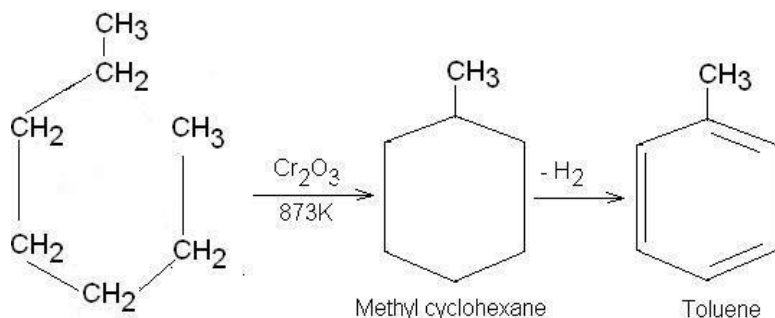


### Mechanism of isomerization

**Isomerization :** The process of conversion of one isomer into other is known as isomerization. Straight chain alkanes on heating with  $\text{AlCl}_3 + \text{HCl}$  at about  $200^\circ\text{C}$  and 35 atm pressure are converted into branched chain alkanes.

### Mechanism of aromatization



The process of conversion of aliphatic compound into aromatic compound is known as aromatization.

Alkanes having six to 10 carbon atoms are converted into benzene and its homologues at high pressure and temperature in presence of catalyst.

Mechanism: Is given above.

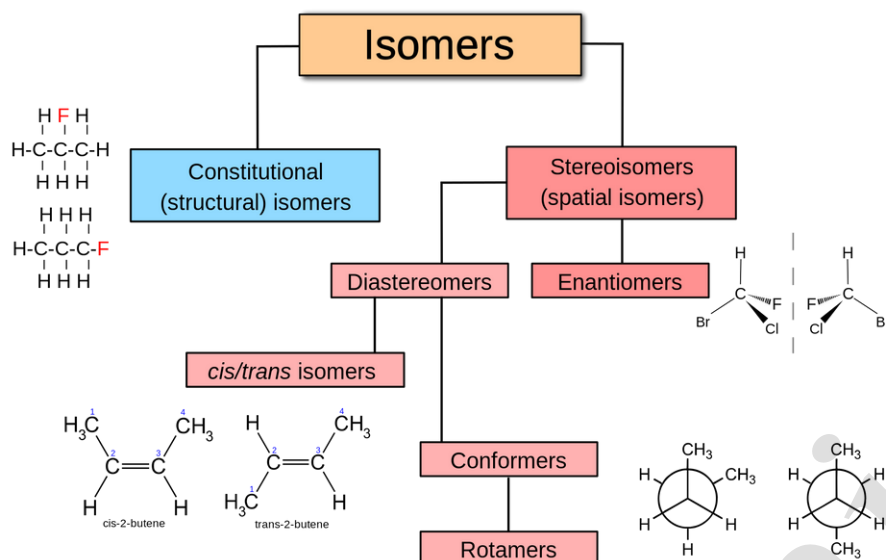
### State the uses of alkanes

Methane and Ethane are the main components of natural gas.

LPG contains butane and propane.

Alkanes are used to produce different product like waxy solids , Vaseline gelly etc.

## Stereoisomerism of alkane



**Stereoisomers** are isomers that have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space. This phenomenon is called is stereoisomerism.

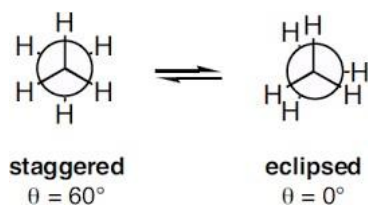
### Newman projections

A newman projection, useful in alkane stereo chemistry, visualizes chemical conformations of a carbon-carbon chemical bond from front to back, with the front carbon represented by a dot and the back carbon as a circle.

### Sawhorse projections

A sawhorse projection is a view of a molecule down a particular carbon-carbon bond, and groups connected to both the front and back carbons are drawn using sticks at 120 degree angles.

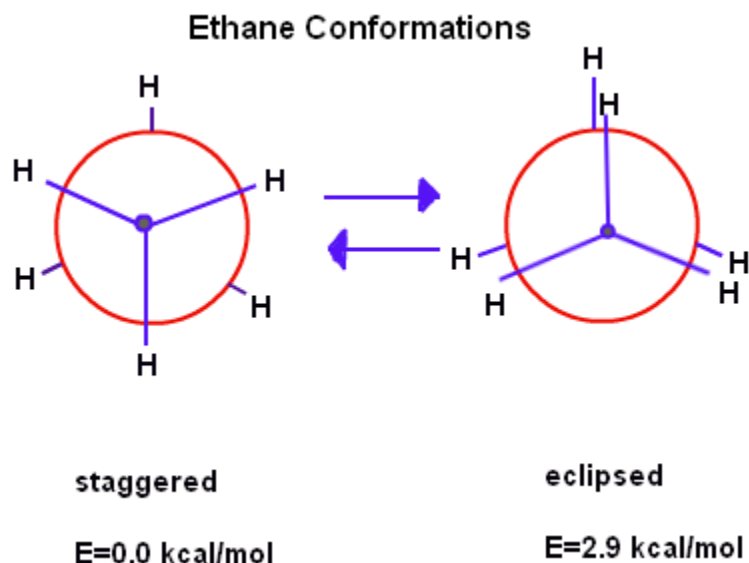
### Conformation of alkane



Any of the spatial arrangements which the atoms in a molecule may adopt and freely convert between, especially by rotation about individual single bonds, is called as conformation. In alkane staggered, eclipsed conformation is seen.

Example : Ethane molecule shows both type of conformation which is shown in diagram.

#### Conformation of ethane



Ethane shows two types of conformation, staggered and eclipsed.

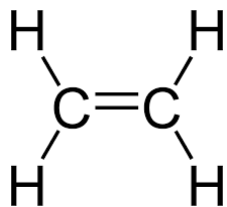
#### Properties of ethane

At standard temperature and pressure, ethane is a colorless, odorless gas. It has a boiling point of  $-88.5^{\circ}\text{C}$  and melting point of  $-182.8^{\circ}\text{C}$ . Solid ethane exists in several modifications. On cooling under normal pressure the first modification to appear is a plastic crystal, crystallizing in the cubic system. In this form, the positions of the hydrogen atoms are not fixed; the molecules may rotate freely around the long axis. Ethane is only very sparingly soluble in water.

#### Uses of ethane

The chief use of ethane is the production of ethene by steam cracking. Ethane can be used as a refrigerant in cryogenic refrigeration systems.

### Structure of double bond



Alkenes are prepared by removing 2 H atom from corresponding alkane. Hence it contain C-C sigma and pi bond. The double character is due to the formation of pi bond takes place on alkene.

### Isomerism of alkene

Alkenes due to the presence of double bond, shows geometrical and structural isomerism.

#### Isomerism of alkene

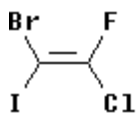
Alkenes have two types of geometrical isomers :

1. Cis isomer: The isomers which are formed by cis isomerism is called as cis isomers.
2. Trans isomer: The isomers which are formed by trans isomerism is called as trans isomers.

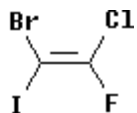
#### Properties of geometrical isomers of alkene

1. Melting Point : In general , the melting point of trans-isomers is higher than that of the cis-isomers.
2. Solubility : In general , the solubility of a cis-isomers is higher than that of the trans-isomers.
3. Dipole moment : Cis-isomers of an alkene is found to be more polar than the trans-isomers mostly.
4. Boiling point : The boiling point of the cis-isomers are higher than those of the trans-isomers in general.

## E,Z NOMENCLATURE



**(Z)-**



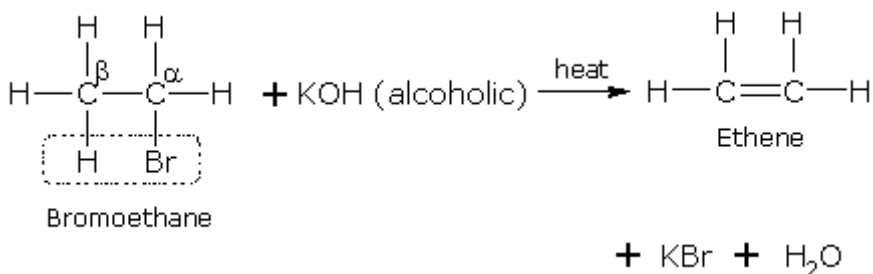
**(E)-**

If three or all four atoms or groups attached to the carbon atoms of the double bond are different, cis and trans isomers can not be used.

Therefore E, Z nomenclature has been introduced to name all types of geometrical isomers.

According to this, if the atoms or groups of highest priority are on the same side of the double bond, the isomer is designated as Z and if the two atoms of highest priority are on the opposite sides, the isomer is E.

### Preparation of alkenes from alkyl halides

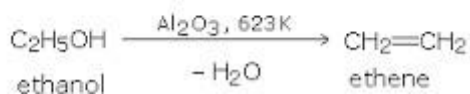
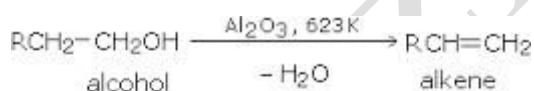


Alkyl halides on heating with a strong base such as sodium ethoxide or a concentrated alcoholic solution of potassium hydroxide undergo dehydrohalogenation to give alkenes.

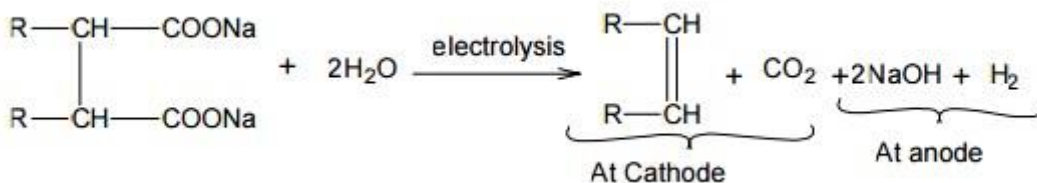
### Alkenes from vicinal dihalides



Dihalogen derivatives of alkanes in which the two halogen atoms are present on adjacent carbon atoms are called vicinal or 1, 2 -dihaloalkanes. Alkenes can be prepared by heating a suitable 1, 2 -dihaloalkane with zinc dust in methanol.



### Preparation of alkenes from sodium or potassium salts



Electrolysis of sodium or potassium salts of saturated dicarboxylic acids gives alkenes.

### Sources of alkenes

Natural sources of alkenes are natural gases and petroleum products.

### Nomenclature of alkenes

In the IUPAC system, they are called alkenes. Their general formula is  $\text{C}_n\text{H}_{2n}$  where  $n = 2, 3, 4, \dots$  etc. The name of any individual alkene is obtained by replacing terminal one of the corresponding alkane by suffix ene.

### Methods involved in preparation of alkenes

1. By partial reduction of alkynes
2. From alkyl halides or haloalkanes
3. From vicinal dihalide
4. From monohydric alcohols
5. From sodium or potassium salt of saturated dicarboxylic acids.

Carbon-carbon double bond changes the physical properties of alkenes. At room temperature, alkenes exist in all three phases, solid, liquids and gases.

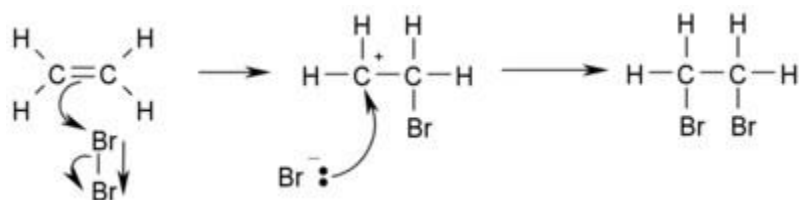
Melting and boiling points of alkenes are similar to that of alkanes, however, isomers of cis alkenes have lower melting points than that of trans isomers.

Alkenes give addition, substitution, elimination reactions to form different compounds.

### Physical properties of alkene

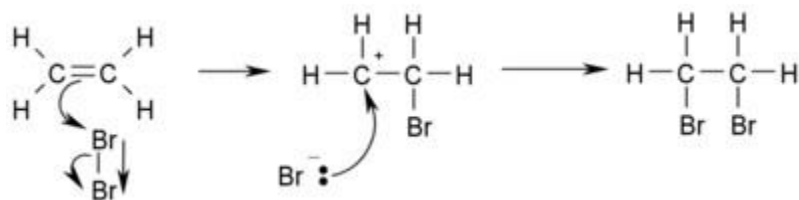
The physical properties of alkenes and alkanes are similar. They are colourless, nonpolar, combustible, and almost odorless. The physical state depends on molecular mass: like the corresponding saturated hydrocarbons, the simplest alkenes, ethene, propene, and butene are gases at room temperature.

### Addition of halogens to alkene

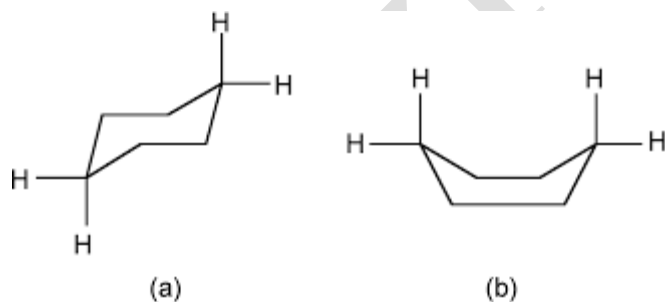


Halogens like bromine or chlorine add up to alken to form vicinal dihalides. However, iodine does not show addition reaction under normal condition. Addition of halogen to alkene is an example of electrophilic addition reaction.

### Mechanism of addition of halogen halide to alkenes



Halogens like bromine or chlorine add up to alken to form vicinal dihalides. However, iodine does not show addition reaction under normal condition. Addition of halogen to alkene is an example of electrophilic addition reaction.

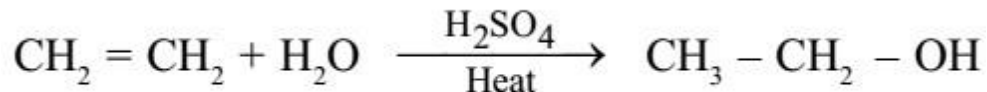


### Stability of alkene

Stability of alkenes is given by its value of heat of hydrogenation. If it is high the alkene is stable.

### Addition of water to alkene



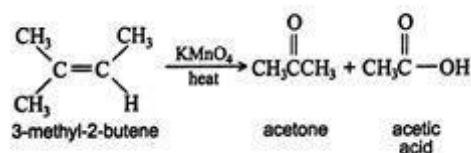


### Ethene

### Ethanol

In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols.

### Oxidation of alkenes

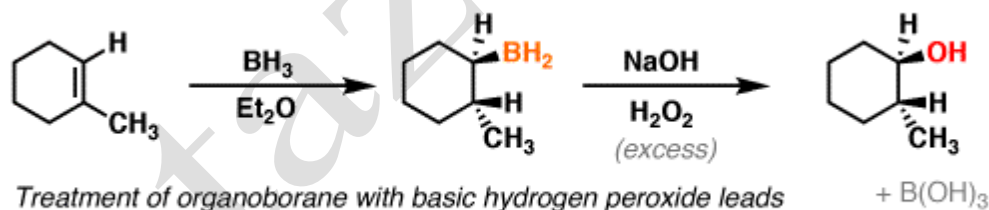


When more concentrated solutions of potassium permanganate and higher temperatures are employed, the glycol is further oxidized, leading to the formation of a mixture of ketones and carboxylic acids. Oxidation of alkenes by ozone leads breaks the double bond and oxidise both double bonded carbons.

The reactions of haloalkenes under substitution reaction can prepare alkanes.

### Hydroboration-oxidation reactions of alkenes

#### Hydroboration - oxidation

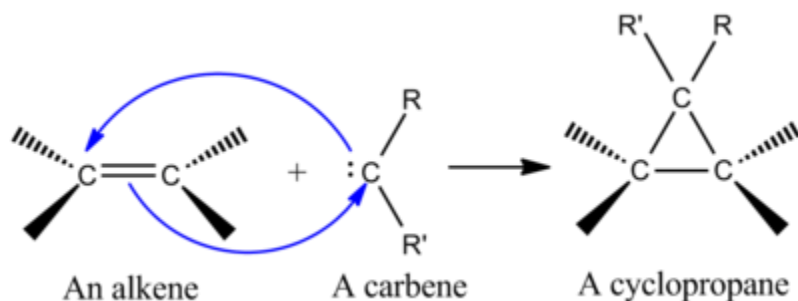


*Treatment of organoborane with basic hydrogen peroxide leads to formation of an alcohol*

#### Stereochemistry is preserved!

Hydroboration-oxidation reactions leads to formation of alcohol, by antimarkonikoff addition of water molecule to double bonded carbon .

### Reaction of carbene with alkenes



Reaction of carbene with alkene leads to formation of cyclopropane.

### Methods of preparation of alkene

1. From alkynes by catalytic reduction.
2. From alkyl halide by dehydrohalogenation.
3. From vicinal dihalide by dehalogenation.
4. From alcohol by acidic dehydration.

Colourless gas at room temperature and pressure. Melting point  $-169^{\circ}\text{C}$ – $169^{\circ}\text{C}$

Slightly sweet smell

Flammable

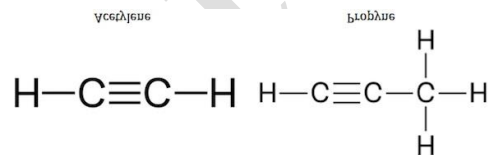
Non-polar molecule. soluble in non-polar solvents & insoluble in polar solvents like water

Reactive: the active site is the double bond. Readily undergoes addition reactions

### Uses of alkenes

Alkenes are used in the synthesis of alcohol, plastics, detergents or fuels, butadiene etc.

### Structure of alkynes



An alkyne is an unsaturated hydrocarbon containing at least one carbon carbon triple bond. The simplest acyclic alkynes with only one triple bond and no other functional groups form a homologous series with the general chemical formula  $\text{C}_n\text{H}_{2n-2}$ .

### Isomerism of alkynes

Alkynes shows structural isomerism in which positional isomerism is common.

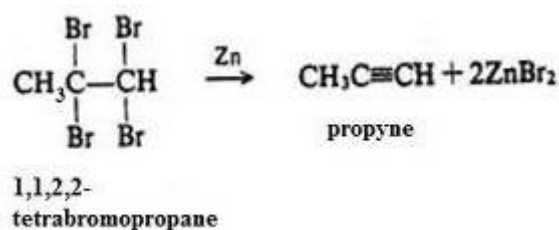
Example: Pent-1-yne and Pent-2-yne are positional isomers.

### Sources of alkynes

A thousand naturally occurring acetylenes have been discovered and reported from terpenes, a subset of this class of natural products, have been isolated from a wide variety of plant species, cultures of higher fungi. So alkynes are obtained by plant sources, fungi culture etc.

### Nomenclature of alkynes

In common name system, alkynes are named as derivatives of acetylene. In IUPAC, they are named as derivatives of the corresponding alkanes replacing ane by the suffix yne.



Tetrahalide in presence of zinc undergoes with dehalogenation to form alkyne and zinc dihalide.

### Method of preparation of alkynes by carbon and hydrogen

1. Calcium carbide is the method in which Carbon is used for preparation of alkynes.
2. Vicinal dihalide is the method in which hydrogen is used for preparation of alkynes.

### Test for position of triple bond

Position of triple bond can be detected by ozonolysis.

### Addition reactions of alkenes and alkynes

The double or triple bonds form radicals and bonds with other free radicals to make new products. e.g. in halogenation bromine gas reacts with alkenes or alkynes to add 2 bromine atoms per double bond and 4 bromine atoms per triple bond.

### **Physical properties of alkyne**

They are insoluble in water.

They are quite soluble in the usual organic solvents of low polarity (e.g. ligroin, ether, benzene, carbon tetrachloride, etc.).

They are less dense than water.

Their boiling points show the usual increase with increasing carbon number.

### **Reactivity of alkynes versus alkenes**

Alkenes are more reactive than alkynes. In order to understand this, we need to first realize that the pi bonded electrons in alkenes and alkynes are inherently nucleophilic and react with electrophiles to form a carbocation. Carbocations are stabilized by hyperconjugation and, the more conjugation in the system, the more stability. That said, tertiary are most stable (followed by secondary, etc). Now, when alkynes react with electrophiles, a vinylic carbocation will be formed (positive charge residing on an sp hybridized carbon atom). These vinylic carbocations are inherently less stable than alkenes.

### **Polymerization reaction of alkynes**

Under suitable conditions, linear polymerization of ethylene takes place to produce polyacetylene or polyethyne.

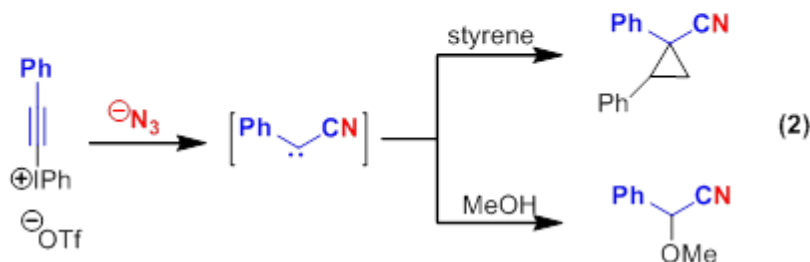
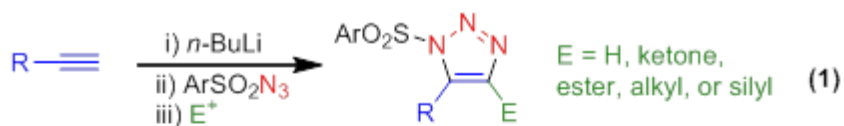
### **Uses of alkynes**

as the fuel for the oxyacetylene blow-lamp used in cutting and welding metals.

to prepare ethanal (i.e. acetaldehyde), and.

many important organic chemicals, including vinyl chloride monomer, which is used in the manufacture of the industrially important plastic polyvinyl chloride, PVC.

### **Reaction of carbenes with alkynes**



### Methods involved in preparation of alkynes

1. Calcium carbide.
2. From vicinal dihalides.

### USES OF ETHYNE

as the fuel for the oxyacetylene blow-lamp used in cutting and welding metals.  
to prepare ethanal (i.e. acetaldehyde), and.  
many  
important organic chemicals, including vinyl chloride monomer, which is used in the  
manufacture of the industrially important plastic polyvinyl chloride, PVC.

### Define aromatic hydrocarbon

An aromatic hydrocarbon or arene (or sometimes aryl hydrocarbon) is a hydrocarbon with sigma bonds and delocalized pi electrons between carbon atoms forming rings.

Example : Benzene.

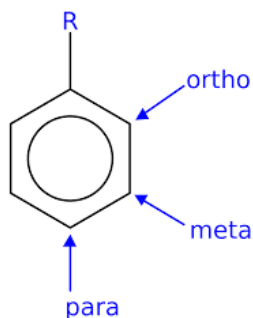
### Arenes depending upon number of fused benzene rings

Arenes depending upon number of fused benzene ring is classified as :

1. Single ring structure : Benzene.

2. Double ring structure : Naphthalene.
3. Triple ring structure : Anthracene.

### Nomenclature and isomerism of arenes



All six hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible.

The 1, 2 or 1, 6 is known as the ortho .

The 1, 3 or 1, 5 is known as meta.

The 1, 4 is known as para isomers.

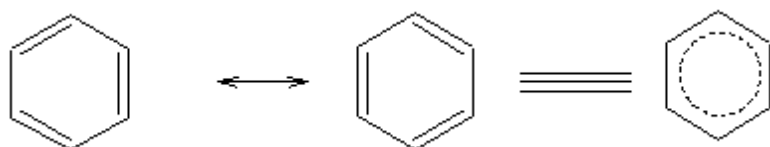
### Structure of benzene

All six carbon-carbon bonds in benzene are of the same length, at 140 (pm).

The C-C bond length are greater than a double bond (135 pm) but shorter than a single bond (147 pm).

This intermediate distance is consistent with electron delocalization the electrons for CC bonding are distributed equally between each of the six carbon atoms.

### Concept of benzene ring resonance



Benzene is a hybrid of various resonating structures .The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon.The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring.

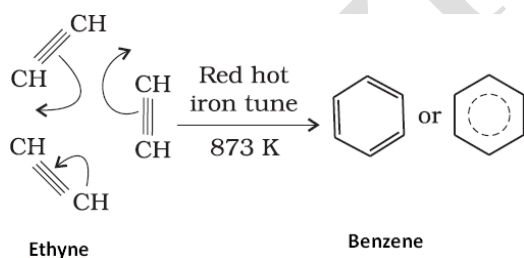
### Define and calculate resonance energy

The resonance energy of a compound is a measure of extra stability of the conjugated system compared to number of isolated double bonds.

### benzenoid aromatics and Non benzenoid aromatics

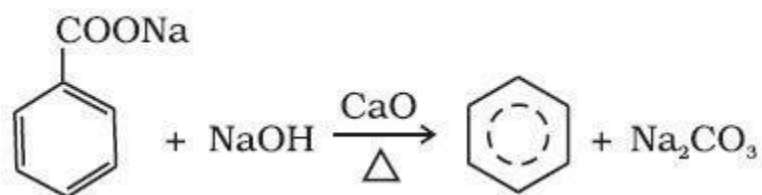
Benzenoid aromatic compounds are the aromatic compound containing benzene ring and none benzenoid aromatic compounds are the aromatic compound containing ring other than benzene.

### Method of preparation of arenes from ethyne by cyclic polymerization



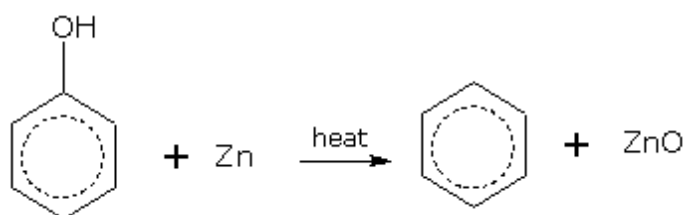
Ethyne on passing through red hot iron tube at 873 K undergoes cyclic polymerization and gives benzene.

### Arenes preparation by sodium benzoate



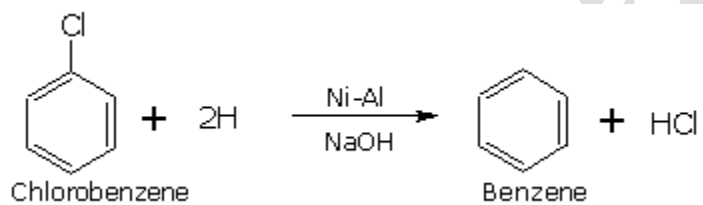
Sodium salt of benzoic acid on heating with soda lime gives benzene.

#### Preparation of arenes from phenol by reduction with zinc dust



Phenol is reduced to benzene by passing its vapour over heated zinc dust.

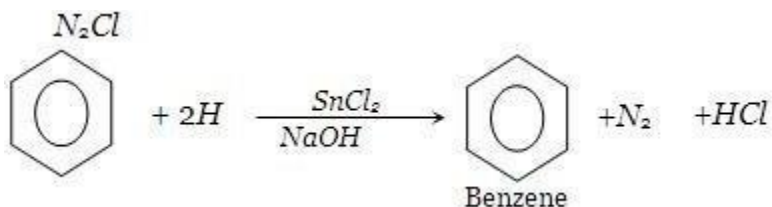
#### Arenes from chlorobenzene by reduction



Arenes by dehalogenation gives benzene.

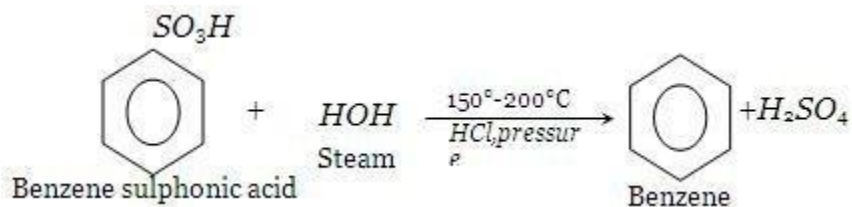


### Arenes by benzenediazonium chloride by reduction



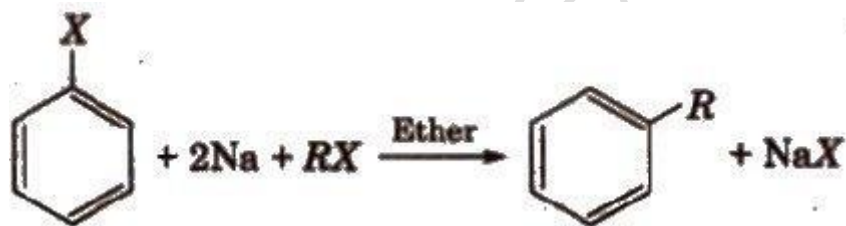
Benzenediazonium chloride produces benzene by reduction.

### Preparation of arenes by benzene sulphonic acid



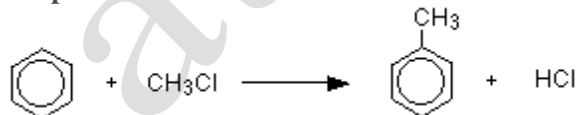
Benzene sulphonic acid on reaction with heated steam frees the sulphonic group and formation of benzene and sulphuric acid takes place.

### Arenes from wurtz-fittig reaction



In the wurtz fittig reaction the substituted halo benzene in the presence of sodium metal and alkyl halides and ether forms substituted alkyl benzene

### Preparation of arenes from friedal-crafts reaction



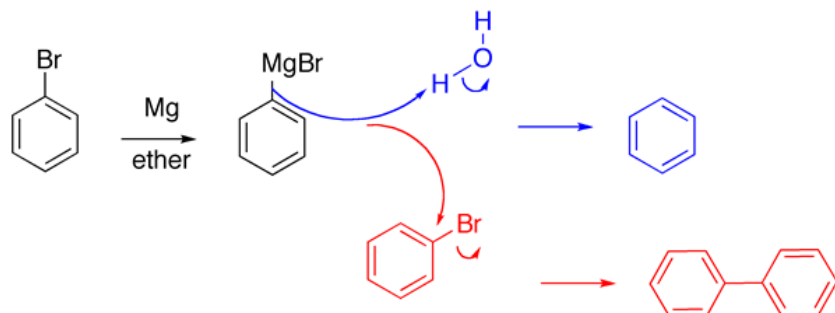
Benzene reacts with alkyl halides in presence of Lewis acid catalyst such as anhydrous  $\text{AlCl}_3$  to form alkylbenzene or arenes.

For example, formation of toluene.

### Method of preparation of benzene

1. Cyclic polymerisation of ethyne.
2. Decarboxylation of aromatic acids.
3. Reduction of phenol.

### Preparation of arenes from grignard reagents



Arenes can be prepared from grignard reagent in which bromo benzene is treated with Mg in presence of ether to form substituted benzene which further reacts with water to give benzene.

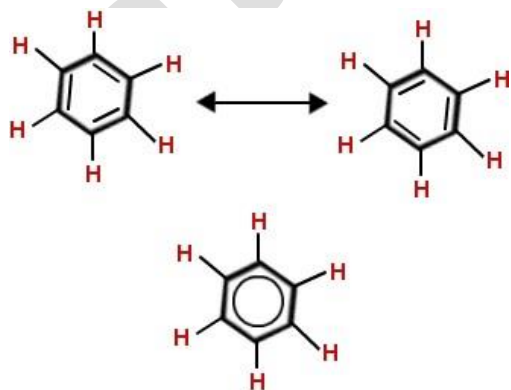
### Physical properties of arenes

Benzene boils at 80°C, which is higher than other hydrocarbons of similar molecular size. The higher boiling point is presumably due to the ease with which temporary dipoles can be set up involving the delocalized electrons.

The arenes are insoluble in water.

Benzene melts at 5.5°C; methylbenzene at -95°C.

### delocalisation of electrons in benzene ring

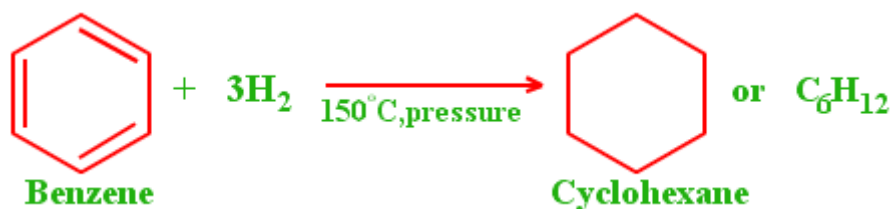


### Substitution reaction of arenes

Arenes are characterised by electrophilic substitution reaction. Common reactions are nitration, sulphonation, halogenation, friedal-crafts alkylation.

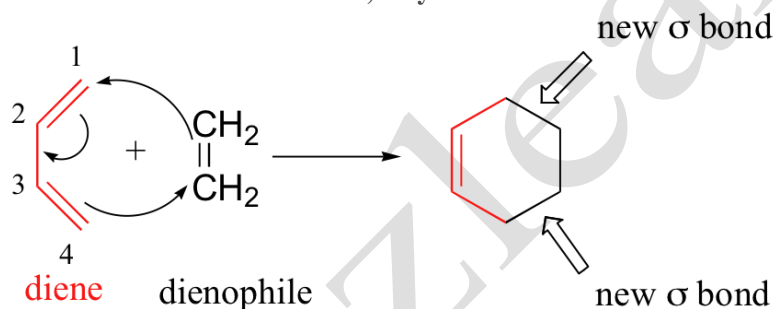
In this reaction first the electrophile generation takes place then electrophile attack on the substrate to form carbocation. Afterwards proton removes from carbocation intermediate to form substituted benzene.

### Addition reaction of arenes



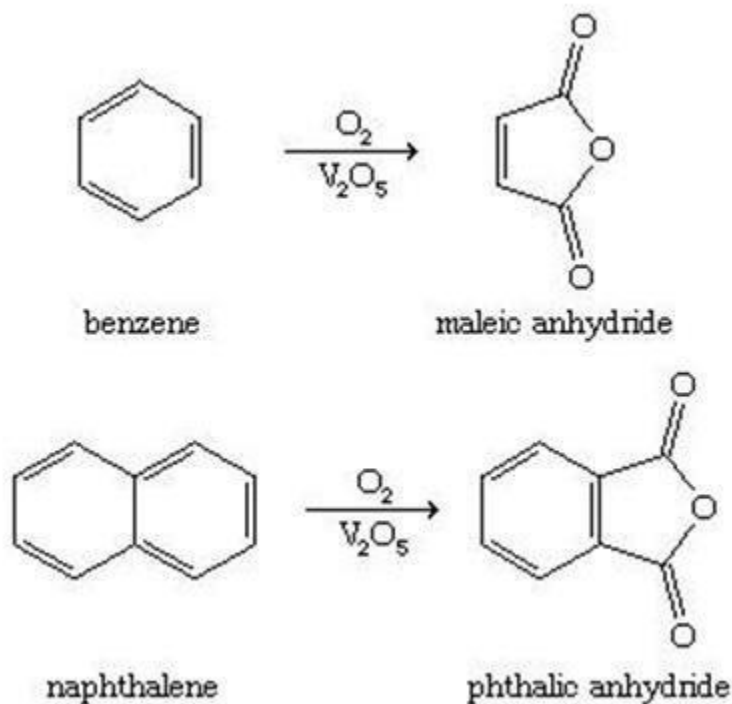
Under vigorous condition i.e. at high temperature or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.

### Diels alder reaction for alkane, alkyne and arenes



Diels alder reaction of alkenes produces cyclic product.

### Directive influence of substituents and their effect on reactivity



### Uses of arenes

Benzene is used in the manufacture of plastics, detergents, pesticides and other chemicals.

### Mechanism of electrophilic substitution reaction of arenes

According to experimental evidences electrophilic reaction supposed to proceed via the following three steps :

- 1.Generation of the electrophile.
- 2.Formation of carbocation intermediate.
- 3.Removal of proton from the carbocation intermediate to regain aromaticity.

### Reactions carbene with arenes

Reaction of carbenes with arenes produces substituted product.

The electron releasing groups direct the incoming group to ortho and para positions are called ortho and para directing groups, as the electron density is more on o-and p-positions.Hence the electrophilic substitution takes place mainly at these positions.Aromatic ring become reactive at these position.

**Directive influence of substituents and their effect on reactivity**

Where as at meta position electron density is less hence it is less reactive. Where as the electron withdrawing groups are meta directing.

**effect of ortho, meta and para directing groups in substituted benzenes**

In substituted benzene, the electron withdrawing groups decrease the reactivity whereas electron releasing group increases the reactivity.

**Method is isolation of aromatic compounds from coal**

Pyrolysis gasoline is the by-product of steam cracking of petroleum by products like paraffin gases, naphthas, gas oils. Pyrolysis gasoline contains 5 per cent diolefins. In addition it also contains 60 per cent aromatic compounds, 50 per cent of benzene. Different techniques are applied on diolefins to produce benzene, these are

Distillation of diolefins to olefins

Saturation of olefins to remove sulphur content

Execution of solvent extraction and distillation process to obtain benzene

**Define and give example of aromaticity**

Aromaticity is a characteristic in which any planar system in which there is complete delocalisation of pi electron in the ring, and the system contain  $4n+2$  pi electrons in the ring is called aromatic.

Example : Benzene, naphthalene, anthracene etc.

Benzene and polynuclear hydrocarbons containing more than two benzene fused together are toxic and said to possess cancer producing property. Such hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer.

## Isomerism in alkanes, alkenes and alkynes

The compounds which are having same molecular formula but different structural formula are known as isomers and the phenomenon is known as isomerism. Isomerism can be classified into different types structural isomerism and stereo isomerism. Structural isomerism is again classified into different types -chain isomerism, position isomerism, functional isomerism and metamerism.

## Hydrocarbons

**Hydrocarbons** are the simplest organic compounds containing only carbon and hydrogen.  
e.g. methane, butane, etc.

## Tests for hydrocarbons

To test whether the hydrocarbon is unsaturated or saturated Bromine test is performed, which involves the addition of bromine water to the hydrocarbon in question; unsaturated hydrocarbons decolourised the bromine water, whereas saturated hydrocarbon will not decolourise it.

## SATURATED AND UNSATURATED HYDROCARBON

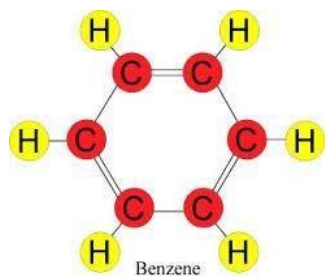
Saturated hydrocarbon : Hydrocarbon which contain C-C single bond are called as saturated hydrocarbon.

Unsaturated hydrocarbon : Hydrocarbon which contain C=C double bond or triple bond are called as unsaturated hydrocarbon.

## Explain hydrocarbon

The organic compound containing H and O along with large amount of Carbon are called as Hydrocarbon. Hydrocarbons can be Alkenes, Alkenes, Alkynes depending upon their structures. When Hydrocarbons contain single bond they are called as alkanes, when it contain double bond called as alkene and when it contain triple bond called as alkyne.

### Cyclic or closed chain hydrocarbon



The hydrocarbon with cyclic structure is called as cyclic hydrocarbon.

Example : Benzene etc.

### Sources of alkanes

The alkanes are isolated from natural gas and petroleum. Natural gas contains mainly methane, with smaller amounts of other low molecular weight alkanes. Petroleum, is the main source of all other alkanes.

### Properties of alkanes

All alkanes are colourless and odourless.

Alkanes experience intermolecular vander waal force of attraction.

Stronger intermolecular van der Waals forces give rise to greater boiling points of alkanes.

The melting point of the alkanes follow a similar trend to boiling point for the same reason as outlined above.

That is, (all other things being equal) the larger the molecule the higher the melting point.

Alkanes under normal conditions shows addition, substitution as well as rearrangement reactions to form different products.

### Physical properties of alkane

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