparation of Alkenes

1. **From alkyl halides: (RX)** by the process of dehydrohalogenation, it is also called Beta elimination .

$CH_3 - CH_2\ Br + KOH\ (Alc.) \rightarrow CH_2 = CH_2 + KBr + H_2O$ (ethene)

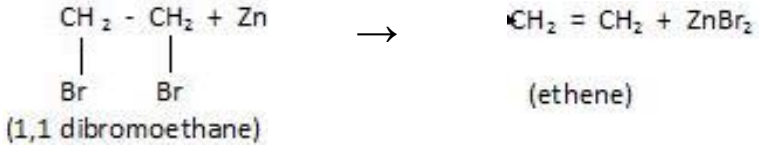
$CH_3\ CH_2\ CH_2\ Br + KOH\ (Alc.) \rightarrow CH_3\ CH = CH_2 + KBr + H_2O$

Proply Bromide — Propene

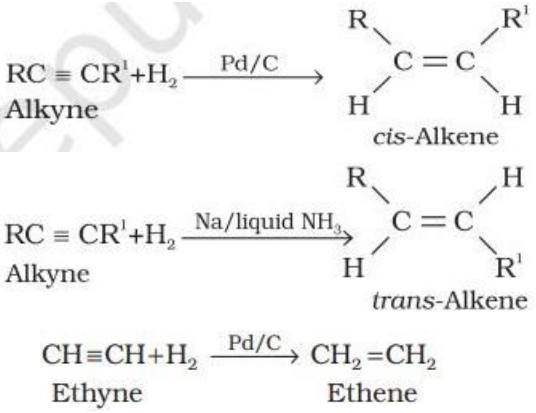
If we see ease of elemination the order is : I > Br > Cl > F

The reactivity of alkanes towards this reaction is : tertiary > secondary > primary

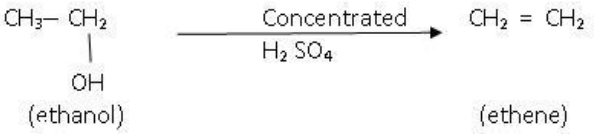
2. **From dihalogen derivatives:**



3. **From alkynes:**



4. **From Alcohols:**

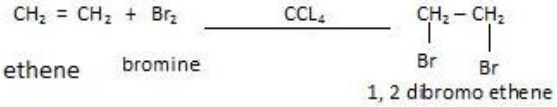


Physical Properties:

1) **Melting Point**: Alkenes have higher melting point than alkanes because π e^- cloud will be more polarized.
   - If we compare melting point of Cis and Trans then, Trans possess high melting point then Cis.
2) **Boiling Point**:
   - With increase in Carbon atoms, boiling point increases.
   - Boiling point decreases with increase in branching.
   - Trans has low boiling point and cis possess high boiling point due to polarity.
3) **Dipole moment**: C is have certain dipole moment, but Trans have zero dipole moment as both the dipoles are in opposite direction therefore, they cancel each other effect.
4) **Solubility**: - Alkenes have greater solubility then alkanes.
   - Solubility increase with increase in C atoms.

Chemical properties of alkenes:

1. **Addition of halogen**



- Order of reactivity of halogens towards this reaction is: F_2 > Cl_2 > Br_2 > I_2

2. **Addition of hydrogen halide**

$CH_2 = CH_2 + H\ Br \rightarrow CH_3 - CH_2Br$

In case of unsymmetrical alkenes, Markovnikov's rule is followed.

- **Markovnikov's rule**: The negative part of the reagent will attach itself to the Carbon atom carrying lesser number of Hydrogen and Hydrogen goes to the Carbon with maximum number of hydrogen.

$$CH_3-CH=CH_2+H-Br \longrightarrow \underset{\text{2-Bromopropane}}{CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3}$$

- But if Reaction occurs in presence of peroxide like benzoyl peroxide, The rule that is followed is Anti-Markovnikov's Rule or Kharasch effect (and this valid only for HBr).

- **Anti Markovnikov's Rule**: According to it the negative part attaches to the carbon atom with maximum number of hydrogen and positive part attaches to the carbon atom with lesser hydrogen .

$$\underset{\text{propene}}{CH_3 - CH = CH_2} + \underset{\text{hydrogen bromide}}{HBr} \xrightarrow[\text{Peroxide}]{\text{benzoyl}} \underset{\text{Bromo propane}}{CH_3 - CH_2 - CH_2Br}$$

3. **Addition of H_2O**

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 + HOH \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3$$

4. **Oxidation Reactions:**

$$\underset{\text{ethene}}{CH_2 = CH_2} + \underset{\text{nascent}}{[O]} \xrightarrow{KMnO} \underset{\text{Ethylene glycol (antifreeze)}}{HO-CH_2-CH_2-OH}$$

$$\underset{\text{(Propene)}}{CH_3-CH=CH_2} + [O] \rightarrow \underset{\text{propan-1-2 diol}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}}$$

Alkynes: In this triple bond is present between carbon atoms (C C bond).The hybridisation is sp and the general formula involved is C_nH_{2n-2}.

Nomenclature: Suffix used is "yne"

For example: (Pentyne) $CH_3 - CH_2 - CH_2 - C\ CH$

Isomerism: Chain isomerism (converting straight chain to branched).

$CH_3 - CH_2 - CH_2CH_2 - C\ CH$ (Hexyne)

$CH_3 - CH_2 - CH(CH_3) - C\ CH$ (3 methyl pent – 1 – yne)

2. Position isomerism (change in the position of triple bond).

$CH_3 - CH_2 - CH_2 - CH_2 - C\ \ CH$ Hexyne

$CH_3 - CH_2-C\ C-CH_2- CH_3$ Hex – 3 – yne

3. Functional isomerism: It involves conversion of one triple bond to two double bonds.

$CH_3\ CH_2- C\ CH$ $(C_4\ H_6)$

$CH_2 = CH- CH = CH_2$ $(C_4\ H_6)$ same molecular formula

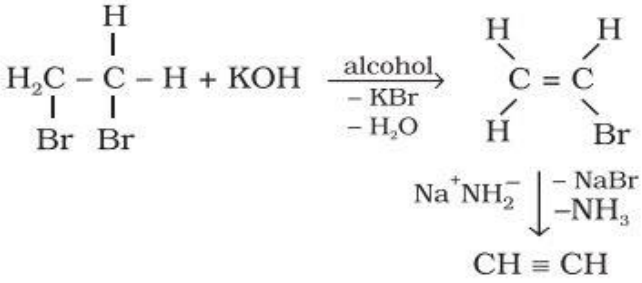
Preparation of Alkynes

1. **Laboratory preparation** –It is prepared in by action of H_2O on Calcium carbide (CaC)

$$CaC_2 + H_2O \rightarrow Ca(OH_2) + CH \equiv CH$$

- This reaction can lead to explosion so, in order To avoid explosion we need to remove air and for that we take oil gas.

2. **By dehydrohdogenation of vicinal dihalide**



Physical Properties:

1. **Existence**: Acetylene, propyne, butyne are gases and other with carbon 4 to 12 are liquids, more than 12 are solids.
2. **Solubility**: They are weekly polar in nature and not soluble in H_2O but soluble in organic solvents.
3. **Melting point and boiling point**: Because of triple bond they have higher melting point and boiling point.

- With increase in number of carbon atoms the boiling point increases.
- With increase in branching the boiling point decreases.

Chemical properties of alkynes

1. **Acidic Character** – This is shown by replacement of one of the hydrogen atom by metal atom.

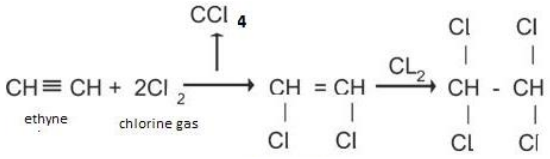
$$CH \equiv CH + Na \rightarrow CH \equiv CNa + H^+$$

ethyne sodium Acid Acetylide

- Alkynes are acidic because of sp hybridisation of Carbon atom.
- Application: By this we can upgrade number of carbon atoms in alkynes.

2. **Addition reaction:**

- **Addition of halogens**



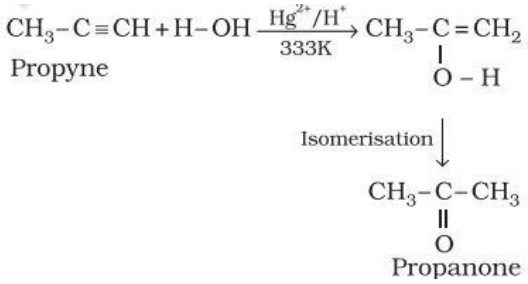
- **Addition of halogen acids**: The order of reactivity of this reaction is:

  HF < HCl < HBr < HI

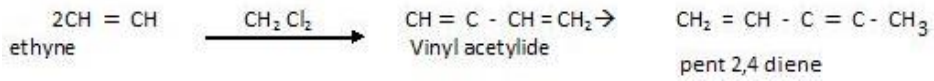
  The reaction involved is: $CH \equiv CH + HCl \longrightarrow CH_2 = CHCl \xrightarrow{HCl} CH_3 - CHCl_2$

  Anti-markoniov's rule is followed in case of addition of HBr:

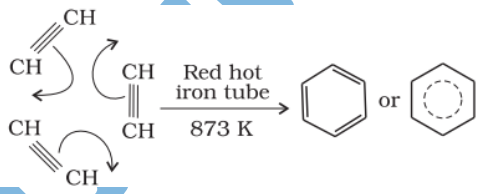
- **Addition of H_2O (hydration Reaction)**



3. **Polymerisation**

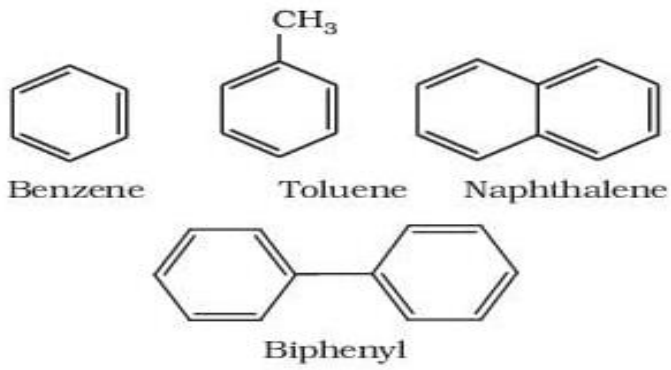


- Cyclic Polymerisation

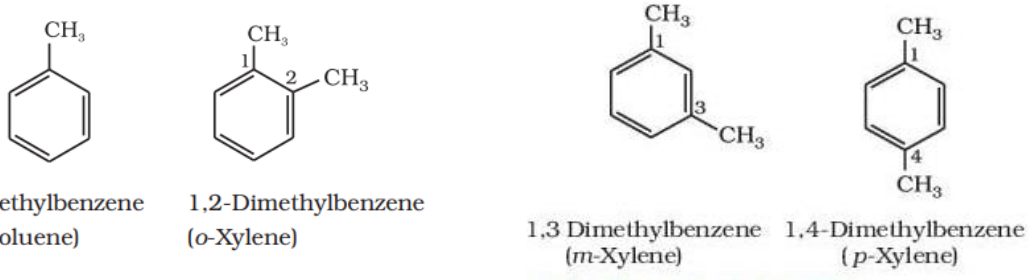


Aromatic Compounds: It means aroma (pleasant smell).

- They have benzene ring C_6H_6 (alternate 3 double bond with no benzene ring).
- All with benzene ring is called are called Benzenoid compound and with no benzene ring is called non-benzenoid compound).

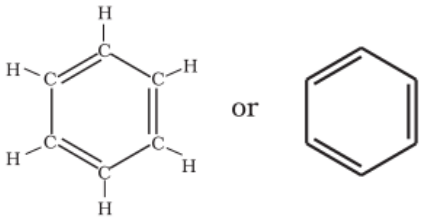


Isomerism: Ortho, Meta and Para isomers are formed.



Methylbenzene (Toluene) | 1,2-Dimethylbenzene (*o*-Xylene) | 1,3 Dimethylbenzene (*m*-Xylene) | 1,4-Dimethylbenzene (*p*-Xylene)

Structure of benzene: In benzene the double bonds keep on moving so, the structure showing double bond can be written in either ways. It has no effect on the chemical reactions of benzene.

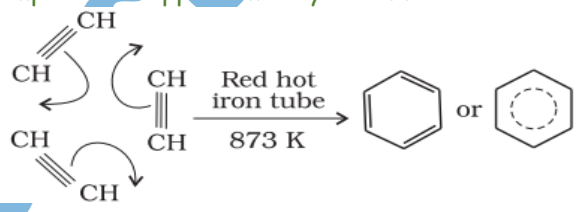


Huckle rule of Aromatic compounds: It gives criteria of aromaticity that is:

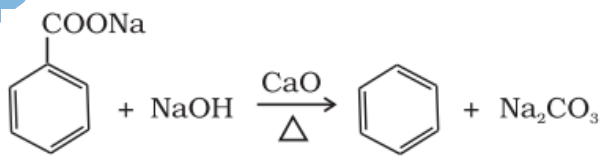
1. Planarity
2. Complete delocalization of the π electron in the ring.
3. All aromatic compound should have $(4n + 2)\ \pi$ electrons , Where n = 2 , 6, 10 , or 14.

Preparation of Benzene

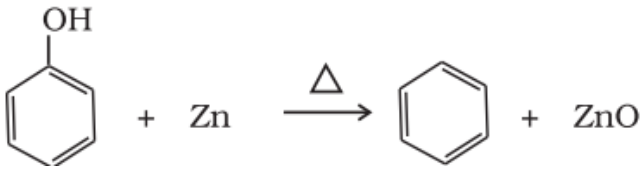
1. **Polymerisation of alkynes:** In this the 3 molecules of alkynes undergo polymerisation as shown in presence of iron at temperature approximately 873 K.



2. **Decarboxylation of aromatic acids:**



3. **Reduction of phenol:** In this reduction of phenol is carried in presence of zinc on heating as given.



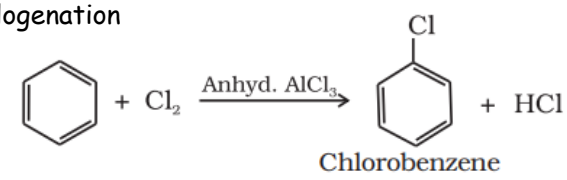
Physical Properties:

1. **Solubility:** They are insoluble in water but soluble in organic solvent.
2. **Flammability:** They are inflammable and burn with sooty smell.
3. **Melting point and boiling point:** It increases with increase in number of carbon atoms in chain.
4. **Nature:** They are toxic and carcinogenic in nature.

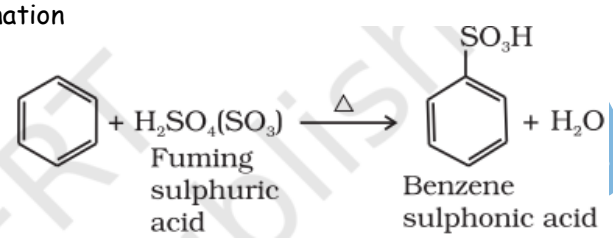
Chemical properties of benzene

1. **Electrophilic Substitution Reaction** In this hydrogen is going to get substituted by some other group.

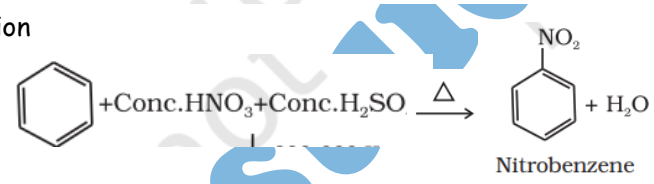
- Halogenation



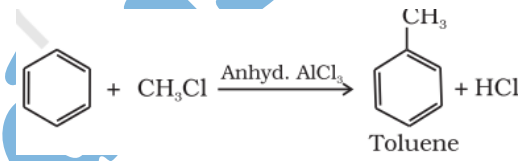
- Sulphonation



- Nitration

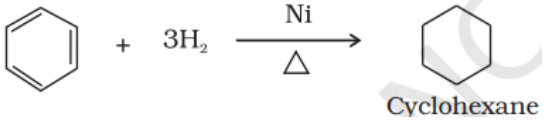


- Alkylation

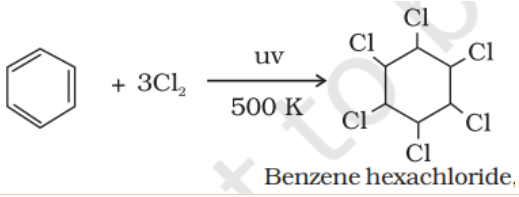


2. **Addition Reaction:** It involves the addition of group or group of atoms to benzene.

- Hydrogenation



- **Halogenation**



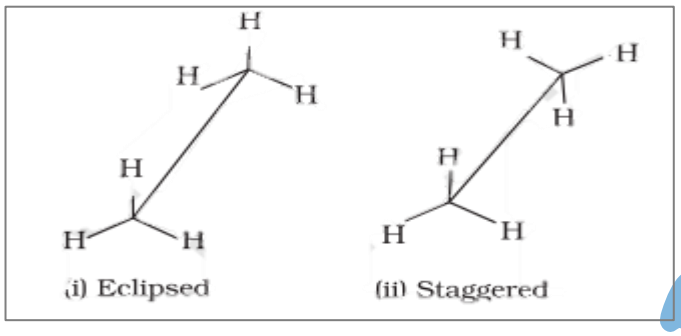
Combustion (Complete oxidation):

$$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O$$

Conformational Isomerism: The different arrangement of atoms in space which can be obtained due to rotation about C – C bond are called Conformation.

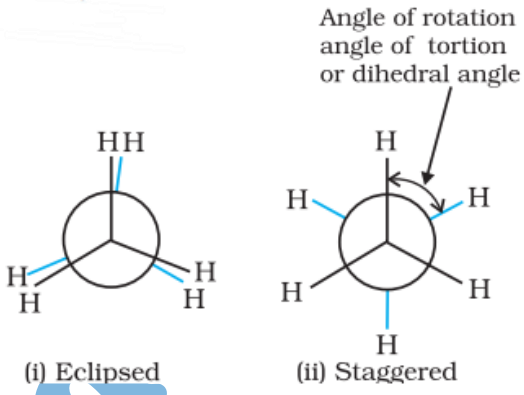
Conformations of ethane: There are two projections.

- Sawhorse projection: In this H and C are bonded to each other and is represented in form of lines.



(Sawhorse)

- Newman projection: In this carbon is represented by drawing circles and hydrogen are represented by drawing lines as shown.



KHATAM