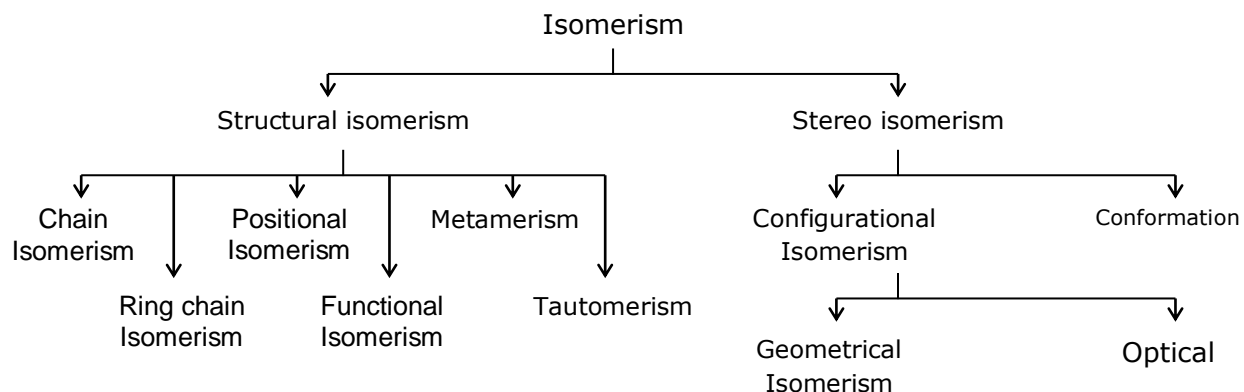


ISOMERISM AND HYDROCARBONS- IPUC

ISOMERISM

Compounds having same molecular formula but different physical and chemical properties show isomerism.

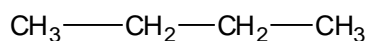
- Isomerism is of 2 types: (a) Structural isomerism (b) Stereoisomerism



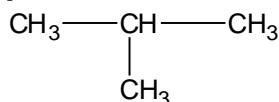
Structural isomerism

Structural isomerism is due to the difference in the arrangement of atoms in the molecule resulting in two or more structures. It is further divided into the following types

a) Chain isomerism: Structure of the parent chain is different



Butane



2 - methyl propane

- Hexane (C₆H₁₄) has five chain isomers : Hexane (n-hexane), 2-methylpentane (isohexane), 3-Methylpentane, 2, 3-Dimethylbutane and 2, 2-Dimethylbutane (neohexane)
- Like alkanes, cycloalkanes also show chain isomerism. For example



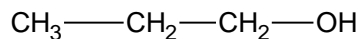
Cyclobutane

and

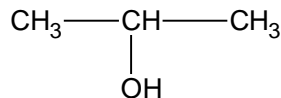


Methylcyclopropane

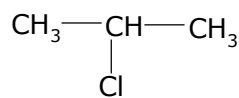
b) Position isomerism: Here position of the functional group is different.



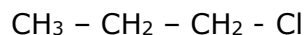
Propanol



2 - propanol

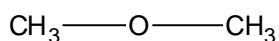


(2 - chloropropane)

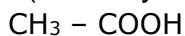


(1 - Chloropropane)

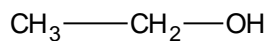
- c) Functional isomerism:** Here functional groups are different.



(methoxy methane)



(acetic acid)



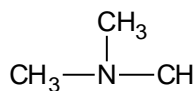
Ethanol



(methyl formate)

- Carboxylic acids and esters ($\text{C}_n\text{H}_{2n}\text{O}_2$)
 $\text{C}_3\text{H}_6\text{O}_2$: $\text{CH}_3\text{CH}_2\text{COOH}$
 represents Propionic acid
 $\text{CH}_3\text{COOCH}_3$ and $\text{HCOOCH}_2\text{CH}_3$
 Methyl acetate Ethyl formate
- Aldehydes, ketones, unsaturated alcohols and unsaturated ethers ($\text{C}_n\text{H}_{2n}\text{O}$)
 $\text{C}_3\text{H}_6\text{O}$: CH_3COCH_3 , $\text{CH}_3\text{CH}_2\text{CHO}$,
 Represents Acetone Propionaldehyde
 $\text{CH}_2 = \text{CH}-\text{CH}_2\text{OH}$ and $\text{CH}_2 = \text{CH}-\text{O}-\text{CH}_3$
 Ally Alcohol Methyl vinylether
- Dienes, allenes and alkynes ($\text{C}_n\text{H}_{2n-2}$) C_4H_6 represents :
 $\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}_2$, $\text{CH}_2 = \text{C} = \text{CHCH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
 1, 3-Butadiene 1, 2-Butadiene 1-Butyne
 or $\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_3$
 2-Butyne
- Nitroalkanes and alkyl nitrites ($\text{C}_n\text{H}_{2n+1}\text{NO}_2$) $\text{C}_2\text{H}_5\text{NO}_2$ represents: $\text{CH}_3\text{CH}_2-\text{NO}_2$
 Nitroethane
 and $\text{CH}_3\text{CH}_2-\text{O}-\text{N} = \text{O}$ (Ethyl nitrite)

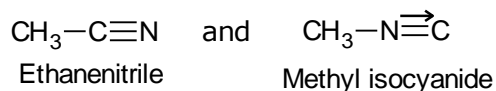
- 1°, 2°, and 3° Amines
 $\text{C}_3\text{H}_9\text{N}$ represents: $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{NHCH}_3$ and
 Propanamine N-Methylethanamine
 (1° Amine) (2° Amine)



N,N-Dimethylmethanamine

(3° Amine)

- Cyanides and isocyanides ($C_nH_{2n-1}N$) C_2H_3N represents:



d) Metamerism

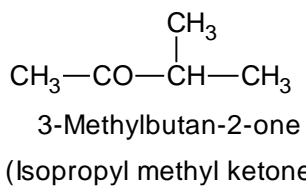
Different distribution of groups on either side of the functional group is called metamerism.

Eg: $CH_3 - O - C_3H_7$ and $C_2H_5 - O - C_2H_5$,



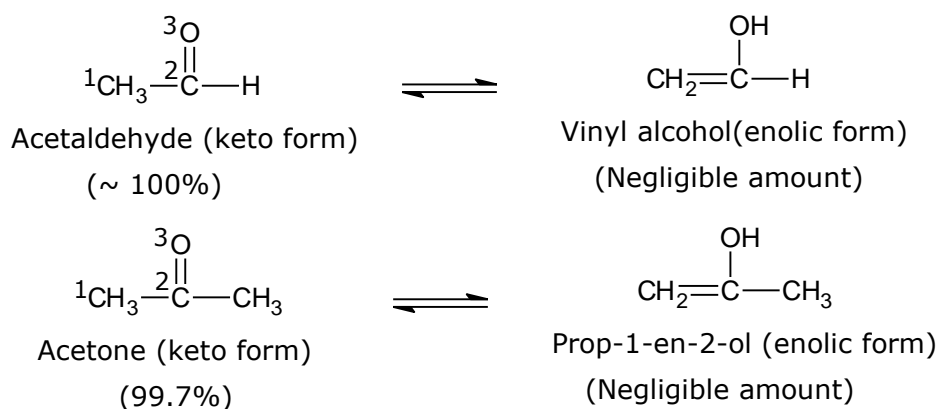
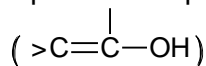
Here functional group remains the same.

- $CH_3CH_2-S-CH_2CH_3$ is a metamer of $CH_3-S-CH_2CH_2CH_3$ or
Diethyl thioether Methyl n-propyl thioether
- $CH_3-S-CH(CH_3)_2$
Methyl isopropyl thioether
- $CH_3CH_2-NH-CH_2CH_3$ is a metamer of $CH_3-NH-CH_2CH_2CH_3$ or
Diethylamine Methyl n-propylamine
- $CH_3-NH-CH(CH_3)_2$
Isopropylmethylamine
- $CH_3CH_2-CO-CH_2CH_3$ is a metamer of $CH_3COCH_2CH_2CH_3$ or
Pentan-3-one Pentan-2-one
(Diethyl ketone) (Methyl n-propyl ketone)

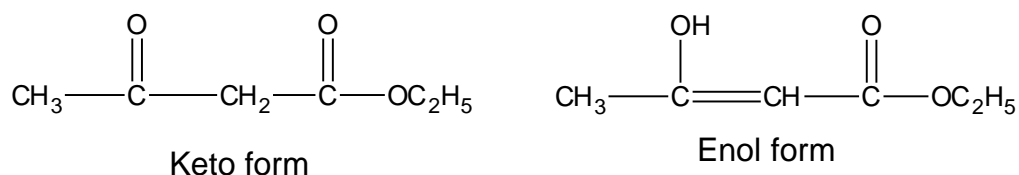


- e) Tautomerism:** This is a type of functional isomerism where the isomers have different functional groups and are spontaneously inter convertible and exist in a dynamic equilibrium with each other.

In this type of tautomerism, one form (tautomer) contains the keto group ($>C=O$) while the other contains the enolic group. Two simplest examples of keto-enol tautomerism are acetaldehyde and acetone.



Eg: **Ethyl acetoacetate exists in two forms.**



- Essential conditions of Tautomerism.** There are two essential conditions for a molecule to exhibit tautomerism. There are
 - The compound must have an electronegative atom (i.e., N, O or S) bonded by a double or a triple bond, i.e., $C=O$, $C\equiv N$, $N\equiv O$, $C=NH$, etc.).
 - The compound must have atleast one labile α -hydrogen, i.e., α -hydrogen present on a saturated carbon. Thus, acetophenone, butan-2-one and propionaldehyde all contain α -hydrogen atoms on a saturated carbon and hence show keto-enol tautomerism.

Racemic Mixture

An equimolar mixture of (+) and (-) enantiomers is called racemic mixture or

Stereo Isomerism:

- Compounds having same molecular formula but different arrangements of atoms in space show stereoisomerism
- Stereoisomerism is of 2 types: (i) Geometrical isomerism (ii) Optical isomerism

Geometrical isomerism:

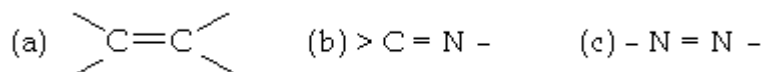
- This arises due to the restricted rotation of the groups across multiple bond or across single bond in cyclic compounds.

Conditions for a molecule to show geometrical isomerism

- The molecule should have a carbon - carbon double bond.
 - Each carbon atom should be attached to two different groups or There should be a cyclic compound and at least two carbon atom should contain two different groups attached to them
- Geometrical isomers which contain two similar groups on the same side of the double bond are called **cis isomers**. If two groups are present on the different side of the double bond they are called **trans isomers**.
 - 2-butene exhibits geometrical isomerism but 1-butene does not because 1-butene contains two similar groups (hydrogen atoms) present on the double bonded carbon atom)
 - Maleic acid is the cis isomer whereas fumaric acid is trans isomer.

(A) GEOMETRICAL ISOMERISM AROUND DOUBLE BONDED ATOMS :

Following three types are possible in this case



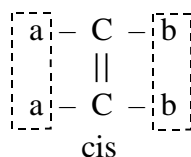
(a) Geometrical isomerism in compounds containing : $>C=C<$

Following two types of compounds are observed to give geometrical isomerism in this class.

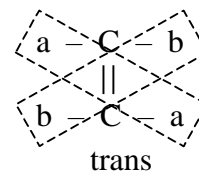
(i) $abC = Cab$ type and (ii) $abC = Cad$ type

where a, b & d are different atoms and groups & C is carbon atom.

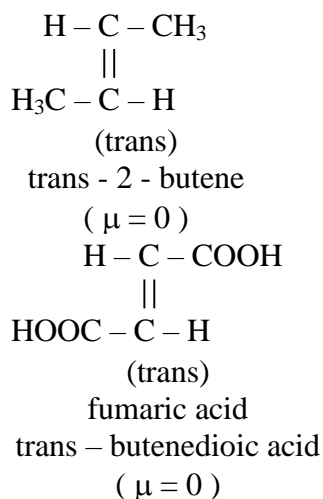
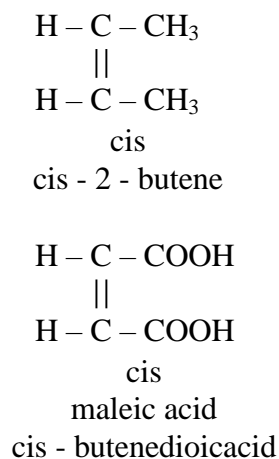
(i) $abC = Cab$ type :



e.g.

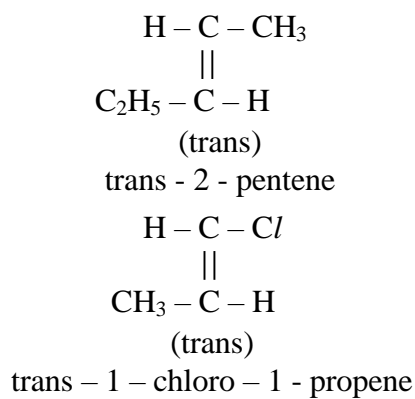
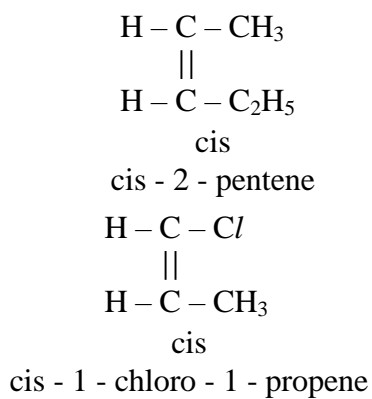
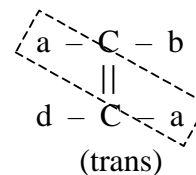
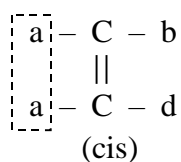


(dipole moment = 0)

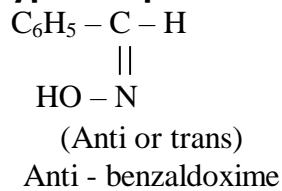
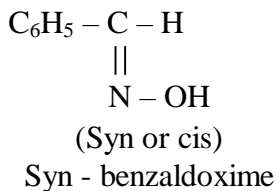


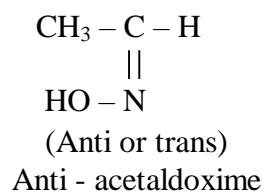
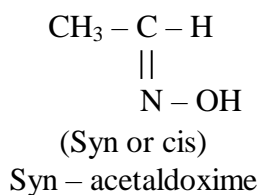
(where μ = dipole moment)

(ii) abC = Cad type :

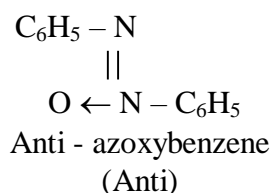
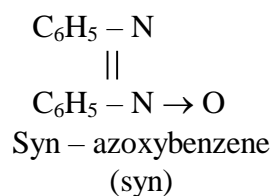
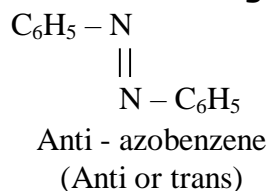
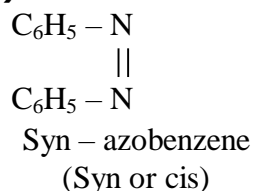


(b) Geometrical isomerism in > C = N - type compounds :





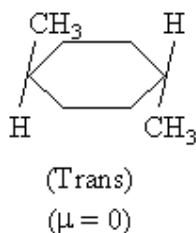
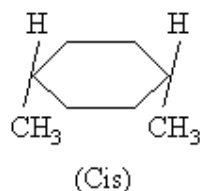
(c) Geometrical isomerism in compounds containing - N = N - :



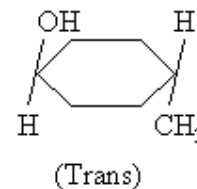
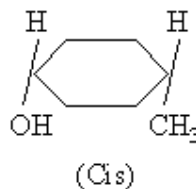
Cis - Trans Isomerism in Cyclic Compounds :

e.g.,

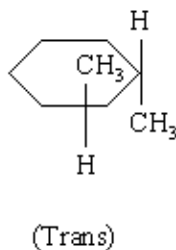
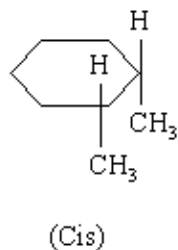
(i)



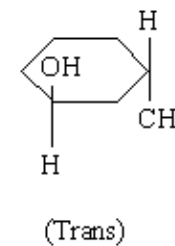
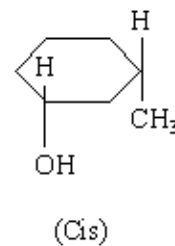
(ii)



(iii)



(iv)



Properties of geometrical isomers

Dipole moment:

Trans-isomers practically have zero dipole moment whereas the cis-isomers have the net dipole moment.

Melting point:

Trans-isomer is more symmetrical and hence has high melting point than the corresponding cis-isomer.

Chemical properties:

Maleic acid can form the anhydride whereas fumaric acid cannot form the anhydride.

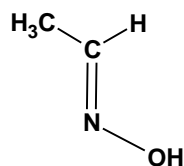
Degree of dissociation:

Maleic acid has high value for first dissociation constant but a low value for second dissociation constant due to the extra stability of anion formed by first ionisation. Whereas in the case of fumaric acid both dissociation constants have almost same value

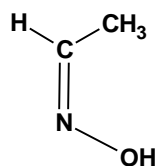
Aldoximes and Ketoximes

also show geometrical isomerism. In aldoxime – H and – OH groups are on same side of the C = N, then that isomer is called **syn** isomer. If they are present on the opposite side they are called **anti** isomer. In the case of ketoximes the relative position of the group which appears first in the name and the – OH group on nitrogen is considered to name it as **syn** or **anti**.

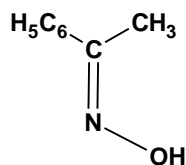
Example



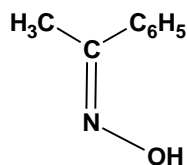
Syn-acetaldoxime



Anti-acetaldoxime



Syn-methylphenylketoxime



Anti-methylphenylketoxime

Optical Isomerism

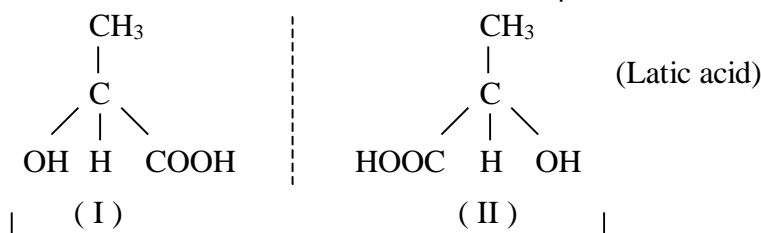
- Compounds which rotate the plane of polarised light are called optically active compounds.
- Compounds which rotate the plane of polarised light to the right are called **dextrorotatory** compounds and to the left are called **laevorotatory** compounds.

Conditions for a molecule to show optical activity

- a) The molecule should not have plane of symmetry
 - b) The molecule should have a non super imposable mirror image.
- All molecules which do not have a plane of symmetry have non super imposable mirror images. (Object and mirror image will be non identical). These molecules are called **chiral molecules** or **asymmetric molecules**.
 - Molecules having plane of symmetry and hence not showing optical activity are called **achiral molecules**.
 - A carbon which is attached to four different groups is called **chiral carbon atom**.

- If a molecule contains only one chiral carbon atom, it does not have plane of symmetry and hence will be optically active.
- Lactic acid contains a chiral carbon which is attached to four different groups and hence shows optical activity.
- In a chiral compound the molecule and its mirror image will be non superimposable and hence they constitute a pair of optical isomers.
- A mixture containing 50% of d isomer and 50% 'l' isomer of the same compound is called **racemic mixture**.

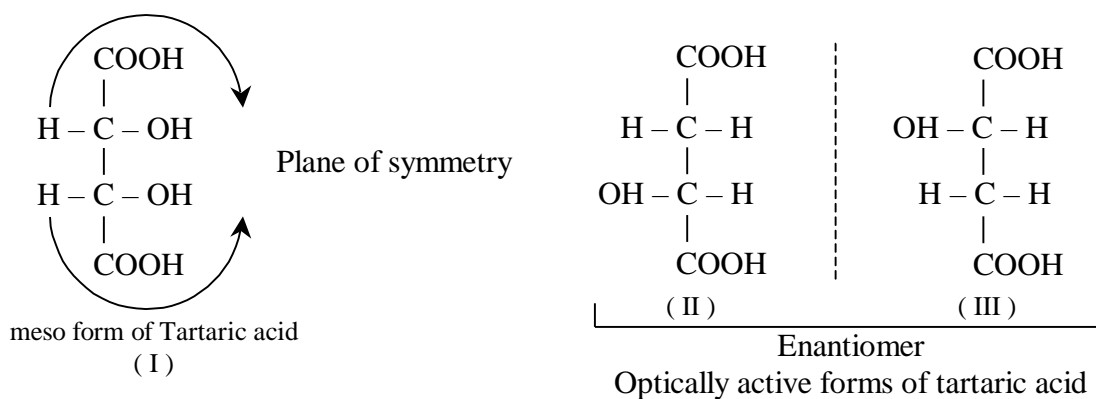
Enantiomer or enantiomorphous : The nonsuperimposable mirror image pair of a compound is called enantiomer or enantiomorphous.



Enantiomer or enantiomorphous in I & II if first is d-form then II will be l-form & vice-versa.

Meso form or m-form or inactive form or i-form : The compound containing more than one asymmetric centre with a plane of symmetry has no tendency to rotate plane of polarised light either left or right and therefore, optically inactive. Such form is called meso-form.

- Tartaric acid contains two similar chiral carbon atoms. Hence the compound also exists as meso form.



In meso compounds the optical inactivity is due to the **internal compensation**. In racemic mixture the optical inactivity is due to the **external compensation**.

Diastereoisomers: A pair of stereoisomers having no mirror-image relationship is known as diastereoisomers.

- (i) cis-trans isomers may be called diastereoisomer.
- (ii) meso form & d or l-form of a compound are diastereoisomer.
- (iii) optically active isomers which are not enantiomers are called diastereoisomers.

Configuration: By the term configuration we mean the arrangement of atoms or groups around the asymmetric carbon atom.

Number of Stereoisomers, Optical isomers and meso-Forms

The total number of stereoisomers, optical isomers and meso-forms of any given formula may be derived as follows:

(a) When the molecule is unsymmetrical and contains 'n' chiral carbon atoms.

Number of optical isomers (o) = 2^n

Number of meso isomers (m) = 0

∴ Total number of stereoisomers (o + m) = $2^n + 0 = 2^n$

(b) When the molecule is symmetrical and has even number of chiral carbon atoms.

Number of optical isomers (o) = $2^n - 1$

Number of meso-forms (m) = $2^{\left(\frac{n}{2}-1\right)}$

Total number of stereoisomers (o + m) = $2^{n-1} + 2^{\frac{n}{2}-1}$.

(c) When the molecule is symmetrical and has odd number of chiral carbon atoms.

Number of optical isomers (o) = $2^{n-1} - 2^{\left(\frac{n-1}{2}\right)}$

Number of meso isomers (m) = $2^{\left(\frac{n-1}{2}\right)}$

∴ Total number of stereoisomers (o + m) = $2^{n-1} - 2^{(n-1)/2} + 2^{(n-1)/2} = 2^{n-1}$

Racemic Mixture

An equimolar mixture of (+) and (-) enantiomers is called racemic mixture or modification. It is denoted by the prefix dl or (±) before the name of the compound. A racemic mixture is optically inactive due to external compensation since the rotation due to one enantiomer is cancelled by equal and opposite rotation caused by the other enantiomer.

Retention

Whenever a chemical reaction is carried out on a chiral molecule, the product may have the same configuration as the reactant or may have the opposite configuration. If the relative spatial arrangement of bonds at an asymmetric centre in a chiral molecule remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.

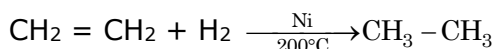
In other words, retention of configuration means preservation of the spatial arrangement of bonds at an asymmetric centre during a chemical reaction.

HYDROCARBONS

Alkanes: General formula of alkanes C_nH_{2n+2} where n is the integer

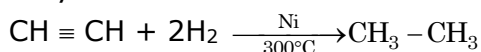
1. By catalytic hydrogenation of unsaturated hydrocarbons:

Hydrogenation takes place in the presence of finely divided nickel as catalyst at 200°C. This reaction is known as Sabatier and Sanderns reaction.



Ethylene

Ethane



Acetylene

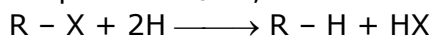
Ethane

Hydrogenation is possible at room temperature when platinum or palladium is used as a catalyst in place of Ni.

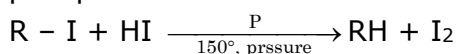
Methane cannot be obtained by this method as no unsaturated hydrocarbon contains a single carbon atom.

2. **By the reduction of alkyl halides:**

Alkyl halide can be reduced with Zn + CH₃COOH, Zn + HCl, Zn + NaOH, Zn-Cu couple in C₂H₅OH, aluminium amalgam in C₂H₅OH or LiAlH₄.



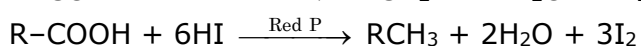
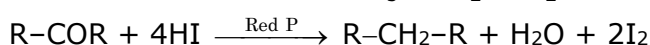
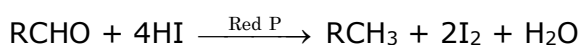
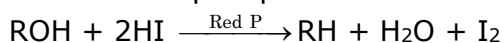
Alkyl halides can also be conveniently reduced by heating with HI and red phosphorous in a sealed tube.



The function of red phosphorous is to remove iodine.

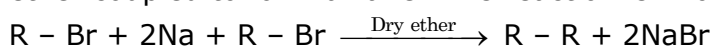
3. **By the reduction of alcohols, aldehydes, ketones and fatty acids:**

The above compounds and their derivatives can be reduced with hot hydroiodic acid and red phosphorous at 150°C in a sealed tube to give alkanes.

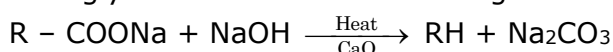


4. **By condensing two molecules of alkyl halides:**

Two molecules of alkyl halides when treated with sodium metal in presence of dry ether coupled to form alkane. This reaction is known as Wurtz synthesis.



5. **By decarboxylation of carboxylic acid:** The sodium salt of carboxylic acid is strongly heated with soda lime to give alkane by elimination of CO₂ as carbonate.



6. **Kolbe's electrolysis:**

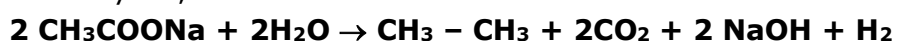
When concentrated solution of sodium or potassium salt of a fatty acid is electrolysed, higher alkane is obtained at the anode.



Methane can't be prepared by this method.

Example:

When a concentrated solution of sodium or potassium salt of a acetic acid is electrolysed, ethane is obtained at the anode



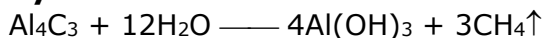
Electrolysis of a single salt will give hydrocarbons which contains even number of carbon atoms. The number of carbon atoms present in the hydrocarbon produced

is double the number of carbon atoms present in the alkyl group of the sodium salt taken

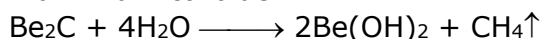
Sodium salt	No. of carbon atoms in the alkyl group	No. of carbon atoms in the hydrocarbon
Sodium acetate	1	2
Sodium propionate	2	4

7. Preparation of methane

By action of water on aluminium carbide or beryllium carbide:



Aluminium carbide



Beryllium carbide

Physical properties of the alkanes

Physical states: Due to the weak van der Waals forces, the first four normal alkanes (C_1 to C_4) are colourless and odourless gases, the next thirteen normal alkanes (C_5 to C_{17}) are colourless and odourless liquids, and from C_{18} onwards, colourless and odourless solids at 298K and 1 atm pressure.

Boiling points: The boiling points of the normal (unbranched) alkanes show a regular (steady) increase with increasing molecular mass. Except for the very small alkanes (C_1 to C_4), the boiling point rises 20 to 30 degrees for each carbon that is added to the chain.

Melting points: The normal alkanes do not exhibit the same smooth increase in melting points with increasing molecular mass that they show in their boiling points.

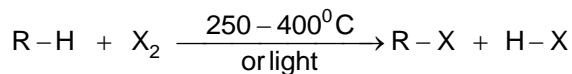
Effect of branching on boiling and melting points: In a group of isomeric alkanes, the normal compound always has the highest b.p. and m.p. Generally, the greater the branching, the lower is the b.p. Thus n-butane has a boiling point of 0°C and isobutane -12°C

Solubility: Alkanes are almost completely insoluble in water. Liquid alkanes are soluble in one another and they generally dissolve in non-polar solvents and solvents of low polarity. Examples of good solvents for alkanes are benzene, carbon tetrachloride, chloroform and ether. The solubility diminishes with increase in molecular mass.

Density: As a class, the alkanes are the least dense of all groups of organic compounds. The density also increases with molecular mass of the alkanes, but tends to level off at about 0.79 g mL^{-1} . Thus all alkanes are considerably less dense than water (1.00 g mL^{-1} , the density of water at 4°C). As a result, petroleum (a mixture of hydrocarbons) floats on water.

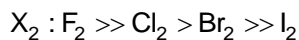
Chemical properties

a) **Halogenation** It involves substitution of hydrogen of an alkane by a halogen. It takes place either at higher temperature ($250 - 400^\circ\text{C}$, *thermal halogenation*) or in the presence of diffused sunlight (*photohalogenation*)



Alkane a mixture of alkyl halides

Relative Order of reactivity



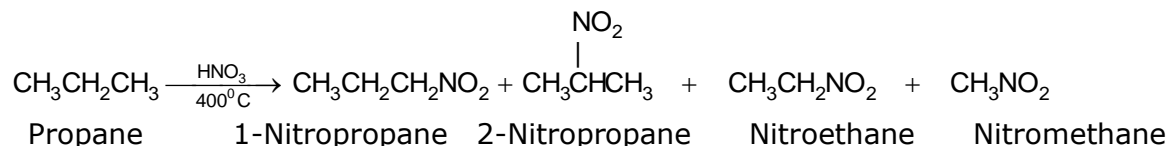
H atom of alkane : $3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{H} > \text{H-CH}_3$

b) Nitration:

Under suitable conditions, alkanes react with nitric acid resulting into substitution of one or more hydrogen atoms by a nitro-group, NO_2 . This process which is called *direct nitration* or just *nitration* is used to prepare nitro-compounds on a large scale [*Industrial preparation*]. It is carried out in two ways:

i) Liquid-phase nitration: Here the alkane is heated with concentrated nitric acid under pressure at 140°C . It is always a slow process and results in the formation of a large amount of poly-nitro compounds.

ii) Vapour – phase nitration: Nitration of the alkanes may be carried in the vapor phase by heating with nitric acid (or with nitrogen oxides or with dinitrogen) at $150-475^\circ\text{C}$. Each alkane has its optimum temperature for nitration. During vapour-phase nitration, a mixture of mononitroalkanes is obtained. The mixture consists of all the possible mononitroderivatives including those which are formed by every possible chain fission of the alkane. For example, vapour-phase nitration of n-propane gives a mixture of four mononitroalkanes:



c) **Sulphonation:** The process of sulphonation of an alkane involves substitution of a hydrogen atom by a sulphonic acid group, SO_3H , leading to the formation of sulphonic acids. The aliphatic sulphonic acids are named either as alkylsulphonic acids or as alkanesulphonic acids:

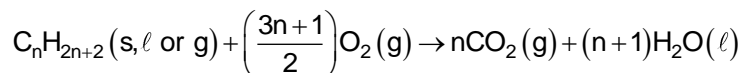
$\text{CH}_3\text{SO}_3\text{H}$	$(\text{CH}_3)_2\text{CHSO}_3\text{H}$
Methylsulphonic acid (methanesulphonic acid)	Isopropylsulphonic acid (propane-2-sulphonic acid)

2) Oxidation

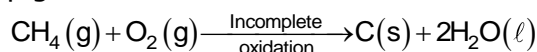
There are two ways to oxidize alkanes:

a) Complete (or uncontrolled) oxidation

All alkanes readily burn on heating in excess of air or oxygen and get completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

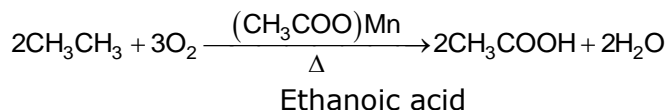
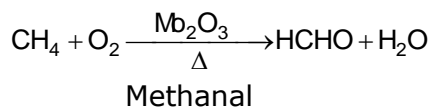
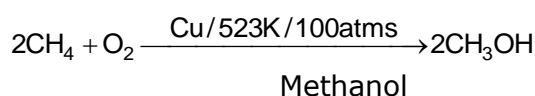
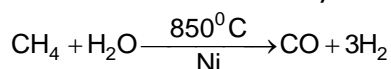
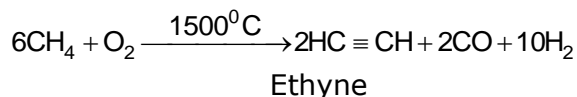


During incomplete combustion of alkanes with limited amount of air or oxygen, *carbon black* is formed which is used in the manufacture of ink, printer ink, black pigments and as filters:

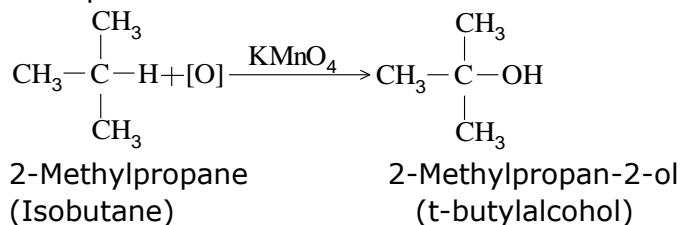


b) **Controlled oxidation:**

On heating with a controlled amount of air or dioxygen at high pressure or temperature and in the presence of suitable catalysts alkanes undergo controlled oxidation to give different useful products.

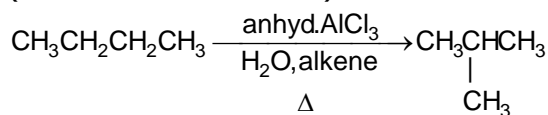


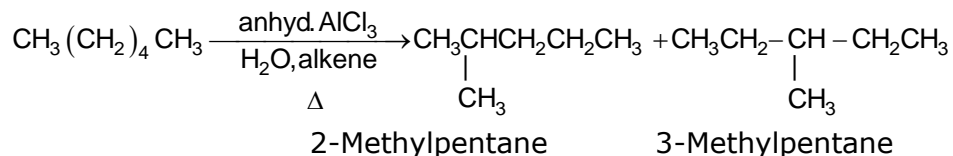
Oxidising reagents such as potassium permanganate normally do not oxidize alkanes but they readily oxidize a tertiary hydrogen atom to a hydroxyl group. For example:



3) **Isomerization:**

It involves conversion of n-alkanes into branched-chain alkanes carrying a methyl group as a side-chain. It is carried out by heating the unbranched alkane with anhydrous aluminium chloride at 300°C. For isomerisation to be feasible a trace of water (to form HCl from AlCl₃) together with a trace of alkyl halide or an alkene (to form a carbocation) is essential.



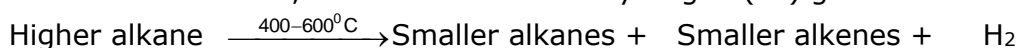


4) **Pyrolysis (cracking):**

The thermal decomposition (i.e., decomposition by the action of heat alone) of an organic compound is known as *pyrolysis*. This word originates from the Greek *pyr* (fire), and *lysis* (a loosing) and hence means "cleavage by heat".

Hydrolysis – cleavage by water:

The pyrolysis of alkanes, particularly petroleum, is known as *cracking*. In *thermal cracking* alkanes are simply passed through a chamber heated to a high temperature. When heated to about 400 – 600°C, higher alkanes are decomposed into smaller alkanes, alkenes and some dihydrogen (H₂) gas:

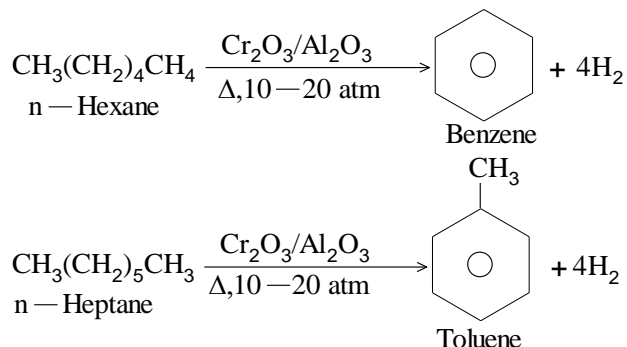


5) **Hydroforming (or catalytic reforming or aromatization):**

It involves conversion of normal alkanes having six or more carbon atoms into benzene and its derivatives. It is carried out under pressure at 480–550°C in the presence of oxides of vanadium, molybdenum or chromium on an alumina support. The process is based on the following sequence:

Dehydrogenation → Cyclisation → Aromatization → Isomerisation

The aromatic compounds obtained contain the same number of carbon atoms as the aliphatic starting materials as shown by the following examples:



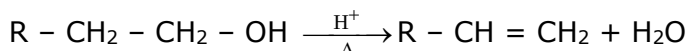
Alkenes:

Alkenes have general formula C_n H_{2n}

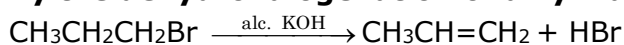
Ethylene:

1. **By dehydration of alcohols:**

Dehydration of alcohols in presence of acids forms alkene. This is elimination reaction. Passing ethanol vapour over alumina catalyst at 350°C or by heating ethanol with conc. H₂SO₄ at 170°C



2. **By the dehydrohalogenation of alkyl halides:**



If dehydrogenation of alkyl halide gives two products, the major product will be according to Saytzeff's rule, i.e. the alkene which is most substituted is the major product.

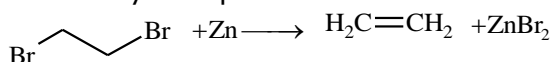
The ease of dehydrohalogenation follows the order,

Tertiary alkyl halide > secondary alkyl halide > primary alkyl halide.

Among the different halides, the order is alkyl iodide > alkyl bromide > alkyl chloride.

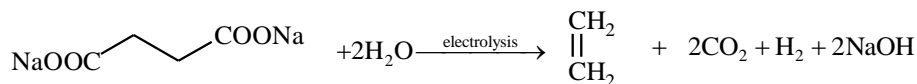
3. By the dehalogenation of vicinal dihalides:

Dehydrohalogenation of vicinal dihalides in presence of Zn dust in alcoholic solution yields pure alkene.



4. Kolbe's electrolysis method:

The electrolysis of sodium or potassium salts of dicarboxylic acid gives alkene at anode.



However, if Na/ liq NH₃ is used, *trans* alkene is formed, and in presence of Ni *cis* alkene is formed.

Properties:

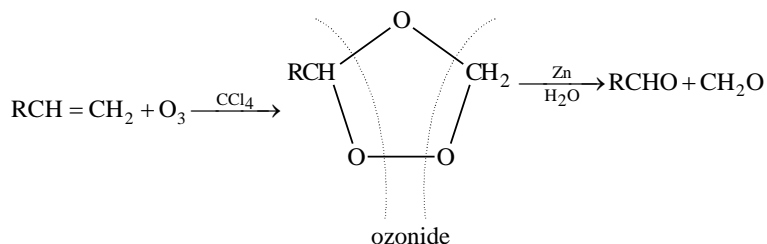
Reduction: Reduced to ethene by hydrogen gas in the presence of Ni catalyst at 200°C

Addition reaction: Chlorine adds to the double bond giving 1, 2-dichloroethane,

HCl adds giving ethyl chloride

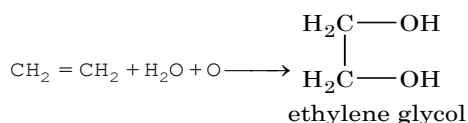
Reactivity of hydrogen halides are in the order HI > HBr > HCl

Ozonolysis:

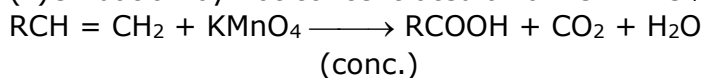


Ethylene ozonide is formed. This on heating with zinc dust and water decomposes giving formaldehyde.

Oxidation (i) Oxidation by cold alkaline KMnO₄ (Bayer's reagent) Ethylene glycol (1, 2 - Ethanediol) is formed.



(ii) Oxidation by hot concentrated alkaline KMnO_4



Polymerisation: Gives polythene

Zeigler Natta catalyst consists of a mixture of triethyl aluminium and titanium tetra chloride.

Uses: Oxy - ethylene flame, artificial ripening of fruits, Preparation of polythene, ethylene glycol, mustard gas.

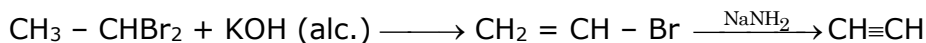
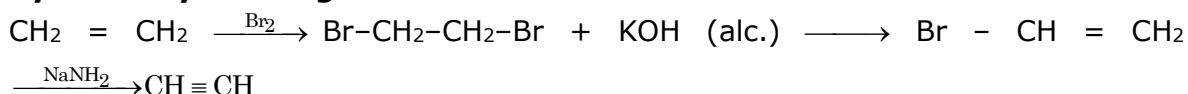
Alkynes:

Alkynes have general formula $\text{C}_n\text{H}_{2n-2}$

Acetylene (Ethyne)

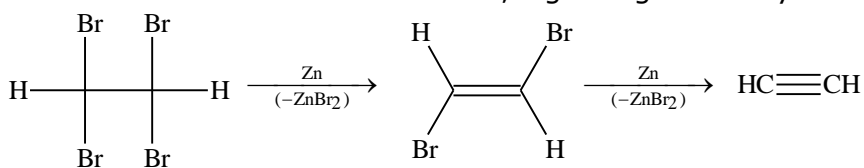
Preparation

1. **By the dehydrohalogenation of vicinal dihalides:**



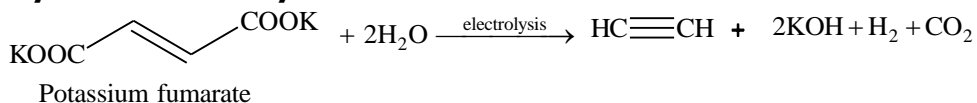
2. **By dehalogenation of vicinal tetrahalides:**

Reaction with active metals like Zn, Mg etc. gives acetylene.



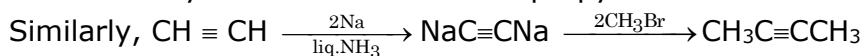
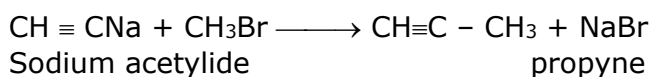
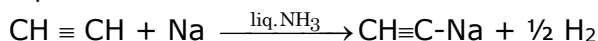
1,1,2,2-tetrabromoethane

3. **By Kolbe electrolysis method:**



4. **From acetylene:**

Higher alkynes can be prepared from acetylene when treated with sodium metal in liquid ammonia.



Electrophilic Addition Reactions to Alkynes

Despite presence of two π -bonds, alkynes are less reactive than alkenes towards electrophilic addition reactions because of the following reasons.

- (i) The C-atoms of alkynes being sp -hybridized are more electronegative and hence hold the π -electrons more tightly.
- (ii) Due to cylindrical nature, the π -electrons of alkynes are more delocalized and hence are less easily available for reaction.
- (iii) The vinyl carbocation formed after the addition of an electrophile to the alkyne is far less stable than the alkyl carbocation obtained by the addition of an electrophile to the alkene.

The gas liberated when calcium carbide reacts with water is Acetylene

Properties:

Adds to H_2 , Cl_2 , HCl , etc.

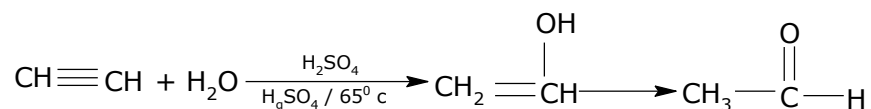
Addition takes place according to Markownikoff's rule

Hydration of Alkynes

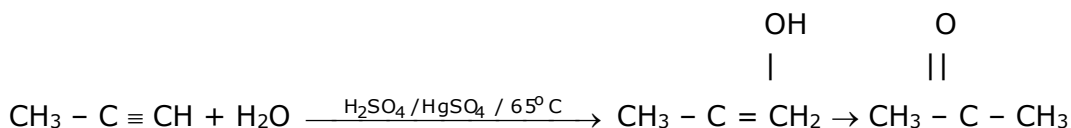
Hydration of ethyne in presence of dil. H_2SO_4 and Hg^{2+} salts gives ethanal while all other terminal alkynes give methyl ketones.

In the presence of dilute sulphuric acid and $HgSO_4$ catalyst at $65^\circ C$, alkynes react with water forming carbonyl compounds

Acetylene gives acetaldehyde



Propyne gives acetone



Markownikoff's Rule:

When a hydrogen halide adds to a double-bond, hydrogen atom adds to that carbon which contains more number of hydrogen atoms.

Anti - Markownikoff's rule: In the presence of an organic peroxide, addition takes place against Markownikoff's rule. This is called Kharasch peroxide effect.

Ozonolysis : Acetylene ozonide - Hydrolysed with water in the presence of Zn gives glyoxal.

Oxidation: On oxidation with alkaline $KMnO_4$, oxalic acid is obtained.

Polymerisation: On passing through a red hot tube benzene is obtained.

Reduction of Alkynes

Reduction of alkynes in presence of Lindlar's catalyst (H_2 , $Pd/BaSO_4 + S$ or quinoline) gives cis-alkenes while Birch reduction ($Na/liq. NH_3$, 200 K) gives trans-alkenes.

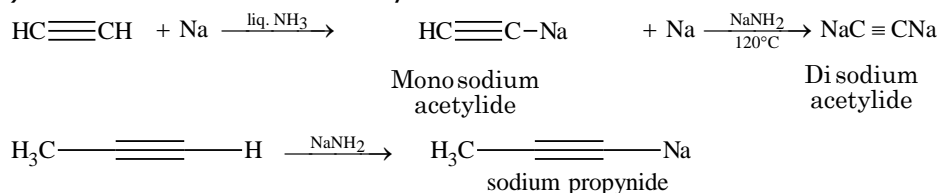
Acidic Nature of Alkynes

- (i) Due to sp -hybridized carbon being more electronegative than sp^2 or sp^3 - hybridized carbons, the relative acidic strength of ethyne, ethene and ethane follows the order:
ethyne > ethene > ethane.
- (ii) All terminal alkynes form Grignard reagents on treatment with CH_3MgBr with evolution of CH_4 .
- (iii) The relative acidic strength of water, alcohols, phenols, carboxylic acids, acetylene, ammonia, ethylene and ethane follows the order: $\text{RCOOH} > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{NH}_3 > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$.
Obviously, the basic character of their conjugate bases follows the reverse order, i.e., basicity decreases in the order:
 $\text{CH}_3\text{CH}_2^- > \text{CH}_2 = \text{CH}^- > \text{NH}_2^- > \text{HC} \equiv \text{C}^- > \text{RO}^- > \text{HO}^- > \text{C}_6\text{H}_5\text{O}^- > \text{RCOO}^-$.

Formation of acetylide:

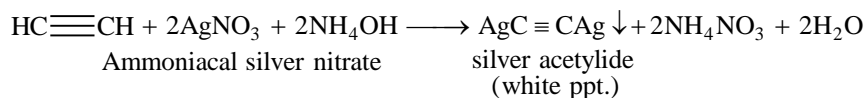
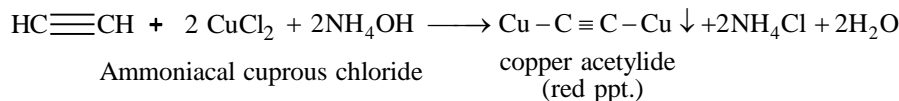
The group $-\text{C} \equiv \text{C}-\text{H}$ in alkynes is slightly acidic in nature and hence its hydrogen atom can be easily replaced by certain metals to give metallic derivatives called acetylides or alkynides .

(i) Formation of sodium acetylides



(ii) Formation of copper and silver acetylides

With ammoniacal cuprous chloride red precipitate of cuprous acetylide is obtained.
With ammoniacal silver nitrate a white precipitate of silver acetylide is formed.



These reactions are used for detecting the presence of acetylinic hydrogen atom.

Uses of acetylene:

Oxy-acetylene flame, synthetic polymers, preparation of compounds like acetaldehyde, acetic acid, solvent - Westron etc.

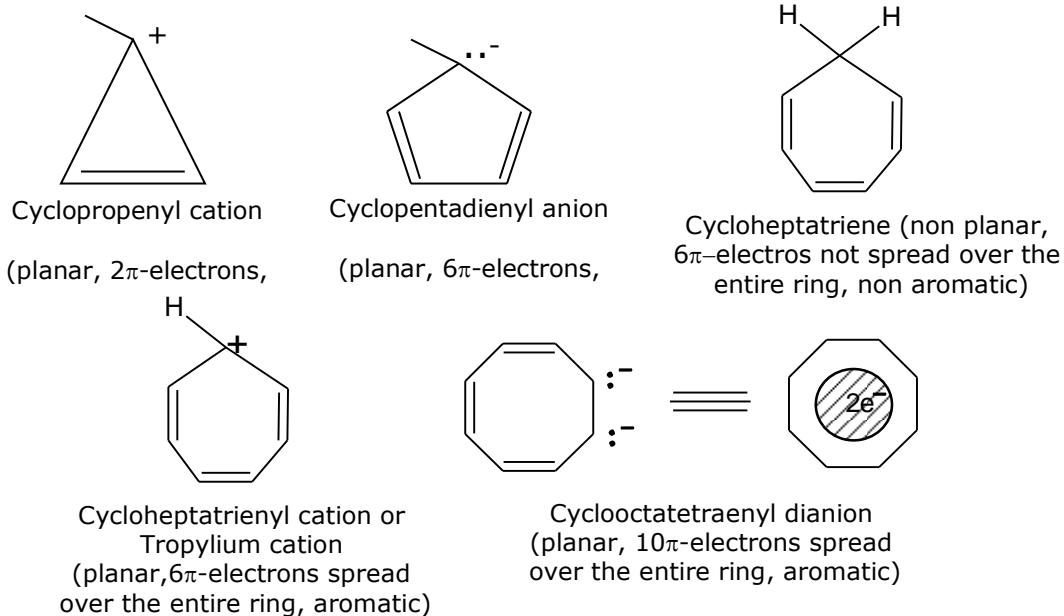
Aromatic Hydrocarbons

Aromatic hydrocarbons satisfy the following requirements.

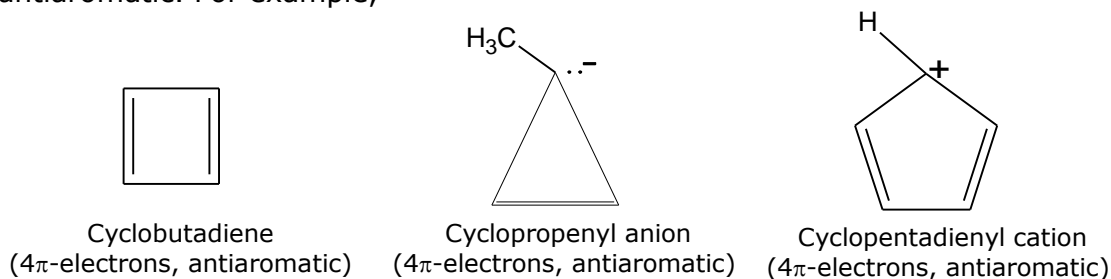
- They should have a ring structure with alternative single and double bonds so that complete delocalisation of the electrons is possible.
- They should have a planar structure which allows the delocalisation of the electrons.
- The bonding orbitals in the conjugated ring system should be completely filled. This can be easily predicted by **Huckel Rule** which states that if a compound has to become aromatic it should have $(4n + 2)$ delocalised electrons, where $n = 0, 1, 2, 3, \dots$

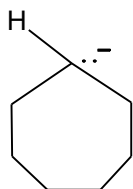
Aromaticity – Huckel Rule

According to Huckel or $(4n + 2) \pi$ rule, any planar cyclic system containing 2, 6, 10, 14, 18..... π -electrons and having a single cyclic π -electron cloud encompassing all the carbon atoms in the ring is aromatic. For example,

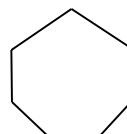


Further, In terms of Huckel rule, monocyclic planar, completely conjugated polyenes containing $4n \pi$ electrons are destabilized by resonance and hence are antiaromatic. For example,



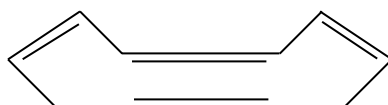


Planar cycloheptatrienyl anion
(8π -electrons, antiaromatic)



Planar cyclooctatetraene
(8π -electrons, antiaromatic)

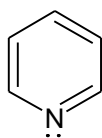
In contrast, cyclooctatetraene (COT) contains 8π -electrons but it is not antiaromatic since it adopts a non-planar (tub-shaped) geometry.



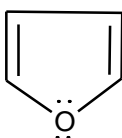
Cyclooctatetraene (COT)
(tub shaped, non planar,
 8π -electrons, non aromatic)

Actually, it behaves like a typical alkene and hence it is better called as non-aromatic.

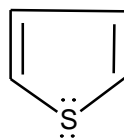
- Heterocyclic compounds such as pyridine, furan, thiophene and pyrrole are all aromatic since each one of these is planar and has a cyclic system of 6π -electrons which are completely delocalized over the entire ring.



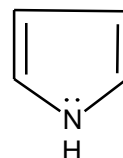
Pyridine



Furan

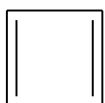


Thiophene

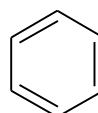


Pyrrole

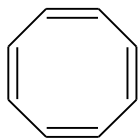
- Completely conjugated monocyclic polyenes containing an even number of carbon atoms are called annulenes. Their general formula is $(\text{CH} = \text{CH})_n$ where $n = 2, 3, 4$, etc. For example,



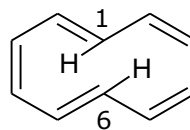
[4]-Annulene
(Cyclobutadiene,
 4π -electrons, antiaromatic)



[6]-Annulene (Benzene,,
 6π -electrons, aromatic)



[8]-Annulene
(Cyclooctatetraene, non planar
8 π -electrons, non-aromatic)



[10]-Annulene
(Cyclodecapentaene, non planar
10 π -electrons, non-aromatic)

It may be noted here that [10]-annulene contains Huckel number of electrons, (10, i.e., $n = 2$) and thus should be aromatic if planar. But due to severe non-bonded interactions between the internal hydrogens (shown in the formula above), the ring assumes non-planar geometry. This non-planarity of the ring prevents delocalization of π -electrons and hence [10]-annulene is non-aromatic and gives typical addition and oxidation reactions of alkenes.

Isolation of Benzene & Toluene

Fractional distillation of coal tar

Coal is destructively distilled. Coal tar is obtained.

Coal tar obtained is fractionally distilled

Benzene and toluene are separated from light oil fraction.

Naphthalene is isolated from the middle oil fraction.

The basic impurity present in light oil fraction is thiophene.

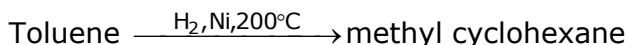
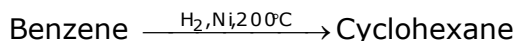
The acidic component of middle oil fraction is phenol (and cresols).

Biogas contains 70% to 80% methane. Rest of it are CO₂, SO₂, N₂, H₂ etc.

Producer gas obtained by passing air over red hot coke

Producer gas consists of CO and N₂

Addition reaction:



Substitution reaction

Nitration: Heating with a mixture of conc.HNO₃ and conc. H₂SO₄ acid.

Benzene \rightarrow Nitrobenzene

Toluene \rightarrow A mixture of o – and p – nitrotoluenes

With fuming nitric acid toluene gives TNT

Cl₂: Presence of anhydrous ferric chloride as halogen carrier.

Benzene \rightarrow Chlorobenzene

Toluene \rightarrow A mixture of o and p – chlorotoluenes

Side chain substitution of Toluene: In the presence of direct sunlight – boiling toluenes gives a benzyl, benzal and benzotrichlorides.

Etard's Reaction: Chromyl chloride in CCl_4 oxidises toluene to benzaldehyde.
Alkaline KMnO_4 oxidises toluene to benzoic acid

Friedel – Crafts reaction:

In the presence of anhydrous aluminium chloride catalyst both benzene and toluene undergo alkylation.

Elucidation of structure of benzene

- The elemental analysis and molecular mass determination show that the molecular formula of benzene is C_6H_6 .
- One mole of benzene on catalytic hydrogenation reacts with three moles of hydrogen or chlorine or ozone. These reactions show that benzene contains three double bonds
- It does not decolourise alkaline potassium permanganate. Hydracids of halogens do not add to benzene. Hence the three double bonds of benzene are not free to react.
- In the presence of ferric chloride catalyst benzene reacts with chlorine to give only one type of mono substituted product. This shows that all the six hydrogen atoms present in benzene are identical.
- To account for the above facts Friedrich August Kekule in 1865 proposed a ring structure for benzene. He assumed the presence of alternative single and double bonds in the molecule which gives 2-ortho disubstituted products.
- But actually only one type of ortho disubstituted product is found.
- Moreover all the bonds present in benzene are of same type which have partial double bond character. Hence the structure of benzene is resonance hybrid of two structures.

Molecular orbital picture of benzene

- Each carbon atom in benzene is sp^2 hybridised. Two hybrid orbitals are involved in bonding with the adjacent carbon atom and one with the hydrogen.
- Each carbon atom contains an unhybridised p orbital with an electron which is used for bonding with similar orbital of adjacent carbon atom to form bond.

Electrophilic substitution reactions of benzene

The reactions involved are

- | | |
|--------------------------------|------------------------------|
| a) Nitration | b) Sulphonation |
| c) Halogenation | d) Friedel-Crafts alkylation |
| e) Friedel-Crafts acetylation. | |

All mechanism involves following steps

- a) Generation of electrophile
- b) Attack of electrophile on electrons of the benzene ring
- c) Abstraction of proton to form the final product.

Some Common Electrophilic Substitution Reactions Given by Benzene:

Substrate	Reagent/Catalyst/ Δ	Reaction species (E^\oplus or E)	Product	Name of reaction
$C_6H_5 - H$	Conc. HNO_3 , conc. NHO_3 /cone. H_2SO_4 or $NO_2^+ BF_4^-$	$N^+ \begin{array}{l} // O \\ \searrow O \end{array}$	$C_6H_5 - NO_2$	Nitration
$C_6H_5 - H$	Conc. H_2SO_4/Δ or fuming sulphuric acid	SO_3H^+, SO_3	$C_6H_5 - SO_3H$	Sulphonation
$C_6H_5 - H$	$X_2(Cl_2 \text{ or } Br_2)/\text{Anhy. } AlX_3/\Delta$ or $I_2/\Delta, Fe/\Delta$	X^+	$C_6H_5 - X$	Halogenation
$C_6H_5 - H$	$R - X/\text{Anhy. } AlX_3/\Delta$	R^+	$C_6H_5 - R$	Alkylation, Friedel Crafts alkylation
$C_6H_5 - H$	$\begin{array}{c} O \\ \\ R - C - Cl \end{array} / \text{Anhy. } AlCl_3/\Delta$	$\begin{array}{c} O \\ \\ R - C \\ \oplus \end{array}$	$\begin{array}{c} O \\ \\ C_6H_5 - C - R \end{array}$	Friedel-Crafts acylation
$C_6H_5 - H$	$CO + HCl/\text{Anhy. } AlCl_3/Cu_2Cl_2$	$\begin{array}{c} O \\ \\ H - C \\ \oplus \end{array}$	$\begin{array}{c} O \\ \\ C_6H_5 - C - H \end{array}$	Gattermann-Koch formylation
$C_6H_5 - H$	$CH_2O + HCl/\text{Anhy. } ZnCl_2/\Delta$	CH_2OH^+	$C_6H_5 - CH_2Cl$	Chloromethylation (Blanc reaction)
$C_6H_5 - H$	i) $HCN/\text{Anhy. } ZnCl_2$ or $\text{Anhy. } Zn(CN)_2/HCl$ ii) H_2O/Δ	$H - C^+ = NH$	$C_6H_5 - CHO$	Gattermann formylation

- During nitration of benzene concentrated sulphuric acid acts as catalyst and also helps in the generation of the electrophile. Concentrated nitric acid acts as base.
- During Friedel-Crafts acylation the product ketone formed acts as a Lewis base and donates lone pair of electron to aluminium chloride to form a complex. Here the complex to be hydrolysed to get the final product.