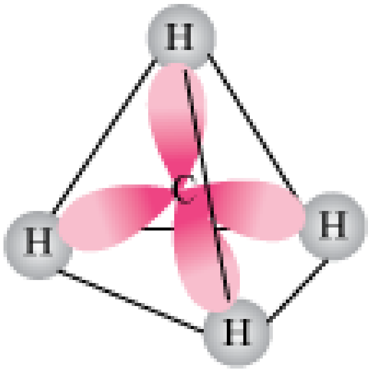
Hydrocarbons

Alkanes - Nomenclature, Isomerism, and Conformations

- General formula is C_nH_{2n+2}.
- Structure of methane is



- Four hydrogen atoms are at the four corners of a regular tetrahedron.
- H − C − H bond angle is of 109.5°.
- In alkanes, C − C bond length is 154 pm and C − H bond length is 112 pm.

Nomenclature and isomerism

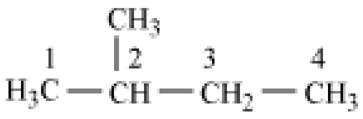
- **Nomenclature**

Example − Pentane (C_5H_{12})

$CH_3-CH_2-CH_2-CH_2-CH_3$

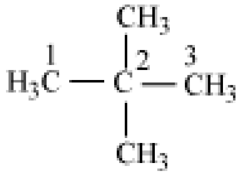
n-Pentane(I)

(b.p – 309 K)



$$\overset{1}{H_3C}-\overset{\overset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

2 – Methylbutane (II)
(b.p = 301 K)



$$\overset{1}{H_3C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{3}{CH_3}$$

2, 2 – Dimethylpropane (III)
(b.p = 282.5 K)

- **Isomerism**
- **I**, **II**, and **III** have the same molecular formula, but have different properties (such as boiling points). The difference in properties arises due to their difference in structures. Hence, they are known as structural isomers.
- Structure **I** is continuous chain and structure **II** and **III** represent branched chain. Hence, **I** and **II**; **II** and **III;** and **I** and **III** represent chain isomers.
- Primary carbon (1°) − Carbon atom is attached to one carbon atom (as in ethane) or no carbon atom (as in methane). Terminal carbons are always primary.
- Secondary carbon (2°) − Carbon atom is attached to two carbon atoms.
- Tertiary carbon (3°) − Carbon atom is attached to three carbon atoms.
- Neo or quaternary (4°) − Carbon atom is attached to four carbon atoms.

Writing the Structure of 3-Ethyl-2-Methylhexane

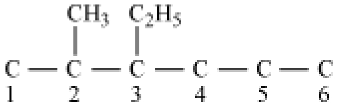
- Chain of six carbon atoms

C − C − C − C − C − C

- Numbering to carbon atoms

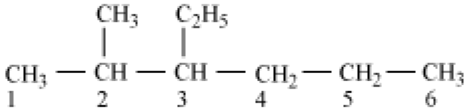
$$\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

- Ethyl group is attached at carbon 3 and methyl group is attached at carbon 2.



$$\underset{1}{\mathrm{C}}-\underset{2}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}-\underset{3}{\overset{\overset{\mathrm{C_2H_5}}{|}}{\mathrm{C}}}-\underset{4}{\mathrm{C}}-\underset{5}{\mathrm{C}}-\underset{6}{\mathrm{C}}$$

- Valence of a carbon atom is satisfied by requisite number of hydrogen atoms.



$$\underset{1}{\mathrm{CH_3}}-\underset{2}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}}-\underset{3}{\overset{\overset{\mathrm{C_2H_5}}{|}}{\mathrm{CH}}}-\underset{4}{\mathrm{CH_2}}-\underset{5}{\mathrm{CH_2}}-\underset{6}{\mathrm{CH_3}}$$

Conformations

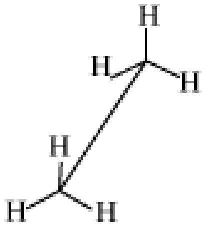
- Rotation about C − C single bond results into different spatial arrangements of atoms, which can change into another. Such spatial arrangements are called conformations or conformers or rotamers.

- C − C bond is not completely free for rotation.

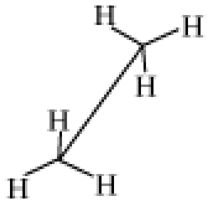
- Rotation of C − C bond is hindered by a small energy barrier of 1− 20 kJ mol^{-1} due to weak interaction between the adjacent bonds. Such type of repulsive interaction is called **torsional strain**.

- **Conformations of Ethane −** Staggard conformation and eclipsed conformation

- Sawhorse projection of ethane

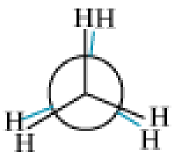


(i) Eclipsed

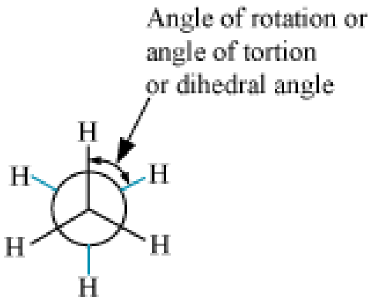


(ii) Staggered

- Newman's projection of ethane



Eclipsed



Staggered.

- **Relative stability of conformations**
- The repulsive interaction between the electron clouds which affects the stability of a conformation is called **torsional strain**.
- Magnitude of torsional strain depends upon the angle of rotation about C − C bond called dihedral angle (or torsional angle).
- Staggered form has the least torsional strain and the eclipsed form has the maximum torsional strain.
- The energy difference between these two extreme forms of ethane (staggered and eclipsed) is of the order of 12.5 kJ mol^{-1}.

Preparation and Properties of Alkanes

Alkanes: As we already know, alkanes are the saturated hydrocarbons with all the valencies of the carbon atoms satisfied, having a general formula C_nH_{2n+2}. The main source of alkanes is natural gas and petroleum. The following table gives the sources of some of the important alkanes:

Occurrence of Methane and Ethane
Methane is the main constituent of marsh gas. Methane is exhaled by animals that feed on food containing cellulose. Methane is found in the intestinal gas of humans and animals. Methane is found in cavities in coal. Ethane occurs along with methane.

Preparation

- **From Unsaturated Hydrocarbons**

$$\underset{\text{Ethene}}{CH_2=CH_2}+H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H}+2H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

- The process is called hydrogenation.
- Metals (Pt, Pd, and Ni) adsorb dihydrogen on their surfaces and activate H − H bond.
- **From Alkyl Halides**
- Reduction of alkyl halides (except fluorides) with zinc and hydrochloric acid

$$\underset{\text{Chloromethane}}{CH_3-Cl}+H_2\xrightarrow{Zn/HCl}\underset{\text{Methane}}{CH_4}+HCl$$

$$\underset{\text{1-Chloropropane}}{CH_3-CH_2-CH_2-Cl}+H_2\xrightarrow{Zn/HCl}\underset{\text{Propane}}{CH_3CH_2CH_3}+HCl$$

- **Wurtz reaction −** Alkyl halides on treatment with sodium in presence of dry ether give higher alkanes (containing an even number of carbon atoms).

$$\underset{\text{Bromomethane}}{CH_3Br}\;+\;2Na\;+\;BrCH_3\;\xrightarrow{dry\,ether}\;\underset{\text{Ethane}}{CH_3-CH_3}\;+\;2NaBr$$

- **From Carboxylic Acids**
- **Decarboxylation** (i.e., elimination of CO_2) of sodium salts of carboxylic acids on heating with soda lime (mixture of NaOH and CaO) gives alkane. The alkanes thus obtained contain one carbon atom less than the carboxylic acid.

$$\underset{\substack{\text{Sodium}\\\text{ethanoate}}}{CH_3COONa}+NaOH\xrightarrow[\Delta]{CaO}\underset{\text{Methane}}{CH_4}+Na_2CO_3$$

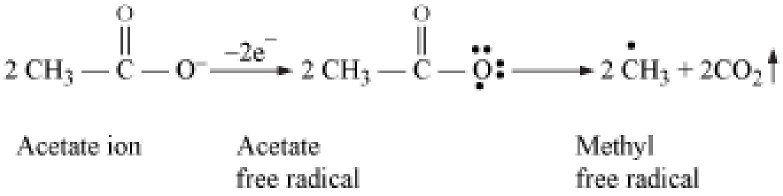
- **Kolbe's Electrolysis Method**

Electrolysis of an aqueous solution of sodium or potassium salt of a carboxylic acid gives alkane (containing an even number of carbon atoms) at the anode.

$$2CH_3CO\overset{-}{O}\overset{+}{N}a + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

Sodium acetate

At Anode



$$2\,CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2\,CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\dot{\ddot{O}}: \longrightarrow 2\,\dot{C}H_3 + 2CO_2\uparrow$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3\uparrow$$

At Cathode

$$2H_2O + e^- \longrightarrow \overset{-}{O}H + \dot{H}$$

$$2\dot{H} \longrightarrow H_2\uparrow$$

Important Note: Methane cannot be prepared by this method.

Physical Properties of Alkanes

- Non-polar molecules
- Due to weak forces, members from C_1 to C_4 are gases, C_5 to C_{17} are liquids, and those containing 18 carbon atoms or more are solids at 298 K.
- Colourless and odourless
- Soluble in non-polar solvents
- Hydrophobic in nature
- Boiling point increases with the increase in molecular mass.

Question: Pentane having a continuous chain of five carbon atoms has a boiling point of 309.1 K whereas 2,2-dimethylpropane boils at 282.5 K though they have same molecular mass. Why?

Answer:

When the number of branched chains increases, the molecule attains the shape of a sphere, which results in a smaller area of contact. As a result of this, there are weak intermolecular forces between spherical molecules which can be overcome at low temperatures. Hence the boiling point of pentane is higher than that of 2,2-dimethylpropane.

Chemical properties of alkanes

- **Combustion**

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_c H^\ominus = -890\,\text{kJ mol}^{-1}$$

In general for alkanes,

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

Methane and ethane undergo complete combustion due to low carbon content and thus burn with a blue non-sooty flame.

- **Controlled Oxidation**
- Yield a variety of products on heating with regulated supply of air or dioxygen at high pressure and in the presence of suitable catalysts

$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} \underset{\text{Methanol}}{2CH_3OH}$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$

$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$$

$$2\,C_2H_6 + O_2 \xrightarrow[\text{Cu Tube, 475 K}]{\text{120 atm}} \underset{\text{Ethanol}}{2\,C_2H_5\,OH}$$

$$C_2H_6 + O_2 \xrightarrow{MoO} \underset{\text{Acetaldehyde}}{CH_3\,CHO} + H_2O$$

$$C_2H_5\,OH + O_2 \xrightarrow[300\,^\circ C]{Pt} \underset{\text{Ethanoic acid}}{CH_3\,COOH} + H_2O$$

- Generally, alkanes resist oxidation. However, alkanes having tertiary H atom can be oxidized to corresponding alcohols by acidified $KMnO_4$ or acidified $K_2Cr_2O_7$.

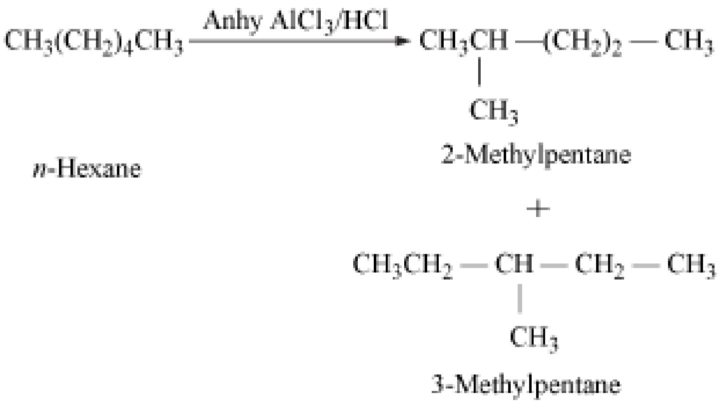
$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH} \xrightarrow{KMnO_4} (CH_3)_3COH$$

- When methane and ethane are burnt in a limited supply of oxygen with no catalyst they form carbon monoxide and water. Further decreased amount of oxygen produces **soot** that is used in the manufacturing of printing inks and tyres.

$$2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$
$$2\,C_2H_6 + 5\,O_2 \longrightarrow 4\,CO + 6\,H_2O$$
$$CH_4 + O_2 \longrightarrow \underset{\text{Soot}}{C} + 2\,H_2O$$

- **Isomerisation**

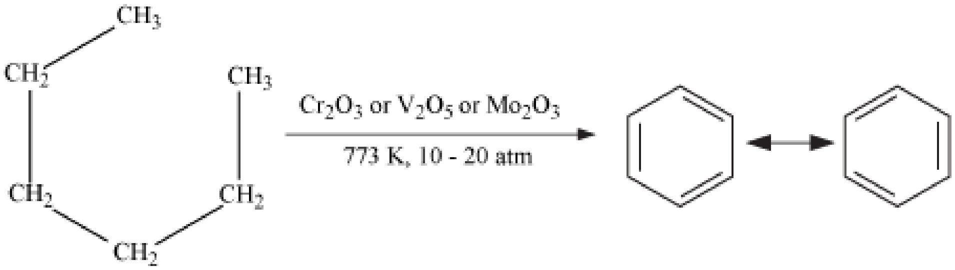
  On heating in the presence of anhydrous $AlCl_3$ and HCl gas, *n*-alkanes isomerise to branched-chain alkanes.



$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhy } AlCl_3/HCl} CH_3CH(CH_3)-(CH_2)_2-CH_3 + CH_3CH_2-CH(CH_3)-CH_2-CH_3$$

- **Aromatization (or Reforming)**

  Heating *n*-alkanes (with six or more carbon atoms) to 773 K at 10−20 atmospheric pressure in the presence of the oxides of V, Mo, or Cr supported over alumina produces benzene and it's homologues.

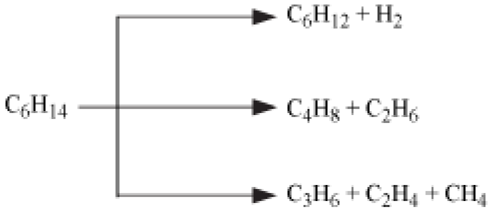


- **Reaction with Steam**

  $$CH_4 + H_2O \xrightarrow[1273K]{Ni} CO + 3H_2$$

- **Pyrolysis or Cracking**

  On heating to a higher temperature, higher alkanes decompose into lower alkanes or alkenes.



$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973K]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{Other products}$$

- **Substitution Reactions**
- Undergo substitution reactions in which one or more hydrogen atoms of alkanes are substituted (replaced) by halogens, nitro group, and sulphonic group
- Example − Halogenation, which takes place either at high temperature or in the presence of UV light (or sunlight)

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

- Rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$
- Rate of replacement of hydrogens of alkanes is 3° > 2° > 1°
- Mechanism of halogenation (free radical mechanism)

(i) Initiation

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \underbrace{\dot{C}l + \dot{C}l}_{\text{Chlorine free radicals}}$$

(ii) Propagation

$$CH_4 + C\dot{l} \xrightarrow{h\nu} \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \underset{\text{Chlorine free radical}}{\dot{C}l}$$

$$CH_3Cl + C\dot{l} \longrightarrow \dot{C}H_2Cl + HCl$$

$$C\dot{H}_2Cl + Cl-Cl \longrightarrow CH_2Cl_2 + \dot{C}l$$

(iii) Termination

$$\dot{\mathrm{Cl}}+\dot{\mathrm{Cl}}\longrightarrow \mathrm{Cl-Cl}$$

$$\dot{\mathrm{C}}\mathrm{H_3}+\dot{\mathrm{C}}\mathrm{H_3}\longrightarrow \mathrm{H_3C-CH_3}$$

$$\dot{\mathrm{C}}\mathrm{H_3}+\dot{\mathrm{Cl}}\longrightarrow \mathrm{H_3C-Cl}$$

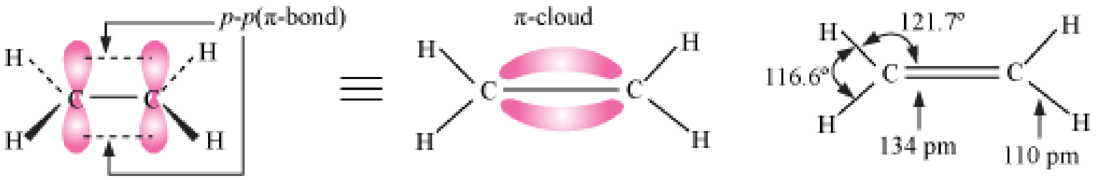
Uses of Some Important Alkanes: Methane and Ethane

Methane	Ethane
Source of CO and H_2O Preparation of acetylene, formaldehyde, methanol, chloromethane and tetrachloromethane Domestic fuel	Preparation of ethene, ethanol, ethanal, ethanoic acid Preparation of a useful solvent in dry cleaning (tetraethyllead-1,1,1,-trichloroethane) Fuel

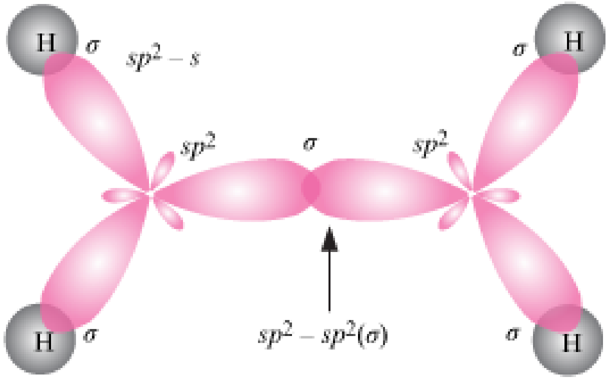
Alkenes: Nomenclature and Isomerism

Alkenes

- Unsaturated hydrocarbons containing at least one double bond
- General formula: C_nH_{2n}
- Also know as olefins
- **Structure of double bond:**
- C = C bond in alkenes contains one strong sigma (σ) bond (bond enthalpy = 397 kJ mol^{-}), and one weak pi (π) bond (bond enthalpy = 284 kJ mol^{-1})
- Pi (π) bonds are obtained by lateral or sidewise overlapping of two 2*p* orbitals of C atoms (shown in the figure).



- Sigma (σ) bond is formed by the head-on overlapping of sp^2 hybridised orbitals.



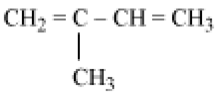
- C = C bond length = 134 pm (bond enthalpy = 681 kJ mol^{-1})

  C − C bond length = 154 pm (bond enthalpy = 348 kJ mol^{-1})

- The presence of pi (π) bond makes alkenes behave as sources of loosely held mobile electrons.

Nomenclature of Alkenes

- Longest chain of carbon atoms containing double bond is selected
- Numbering of the chain is done from the end which is nearer to the double bond
- The suffix '−ane' of alkanes is replaced by the suffix '−ene'.

Structure	IUPAC name
$CH_3 - CH_2 - CH = CH_2$	But-1-ene
 $\underset{\displaystyle CH_3}{CH_2 = \underset{\vert}{C} - CH = CH_3}$	2-Methylbuta−1,3-diene
$CH_3 - CH_2 - CH = CH - CH_2 - CH_3$	Hex-3-ene

Isomerism

- **Structural isomerism** (property of compounds to have the same molecular formula, but different structures)

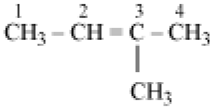
- Alkenes higher than propene have different structures.

- Example: C_5H_{10}

  (I) $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_2 - \overset{5}{C}H_3$

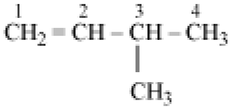
  (II) $\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_2 - \overset{5}{C}H_3$

  (III)



$$\overset{1}{C}H_3 - \overset{2}{C}H = \underset{\displaystyle CH_3}{\overset{3}{C}} - \overset{4}{C}H_3$$

  (IV)



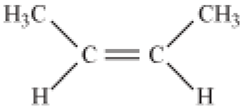
$$\overset{1}{C}H_2 = \overset{2}{C}H - \underset{\displaystyle CH_3}{\overset{3}{C}H} - \overset{4}{C}H_3$$

  I and III; II and III; I and IV; II and IV → structural isomers

  I and II; III and IV are position isomers

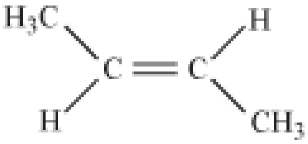
- **Geometrical isomerism** (Isomerism in which compounds have different spatial arrangement of atoms or groups about a double bond)

- *Cis*-isomer: Two identical atoms or groups are on the same side of the double bond



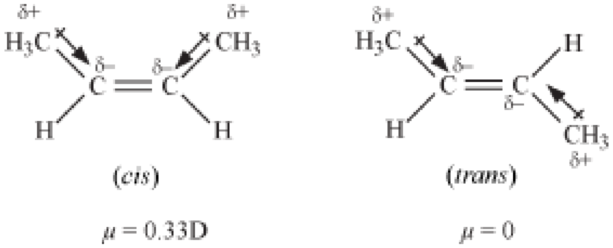
cis-But-2-ene

- *Trans*-isomer: Two identical atoms or groups lie on the opposite side of the double bond



trans-But-2-ene

- *Trans*-but-2-ene is non-polar (dipole moment = 0) while *cis*-but-2-ene is polar (dipole moment = 0.33D).



- B.p of *cis*-but-2-ene = 277 K

  B.p of *trans*-but-2-ene = 274 K

- Melting point of the *trans*-isomer is higher than that of the *cis*-isomer.

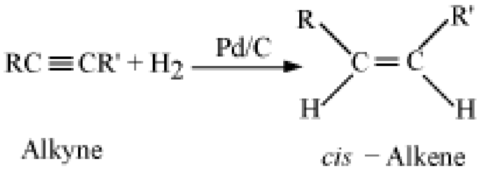
- *Cis-trans* isomerism (or geometrical isomerism) is also shown as XYC = CXZ and XYC = CZW

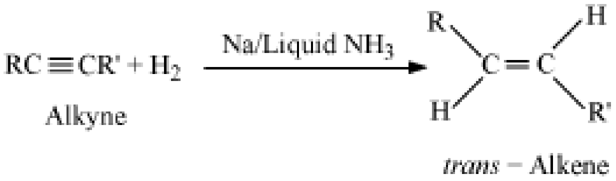
Preparation and Properties of Alkenes

Alkenes : We have studied that alkenes are unstaturated hydrocarbons containing carbon-carbon double bonds with general formula C_nH_{2n} . They are reactive in nature, so they are hardly found in free state.

Preparation

- **From alkynes**: Partial reduction of an alkyne in the presence of partially deactivated palladised charcoal (known as Lindlar’s catalyst), or in the presence of sodium, in liquid NH_3.





- **From Alkyl Halides**: On heating alkyl halides (R − X) with alcoholic potassium hydroxide

- The reaction is known as dehydrohalogenation.

- It is an example of β-elimination (H atom is eliminated from the β carbon atom).

- The rate of reaction depends upon both the nature of halogen atom and the alkyl group. For halogens, the rate of reaction decreases in the order

  Iodine > Bromine > Chlorine

  while for alkyl groups, the rate of reaction decreases in the order

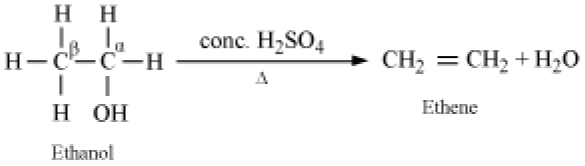
  Tertiary > Secondary > Primary (for alkyl groups)

- **From Vicinal Dihalides**: On treatment with zinc metal, vicinal dihalides (dihalides − with two halogen atoms attached to two adjacent carbon atoms) give alkenes.

  $$CH_2Br-CH_2Br+Zn \longrightarrow CH_2=CH_2+ZnBr_2$$
  $$CH_3CHBr-CH_2Br+Zn \longrightarrow CH_3CH=CH_2+ZnBr_2$$

  → This reaction is called dehalogenation.

- **From Alcohols by Acidic Dehydration:**



- **From Alcohols by Dehydration using Al_2O_3 as catalyst**

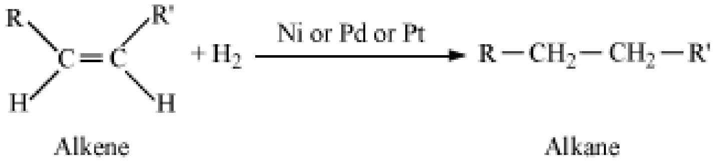
$$C_2H_5\,OH \xrightarrow[300\ °C]{Al_2\,O_3} C_2H_4 + H_2O$$

Physical Properties of Alkenes

- First three members are gases; the next fourteen are liquids; and the higher ones are solids.
- Ethene is a colourless gas, with a faint sweet smell.
- All the alkenes are colourless, odourless, insoluble in water and fairly soluble in non-polar solvents.
- Boiling point of alkenes increases regularly with increase in size.
- Boiling points of straight chain alkenes are higher than those of isomeric branched-chain compounds.

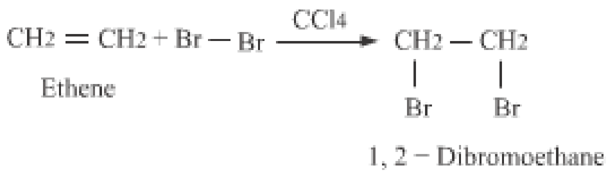
Chemical Properties of Alkenes

- **Addition of hydrogen:**

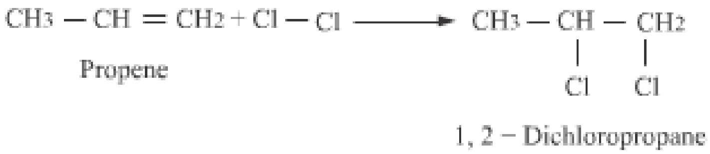


- **Addition of halogens:**

Bromine and chlorine react with alkene to form vicinal dihalides (iodine does not undergo addition reaction under normal conditions).



$$\underset{\text{Ethene}}{CH_2 = CH_2} + Br - Br \xrightarrow{CCl_4} \underset{\text{1, 2 − Dibromoethane}}{\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}}}$$



$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + Cl - Cl \longrightarrow \underset{\text{1, 2 − Dichloropropane}}{CH_3 - \underset{Cl}{\underset{|}{CH}} - \underset{Cl}{\underset{|}{CH_2}}}$$

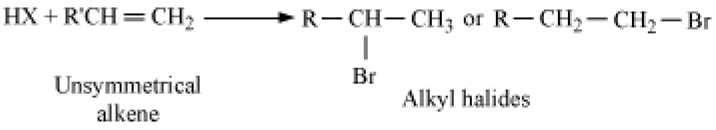
Addition of hydrogen halides: (HX; X = Cl, Br, I)

- Addition of hydrogen halides to alkenes is an electrophilic addition reaction which results in the formation of alkyl halides.
- Order of reactivity of hydrogen halides is HI > HBr > HCl

Addition of hydrogen halides to symmetrical alkenes

$$HX + \underset{\text{Symmetrical alkene}}{CH_2 = CH_2} \longrightarrow CH_3 - CH_2 - Br$$

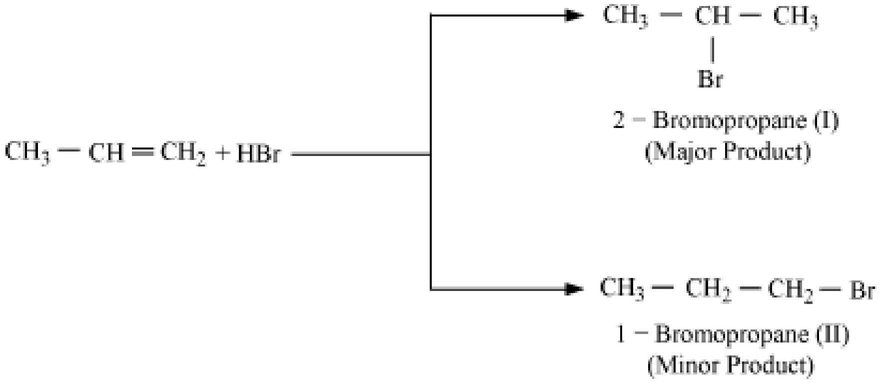
Addition of hydrogen halides to unsymmetrical alkenes



$$HX + \underset{\text{Unsymmetrical alkene}}{R'CH = CH_2} \longrightarrow \underset{\text{Alkyl halides}}{R - \underset{Br}{\underset{|}{CH}} - CH_3 \text{ or } R - CH_2 - CH_2 - Br}$$

Addition of hydrogen halides to unsymmetrical alkenes follows Markovnikov's rule.

Markovnikov's Rule

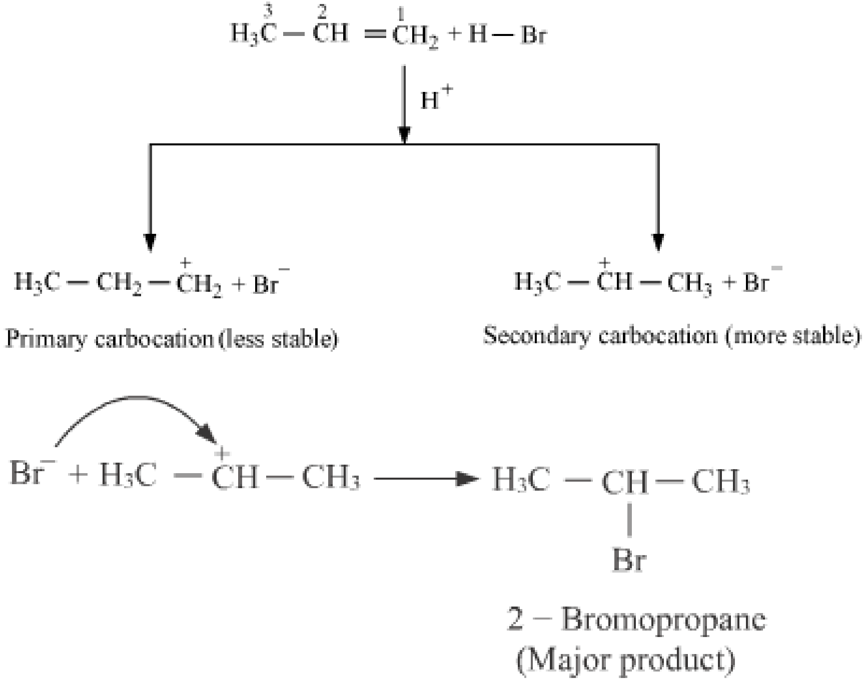


$$CH_3 - CH = CH_2 + HBr \longrightarrow \begin{cases} CH_3 - \underset{Br}{\underset{|}{CH}} - CH_3 & \text{2 − Bromopropane (I) (Major Product)} \\ CH_3 - CH_2 - CH_2 - Br & \text{1 − Bromopropane (II) (Minor Product)} \end{cases}$$

- Negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

  I is the major product.

- **Mechanism:**



Anti-Markovnikov's Addition (Or Peroxide Effect or Kharash Effect)

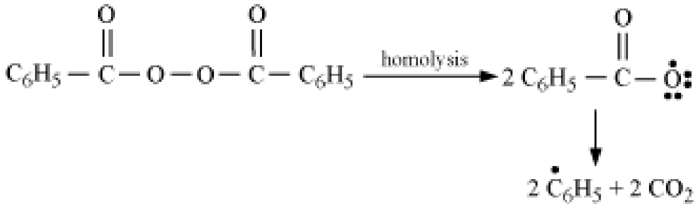
- Addition of HBr to unsymmetrical alkenes in the presence of peroxide gives a product contrary to Markonikov's rule.

$$CH_3-CH=CH_2+HBr\xrightarrow{(C_6H_5CO)_2O_2}CH_3-CH_2-CH_2-Br$$

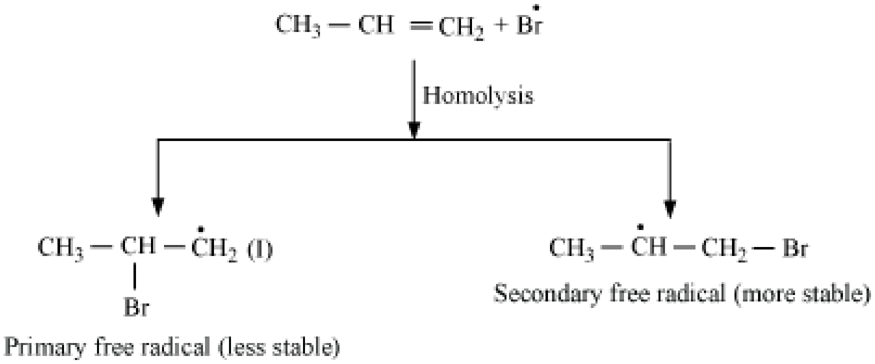
1-Bromopropane

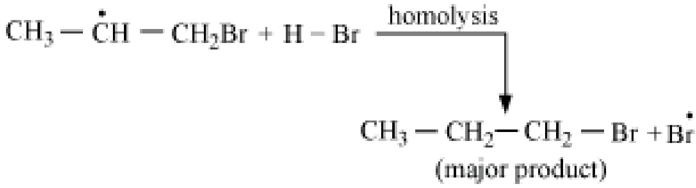
- **Mechanism:**

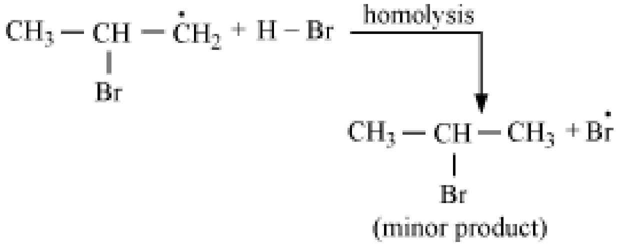
-



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5\xrightarrow{\text{homolysis}}2\,C_6H_5-\overset{O}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{O}}{:}\longrightarrow 2\,\dot{C}_6H_5+2\,CO_2$$

- $\dot{C}_6H_5 + H - Br \xrightarrow{\text{homolysis}} C_6H_6 + \dot{B}r$
- 

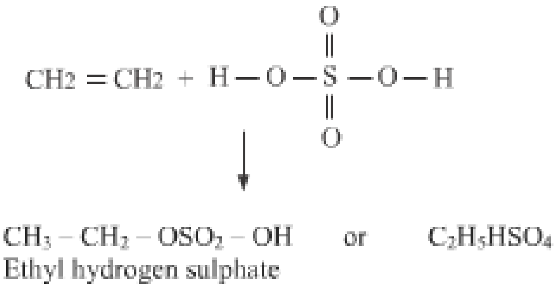
- 

- 

- Peroxide effect is observed only with HBr, and not with HCl and HI
- Reason:
- HCl bond is stronger (430.5 kJ/mol) and is not cleaved by the free radicals.
- HI bond is weaker and the iodine free radicals combine to form iodine molecules, instead of adding to the double bond.

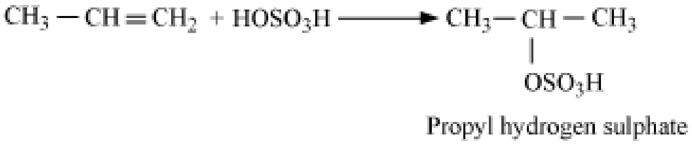
Some Other Chemical Properties of Alkenes

- **Addition of H_2SO_4** (In accordance with Markovnikov's rule)



$$CH_2=CH_2 + H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H \downarrow CH_3-CH_2-OSO_2-OH \text{ or } C_2H_5HSO_4$$

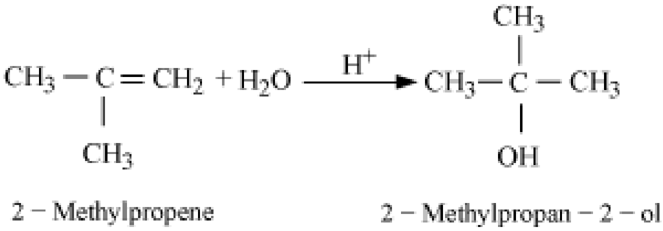
Ethyl hydrogen sulphate



$$CH_3-CH=CH_2 + HOSO_3H \longrightarrow CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$$

Propyl hydrogen sulphate

- **Addition of water** (In accordance with Markovnikov's rule)

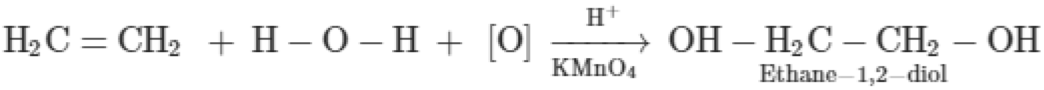


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

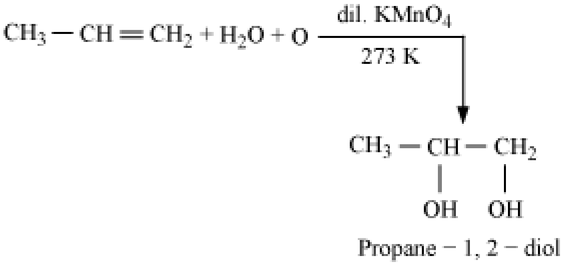
2 − Methylpropene 2 − Methylpropan − 2 − ol

- **Oxidation**

- With a cold, dilute, aqueous solution of $KMnO_4$ (Baeyer's reagent), alkenes are oxidised to give vicinal glycols.



$$H_2C=CH_2 + H-O-H + [O] \xrightarrow[KMnO_4]{H^+} OH-\underbrace{H_2C-CH_2}_{\text{Ethane}-1,2-\text{diol}}-OH$$



$$CH_3-CH=CH_2+H_2O+O \xrightarrow[273\ K]{dil.\ KMnO_4} CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

Propane − 1, 2 − diol

- Acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ oxidises alkenes to give ketones or acids (depending upon the nature of alkenes).

$$(CH_3)_2C=CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C=O+CO_2+H_2O$$

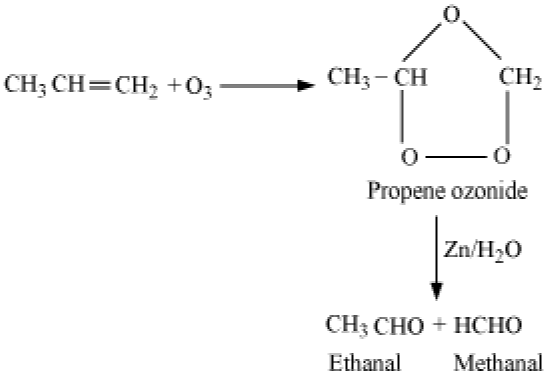
2-Methylpropene Propan-2-one

$$CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$$

But-2-ene Ethanoic acid

- **Ozonolysis**

$$H_2C=CH_2 + O_3 \xrightarrow[H_2O]{Zn} 2\ HCHO$$



- **Polymerisation**

$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp/pressure}} +\!\!\left(CH_2-CH_2\right)\!\!+_n$$

Polythene (Polymer)

$$n(CH_3-CH=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp/pressure}} +\!\!\left(\underset{\substack{|\\CH_3}}{CH}-CH_2\right)\!\!+_n$$

Polypropene (Polymer)

- **Combustion**

$$C_2H_4 + 3\,O_2 \longrightarrow 2\ CO_2 + 2\,H_2O + \text{Heat}$$

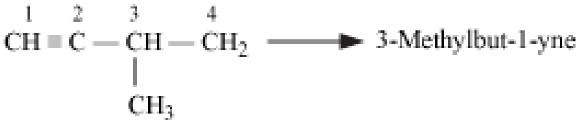
Uses: Some of the common uses of ethene are as follows:

- Manufacture of polyethene
- Making ethanol which is required for making cosmetics and toileteries
- Ripening of fruits
- Manufacture of raw material for detergents (epoxyethane)
- Producing oxy-ethylene flame (used for cutting and welding purposes)
- Manufacture of synthetic chemicals

Alkynes

- The general formula is CnH_{2n-2} .
- Contain at least one triple bond between two carbon atoms
- In IUPAC nomenclature:
- They are named as derivatives of the corresponding alkanes replacing ‘ane’ by the suffix ‘yne’.
- The position of the triple bond is indicated by the first the triply bonded carbon.

$$H_3\overset{1}{C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_3 \longrightarrow \text{Pent}-2-\text{yne}$$



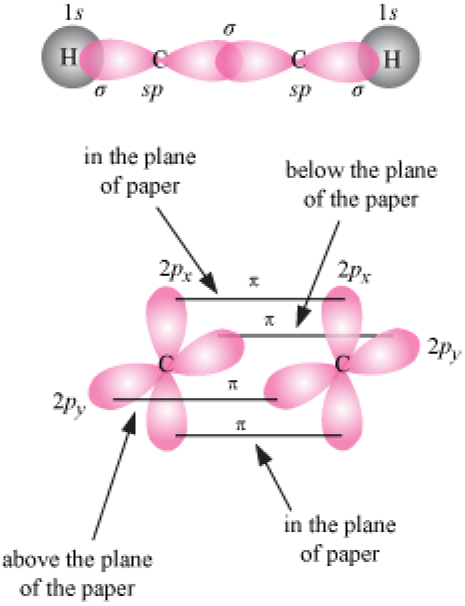
$$\overset{1}{CH}\equiv\overset{2}{C}-\underset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_2}\longrightarrow \text{3-Methylbut-1-yne}$$

- But-2-yne and but-1-yne differ in their structures due to the position of the triple bond. Hence, they are known as **position isomers.**

$CH_3-C\equiv C-CH_3$ But-2-yne

$CH_3-CH_2-C\equiv CH$ But-1-yne

Structure of Triple Bond (Ethyne)



- Each carbon atom of ethyne has two *sp* hybridised orbitals.
- C − C sigma bond is formed by head-on overlapping of two *sp* hybridised orbitals of the two C atoms.
- 2*p* orbitals of one carbon atom undergo lateral or sideways overlapping with 2*p* orbitals of other carbon atoms to form two *pi* (π) bonds.
- H − C − C bond angle is 180°.
- C ≡ C bond enthalpy = 823 kJ mol^{-1}
- C ≡ C bond length is 120 pm, which is shorter than those of C = C (133 pm) and C − C (154 pm) bonds.

Preparation of Ethynes

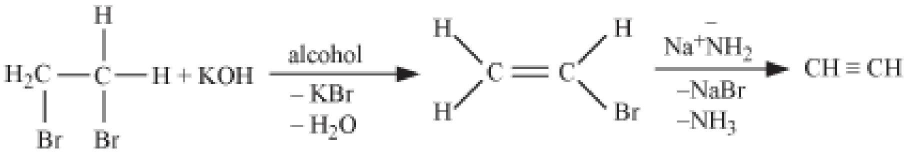
- **From calcium carbide (CaC_2)** − Ethyne is prepared by treating calcium carbide (which is obtained by heating quick lime with coke) with water.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \longrightarrow \underset{\substack{\text{Calcium} \\ \text{carbide}}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

- **From vicinal dihalides**



Physical Properties of Alkynes

- First three members are gases; the next eight are liquids; and the higher ones are solids.
- Colourless, odourless (except ethyne)
- Weakly polar in nature

- Lighter than water; immiscible with water, but soluble in organic solvents such as ethers, CCl_4, benzene, etc.

- Melting point, boiling point, and density increase with the increase in molar mass.

Chemical Properties of Alkynes

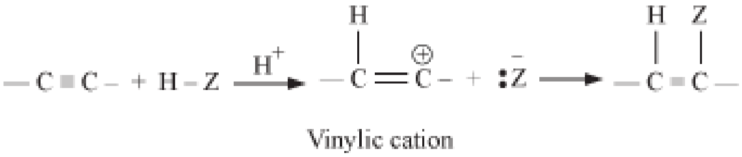
- Hydrogen atoms of ethyne (or any other alkyne), attached to the triply bonded carbon atom, are acidic in nature.

$$HC\equiv CH + Na \longrightarrow \underset{\substack{\text{Monosodium}\\ \text{ethynide}}}{HC\equiv C^{-}Na^{+}} + \frac{1}{2}H_2$$

$$HC\equiv C^{-}Na^{+} + Na \longrightarrow \underset{\substack{\text{Disodium}\\ \text{ethynide}}}{\overset{+}{Na}\overset{-}{C}\equiv\overset{-}{C}\overset{+}{Na}} + \frac{1}{2}H_2$$

$$CH_3-C\equiv C-H + \underset{\substack{\text{Sodamide}\\ \text{(base)}}}{\overset{+}{Na}\overset{-}{NH_2}} \longrightarrow \underset{\text{Sodium propynide}}{CH_3-C\equiv\overset{-}{C}\overset{+}{Na}} + NH_3$$

- **Addition Reactions of Alkynes**



$$-C\equiv C- + H-Z \xrightarrow{H^+} \underset{\text{Vinylic cation}}{-\overset{\overset{H}{|}}{C}=\overset{\oplus}{C}-} + \overset{-}{:Z} \longrightarrow -\overset{\overset{H}{|}}{C}=\overset{\overset{Z}{|}}{C}-$$

- In unsymmetrical alkynes, addition takes place according to

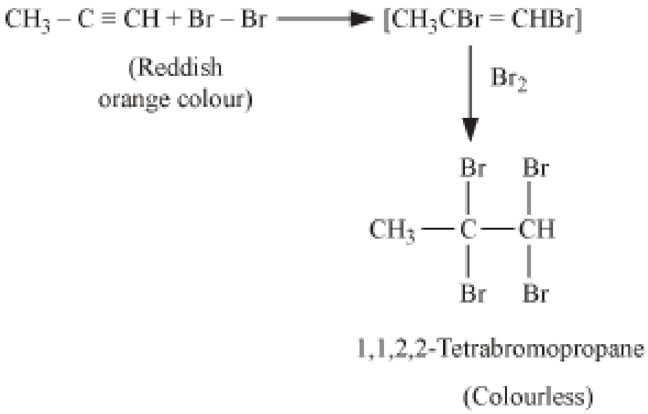
  Markovnikov's rule.

- **Addition of dihydrogen**

$$H-C\equiv C-H \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3$$

$$CH_3-C\equiv CH \xrightarrow[Pt/Pd/Ni]{H_2} [CH_3-CH=CH_2] \xrightarrow{H_2} CH_3-CH_2-CH_3$$

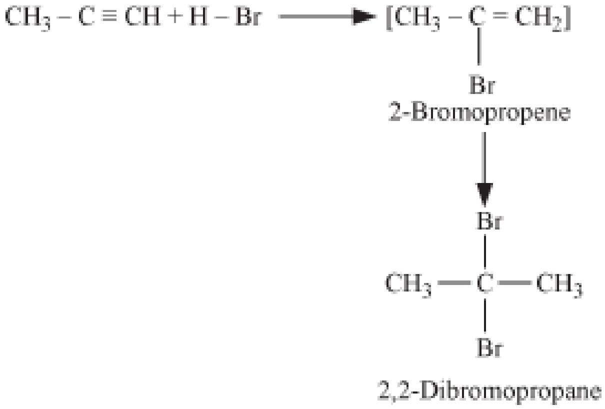
- **Addition of halogens**



-

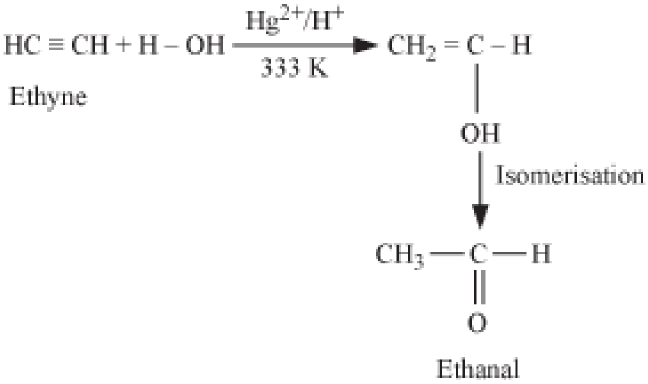
- It is used as a test for unsaturation.
- **Addition of hydrogen halides (HX; X = Cl, Br, I)**

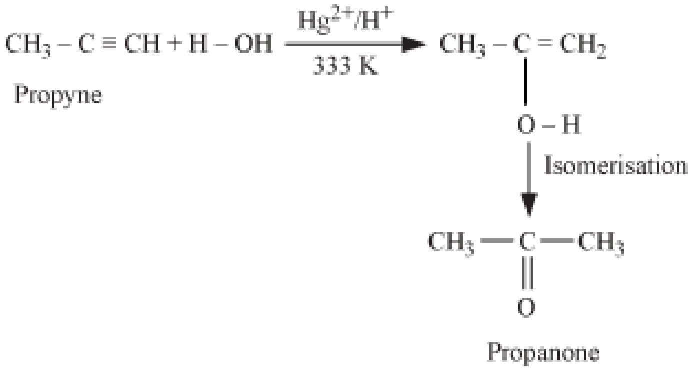
  HX adds to alkynes to form gem halides (in which two halogens are attached to the same carbon atom).



- **Addition of water**

  Generally, these do not react with water. However, on warming alkynes with mercuric sulphate and dilute sulphuric acid at 333 K, one molecule of water adds to them to form carbonyl compounds.

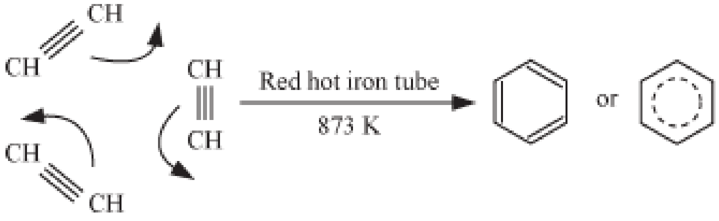




- **Polymerisation**
- **Linear polymerisation −** Polyacetytene or polyethyne is produced by linear polymerisation of ethene.

  Repeating units − CH = CH − CH = CH

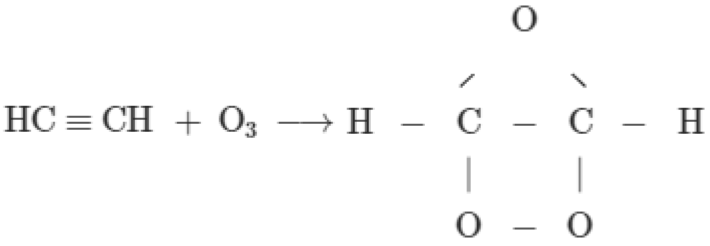
  Represented as − $\left(CH = CH - CH = CH \right)_n$
- **Cyclic polymerisation**



- **Oxidation**

$$2\,HC \equiv CH + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + \text{Heat}$$

- **Ozonolysis**



$$HC \equiv CH + O_3 \longrightarrow H - \overset{\diagup\!\!\!\overset{O}{}\!\!\!\diagdown}{C - C} - H$$

$$H - \underset{O\,-\,O}{\underset{|\quad\;\;|}{C - C}} - H$$

Uses: Some of the uses of ethyne are as follows:

- Oxy-acetylene welding at very high temperatures
- Illuminant in oxy-acetylene lamp
- Ripening and preservation of fruits
- Manufacture of several products like polymers. artificial rubber, oxalic acid, acetaldehyde, acetic acid, etc.

Test to Distinguish between Alkanes, Alkenes and Alkynes

Hydrocarbon	**Reagents**			
	Br$_2$ in CCl$_4$	**Alk. KMnO$_4$**	**Ammoniacal cuprous chloride**	**Ammoniacal silver nitrate**
Alkanes	No change	No change	No change	No change
Alkenes	Decolourisation of Br$_2$ solution	Decolourisation of KMnO$_4$ solution	No change	No change
Alkynes			Red precipitate is formed	White precipitate is formed

Benzene: An Aromatic Compound

Aromatic Hydrocarbons

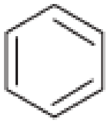
- Also known as arenes

- Most of them possess a pleasant odour (Greek − aroma). Hence, they are called aromatic compounds.

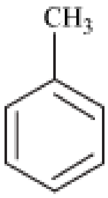
- They were found to contain benzene ring (which is highly unsaturated).

- **Benzenoids** are the aromatic compounds containing benzene ring and **non-benzenoids** are those not containing benzene ring.

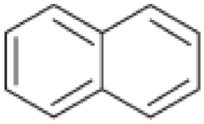
- Examples of arenes:



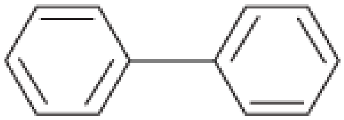
Benzene



Toluene

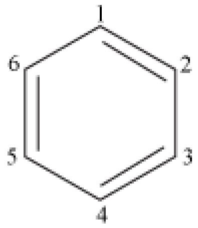


Naphthalene



Biphenyl

- **Nomenclature and isomerism:**

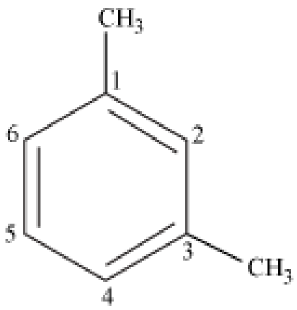


1, 2 or 1, 6 positions → *ortho* (*o*-)

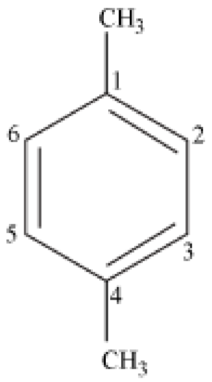
1, 3 or 1, 5 positions → *meta* (*m*-)

1, 4 positions → *para* (*p*-)

- **Structural isomers:**



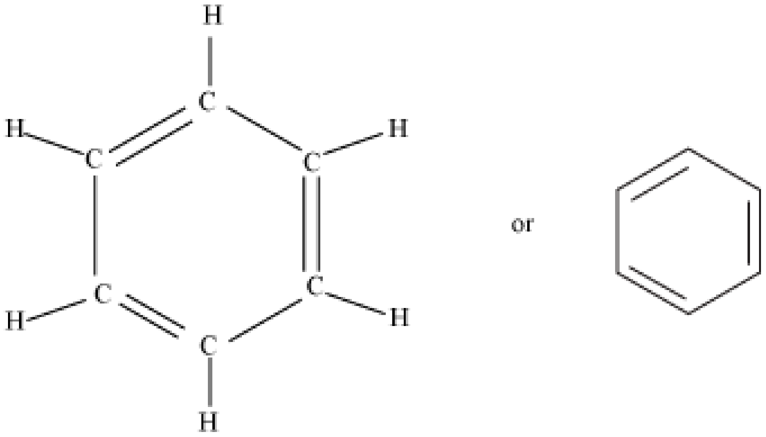
1,3-Dimethylbenzene
(*m* - Xylene)



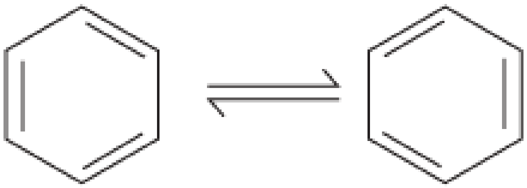
1,4 - Dimethylbenzene
(*p* - Xylene)

Structure of Benzene

- Molecular formula = C_6H_6
- It forms a triozonide, which indicates the presence of three double bonds.
- It produces only one mono-substituted derivative, which indicates that all the six carbon and six hydrogen atoms of benzene are identical.
- Kekule proposed the following structure of benzene:

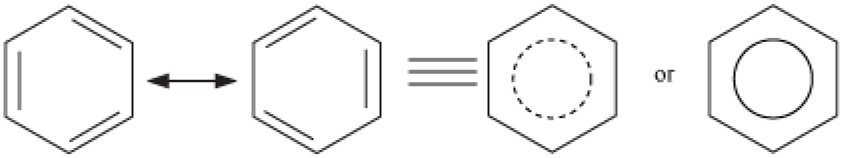


- Kekule suggested the oscillating nature of double bonds in benzene.

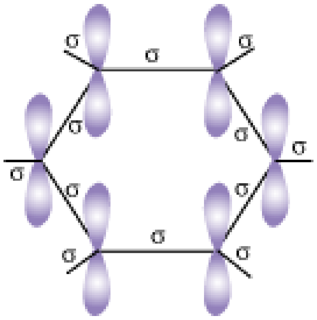


Resonance and Stability of Benzene

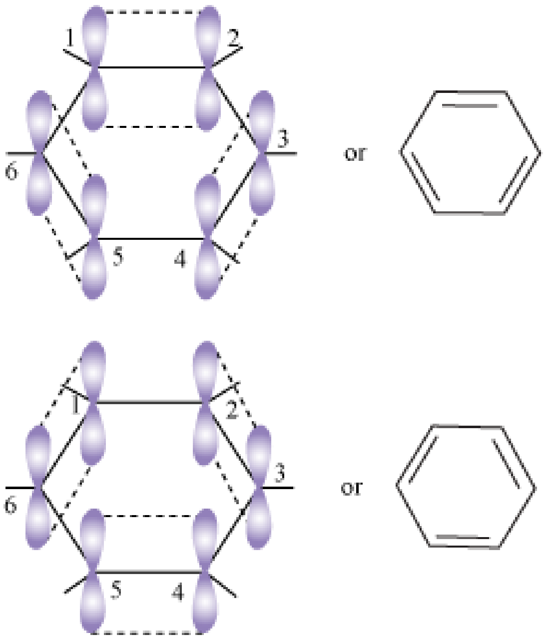
- Benzene is a hybrid of various resonating structures.



- All the six carbon atoms in benzene are sp^2 hybridised.
- There are six C − C σ bonds (formed by the overlapping of sp^2 orbitals) and six C − H σ bonds (formed by overlapping of $sp^2 - s$ orbitals).

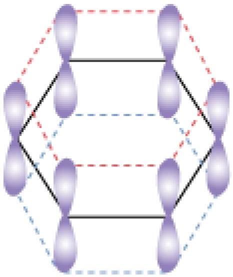


- The un-hybridised p-orbitals of carbon atoms form π bonds by lateral overlapping (shown in the figure).

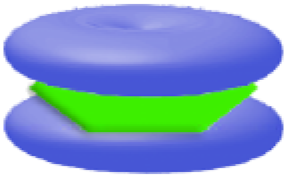


- X-ray diffraction data shows that all the C − C bond lengths are of the same order (139 pm).

- There is equal probability for the *p*-orbital of each carbon to overlap with the *p*-orbitals of the adjacent carbons.



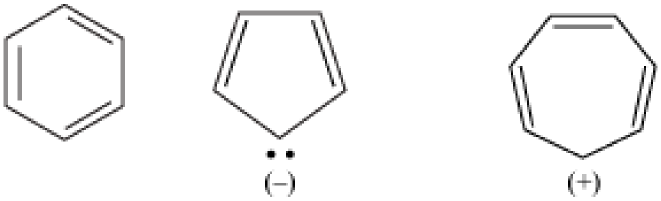
- This overlapping is represented by two rings of electron clouds, one above and one below the plane of hexagonal ring (shown in the figure).



- Six π electrons are delocalised and can move freely about the six-carbon nuclei.

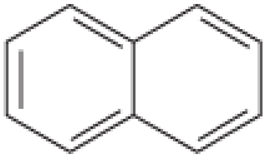
Aromaticity

- A compound is said to be aromatic if:
- It is planar
- There is complete delocalisation of the π-electrons in the ring
- It obeys Huckel Rule ($4n + 2$), i.e., it should have ($4n + 2$) π electrons in the ring, where n is an integer ($n = 0, 1, 2, \ldots$)
- **Aromatic compounds:**



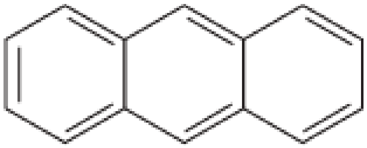
Benzene Cyclopentadienyl ion Cycloheptatrienyl ion

($n = 1$, 6π electrons)



Naphthalene

($n = 2$, 10π electrons)



Anthracene
($n = 3$, 14π electrons)

Uses of Some Common Aromatic Compounds

Benzene:

- It is used in dry cleaning.
- It is used as a solvent for oils, fats, resins, rubber, etc.
- It is used in the manufacture of perfumes, dyes, drugs, etc.

Naphthalene:

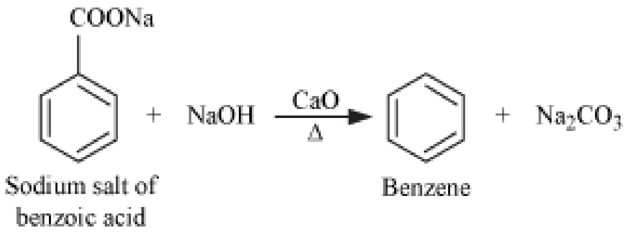
- It used in the synthesis of dyes.
- It is commonly used as an insecticide in the form of moth balls.

Preparation and Properties of Benzene

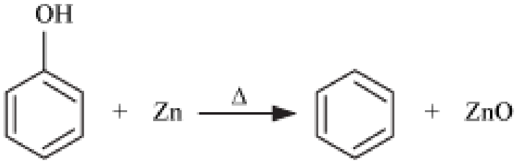
Preparation of Benzene

- By cyclic polymerization of ethyne

- By decarboxylation of aromatic acids



- By reduction of phenols



Physical Properties

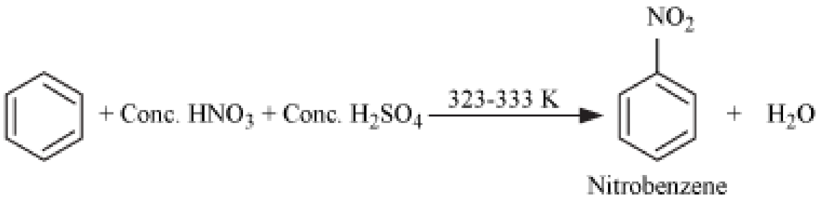
- Non-polar molecule
- Colourless liquid or solid with a characteristic aroma
- Aromatic hydrocarbons are insoluble in water, but readily soluble in organic solvents.
- Burn with sooty flame

Chemical Properties of Benzene

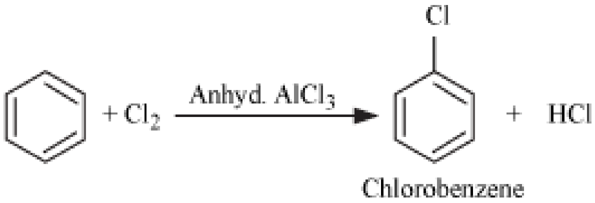
Arenes are characterized by electrophilic substitution reactions.

Electrophilic Substitution Reaction

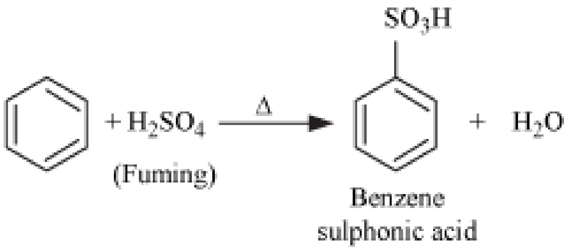
- **Nitration**



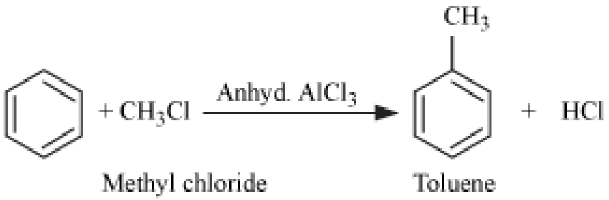
- **Halogenation**

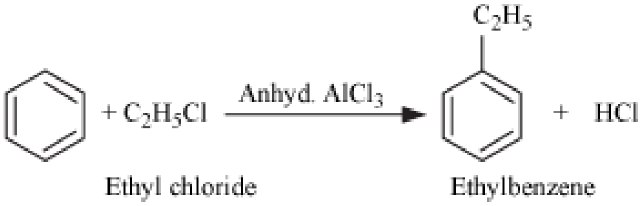


- **Sulphonation**

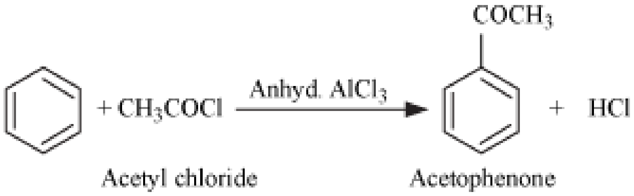


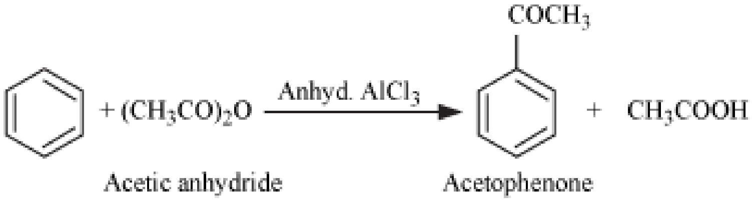
- **Friedel−Crafts alkylation**



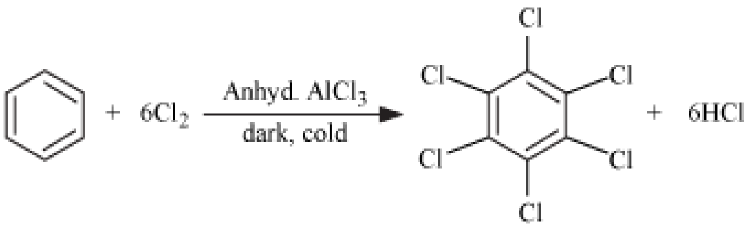


- **Friedel − Crafts acylation**





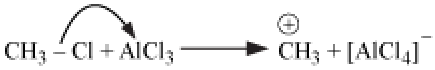
- Treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ gives hexachlorobenzene (C_6Cl_6).



Hexachlorobenzene

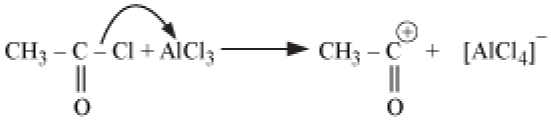
- **Mechanism of electrophilic substitution reaction**
- **Generation of electrophile (E^+)**

  For alkylation −−−



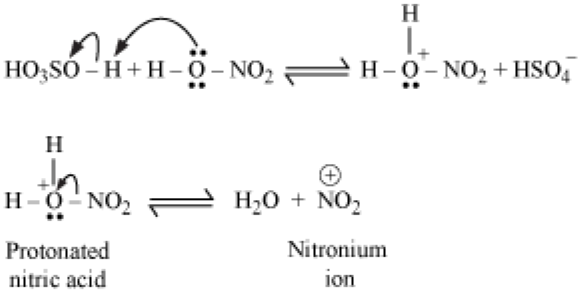
$CH_3-Cl + AlCl_3 \longrightarrow \overset{\oplus}{C}H_3 + [AlCl_4]^-$

  For acylation −−−

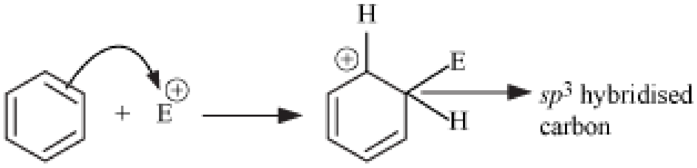


$CH_3-\underset{\underset{O}{\|}}{C}-Cl + AlCl_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{\overset{\oplus}{C}} + [AlCl_4]^-$

  For nitration −−−

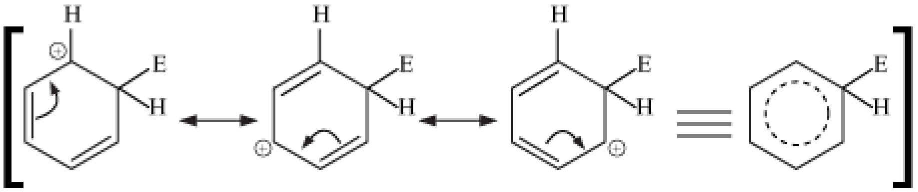


- **Formation of carbocation**



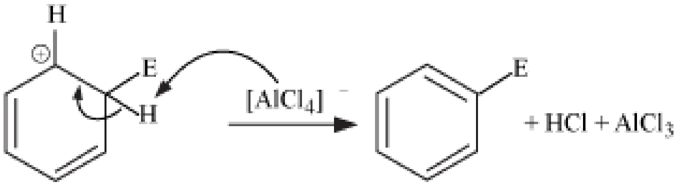
Sigma (σ) complex
[Arenium ion]

- Arenium ion gets stabilized by resonance as follows.



Arenium ion loses its aromatic character because delocalization of electrons stops at *sp*^{3} hybridised carbon.

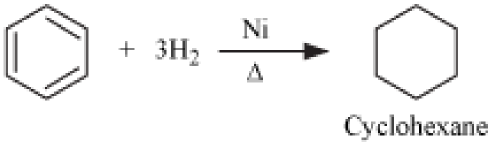
- **Removal of hydrogen**



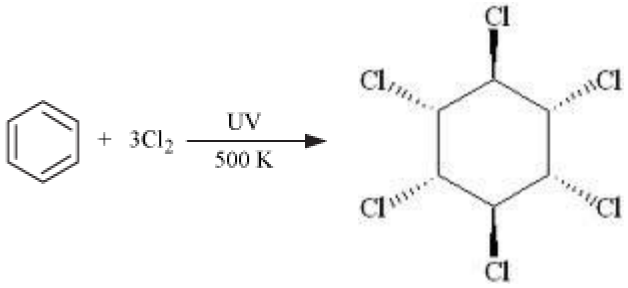
$[AlCl_4]^-$ attacks the a-complex and releases proton from *sp*^{3} hybridised carbon.

Addition Reactions

- Hydrogenation of benzene to give cyclohexane



- Three chlorine molecules add to benzene under ultraviolet light to give benzene hexachloride $C_6H_6Cl_6$ (BHC).



Combustion

Benzene burns in air with sooty flame to produce CO_2 and H_2O.

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

In general, for hydrocarbons,

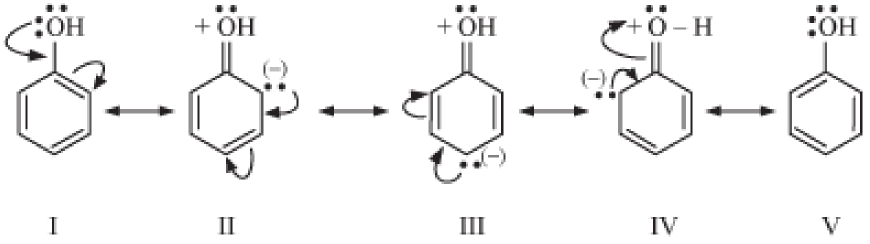
$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

Directive Influence of a Functional Group in Mono-substituted Benzene

- **Ortho and Para Directing Groups**
- Examples:

$-NH_2$, $-NHR$, $-NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$, halogens, etc.

- These groups direct the incoming group to the ortho and para positions.
- − OH group activates benzene for the attack by an electrophile at the *ortho* and *para* positions.



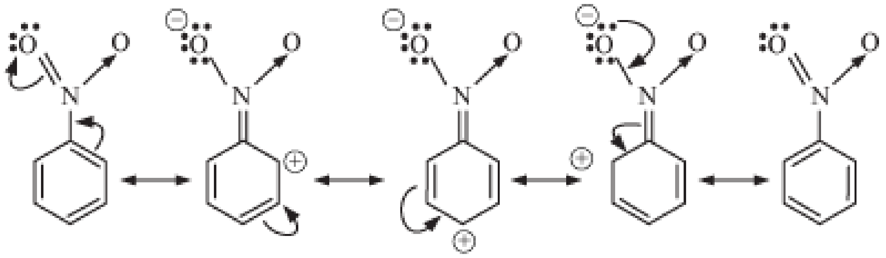
- Halogens are moderately deactivating because of their strong −I effect due to which overall electron density on benzene ring decreases. However, electron density on *o*− and *p*− positions is greater than that at the *m*-position due to resonance. Hence, halogens are also *o*− and *p*− directing groups.

- **Meta −Directing Groups (Or Deactivating Groups)**
- Examples:

$-NO_2$, $-CN$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$, etc.

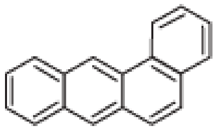
These groups direct the incoming group to *meta* position and hence, are called metal directing groups.

- Electron density is less on *o*− and *p*− positions as compared to *meta* position. Therefore, electrophile will attack at the *meta* position.

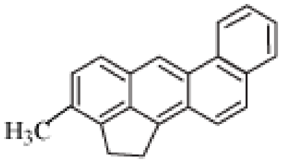


Carcinogencity and Toxicity

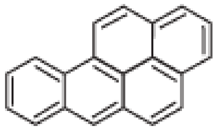
- Benzene and polynuclear hydrocarbons (containing more than two fused benzene rings) are carcinogenic.
- Polynuclear hydrocarbons are produced on incomplete combustion of tobacco, coal, and petroleum.
- These compounds enter into human body, damage DNA, and cause cancer.
- Some carcinogenic hydrocarbons are



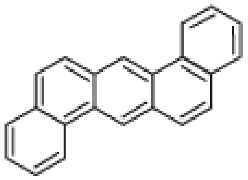
1,2-Benzanthracene



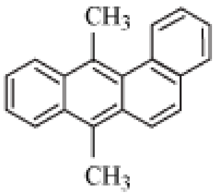
3-Methylcholanthrene



1,2-Benzpyrene



1,2,5,6-Dibenzanthracene



9,10-Dimethyl-1,2-benzanthracene