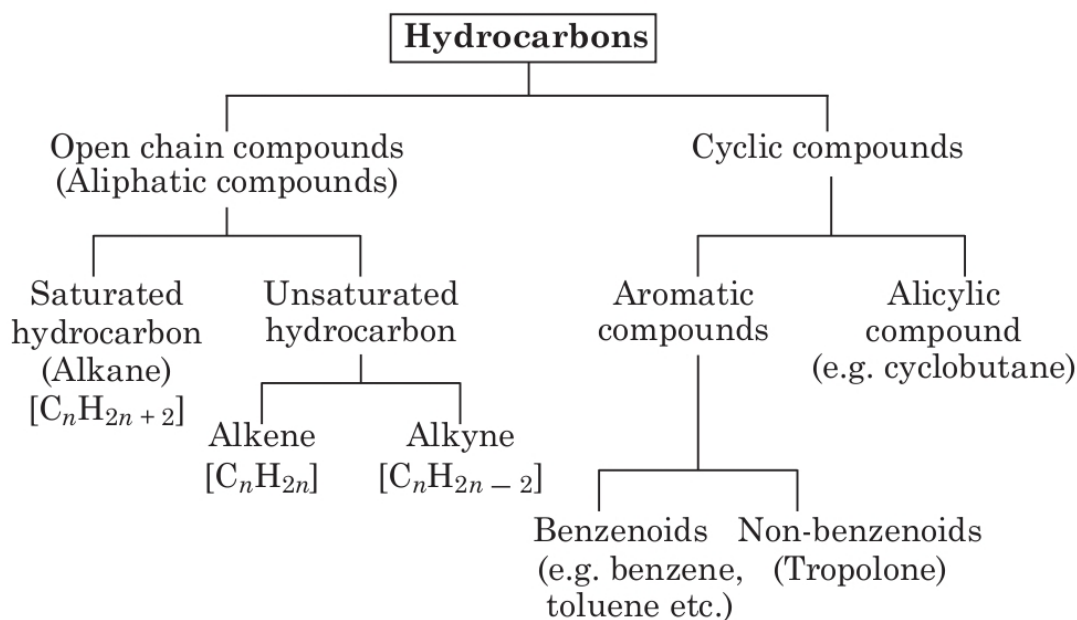


Hydrocarbons

Hydrocarbons are the organic compounds containing carbon and hydrogen only, e.g. alkane, alkene and alkynes.

Classification of Hydrocarbons



Alkanes

Alkanes are saturated, open chain hydrocarbons containing carbon-carbon single bonds, e.g. methane (CH₄), ethane (C₂H₆), propane (C₃H₈), etc.

These hydrocarbons are inert under normal conditions [i.e. do not react with acids, bases and other reagents]. Hence, they were earlier known as **paraffins** (Latin : *parum*-little; *affins*-affinity)

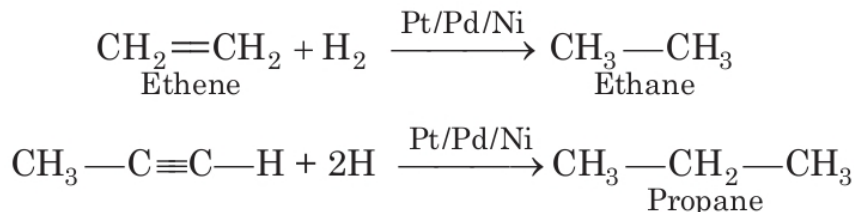
Alkanes exhibit **chain isomerism** and **position isomerism**.

Structure

Alkanes possess only sigma bonds. In these molecules, carbon atom lies at centre and hydrogen atoms lie at the corners of regular tetrahedron. All H—C—H bond angles are 109.5°.

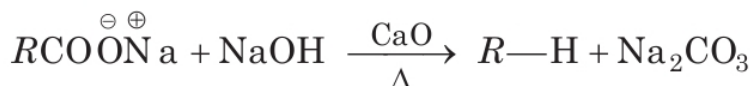
Methods of Preparation of Alkanes

(i) From hydrogenation of alkenes and alkynes



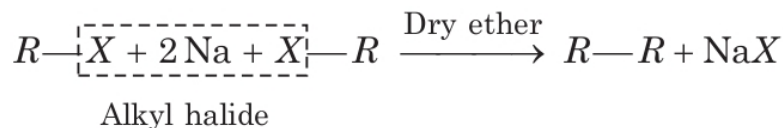
Ease of hydrogenation depends on the steric crowding across the multiple bond. More is the steric crowding, the less is the reactivity towards hydrogenation.

(ii) By sodalime Decarboxylation of sodium or potassium salts of fatty acids [decarboxylation reaction] in presence of NaOH, CaO gives alkane.



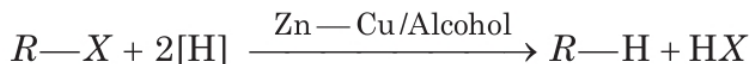
This reaction is used for descending of series as the alkane obtained has one carbon less than the parent compound. CaO is more hygroscopic than NaOH and it keeps NaOH in dry state.

(iii) By Wurtz reaction



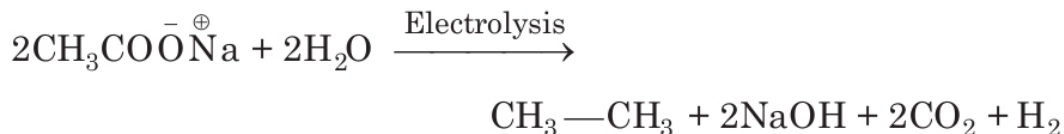
This reaction is used to increase the length of the carbon chain.

(iv) By reduction of alkyl halides



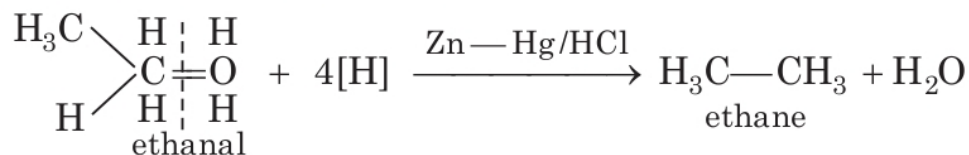
Reducing agents like Zn/HCl, HI/Red P, H₂/Pd can also be used.

(v) By Kolbe's electrolysis

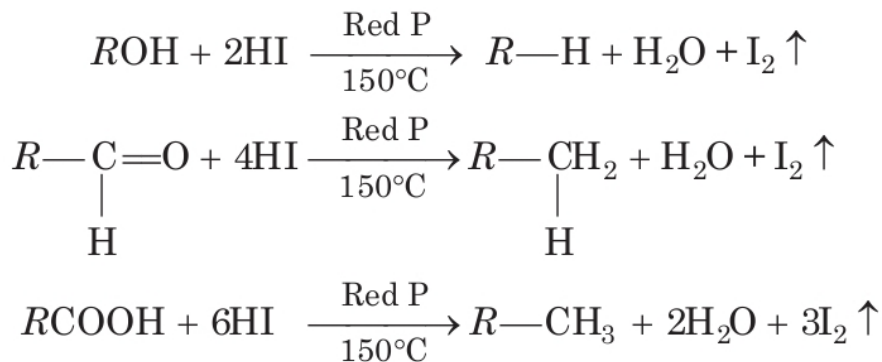


Only alkanes with even number of carbon atoms can be formed. Alkane and CO₂ are liberated at anode while H₂ is liberated at cathode.

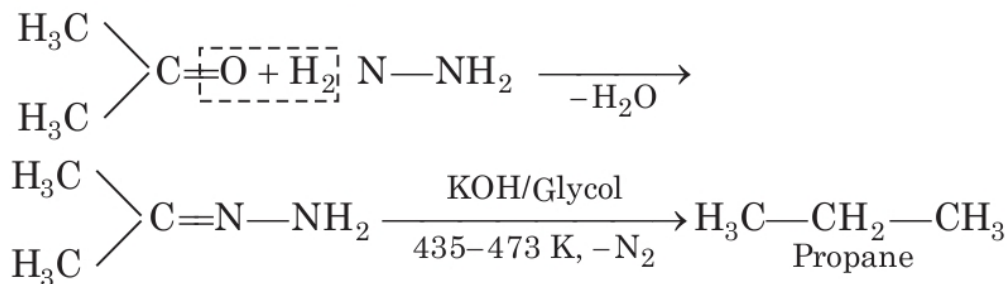
(vi) **Clemmensen's reduction**



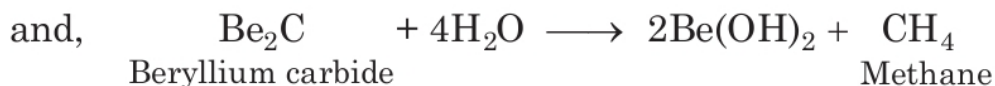
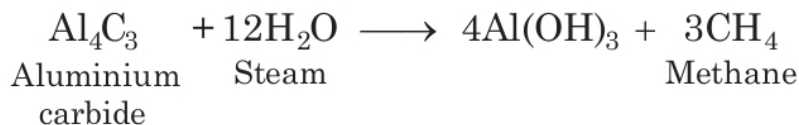
(vii) **From compounds containing oxygen** Alcohols, aldehydes, ketones, carboxylic acids and their derivatives give alkane when treated with hot conc. HI and red P in a sealed tube.



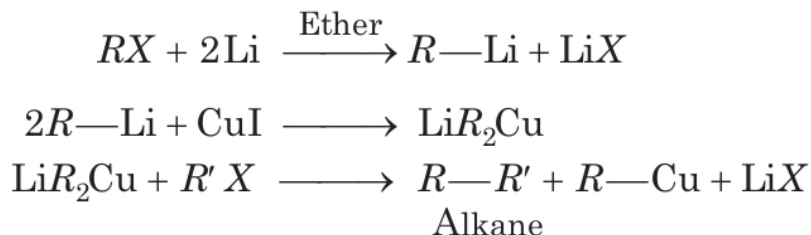
(viii) **Wolff-Kishner's reduction**



(ix) **From carbides**



(x) **Corey-House synthesis** This method can be used to prepare alkanes having odd number of carbon atoms.



Physical Properties of Alkanes

- (i) The first four members are colourless gas, next thirteen members are colourless liquids and next higher members are colourless solids.

(It can be explained on the basis of magnitude of attraction forces.)

- (ii) Boiling point of alkanes decreases on branching.

$$\text{BP} \propto \text{VAF (van der Waals' forces)}$$

$$\text{VAF} \propto \text{molecular mass} \quad \text{or} \quad \text{VAF} \propto \text{SA (Surface area)}$$

So, boiling point order can be given as

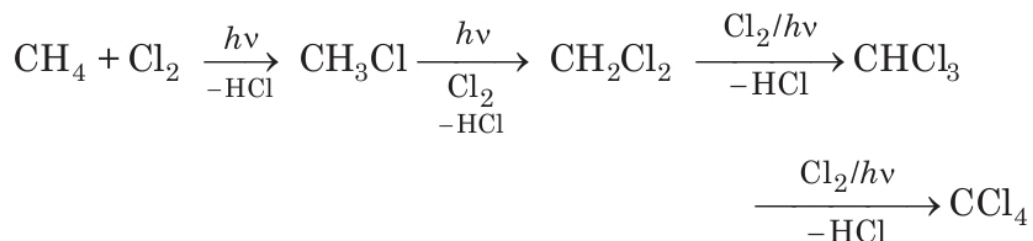
$$n\text{-octane} > \text{iso-octane} > 2, 2, 3, 3\text{-tetramethyl butane}$$

- (iii) Alkanes with even number of carbon atoms have higher melting points as compared to next higher or lower alkanes with odd number of carbon atoms.
- (iv) Alkanes being non-polar in nature, soluble in non-polar solvents but insoluble in polar solvent such as water.

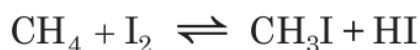
Chemical Properties of Alkanes

- (i) **Halogenation of alkanes**

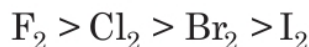
- (a) Chlorination



- (b) Bromination of alkanes proceeds in the same way but not so easily.
- (c) Iodination



Order of reactivity of halogens is

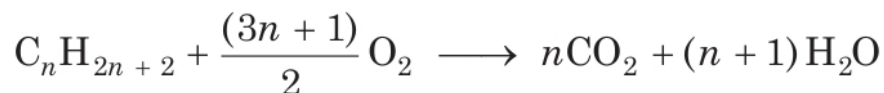


Order of reactivity of hydrogen of alkane is



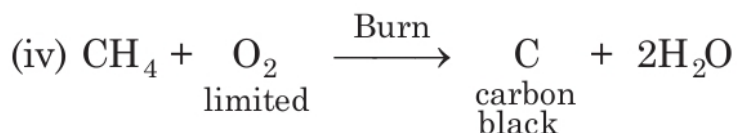
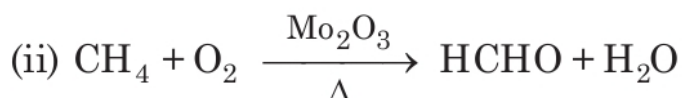
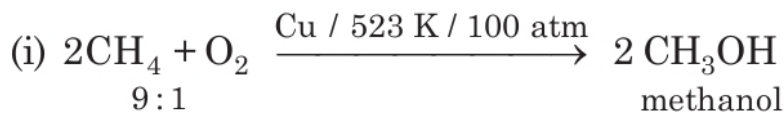
┌ Mechanism of halogenation of alkanes proceed via free radical formation, i.e. the attacking reagent is a halogen free radical (X^\bullet). It is a chain reaction. └

(ii) Combustion

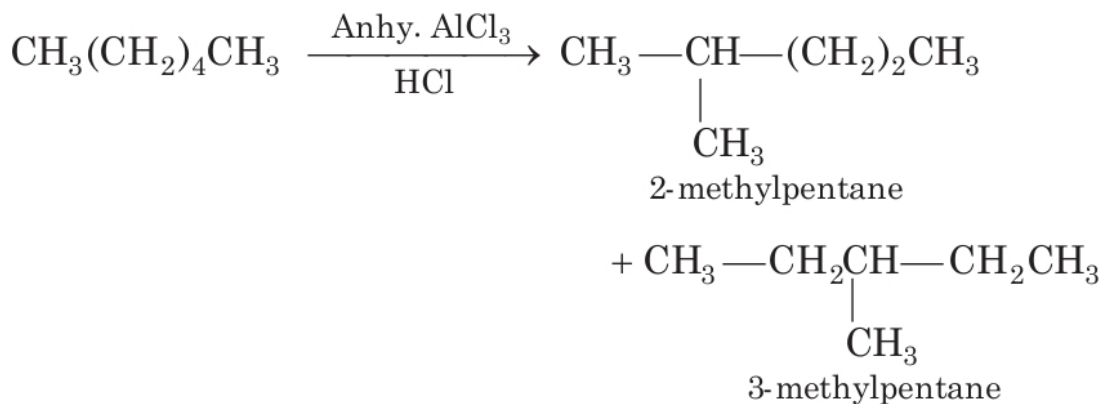


Due to the evolution of a large amount of heat during combustion, alkanes are used as fuels.

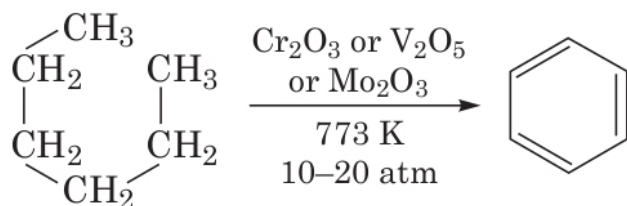
(iii) Controlled oxidation



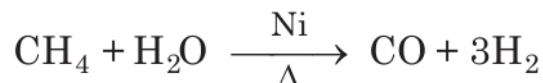
(iv) Isomerisation



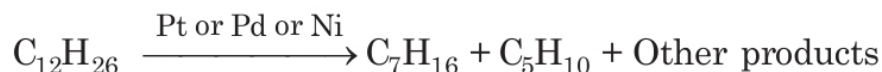
(v) Aromatisation



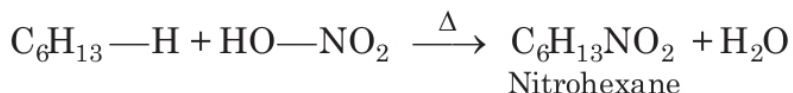
(vi) Reaction with steam



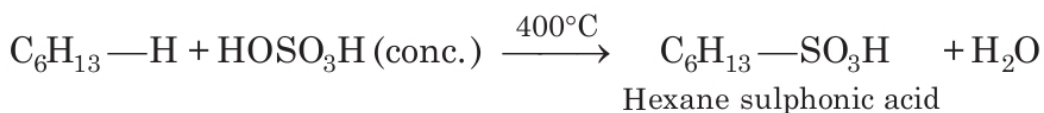
(vii) Pyrolysis



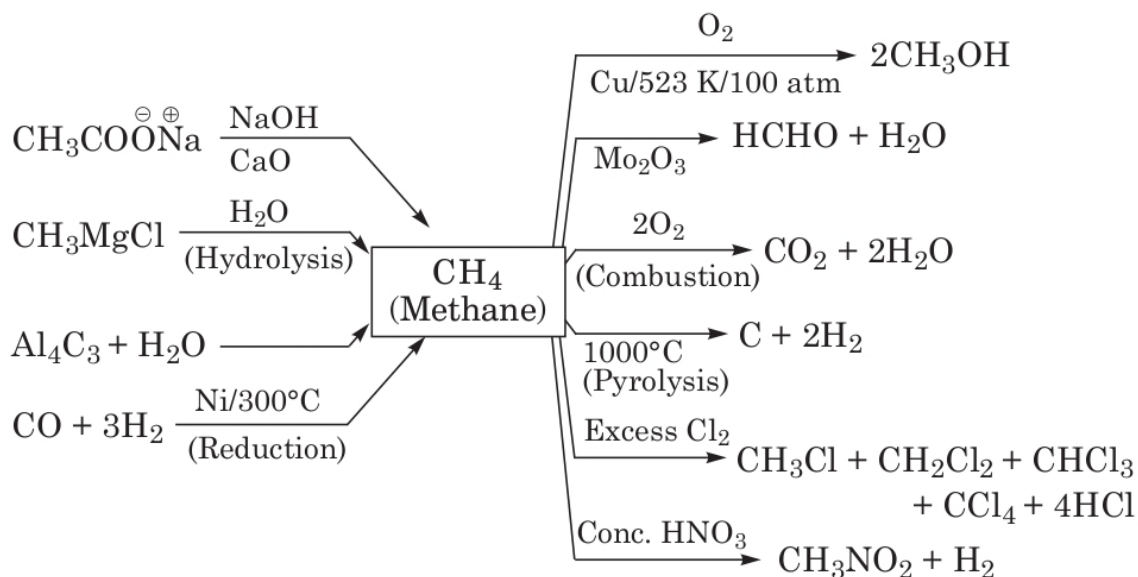
(viii) Nitration



(ix) Sulphonation

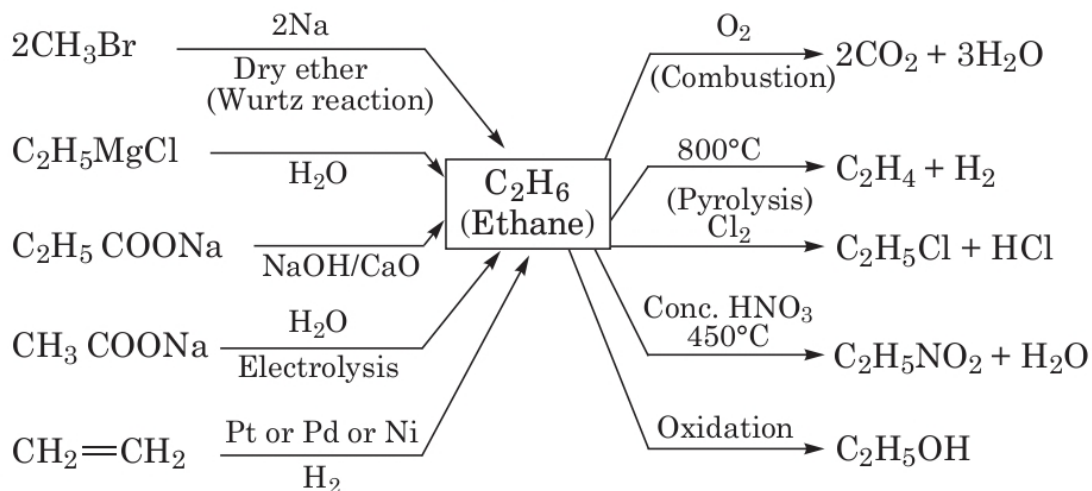


Reactions for Methane (CH₄)



(Methane cannot be prepared by Wurtz reaction, Kolbe's electrolytic process and by reduction of alkenes or alkynes).

Reactions for Ethane (C₂H₆)

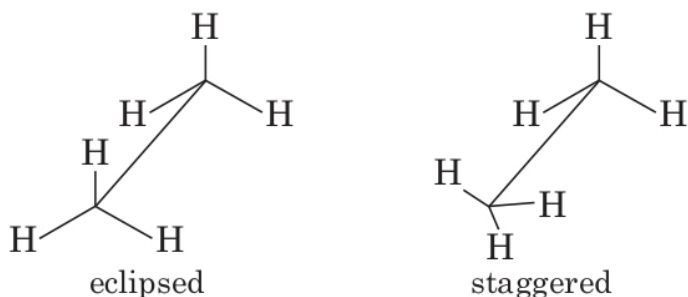


Conformations of Alkanes

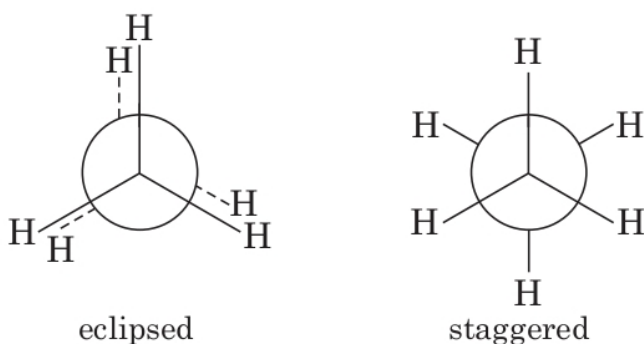
Alkanes have C—C sigma (σ) bonds and rotation about C—C single bond is allowed. This rotation results in different spatial arrangements of atoms in space which can change into one another, such spatial arrangements are called conformations or conformers or rotamers.

Conformations of ethane

(i) Sawhorse projections



(ii) Newman projections



Intermediate conformation between **eclipsed** and **staggered** are known as **skew (gauche) conformations**.

Eclipsed form is least stable but staggered form is most stable due to greater distance between the bond pairs or lesser torsional strain.

The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1} .

Alkenes

These are unsaturated non-cyclic hydrocarbons which have sp^2 -hybridisation with 120° bond angle.

Alkenes are also called **olefins** [oil forming] which indicates their high reactive nature.

Alkenes have general formula C_nH_{2n} , where $n = 2, 3, 4 \dots$

e.g., C_2H_4 (ethene), C_3H_6 (propene), etc.

Structure

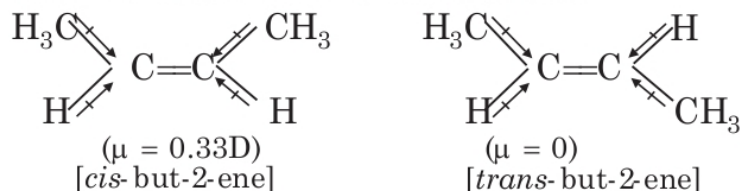
Alkenes possess at least one π bond and have triangular planar shape with a bond angle of 120° between C—H bonds.

Isomerism in Alkenes

Alkenes show both structural isomerism and geometrical isomerism.

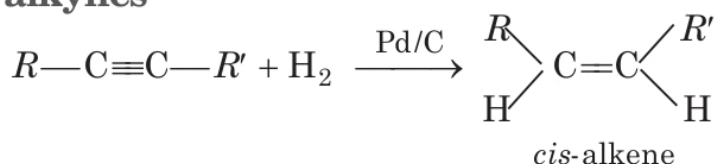
Structural isomerism exhibited by alkenes are chain isomerism and position isomerism.

Alkenes also exhibit stereoisomerism as geometrical (*cis-trans*) isomerism. *cis*-form of alkene is found to be more polar than *trans*-form because dipole moment of *trans*-form is almost zero.

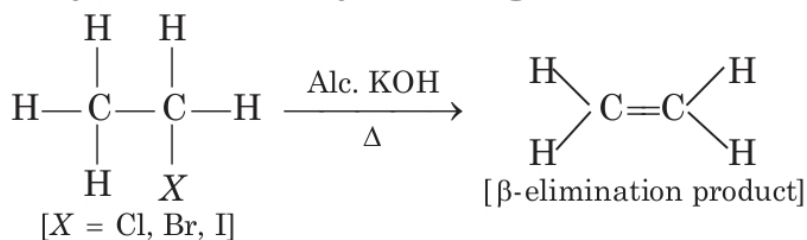


Methods of Preparation of Alkenes

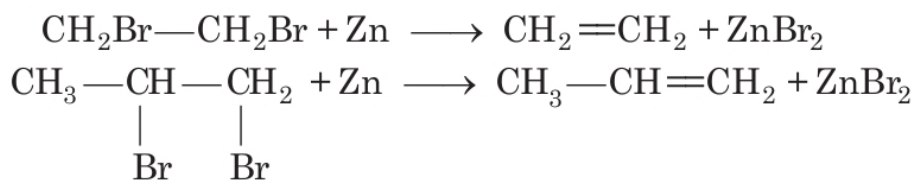
(i) From alkynes



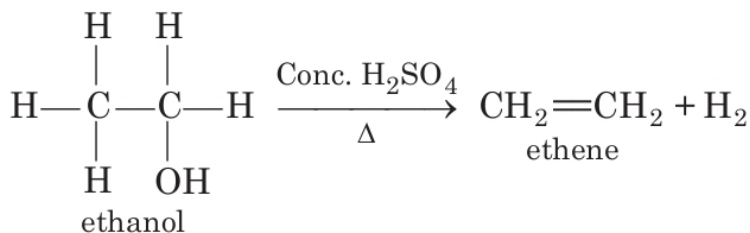
(ii) From alkyl halide [dehydrohalogenation]



(iii) From vicinal dihalides



(iv) From alcohols by acidic dehydrogenation



Physical Properties of Alkenes

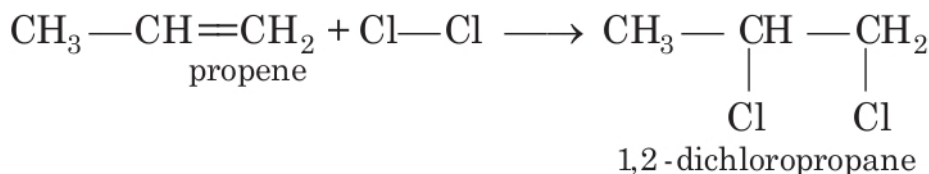
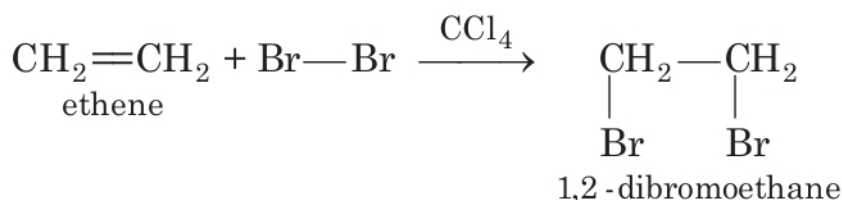
Alkene as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature.

C₁ to C₃ are gases, the next fourteen are liquids and the higher members are solids.

Alkenes show a regular increase in boiling point with increase in size.

Chemical Properties of Alkenes

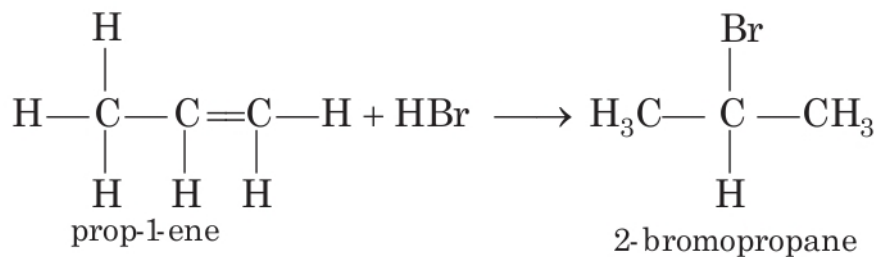
(i) Addition of halogens



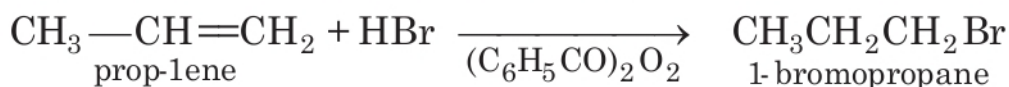
(ii) **Addition of hydrogen halides** HCl, HBr, HI add up to alkenes to form alkyl halides as per their reactivity order



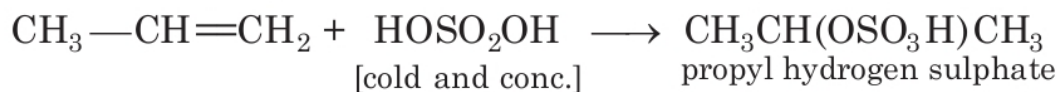
Addition reaction of HBr to unsymmetrical alkenes (Markownikoff's rule) According to Markownikoff's rule, the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atom.



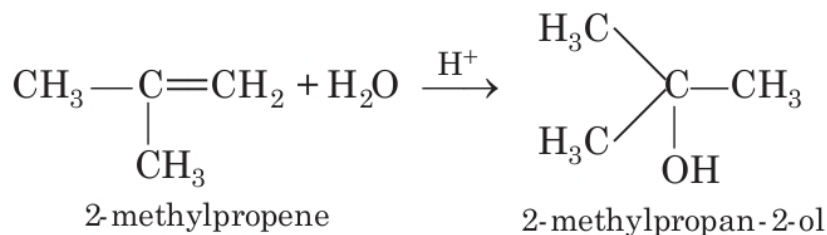
Anti-Markownikoff addition or peroxide effect or Kharash effect In the presence of organic peroxide, addition of only HBr molecule on unsymmetrical alkene takes place contrary to the Markownikoff's rule.



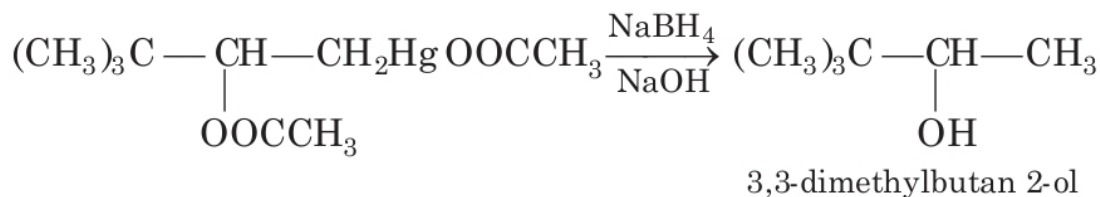
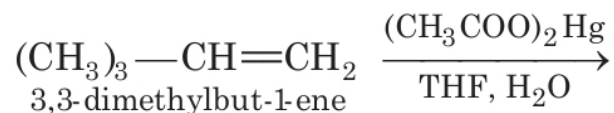
(iii) **Addition of sulphuric acid**



(iv) **Addition of water**



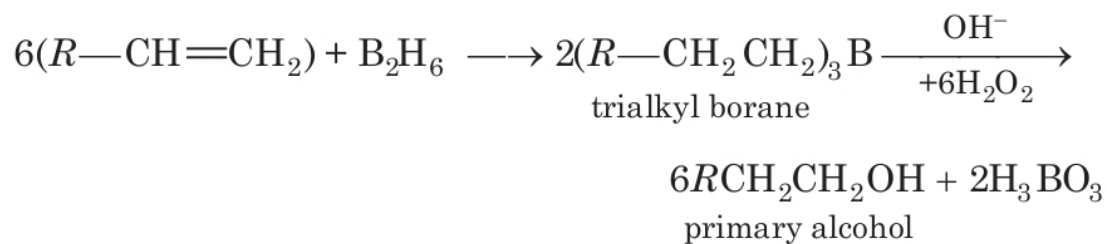
(v) **Oxymercuration-demercuration** This reaction is an example of hydration of alkene according to Markownikoff's rule.



It is an *anti*-addition reaction.

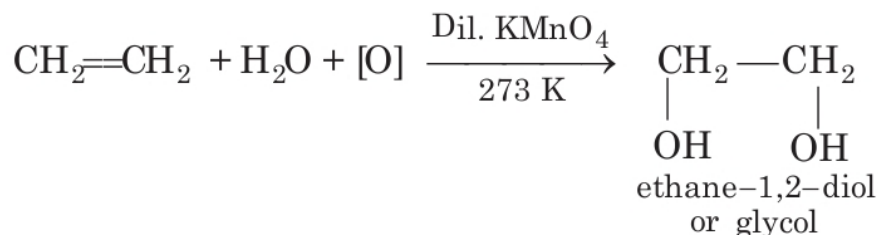
It is better than catalytic hydration by dil. H_2SO_4 , as it avoids rearrangement.

(vi) **Hydroboration oxidation**

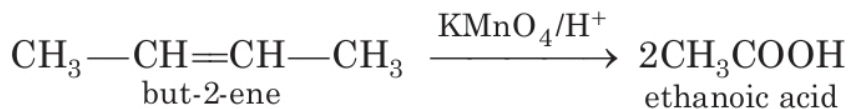
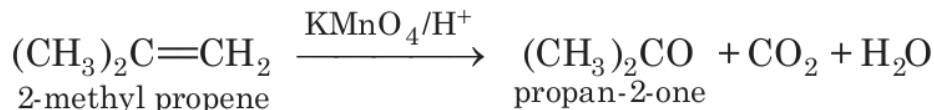


This reaction involved *syn*-addition of reagent.

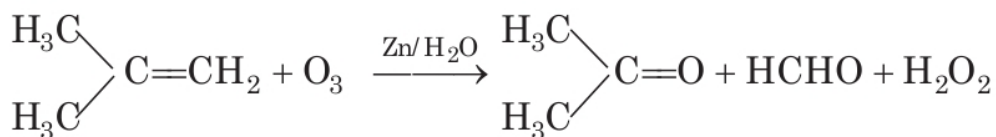
(vii) **Oxidation** Alkenes decolourise cold dilute aqueous solution of potassium permanganate (Baeyer's reagent). It is used as a test for unsaturation.



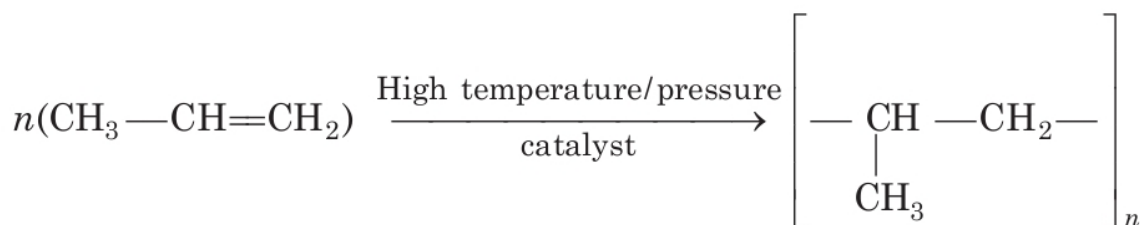
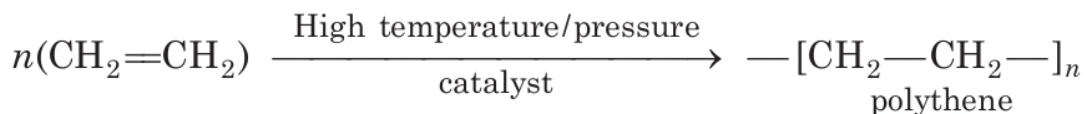
Acidic KMnO_4 or acidic $\text{K}_2\text{Cr}_2\text{O}_7$ oxidise alkenes to ketones and/or acids depending upon the nature of alkene and the experimental conditions.



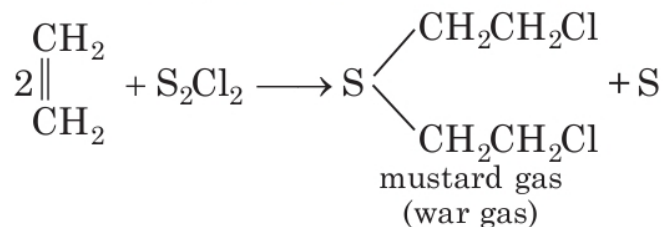
(viii) **Ozonolysis**



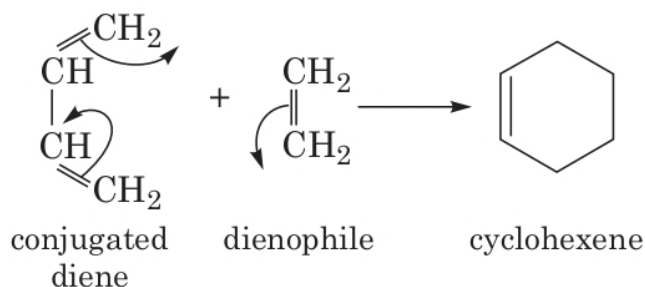
(ix) **Polymerisation**



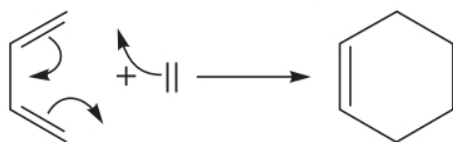
(x) **Reaction with sulphur monochloride**



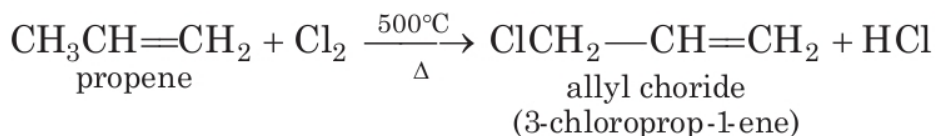
(xii) **Diels-Alder reaction** (via conjugated dienes)



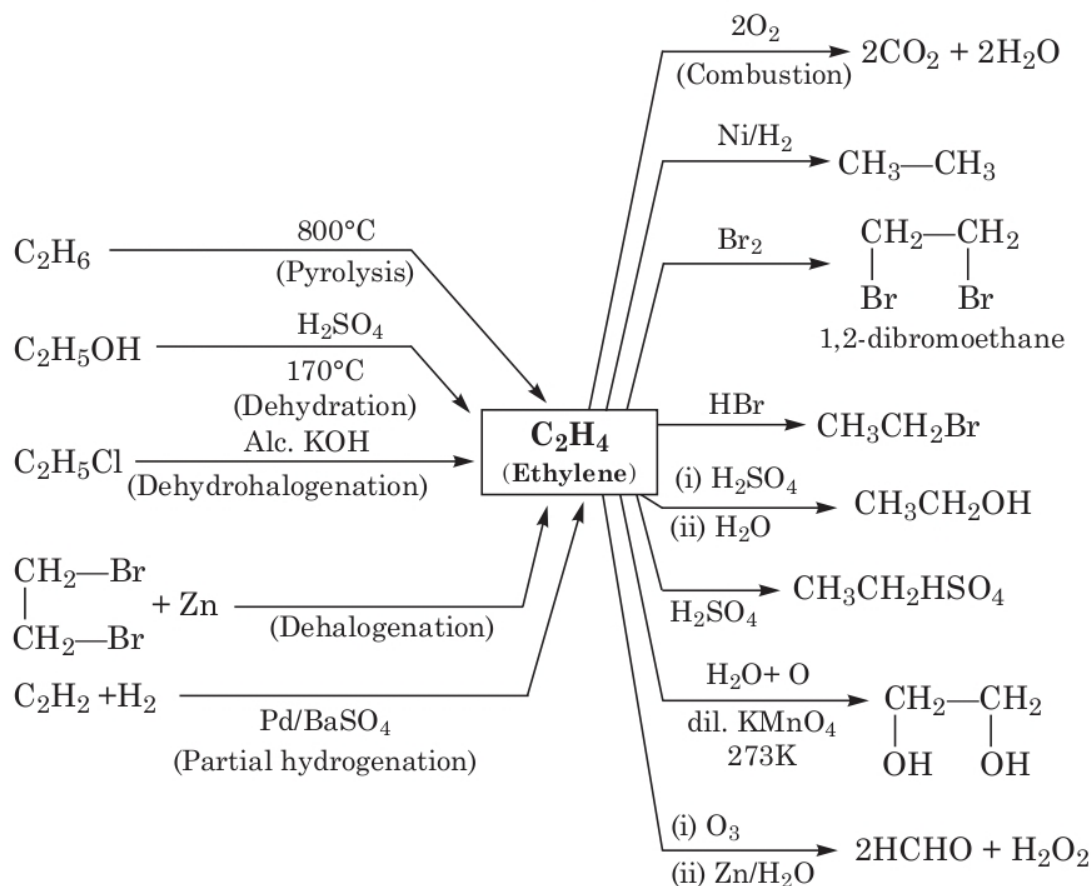
Dienes having alternate single (–) and double bonds (=) are called conjugated alkenes. These give Diels (-) Alder reaction.



(xiii) **Substitution reactions** These occur at very high temperature at allylic position.



Reactions for Ethene [Ethylene] (C₂H₄)



Alkynes

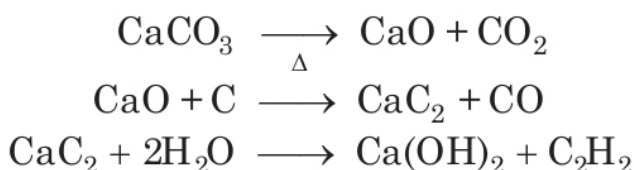
These are unsaturated hydrocarbons with general formula C_nH_{2n-2} e.g. C₂H₂ (ethyne), C₃H₄ (propyne).

Structure

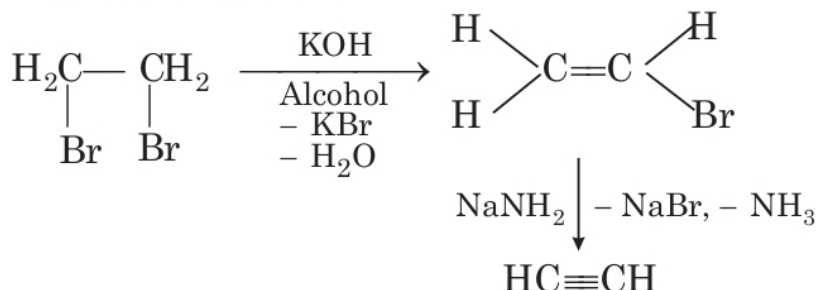
H—C≡C—H contains 3 σ and 2π-bonds and bond length is 120 pm. In acetylene, H—C—C bond angle is 180°. In alkynes, position of triple bond is determined by ozone (O₃). In alkynes show position chain functional and ring **chain isomerism**.

Methods of Preparation of Alkynes

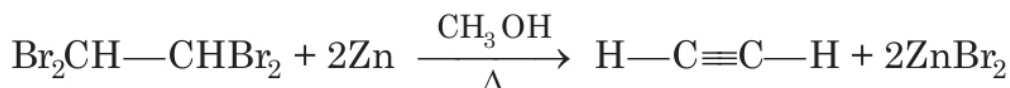
(i) From calcium carbide



(ii) From vicinal dihalides



(iii) From tetrahalides



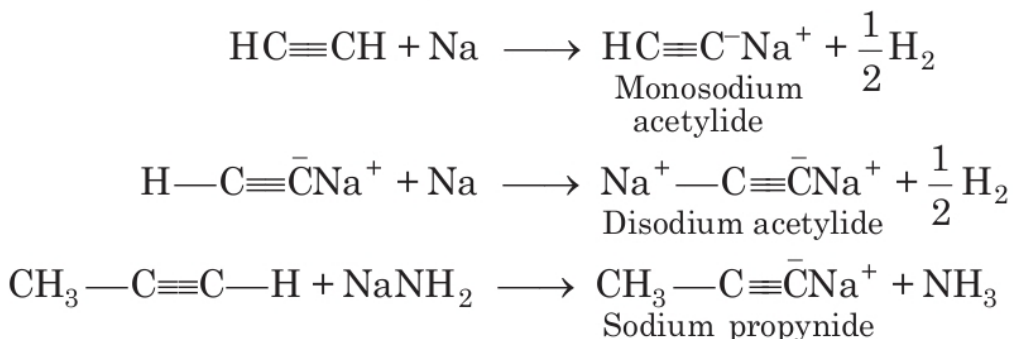
Physical Properties of Alkynes

- (i) The first two members are gases, next eight members ($\text{C}_5 - \text{C}_{12}$) are liquids and higher members are solids.
- (ii) They are all colourless and odourless with the exception of acetylene which has slightly garlic odour due to the presence of PH_3 and H_2S as impurities.
- (iii) Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.
- (iv) Melting point, boiling point and density increase with increase in molar mass.

Chemical Properties of Alkynes

Alkynes also exhibit electrophilic addition reaction but less reactive than alkenes because the dissociation of π -electron cloud requires more energy. Alkynes show electrophilic as well as nucleophilic addition reactions.

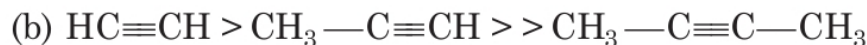
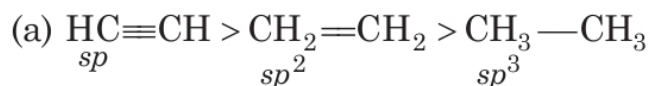
(i) Acidic character of alkyne



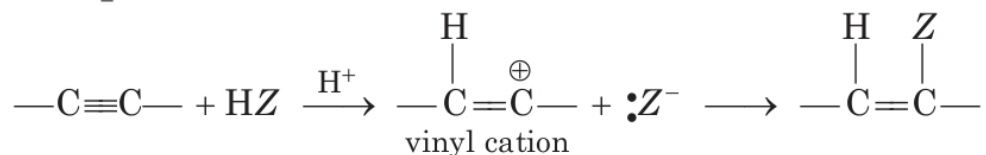
These reactions are not shown by alkenes, alkanes and non-terminal alkynes, hence used for distinction between alkane, alkene and alkyne. Acetylenic hydrogens are acidic in nature due to 50% s-character in sp -hybridised orbitals.

Acidity of alkynes is lesser than water.

Acidic behaviour order



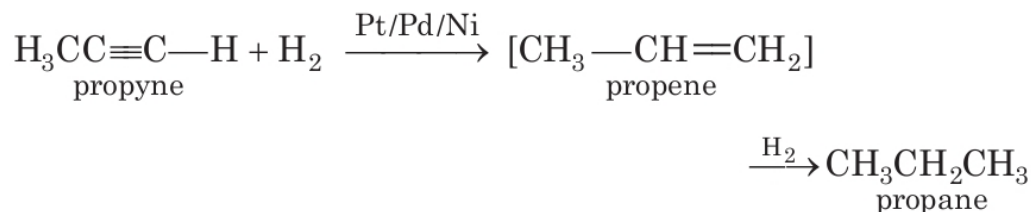
(ii) **Electrophilic addition reactions**



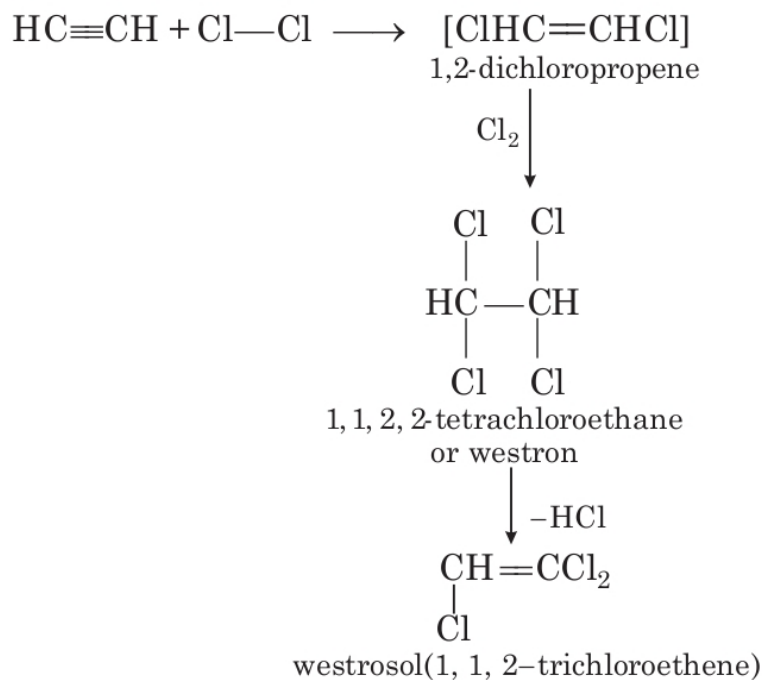
The addition product formed depends upon the stability of vinylic cation. Addition on unsymmetrical alkynes takes place according to Markownikoff's rule.

Few addition reactions are as follows :

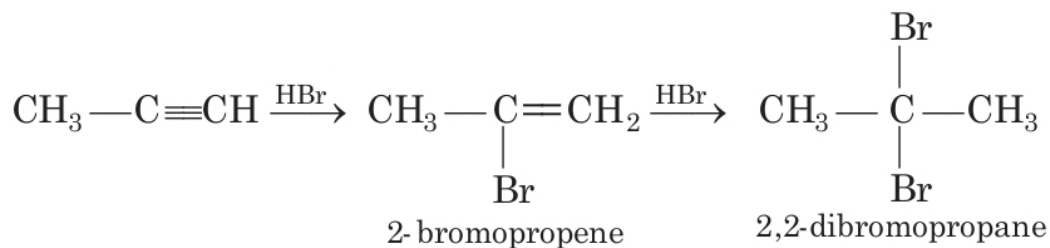
(a) Addition of dihydrogen



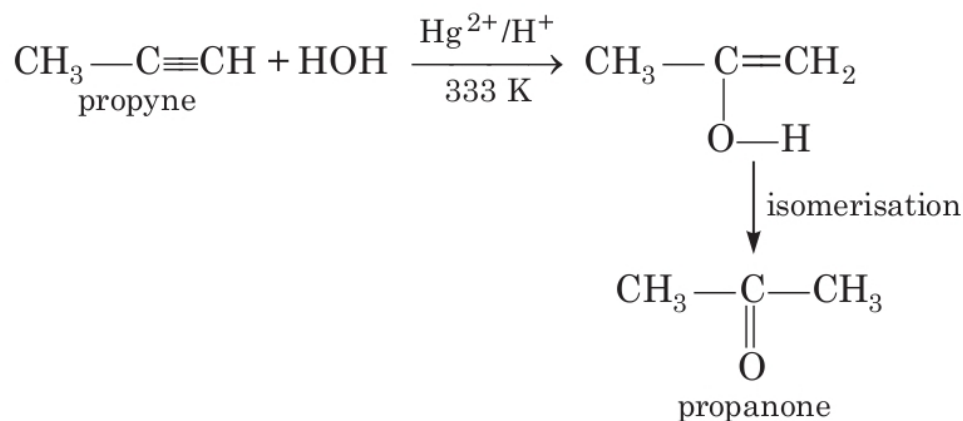
(b) Addition of halogens



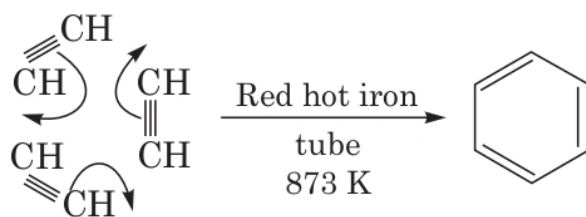
(c) Addition of hydrogen halides



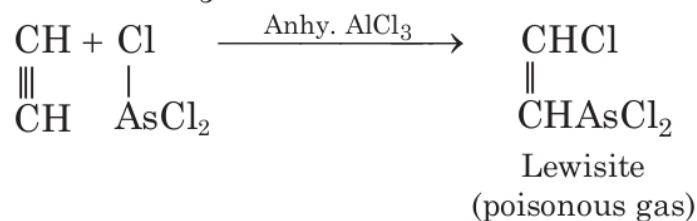
(d) Addition of water



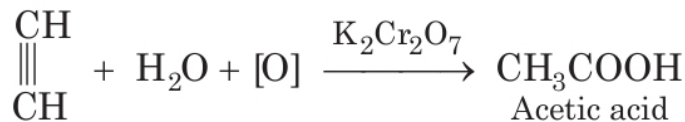
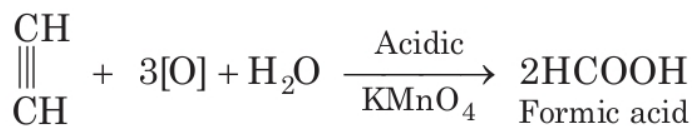
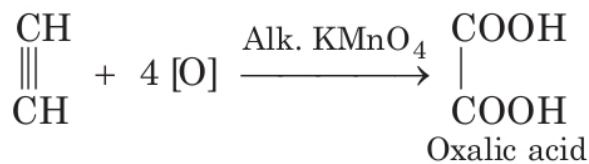
(iii) Cyclic polymerisation



(iv) Reaction with AsCl_3 (arsenic trichloride)



(v) Oxidation

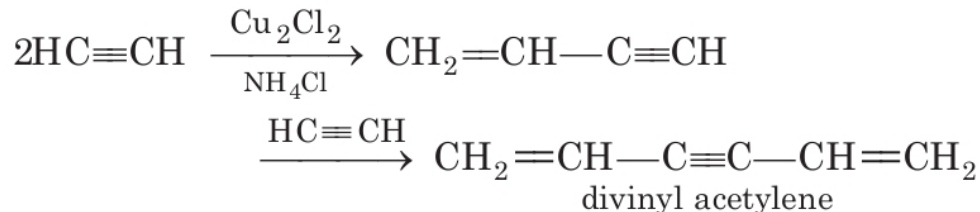


(vi) Ozonolysis

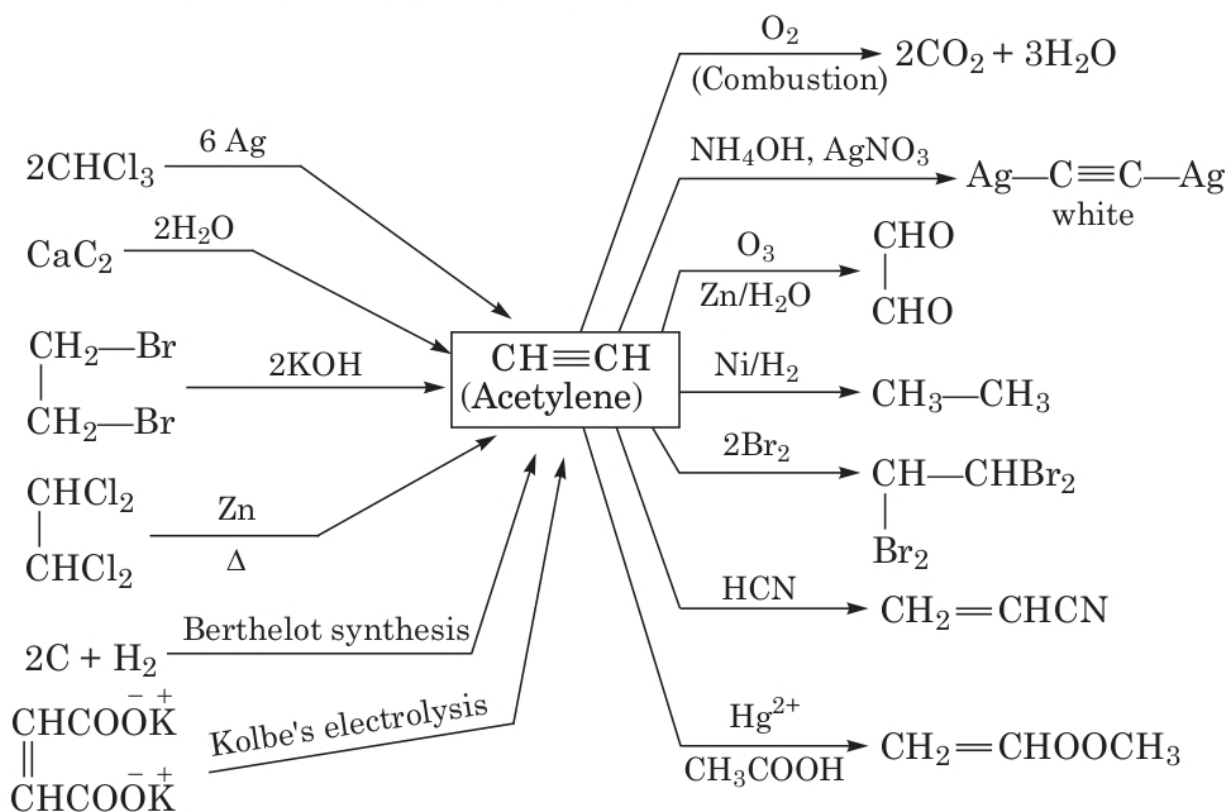


Higher alkynes give diketones which are further oxidised to carboxylic acid.

(vii) Linear polymerisation

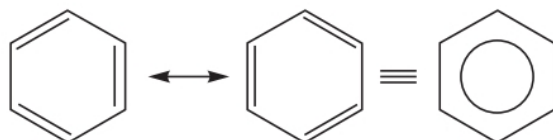


Reactions for Acetylene (C₂H₂)



Benzene

The parent member of the family of aromatic hydrocarbons is benzene (molecular formula: C₆H₆). It has hexagonal ring of six carbon atoms with three double bonds at alternate positions. It is resonance stabilised and the structure may be represented as given ahead.



Structure of Benzene

On the basis of Kekule, structure of benzene has cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.

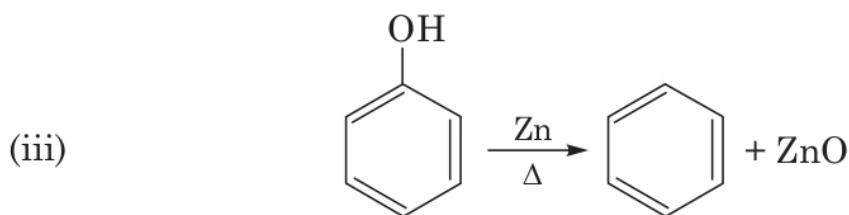
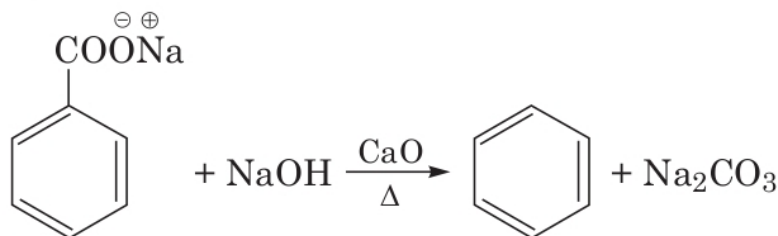
Aromaticity

Aromatic compound should possess the following characteristics :

- (i) Planarity.
- (ii) Complete delocalisation of the π electrons in the ring.
- (iii) Presence of $(4n + 2)\pi$ electrons in the ring where n is an integer ($n = 0, 1, 2, \dots$). This is often referred to as Huckel rule.

Methods of Preparation

- (i) **Cyclic polymerisation of ethyne** Refer to text on page 371.
- (ii) **Decarboxylation of aromatic acids**



Physical Properties of Benzene

Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.

Aromatic hydrocarbons are immiscible with water but readily miscible with organic solvents.

Aromatic compounds burn with sooty flame.

Chemical Reactions of Benzene

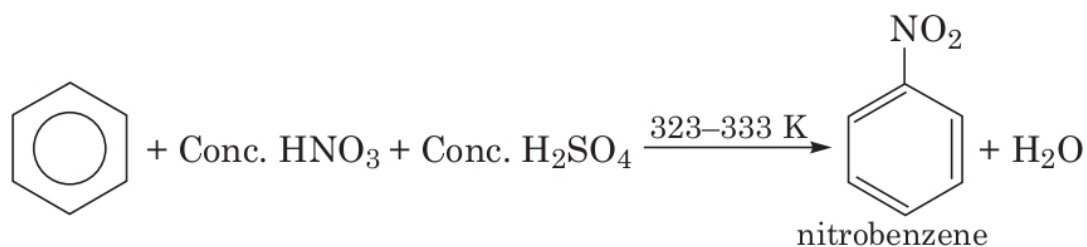
Benzene gives electrophilic substitution reactions.

According to experimental evidences, electrophilic substitution reaction involve following three steps :

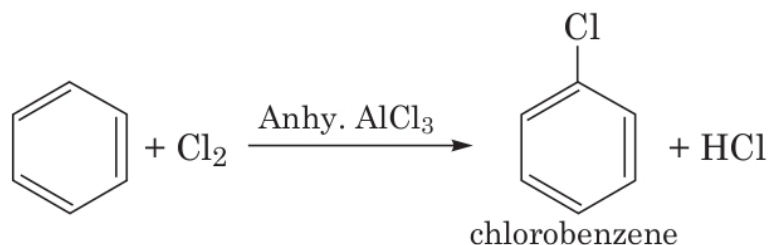
- (a) Generation of electrophile
- (b) Formation of carbocation intermediate
- (c) Removal of proton from the carbocation intermediate.

Common electrophilic substitution reactions are as follows :

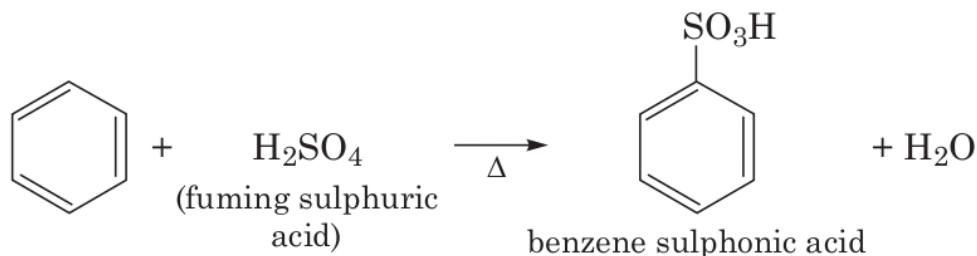
(i) **Nitration**



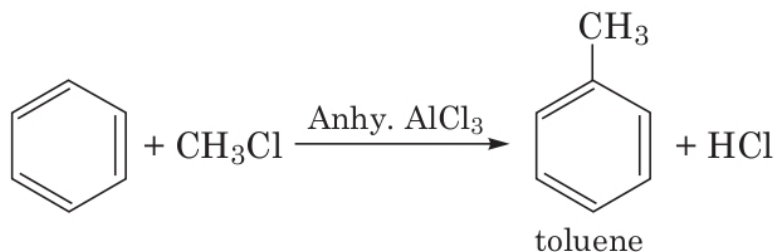
(ii) **Halogenation**



(iii) **Sulphonation**

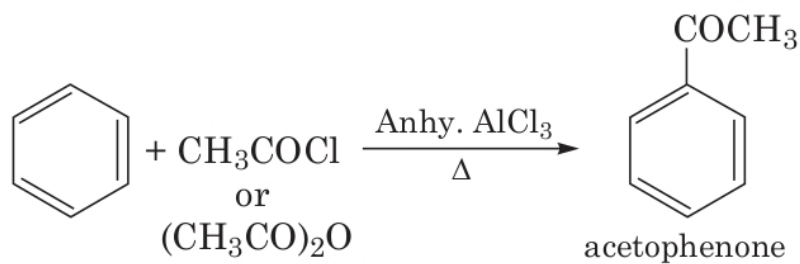


(iv) **Friedel-Crafts alkylation reaction**

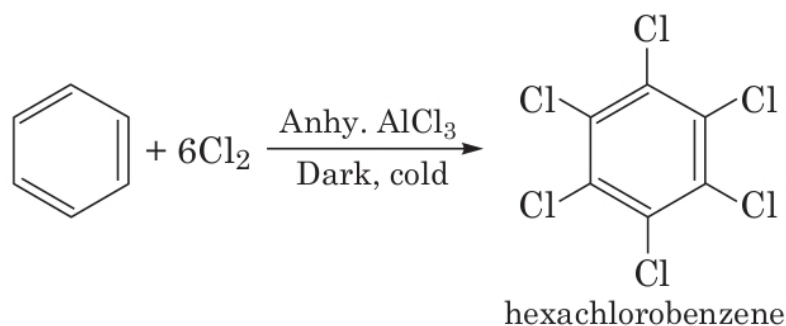


When Friedel-Craft alkylation is carried out with CH_3Cl the product obtained is $\text{C}_6\text{H}_5\text{CH}_3$. In case the alkylation is carried out with higher alkyl halide, e.g. n-propyl chloride, then the electrophile n-propyl carbocation ($\text{CH}_3-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$) which is a primary carbocation rearranges to form more stable secondary carbocation (*iso*-propyl carbocation) and the main product formed will be *iso*-propyl benzene.

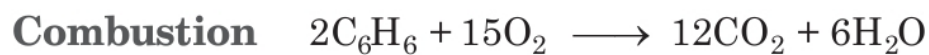
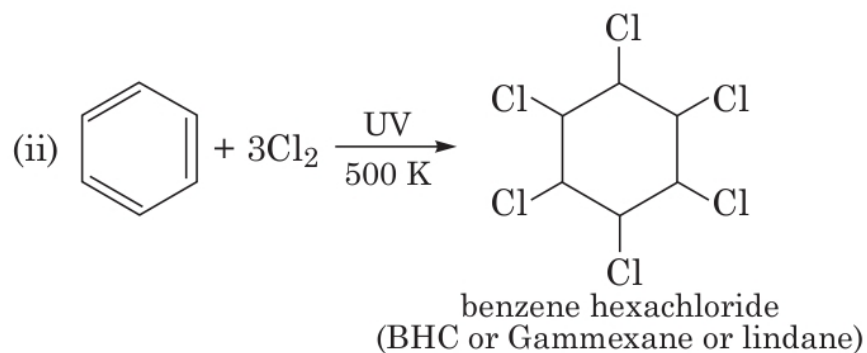
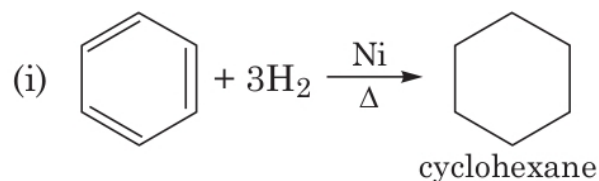
(v) **Friedel-Crafts acylation reaction**



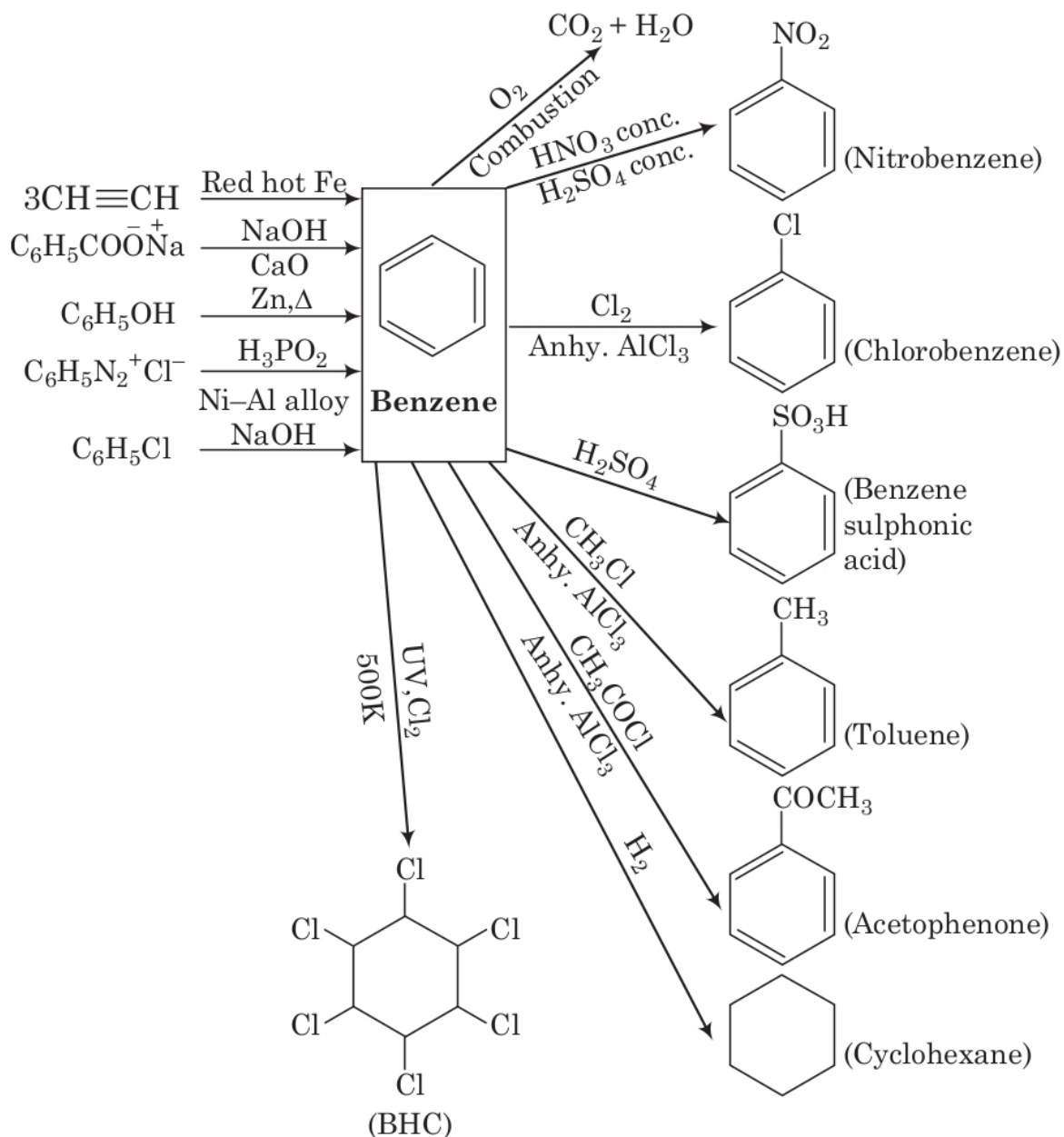
(vi) **With Cl₂** In excess of chlorine, benzene yields hexachlorobenzene [C₆Cl₆].



Benzene also undergoes addition reactions *e.g.*,

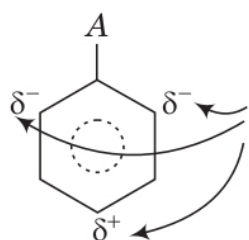


Reactions for Benzene



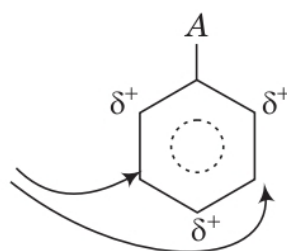
Directive Influence of Substituents on Benzene Ring

The first substituent on benzene ring directs the next incoming group.



E^+ (electrophile)
 [Always attack the positions
 of high electron density]

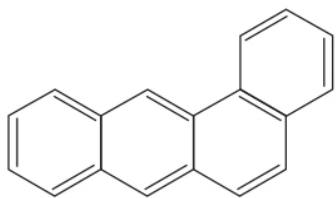
o and *p*-directing
 e.g. $-\text{NH}_2, -\text{OH}, -\text{OR}, -\text{R}$



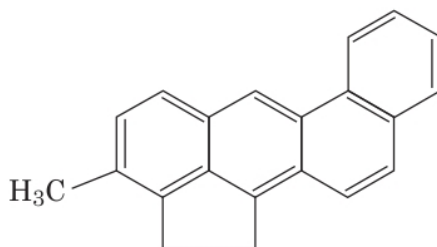
m-directing
 e.g. $-\text{F}, -\text{Cl}, -\text{C}\equiv\text{N}$

Carcinogenicity and Toxicity

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. e.g.



1-2-benzanthracene



3-methylcholanthrene

Petroleum

It is a dark coloured oily liquid with offensive odour, found at various depths in many region below the earth's surface. It is also called **rock oil**, **mineral oil** or **crude oil**. It is covered by an atmosphere of a gaseous mixture known as **natural gas**.

It contains mainly alkanes, cycloalkanes, aromatic hydrocarbons, sulphur, nitrogen and oxygen compounds.

When subjected to fractional distillation, it gives different fractions at different temperatures.

S.No.	Fraction	Boiling range	Composition	Uses
1.	Uncondensed gases	Room temperature	$C_1 - C_4$	Fuel gases, refrigerants, production of carbon black, hydrogen.
2.	Crude naphtha (Its refractionation gives	30–150°	$C_5 - C_{10}$	
	(i) Petroleum ether	30 – 70°	$C_5 - C_6$	Solvent
	(ii) Gasoline	70 – 120°	$C_6 - C_8$	Fuel, petrol gas
	(iii) Benzene derivative	120 – 150°	$C_8 - C_{10}$	Solvent, drycleaning
3.	Kerosene	150–250°	$C_{11} - C_{16}$	Fuel, illuminants, oil gas

S.No.	Fraction	Boiling range	Composition	Uses
4.	Heavy oil (Its refractionation gives (i) Gas oil (ii) Fuel oil (iii) Diesel oil	250–400°	C ₁₅ – C ₁₈	Fuel for diesel engines
5.	Residual oil (Its vacuum distillation gives (i) Lubricating oil (ii) Paraffin wax (iii) Vaseline (iv) Pitch	Above 400°C	C ₁₇ – C ₄₀ C ₁₇ – C ₂₀ C ₂₀ – C ₃₀ C ₂₀ – C ₃₀ C ₃₀ – C ₄₀	Lubrication Candles, boot polish Toilets, lubrication Paints, road surfacing
6.	Petroleum coke			As fuel

LPG (Liquified Petroleum gas)

It is a mixture of butane and *iso*-butane with a small amount of propane. A strong foul smelling substance, called ethyl mercaptan (C₂H₅SH) is added to LPG cylinders, to help in the detection of gas leakage.

CNG (Compressed Natural Gas)

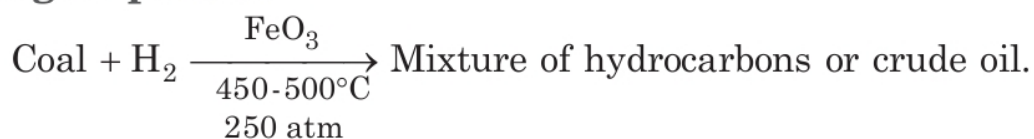
It consists mainly of methane (95%), which is a relatively unreactive hydrocarbon and makes its nearly complete combustion possible.

Artificial Methods for Manufacturing Petrol

From higher alkanes, petrol or gasoline is obtained by cracking or pyrolysis.

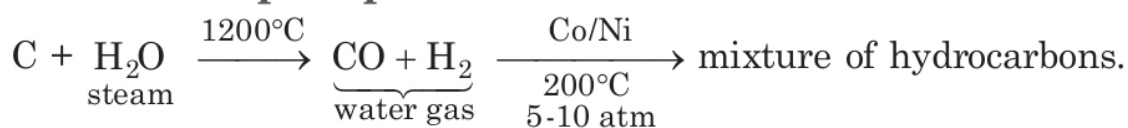
From coal, petrol can be synthesised by following two processes :

(i) Bergius process



The yield of gasoline by this method may be as high as 60%.

(ii) Fischer- Tropsch process



The best catalyst for this process is a mixture of Co, thoria, magnesia and kieselguhr.

The overall yield in this process is slightly higher than Bergius process.

Octane Number

The quality of petrol is expressed in terms of octane number which is defined as the percentage of *iso*-octane by volume in a mixture of *iso*-octane and *n*-heptane which has the same antiknock properties as the fuel under test.

The octane number is 100 for *iso*-octane (2,2,4-trimethylpentane)

Natural gas has octane number 130.

TEL (tetraethyl lead) is used as antiknocking compound.

Octane number is increased by isomerisation, alkylation or aromatisation.

Cetane Number

Quality of diesel oils is measured in terms of cetane number which is defined as the percentage of cetane (hexadecane) by volume in a mixture of cetane and α -methyl naphthalene which has the same ignition property as fuel oil under similar experimental conditions.

It is 100 for cetane and 0 for α -methyl naphthalene.