HYDROCARBONS

PREPARATION OF AN ALKANE-

(1) Hydrogenation Reduction- Reduction of unsaturated HC

Ethyle Helide)(Ethane)

WURTZ REACTION

R - X + 2Na + X - R <u>Dry Ethe</u>r R-R + 2 NaX

alkyl halide (Alkane)

R-X on treatment with Na metal in the presence of a dry ether gives higher alkanes, this is known as Wurtz Reaction. It is used for the preparation of higher alkanes containing an even number of a carbon atom.

->Convert Bromoethane to Butane

CH₃ - CH₂ - Br + 2Na + CH₃ - CH₂ - Br <u>Dry Ethane</u> CH₃ - CH₂ - CH₂ - CH₃ + 2NaBr

Limitations of Wurtg Redⁿ

CH₃ - I + Na + I - C₂H₅ Dry ethane CH₃ - CH₃ + C₂H₅ - C₂H₅ + CH₃ - C₂H₅ + NAI

CH₃ - I +2Na + I - CH₃ Dry ethane CH₃ - CH₃ + 2NAI

Etane

C₂H5 - I + 2Na + I - C₂H₅ <u>Dry ethane</u> C₂H₅ - C₂H₅ + 2 NAI

Butane

CH₃ - I +2Na + I - C₂H₅ Dry ethane CH₃ - C₂H₅ + 2NAI

Propane

If 2 different alkyl halides are taken in the wurtg Redⁿ, then it gives a mixture of 3 alkanes (different). As they are very close in their B.P, so may can't be separated by fractional distillation.

From Carboxylic acid - Decarboxylation (Removal of CO₂)

0
||

$$R - C - O^0$$
 Na + + NaoH Cap R-H + Na₂CO₂

Δ

(sodium salt of carboxylic acid) (Alkane)

The process of elimination of CO₂ from a carboxylic acid is known as decarboxyliation.

Sodium Propanoate

Question: Sodium salt of which acid is used for the preparation of propane. write chemical equation.

$$CH_3 - CH_2 - CH_2 - C - ONa^+ + Naon Cao CH_3 - CH_2 - CH_3 + propane + Na_2CO_3$$

Sodium Butanoate

KOLBE ELECTROLYTIC METHOD

An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing an even number of carbon atoms at the anode.

2CH COO- Na+ 2H O

Sodium acetate

Electrolysis

CH₃- CH₃+ 2CO₂+ H₂ + 2NaOH

The reaction is supposed to follow the following path:

i) 2CH₃ COO⁻ Na → 2CH₃- C- O⁻ + 2Na⁺

ii) At anode:

At Anode: (Oxidation) $2CH_3 - \overset{\parallel}{C} - 0^- \xrightarrow{-2e^-} 2CH_3$ $2CH_3 + 2CO_2$ Methy $2CH_3^{-} - CH_3 - CH_3$ At Cathode: (Reduction) $2H_20 \xrightarrow{+2e^-} 20H^- + 2H^ 2H \rightarrow H_2$

PHYSICAL PROPERTIES

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to the very little difference in electronegativity between carbon and hydrogen atom.

BOILING POINTS

Ethane < Propane < Butane

There is an increase in boiling point with increase in molecular mass. This is due to the fact that the inter molecular forces increase with increase vander Waal in mole.

Pentane > 2- Methylbutane > 2.2 - Dimethylpropane

In the isomeric alkanes, with the increase in a number of branched chains, the molecule attains the shape of a sphere. This result in a smaller area in contact and therefore, there are weak vander waalforces between molecule. so, that have a low boiling point.

CHEMICAL PROPERTIES

Substitution Reaction- The reaction in which hydrogenatom of alkane are substituted are known as substitution reaction.

$$CH_4 + Cl_2 \underline{hy} CH_3Cl + HCl$$

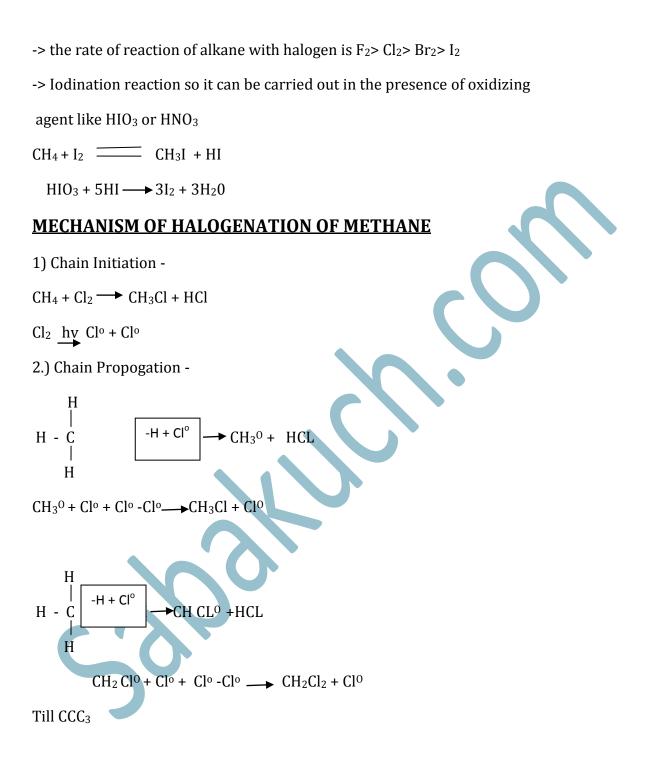
$$CH_3Cl + Cl_2 \underline{hy} CH_3Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \underline{hy} CHCl_3 + HCl$$

$$CnCl_3 + Cl_2 \underline{hy} CCl_3 + HCl$$

$$F_2 > Cl_2 > Br_2 > I_2$$

Reactible gives Reversible reaction



3) Chain Termination If no sunlight -> $Cl_{0} + Cl_{0} \longrightarrow Cl_{2}$ -> $CH_{3}^{0} + Cl_{0} \longrightarrow CH_{3}Cl$

 \rightarrow CH₃^o + CH₃ \rightarrow C₂H₆

COMBUSTION REACTION

When carbon compound reacts with O₂.

Complete oxidation - CH H₂N + 2 + (3n + 1) O₂ \rightarrow HCO₂ + (N+1) H₂O + Δ

Incomplete Oxidation- CH $H_2N + 2 + O_2 \rightarrow HC(S) + {(N+1)} H_2O(I)$

Controlled Oxidation- 2 CH4 + O_2 Cu/523K/100 atm 2CH₃OH

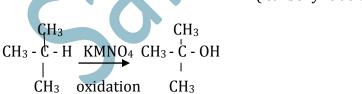
(Alcohol)

 $CH4 + O_2 MO_2O_3 HCH0 + H_2O$

2CH₃ - CH₃ + 3O₂ (CH₃COO)₂Mn _2CH₃COOH + 2H₂O

(Aldehyde)

(carboxylic acid)



= It is making alcohol and not carboxylic because the tertiary carbon does not have valency to hold carboxylic acid.

ISOMERISM REACTION

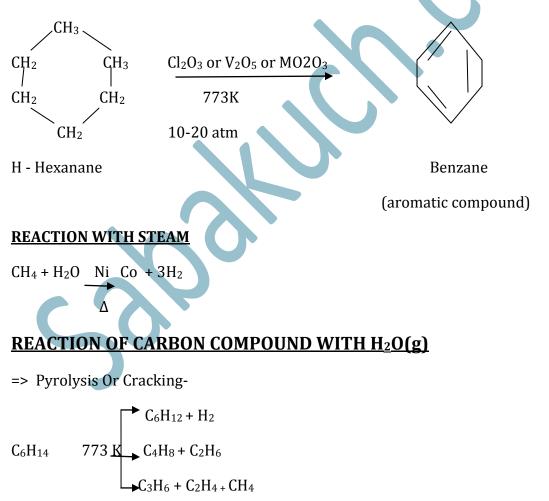
CH₃ - (CH₂)₄ - CH₃ anhydrous CH₃ - CH₂ -

- 2- methylpentane + CH₃. CH₂- CH- CH₂- CH₃ CH₃

3- methylpantane

In presence of anhydrons AlCl₃ + HCL an alkane gives isomers (chain).

AROMATISATION OR REFORMING



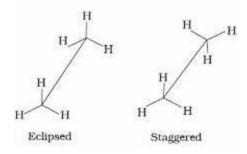
CONFORMATION

Conformations Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis. This permits free rotation about C–C single bond. This rotation results in different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers. Alkanes can thus have an infinite number of conformations by rotation around C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol–1 due to the weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called torsional strain.

Conformations of ethane: Ethane molecule (C2H6) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into an infinite number of spatial arrangements of hydrogen atoms attached to on e carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called conformational isomers (conformers). Thus, there are an infinite number of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called eclipsed conformation and the other in which hydrogens are as far apart as possible are known as the staggered conformation. Any other intermediate conformation is called a skew conformation. It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by Sawhorse and Newman projections.

SAWHORSE PROJECTIONS

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. The Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig-

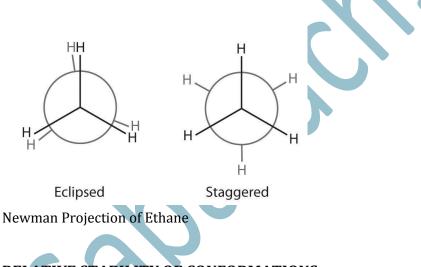


Sawhorse projection of Ethane

NEWMAN PROJECTIONS



In this projection, the molecule is viewed at the C–C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in fig-



RELATIVE STABILITY OF CONFORMATIONS:

As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in an increase in electron cloud repulsions. To check the increased repulsive forces, the molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects the stability of a conformation, is called torsional strain. The Magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called dihedral angle or torsional angle. Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain. Thus, it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol–1, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol–1 through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

ALKENES

ISOMERISM

=> Structural Isomerism-

For e.g., Butane

- 1)- $CH_2 = CH CH_2 CH_3$ But -1-ene
- 2)- CH_3 $CH = CH_1 CH_3$ But -2-ene
- 3)- CH₂ = C -CH₃
- 2-Methylprop-1-ene

Structure 1) & 3) and 2) and 3) are examples of chain isomers.

Whereas 1.) & 2) are examples of positions isomerism.

=> Stereo Isomer

The restricted rotation of an atom around a doubly bonded carbon atom gives rise to different geometries. the stereo isomers of this type are called geometrical isomers.

It is of two types -

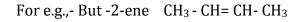
1. Cis Isomers

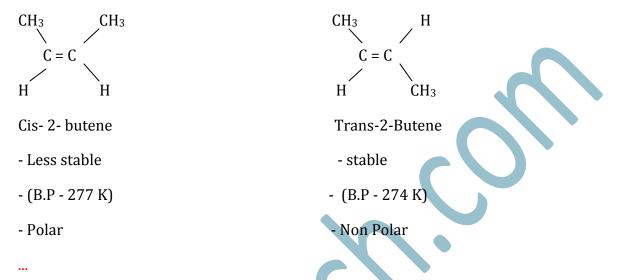
2. Trans Isomers

Solid - trans BP > Cis

Cis- In which two identical atoms or groups lie on the same side of the double bond.

Trans- the isomers of the type in which identical atoms or groups lie on the opposite side of the double bond.





Cis-isomers of alkene is more polar that trans isomer.

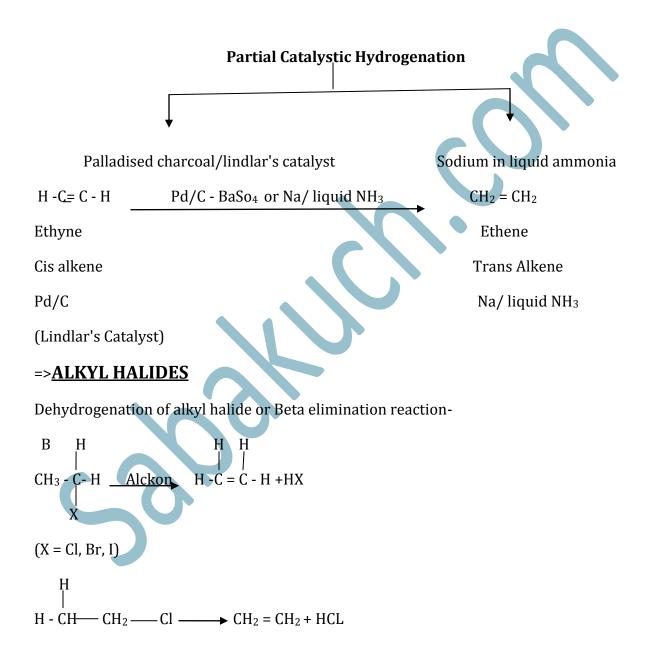
The dipole moment of trans is almost zero. so, trans-but-2-ene is non-polar because in trans the two methyl groups are in the opposite direction.

Triple moment of C-CH₃ bond cancels out the effect of each other. So, trans is non- polar.



PREPARATION OF ALKENE FROM-

Alkyne partial catalystic Hydrogenation Alkene



=><u>ALCOHOL</u>

Dehydration of Alcohol/ Beta elimination reaction

H OH | |R - C - C - H <u>Conc. H₂So₄</u> R - HC = CH₂ + H₂O | | |H H

Ethene

=><u>VICINAL DIHALIDE</u>

 $CH_2 - CH_2 + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$ | | | Br Br

Dibromoethane

Dihalides in which two halogen atoms are attached to two adjacent carbon atom.

Dehalogenation

Chemical properties of alknes

=>Electrophilic addition Reaction - Alkenes are the rich sources of loosely held pi e⁻ due to which they show addition reaction in which electrophiles add on to the C=C to form addition products.

Reaction in Alkenes-

Addition of dihydrogen

 $\begin{array}{ccc} H_2C = CH_2 + H_2 \longrightarrow & CH_2 - CH_2 \text{ Or } CH_3 - CH_3 \\ & & | & | \\ & H & H \end{array}$

Addition of Halogens

Addition of Halogen Acid

$$CH = CH_2 + HCI \longrightarrow H \quad -C - C - H$$

Symmetrical alkene - i.e- Similar groups attached to double bond. For e.g., But-2-ene

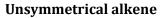
Cl H

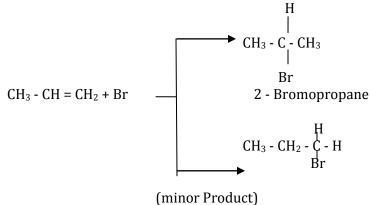
$$H_{3}C - HC - CH - CH_{3}$$

$$H = CH - CH_{3} + HBr_{2}$$

$$H_{3}C - CHBr - CH_{2} - CH$$

$$H_{3}C - CHBr - CH_{2} - CH$$

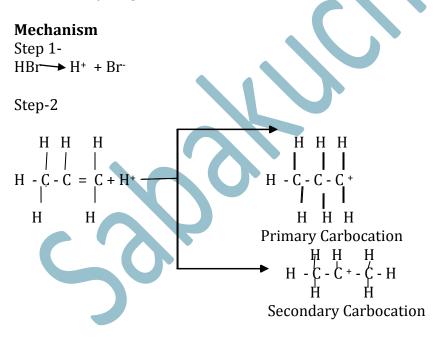




1-Bromopropane

MARKOVNIKOV'S RULE

During the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the attacking reagent is added to the unsaturated carbon which possess lesser number of hydrogen atoms.



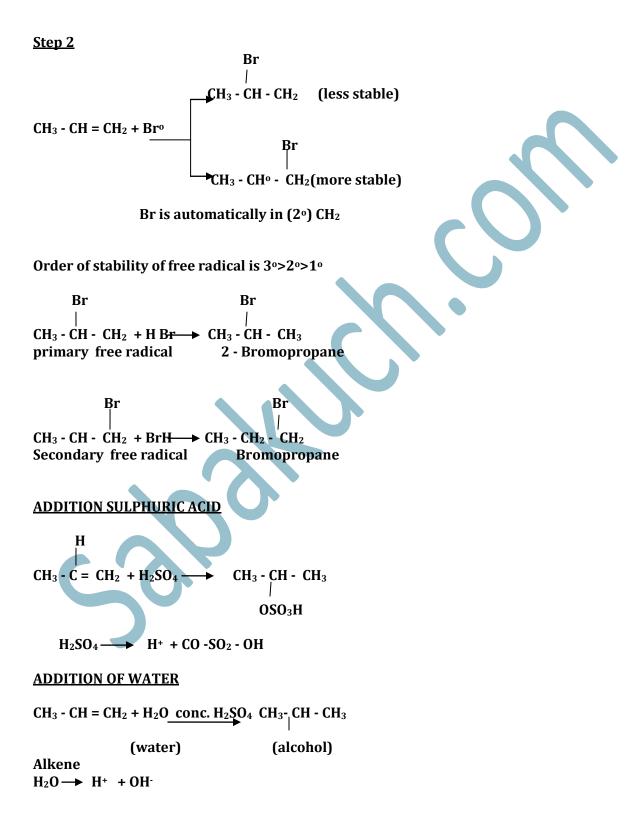
Order of stability of carbocation- $3^0 > 2^0 > 1^0$

 $\begin{array}{c} H \\ | \\ CH_3 - C^+ - CH_3 + Br \longrightarrow CH_3 - C - CH_3 \\ | \\ Br \end{array}$

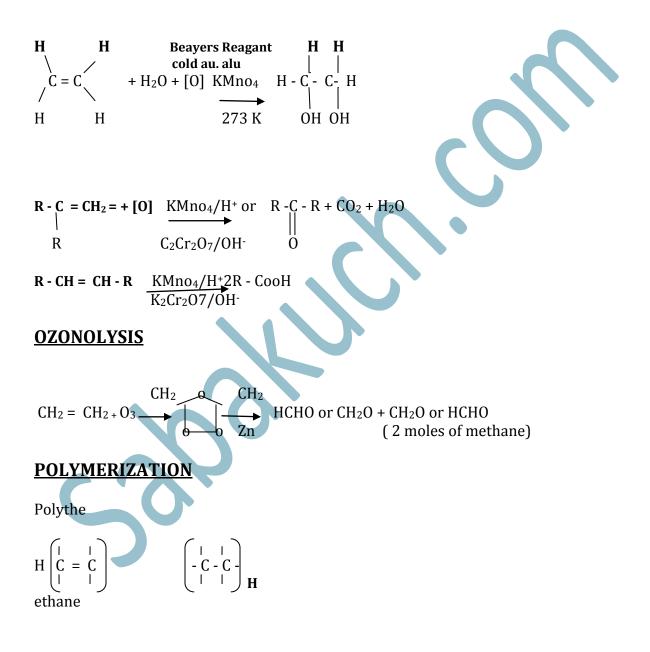
Secondary carbocation 2- Bromopropane

Anti Markovnikov Rule(Periodic effect) (opposite of Markovnikov's Rule)

ΗΗ Η H H Br 1 H - C - C = C + HBr <u>Peroxide</u> H - C- C - C - H Η Η ннн Step-1 0 0 C₆H₅ - C - O - O - C - C₆H₅ (benzoyl peroxide) C₆H₅ - C - O - O - C - C₆H₅ Hemolytic $2C_6H_5C-O$ Clearage ||0 0 2C₆H₅ C - O^o \bullet C₆H₅ \circ + CO₂ phenyl free radical 0 C_6H_5 + HBr \blacktriangleright C₆H₆ + Br **Bromine free radical**



OXIDATION REACTION



Polythene is formed by the combination of a large number of ethane molecules at high temperature, pressure and in the presence of a catalyst. The large molecules obtained are called polymers and the method is called polymerization.

ALKYNES

CnH₂n - 2

Vicinal Dihalide

Eq.of question

H₂C - CH₂alckon A NaNH₂ B

Find A and B

 $H_2 - C - C - H_2$ alckon $H - C = CH_2$ NaN H_2 $HC = CH + NH_2 - Nacl$

From Cal carbide (if comes it is done only for the preparation of Ethyl)

 $\begin{array}{c} CaCO_3 \\ (Lime stone) \end{array} \qquad \begin{array}{c} Cao + CO_2 \\ (quick lime) \end{array}$

CaO+ 3C CaC₂ + CO quick lime coke calcium carbide

 $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC = CH$ calcium carbide calcium hydroxide ethyne

CHEMICAL PROPERTIES

1. Acidic Nature of alkynes- In Ethyne, the carbon is Sp hybridized due to maximum percentage of 'S' character, the Sp hybridized orbital's of carbon atoms in ethyne molecules have the highest electro negatively so these attract the shared electron pair of the CH bond of ethyne to a greater extent than that of the Sp² hybridized of orbital's of carbon in ethene and Sp³ hybridized orbital of carbon in ethane for eg.

HC = CH + Na $HC = CNa + 1/2 H_2$

Ethyne

This reaction is not shown by Alkanes and alkynes so it can be used to distinguish between alkyne, alkane and alkene.

Electrophillic addition reaction

1) Addition of Halogen acid (HX)

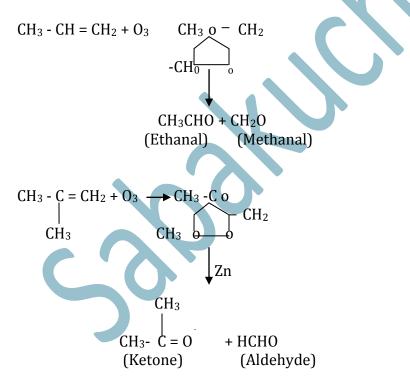
 $\begin{array}{ccc} H3C - C \equiv CH + HCl & C - C = C \\ & & & & \\ Propyne & Cl & H \end{array}$

2) Addition of Halogen

HC = CH + 2 Br
$$CCl_4$$
 H - C - C - H
Br Br
Br Br

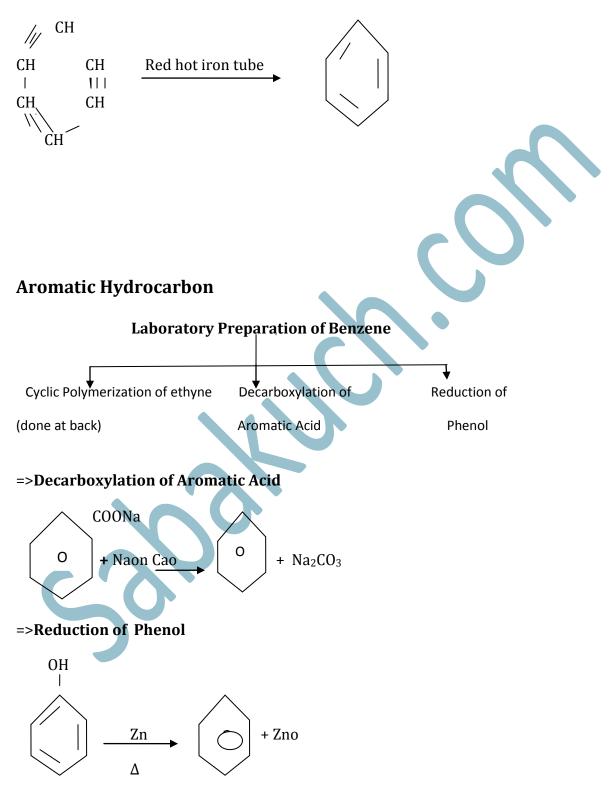
Reddish- orange color of the solution of bromine in CCl₄ is decolorized. This is the test for unsaturation.

OZONOLYSIS



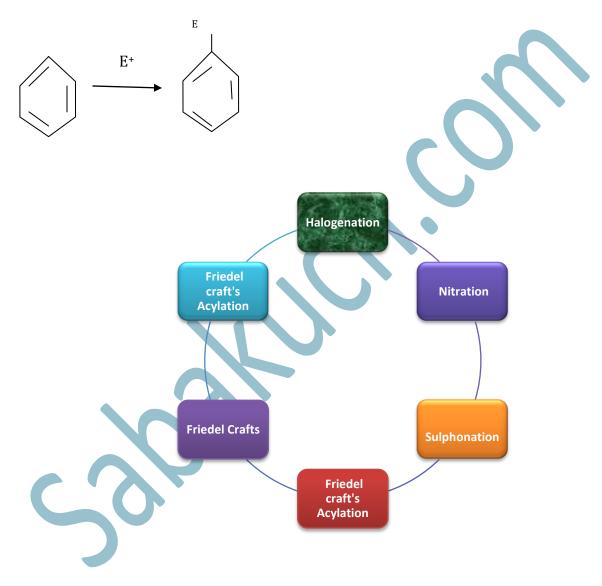
3). Addition of HBr $CH_3 - C = CH + HBr \longrightarrow [CH_3 - C = CH_2] \xrightarrow{HBr} Br$ B_R 2,2-Bromopropene CH₃-C-CH₃ Propyne 4). Addition of Water B_R OH ↓ Η (0 is electronegative) $CH = CH + H_2O$ HgS04 / H2S04 (H+,OH-) **60**⁰ H⁺/ HgSO₄ $CH = CH = \frac{HgS0_4 / H_2S0_4}{H^+ / HgS0_4}$ $CH_3 - C = CH + H_2O - HgSO_4 - CH_3 - C$ = CH Propyne OH Isomerization $CH_3 - C = CH_3$ 0 **POLYMERIZATION** Polymerization-(a) Linear Polyethyne

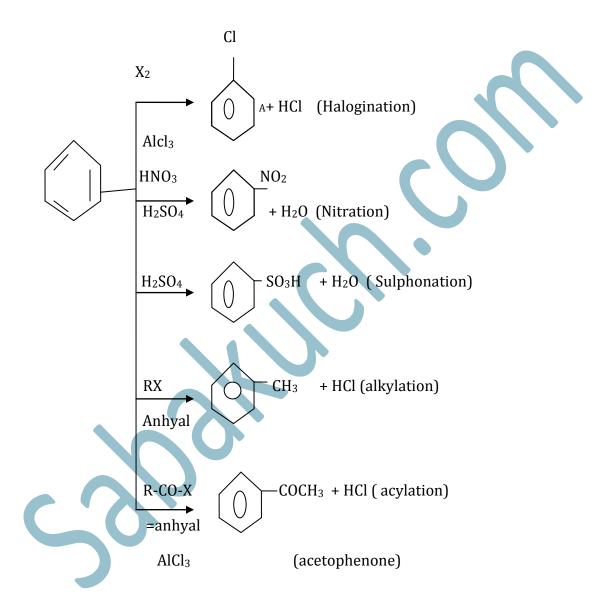




CHEMICAL PROPERTIES OF AROMATIC

1). Electrophillic Substitution Reaction-

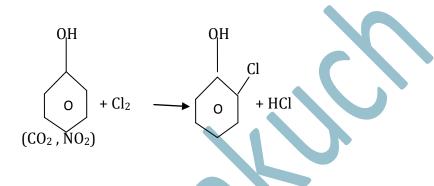




DIRECTIVE INFLUENCE OF FUNCTIONAL GROUP IN MONO-SUBSTITUTION OF BENZENE

COH, (l, OCH₃)

1.) Electron donating group on the benzene ring are ortho- para directing because one pair of a substitutional atom undergoes resonance with the pi e⁻ of the benzene ring and e⁻ density increases at ortho and para e⁻ density increases at ortho and para so, they are ortho-para directing.



2.) Electron Withdrawing group on the benzene ring are meta directing because these groups direct the incoming group to the meta position-

