HYDROCARBON

ALKANE

Introduction :

Alkanes are the saturated non-polar hydrocarbon having general formula C_nH_{2n+2}.
Hydrocarbon – Those organic compounds which contain only carbon and hydrogen atoms are known as hydrocarbons.

Preparation of alkane :

(I) By catalytic reduction of alkenes and alkynes

$$R-C\equiv C-R' \xrightarrow[\text{Ni, Pt or Pd}]{H_2,25^\circ C} R-CH_2-CH_2-R'$$

$$R-CH=CH-R' \xrightarrow[\text{Ni, Pt or Pd}]{H_2,\,25^\circ C} R-CH_2-CH_2-R'$$

Hydrogenation → Addition of H_2 to unsaturated bond.

Hydrogenation is of two kind

(a) Heterogeneous and **(b) Homogeneous**

(a) Heterogeneous → It is two phase hydrogenation, the catalyst is finely divided metal like Ni, Pt or Pd and a solution of alkene.

(b) Homogeneous → It is one phase hydrogenation where both catalyst and alkenes are in solution phase. In this, hydrogenation catalyst are organic complex of transition metal like Rh or Ir.

Hydrogenation is exothermic, qualitative and during the hydrogenation, total heat evolved to hydrogenate one mole of unsaturated compound is called heat of hydrogenation. Heat of hydrogenation is the measurement of stability of isomeric alkenes.

$$\text{Stability of alkene} \propto \frac{1}{\text{Heat of hydrogenation}}$$

(II) From alkyl halide

(A) From organometallic compound →

compound having $\overset{\delta-}{C}-\overset{+\delta}{M}$ bond.

(M → metal)

(i) By Wurtz reaction

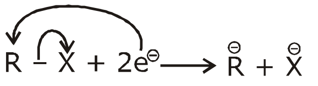
$$2R-X+2Na \xrightarrow{\text{dry ether}} R-R+2NaX$$

$$R-X + R'-X \xrightarrow[\text{ether (dry)}]{Na} R-R,\ R-R',\ R'-R'$$

Mechanism ⟶ Two mechanisms are suggested

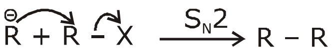
(a) Ionic mechanism

$$2Na \longrightarrow 2Na^{+} + 2e^{-}$$



$$R-X + 2e^{\ominus} \longrightarrow \overset{\ominus}{R} + \overset{\ominus}{X}$$

(1°, 2°)



$$\overset{\ominus}{R} + R-X \xrightarrow{S_N2} R-R$$

(1° or 2°)

$$\overset{\oplus}{Na} + \overset{\ominus}{X} \longrightarrow NaX$$

(b) Free radical mechanism

$$Na \longrightarrow \overset{\oplus}{Na} + \overset{\ominus}{e}$$

$$R-X + \overset{\ominus}{e} \longrightarrow R^{\bullet} + X^{\ominus}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$

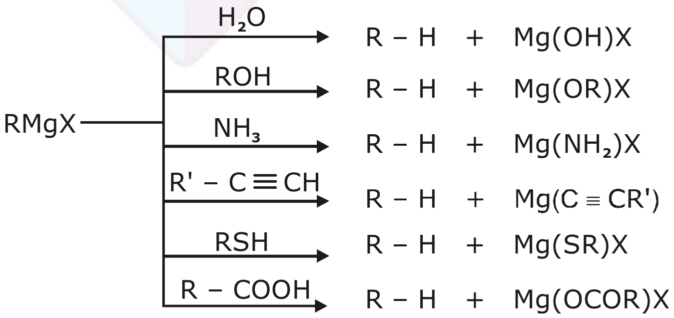
Note :

The alkyl halide should be 1º or 2º, with 3º R – X. S_N2 and free radical coupling is not possible due to steric hinderance, so in that case elimination or disproportionation is possible.

In the ionic mechanism, alkyl sodium $(\overset{\ominus}{R}\overset{\oplus}{Na})$ gives $\overset{\ominus}{R}$ which is strong base as well as nucleophile so it gives S_N2 reaction with R – X. So, ether should be dry otherwise, if moisture is present then $\overset{\ominus}{R}$ forms R – H instead of R – R with H_2O.

(ii) By Grignard Reagent. $\underset{1°,2°,3°}{R-X} \xrightarrow[\text{ether}]{Mg} RMgX$

$$RMgX + \text{All active H containing compound} \longrightarrow R-H$$



$$RMgX \xrightarrow{H_2O} R-H + Mg(OH)X$$

$$RMgX \xrightarrow{ROH} R-H + Mg(OR)X$$

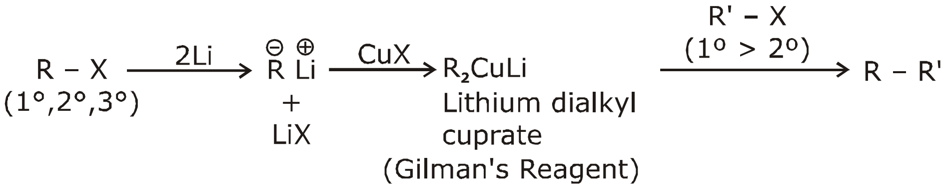
$$RMgX \xrightarrow{NH_3} R-H + Mg(NH_2)X$$

$$RMgX \xrightarrow{R'-C\equiv CH} R-H + Mg(C\equiv CR')$$

$$RMgX \xrightarrow{RSH} R-H + Mg(SR)X$$

$$RMgX \xrightarrow{R-COOH} R-H + Mg(OCOR)X$$

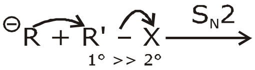
(iii) By Corey house alkane synthesis:



$$\underset{(1^\circ,2^\circ,3^\circ)}{R-X} \xrightarrow{2Li} \underset{\substack{+\\ LiX}}{\overset{\ominus}{R}\,\overset{\oplus}{Li}} \xrightarrow{CuX} \underset{\substack{\text{Lithium dialkyl}\\ \text{cuprate}\\ \text{(Gilman's Reagent)}}}{R_2CuLi} \xrightarrow{\substack{R'-X\\ (1^\circ > 2^\circ)}} R-R'$$

Mechanism :

R_2CuLi is the source of $\overset{\ominus}{R}$



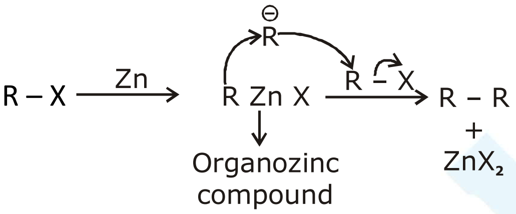
$$\overset{\ominus}{R} + \underset{1^\circ >> 2^\circ}{R'-X} \xrightarrow{S_N2} R-R'$$

R_2 CuLi do not react with $-NO_2$, $-CN$, $> C = O$ etc.

(iv) By Frankland reagent:

$$R-X + Zn + R-X \xrightarrow{Ether} R-R + ZnX_2$$

Mechanism



$$R-X \xrightarrow{Zn} \underset{\substack{\downarrow\\ \text{Organozinc}\\ \text{compound}}}{R\,Zn\,X} \xrightarrow{R-X} \underset{\substack{+\\ ZnX_2}}{R-R}$$

(B) By reduction of alkyl halides

(i) With metal-acid :

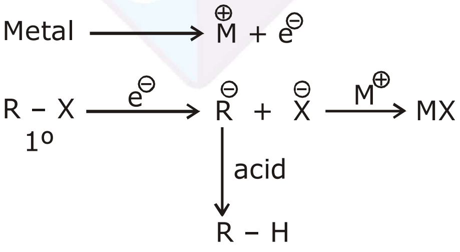
$$\underset{1^\circ}{R-X} \xrightarrow[\text{Metal / acid}]{e^{\ominus}/\ H^{\oplus}} R-H + HX$$

Reducing agent

Zn / acid, Zn – Cu / H_2O or Zn – Cu + acid

Zn – Cu / C_2H_5OH, Na – Hg / acid, Al – Hg / H_2O etc.

Mechanism :



$$\text{Metal} \longrightarrow \overset{\oplus}{M} + e^{\ominus}$$

$$\underset{1^\circ}{R-X} \xrightarrow{e^{\ominus}} \underset{\substack{\downarrow\ \text{acid}\\ R-H}}{\overset{\ominus}{R}} + \overset{\ominus}{X} \xrightarrow{M^{\oplus}} MX$$

(ii) With metal hydrides :

(a) Triphenyltin Hydride (Ph_3SnH) : It reduces 1°, 2° & 3° R – X

$$R-X \xrightarrow{Ph_3SnH} R-H$$

(b) $NaBH_4$

$$\underset{2^\circ\ \&\ 3^\circ}{R-X} \xrightarrow{NaBH_4} R-H$$

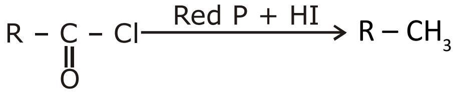
(c) $$\underset{1^\circ\ \&\ 2^\circ}{R-X} \xrightarrow{LiAlH_4} R-H$$

$$\underset{3^\circ}{R-X} \xrightarrow{LiAlH_4} \text{Alkene}$$

(III) By red P & HI

Red P & HI is strong reducing agent.

$$R-COOH \xrightarrow{\text{Red P + HI}} R-CH_3$$



$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{\text{Red P + HI}} R-CH_3$$

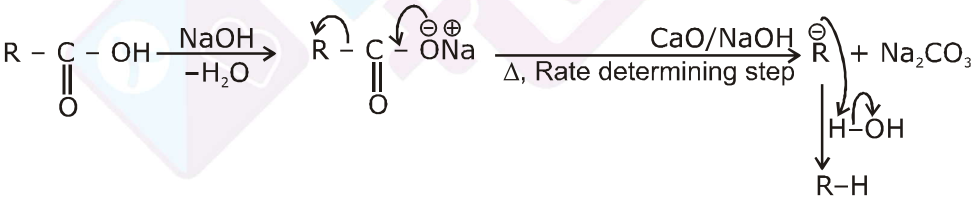
$$R-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow{\text{Red P + HI}} R-CH_3$$

$$R-X \xrightarrow{\text{Red P + HI}} R-H$$

$$R-OH \xrightarrow{\text{Red P + HI}} R-H+H_2O$$

(IV) By soda lime

Fatty acids are good source of hydrocarbons. Heating of sodium salt of carboxylic acid (R – COONa) with soda lime (NaOH – CaO) gives hydrocarbon, which is known as decarboxylation (e.g. replacement of – COOH group by –H) Decarboxylation also takes place on heating only, when compound is geminal dicarboxylic acid or there has keto group or double bond on β carbon.



(V) By Kolbe's electrolysis

$$2RCOOK + 2HOH \xrightarrow{\text{Electrolysis}}$$
$$RR + 2CO_2 + H_2 + 2KOH$$

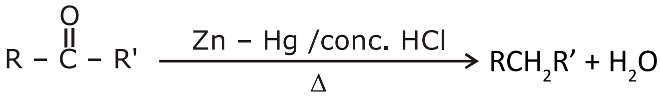
e.g. $2CH_3{-}COOK + 2H_2O \xrightarrow{\text{Electrolysis}}$
$CH_3CH_3 + 2CO_2 + H_2 + 2KOH.$

If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n – 1) carbon atoms.

(VI) Reduction of aldehydes, ketones

(a) By Clemmensen's reduction with Zn – Hg / conc. HCl

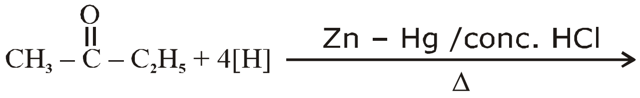
$$R-CHO \xrightarrow[\Delta]{Zn-Hg\ /conc.\ HCl} RCH_3 + H_2O$$



$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow[\Delta]{Zn-Hg\ /conc.\ HCl} RCH_2R' + H_2O$$

e.g. $CH_3-CHO \xrightarrow[\Delta]{Zn-Hg\ /conc.\ HCl} CH_3CH_3$

$+ H_2O$



$$CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5 + 4[H] \xrightarrow[\Delta]{Zn-Hg\ /conc.\ HCl}$$

$CH_3CH_2C_2H_5 + H_2O$

Clemmensen reduction is not used for compound which have acid sensitive groups.

(b) By Wolff-Kishner reduction with NH_2NH_2/ KOH

$$RCHO \xrightarrow[\Delta]{NH_2NH_2\ /\ KOH} RCH_3$$

$$RCO-R' \xrightarrow[\Delta]{NH_2NH_2\ /\ KOH} RCH_2R'$$

Wolff-Kishner reduction is not used for compounds which have base sensitive groups.

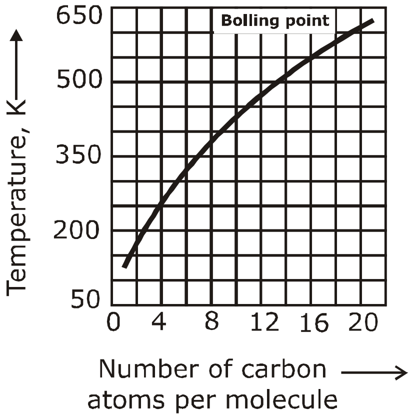
Physical Properties of Alkanes :

(I) Physical State :

The first four members (C_1 to C_4) are gases : the next thirteen members, (C_5 to C_{17}) are liquids while the higher members are waxy solids.

(II) Boiling Points :

The boiling points of n-alkanes increases regularly with the increase in the number of carbon atoms.

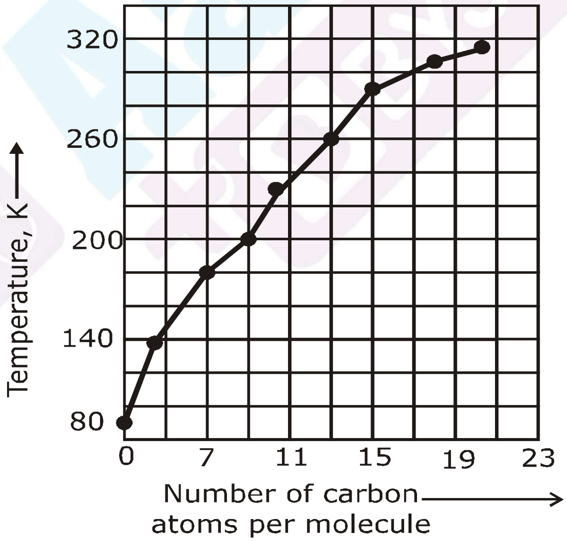


Among the isomeric alkanes, the branched chain isomers have relatively low boiling points as compared to their corresponding straight chain isomers. Greater the branching of the chain, lower is the boiling point. This is due to the fact that branching of the chain makes the molecules more compact and brings it close to a sphere, so the magnitude of van der waals forces decreases.

(III) Melting Points :

It is evident that the increase in melting point is relatively more in moving from an alkane having odd number of carbon atoms to the higher alkane with even no. of ‘C’ while it is relatively less in moving from an alkane with even number of carbon atoms to the higher alkane.

Explanation : The alkanes with even no. of ‘C’ atoms are more closely packed.



(IV) Solubility :

In keeping with the popular rule “like dissolves like”. hydrocarbons are insoluble in polar solvent like water because they are predominantly non-polar in nature.

(V) Density :

The densities of alkanes increase with increasing molecular weight but become constant at about 0.8 g cm^{-3}. This means that all alkanes are lighter than water so they float over water.

Chemical Reactions of Alkanes :

Characteristic reaction of alkanes are free radical substitution reaction, these reaction are generally chain reactions which are completed in three steps mainely.

(i) Chain initiation,
(ii) Chain propagation,
(iii) Chain termination,

Examples of free radical substitution reaction :

$$R-H+X_2 \xrightarrow[250^{o}-400^{o}C]{\text{UV light or}} R-X+HX$$

Eg. $$CH_4 \xrightarrow[hv]{Cl_2} \underset{HCl}{\overset{}{CH_3Cl}} \xrightarrow[hv]{Cl_2} CH_2Cl_2 \xrightarrow[hv]{Cl_2} CHCl_3 \xrightarrow[hv]{Cl_2} CCl_4$$

$$\begin{array}{ccc} CH_3Cl & CH_2Cl_2 & CHCl_3 \\ + & + & + \\ HCl & HCl & HCl \end{array}$$

When equimolar amount of methane and Cl_2 are taken, a mixture of four possible products are formed, but if we take excess of CH_4 then yield of CH_3Cl will be the major product.

Reactivity of X_2 : $F_2 > Cl_2 > Br_2 > I_2$
Reactivity of H : 3° H > 2° H > 1° H

With F_2 alkanes react so vigorously that, even in the dark and at room temperature, reactants are diluted with an inert gas.

Iodination is a reversible reaction, so HI formed as a by-product is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be carried out only in presence of strong oxidizing agent like HIO_3, HNO_3 or HgO

$$R-H+I_2 \rightleftharpoons R-I+HI$$

$$5HI+HIO_3 \longrightarrow 3H_2O+3I_2$$

Mechanism of halogenation of CH_4 :

(i) Chain initiation → It is an endothermic step.

$$X_2 \xrightarrow[250^{o}-400^{o}C]{\text{UV or temp}} 2\dot{X}$$

(ii) Chain propagation →

$$\dot{X}+R-H \longrightarrow \dot{R}+HX$$

$$\dot{R}+X-X \longrightarrow R-X+\dot{X}$$

(iii) Chain termination → It is always exothermic

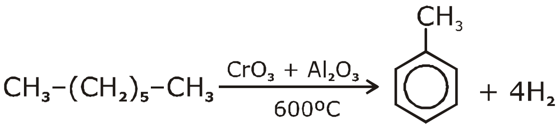
$$\dot{X} + \dot{X} \longrightarrow X_2$$

$$\dot{R} + \dot{R} \longrightarrow R - R$$

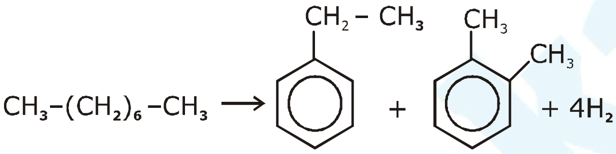
$$\dot{R} + \dot{X} \longrightarrow R - X$$

Each photon of light cleaves one chlorine molecule to form two chlorine radicals, each chlorine atom starts a chain and on an average each chain contains 5000 repetitions of the chain propagating cycle so about 10,000 molecules of CH_3Cl are formed by one photon of light.

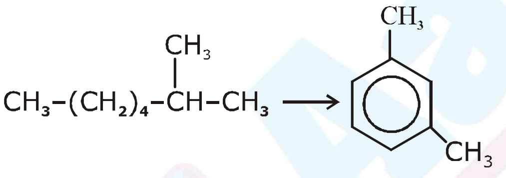
Aromatization :



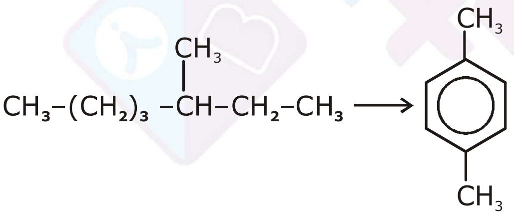
Toluene



ortho-Xylene



meta-Xylene



para-Xylene

Combustion : (i.e. complete oxidation)

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \xrightarrow[\Delta]{\text{Combustion}} nCO_2 + (n+1)\,H_2O\ (\Delta H_{\text{combustion}} = -ve)$$

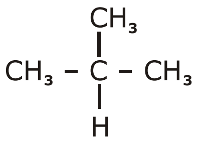
$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow[\Delta]{\text{Combustion}} xCO_2 + \frac{y}{2}\ H_2O$$

$$C_5H_{12} + 8O_2 \xrightarrow[\Delta]{\text{Combustion}} 5CO_2 + 6H_2O$$

Heat of combustion : Amount of heat i.e. liberated when 1 mole of hydrocarbon is completely burnt into CO_2 & H_2O.

Heat of combustion as a measure of stability of alkane :
Combustion is used as a measurement of stability.
More branched alkanes are more stable and have lower heat of combustion.

e.g. (I) $CH_3 - CH_2 - CH_2 - CH_3$ (II)

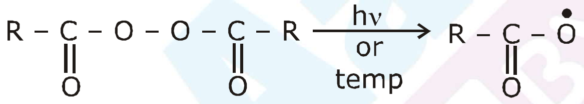


$$CH_3 - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

Stability : II > I
$\Delta H_{comb.}$: I > II
More branched alkane has more no. of primary C – H bonds. (therefore it has more bond energy).
Homologues : Higher homologues have higher heat of combustion.
Isomers : Branched isomers have lower heat of combustion.

(i) Initiators → They initiate the chain reaction, initiators are R_2O_2, peresters, etc.

$$R - O - O - R \xrightarrow[\text{or temp}]{h\nu} R\dot{O}$$



$$R - \underset{\underset{O}{\|}}{C} - O - O - \underset{\underset{O}{\|}}{C} - R \xrightarrow[\text{or temp}]{h\nu} R - \underset{\underset{O}{\|}}{C} - \dot{O}$$

(ii) Inhibitors → A substance that slow down or stop the reaction are known as inhibitors.
For example - O_2 is a good inhibitor.

$$\dot{R} + O_2 \longrightarrow R - O - \dot{O} + \dot{R} \longrightarrow R - O - O - R$$

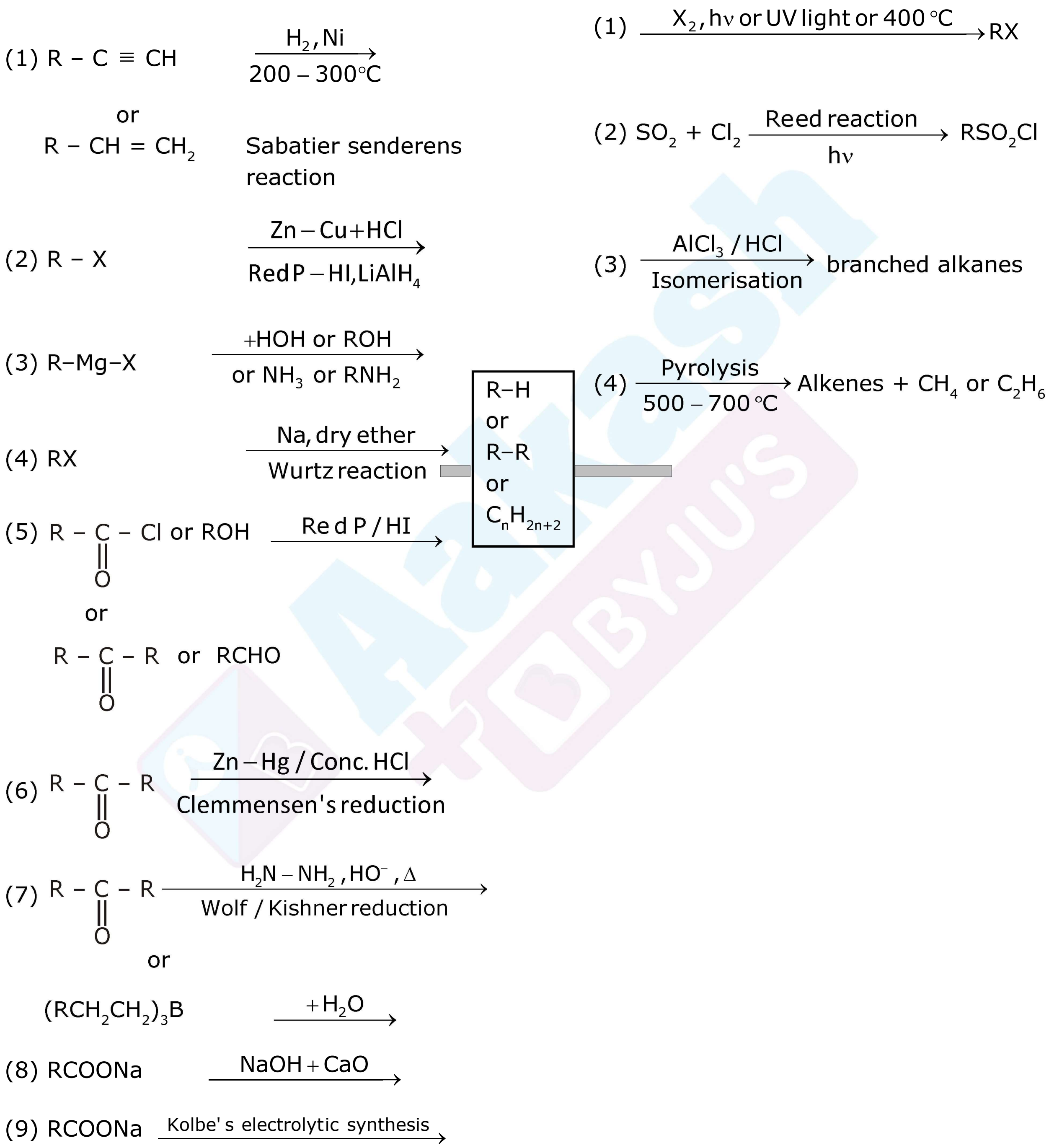
All reactive alkyl free radicals are consumed so reaction will stop for a period of time.
Relative reactivity of halogen towards, methane :
Order of reactivity is $F_2 > Cl_2 > Br_2 > I_2$ which can be explained by the value of ΔH (Energy change)
Steps of halogenation,value of ΔH for each step. (kcal/mol)

		F	Cl	Br	I
(i)	$X_2 \longrightarrow 2X$	+ 38	+ 58	+ 46	+ 38

(ii) $\dot{X} + CH_4 \longrightarrow \dot{C}H_3 + HX$
$-32 \quad +1 \qquad +16 \quad +33$

(iii) $\dot{C}H_3 + X \longrightarrow CH_3X + \dot{X}$
$-70 \quad -26 \qquad -24 \quad -20$

REACTION CHART FOR ALKANES



R–H or R–R or C_nH_{2n+2}

(1) $R-C\equiv CH$ or $R-CH=CH_2$ $\xrightarrow[200-300^\circ C]{H_2, Ni}$ Sabatier senderens reaction

(2) $R-X$ $\xrightarrow[\text{Red P} - HI, LiAlH_4]{Zn-Cu+HCl}$

(3) $R-Mg-X$ $\xrightarrow[\text{or } NH_3 \text{ or } RNH_2]{+HOH \text{ or } ROH}$

(4) RX $\xrightarrow[\text{Wurtz reaction}]{\text{Na, dry ether}}$

(5) $R-\underset{\underset{O}{\|}}{C}-Cl$ or ROH $\xrightarrow{\text{Red P / HI}}$

or

$R-\underset{\underset{O}{\|}}{C}-R$ or RCHO

(6) $R-\underset{\underset{O}{\|}}{C}-R$ $\xrightarrow[\text{Clemmensen's reduction}]{Zn-Hg / \text{Conc. } HCl}$

(7) $R-\underset{\underset{O}{\|}}{C}-R$ $\xrightarrow[\text{Wolf / Kishner reduction}]{H_2N-NH_2, HO^-, \Delta}$

or

$(RCH_2CH_2)_3B$ $\xrightarrow{+H_2O}$

(8) RCOONa $\xrightarrow{NaOH + CaO}$

(9) RCOONa $\xrightarrow{\text{Kolbe's electrolytic synthesis}}$

(1) $\xrightarrow{X_2, h\nu \text{ or UV light or } 400^\circ C}$ RX

(2) $SO_2 + Cl_2 \xrightarrow[h\nu]{\text{Reed reaction}} RSO_2Cl$

(3) $\xrightarrow[\text{Isomerisation}]{AlCl_3 / HCl}$ branched alkanes

(4) $\xrightarrow[500-700^\circ C]{\text{Pyrolysis}}$ Alkenes + CH_4 or C_2H_6

HYDROCARBON (ALKENE)

ALKENE

Introduction :

Alkenes are hydrocarbons with carbon–carbon double bonds. Alkenes are sometimes called olefins, a term derived from olefinic gas, meaning "oil forming gas". Alkenes are among the most important industrial compound and many alkenes are also found in plants and animals. Ethylene is the largest – volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals.

Structure and bonding in Alkenes

(1) Alkenes are unsaturated hydrocarbons having at least one double bond.

(2) They are represented by general formula (G.F.) C_nH_{2n} (one double bond).

(3) In ethene C = C bond length is 1.34 Å.

(4) Its bond energy is 146 kcal mol^{-1}.

(5) The hybridization of (C = C) alkenic carbon is sp^2

(6) The πe^- cloud is present above and below the plane of σ–bonded skeleton.

(7) They are also known as olefins since ethene, the first member of the homologous series forms an oily liquid substance when treated with halogens.

(8) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes.

Note :

That angle between double bond - single bond will be greater than angle between single bond - single bond since repulsion due to p electrons (double bond - single bond repulsion > single bond-single bond repulsion according to VSEPR theory).

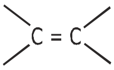
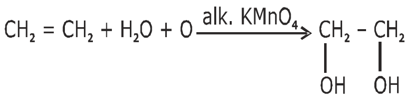
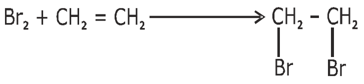
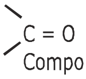
Physical properties of Alkenes / Hydrocarbons

Table : III

	Physical properties	Homologous series	Isomers
1.	Physical state	$C_1 - C_3$gases $C_4 - C_{20}$liquids $>C_{20}$:solids	
2.	Dipole moment (μ)		cis > trans
3.	Polarity		cis > trans (for $C_{ab} = C_{ab}$type of alkenes)
4.	Melting point	increases with M.W.	trans > cis (due to more packing capacity)
5.	Boiling point	increases with M.W.	cis > trans # branching decreases B.P.  $\overset{C}{\overset{\vert}{C}} - C = C < C - C = C - C$ polarity increases, boiling point increases
6.	Solubility	practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc.	cis > trans polarity increases, solubility in polar solvents increases.
7.	Stability		trans > cis (cis isomers has more vander Waal repulsion)

Laboratory test of alkene

Table : IV

Functional Group	Reagent	Observation	Reaction	Remarks
	(1) Bayer's Reagent alk. dil. cold $KMnO_4$	Pink colour disappears	 $CH_2 = CH_2 + H_2O + O \xrightarrow{alk.\ KMnO_4} \underset{OH}{\underset{\vert}{CH_2}} - \underset{OH}{\underset{\vert}{CH_2}}$	Dihydroxylation
	(2) Br_2 / H_2O	Bromine water colour decolourises	 $Br_2 + CH_2 = CH_2 \longrightarrow \underset{Br}{\underset{\vert}{CH_2}} - \underset{Br}{\underset{\vert}{CH_2}}$ White ppt	Dibromination
	(3) O_3 (ozone)	 C = O Compounds	$H_2C = CH_2 + O_3 \xrightarrow{Zn / H_2O} 2HCHO$	Ozonolysis

Preparation of Alkenes

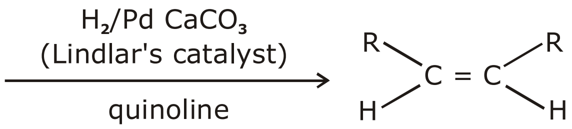
(I) BY PARTIAL REDUCTION OF ALKYNES

(a) By catalytic hydrogenation of alkynes in presence of poisoned catalyst A syn addition of hydrogen : Synthesis of cis-alkenes : This is performed by :

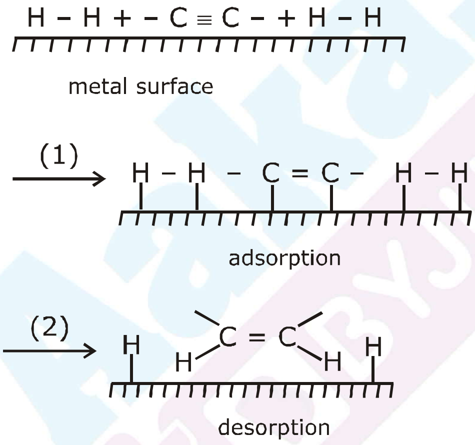
(i) Lindlar's catalyst : Metallic palladium deposited on calcium carbonate with lead acetate and quinoline.

General Reaction

R – C ≡ C – R



Mechanism of hydrogenation :

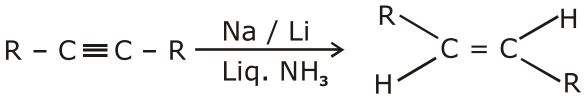


Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

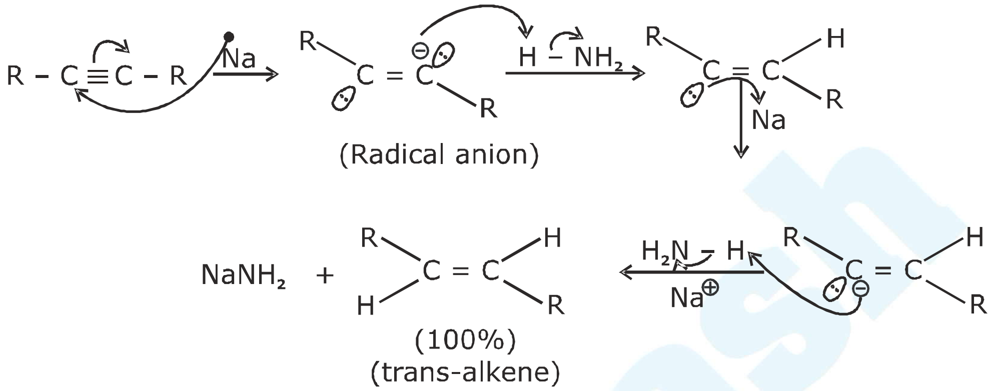
In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atom from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes. **Quinoline** therefore is called **catalyst poison** and **palladium** is called **deactivated catalyst** or **poisoned catalyst**.

(b) Birch reduction : (Anti addition of hydrogen : synthesis of trans-alkenes)

General Reaction



Mechanism : Reagents Na(or Li, K) + liq $NH_3 \longrightarrow Na^{\oplus} + e^{\ominus}$(solvated electron)



e.g. $CH_3-CH_2-C\equiv C-CH_2-CH_3$

trans-hex-3-ene

Note : This process of reduction is not eligible when terminal alkynes are taken ($R-C\equiv CH$) because terminal alkynes form sodium salt with Na metal.

$CH_3–C\equiv CH + Na/NH_3 \longrightarrow CH_3–C\equiv C^-Na^+ + [H]^+$

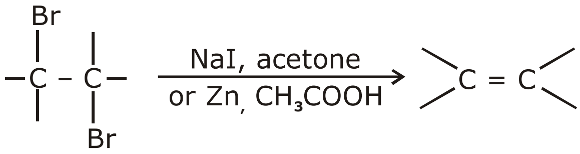
(II) BY DEHALOGENATION OF VICINAL DIHALIDES

There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

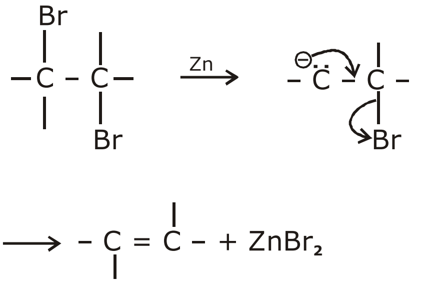
Dehalogenation of vicinal dihalides can be affected either by NaI in acetone or zinc in presence of acetic acid or ethanol.

General Reaction :

(i)



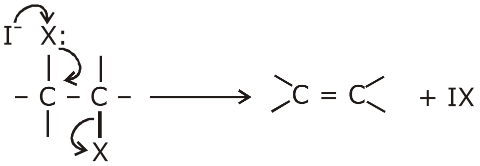
Mech.



(ii) $CH_3–CHBr–CH_2Br \xrightarrow[\text{(CH}_3\text{COOH or C}_2\text{H}_5\text{OH as solvent)}]{\text{Zn dust}} CH_3 - CH{=}CH_2$

Mech.

With NaI in acetone :



It involves an **anti elimination** of halogen atoms

Remarks :

(1) Both are E2 elimination.

(2) Both are stereospecific anti elimination.

(III) DEHYDROHALOGENATION OF ALKYL HALIDES

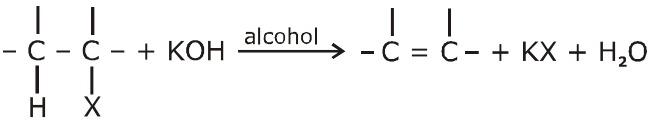
Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

Dehydrohalogenation can take place by E1 and E2 mechanism.

(i) Hot alcoholic solution of KOH $EtO^–$ / EtOH (ii) $NaNH_2$ (iii) t-BuO–K^+ in t-BuOH

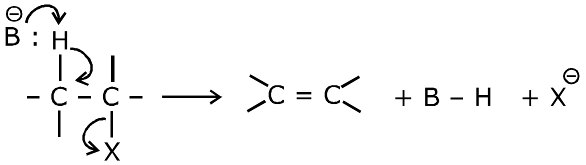
(i) Dehydrohalogenation by the E_2 mechanism : Second-order elimination is a reliable synthetic reaction, especially if the alkyl halide is a poor S_N2 substrate. E2 dehydrohalogenation takes place in one step, in which a strong base abstracts a proton from one carbon atoms and halogen as the leaving group leaves the adjacent carbon.

General reaction :



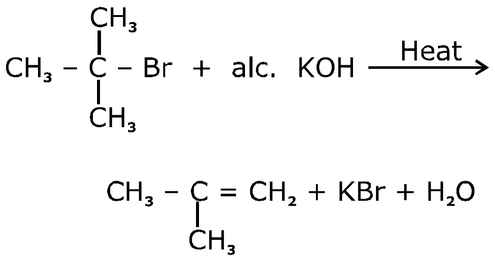
$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + KOH \xrightarrow{\text{alcohol}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

Mechanism :



Undergo elimination of hydrogen halide (HX) leading to the formation of alkenes.

e.g.

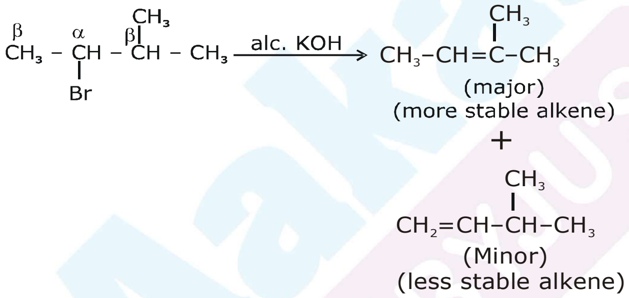


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + alc.\ KOH \xrightarrow{Heat} CH_3-\underset{CH_3}{C}=CH_2 + KBr + H_2O$$

Here β – H is eliminated by base hence called β **elimination** following **Saytzeff rule.**

i.e, (Highly substituted alkene is major product). It also involves an anti elimination of HX.

e.g.



$$\overset{\beta}{CH_3}-\underset{Br}{\overset{\alpha}{CH}}-\overset{CH_3}{\overset{\beta}{CH}}-CH_3 \xrightarrow{alc.\ KOH} CH_3-CH=\overset{CH_3}{C}-CH_3$$

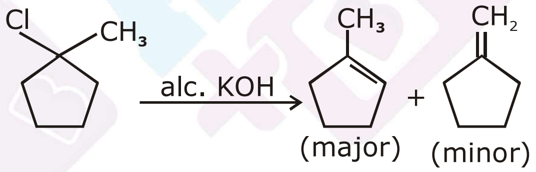
(major)
(more stable alkene)

+

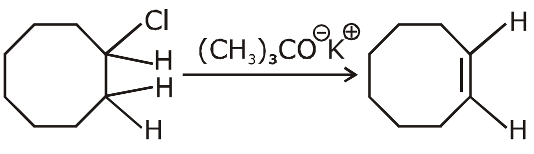
$$CH_2=CH-\overset{CH_3}{CH}-CH_3$$

(Minor)
(less stable alkene)

e.g.

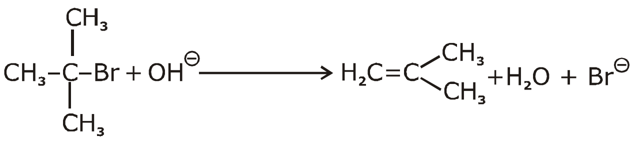


e.g.



Chlorocyclooctane Cyclooctene

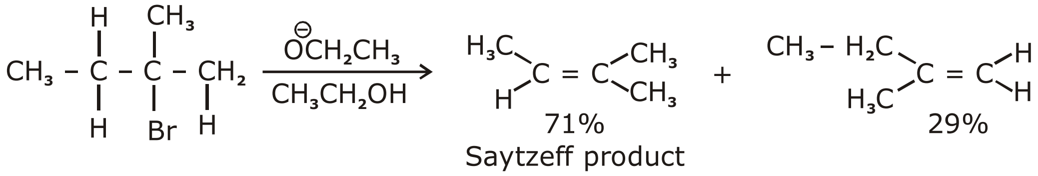
e.g.

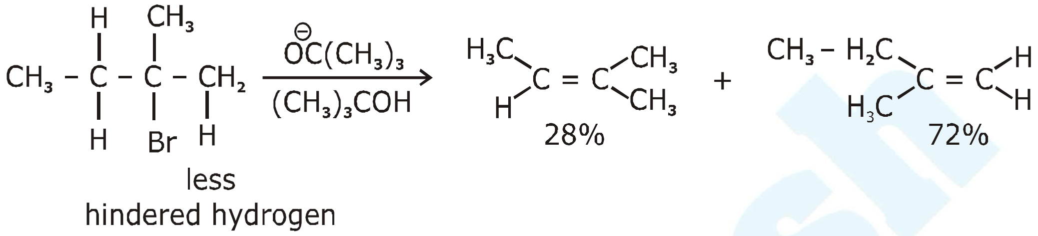


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + OH^{\ominus} \longrightarrow H_2C=C\begin{matrix}CH_3\\CH_3\end{matrix} + H_2O + Br^{\ominus}$$

(ii) Formation of the Hoffmann product:

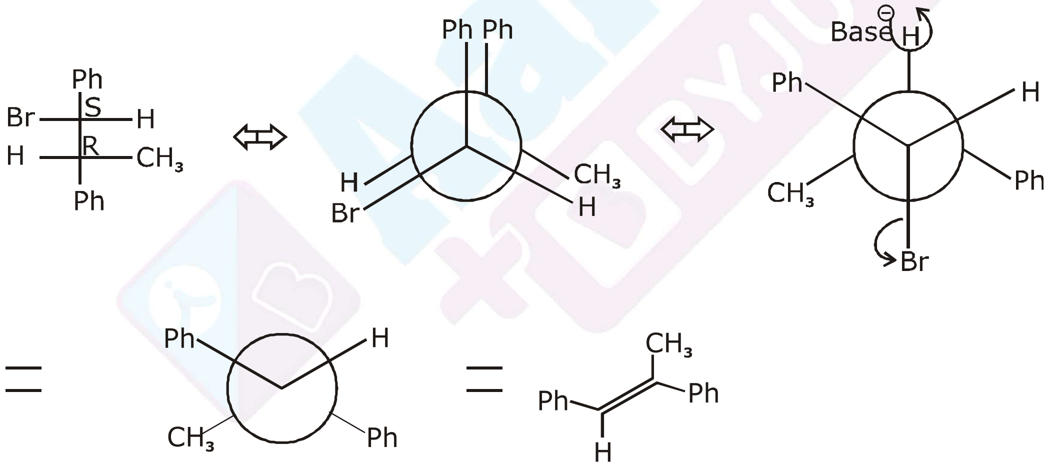
Bulky bases can also accomplish dehydrohalogenation that do not follow the Saytzeff rule. Due to steric hindrance, a bulky base abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the Hoffmann product.





Stereospecific E_2 reactions :

The E2 elimination is stereospecific because it normally goes through an anti and coplanar transition state. The products are alkene, and different diastereomers of starting materials commonly give different diastereomers of alkenes.



Chemical Reactions of Alkenes

(I) CATALYTIC HYDROGENATION OF ALKENES : (HETEROGENEOUS HYROGENATION)

Hydrogenation : The function of catalyst

Hydrogenation of an alkene is exothermic reaction ($\Delta H^o = -120$ kJ mol^{-1})

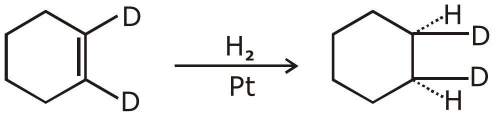
$R - CH = CH - R + H_2 \xrightarrow{Ni} R - CH_2 - CH_2 - R + \text{heat}$

As a consequence, both hydrogen atoms usually add from the same side of the molecule. This mode of addition is called **syn** addition.

Hydrogenation of an alkene is formally a reduction, with H_2 adding across the double bond to give an alkane. The process usually requires a catalyst containing Pt, Pd or Ni.

e.g. $CH_3 - CH = CH - CH_3 + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3$

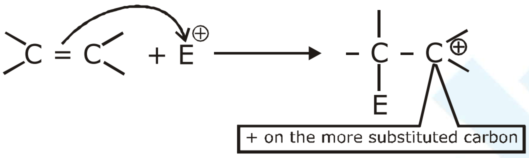
e.g.



(II) ELECTROPHILIC ADDITION REACTIONS

Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.

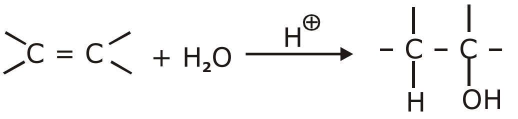


Step 2 : Attack by a nucleophile gives the product of addition.

(i) Acid-Catalyzed Hydration of Alkenes :

Alkenes add water in the presence of an acid catalyst to yield alcohols. The addition takes place with Markovnikov's rule. The reaction is reversible, and the mechanism for the acid-catalyzed hydration of an alkene is simply the reverse of that for the dehydration of an alcohol. The carbocation intermediate may rearrange if a more stable carbocation is possible by hydride or alkanide migration. Thus, a mixture of isomeric alcohol products may result.

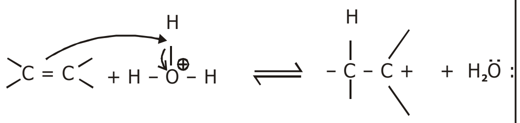
General Reaction :



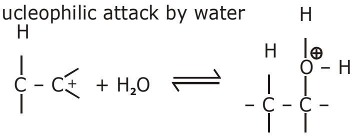
(Markovnikov orientation)

Mech.

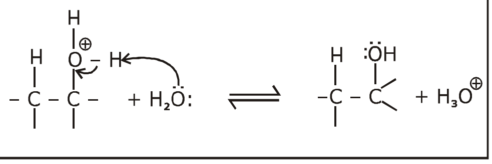
Step 1 : Protonation of the double bond forms a carbocation



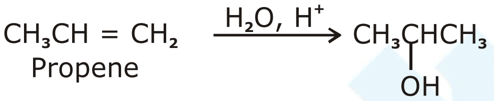
Step 2 : Nucleophilic attack by water



Step 3 : Deprotonation of the alcohol



e.g.

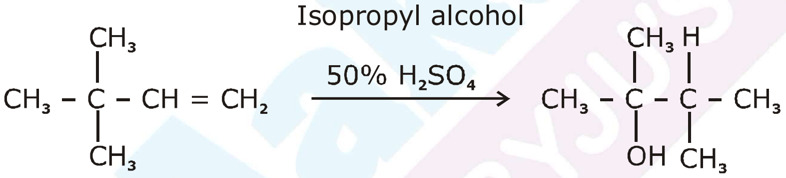


$$CH_3CH = CH_2 \xrightarrow{H_2O,\ H^+} CH_3\underset{OH}{C}HCH_3$$

Propene

Isopropyl alcohol

e.g.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{50\%\ H_2SO_4} CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{H}{\underset{CH_3}{C}}-CH_3$$

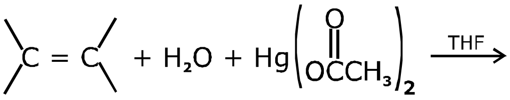
3,3-Dimethyl-1-butene

2,3-Dimethyl-2-butanol
(Major product)

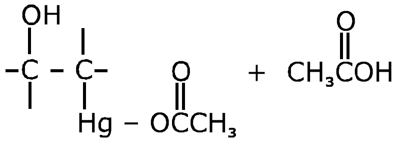
(ii) (a) Oxymercuration - Demercuration :

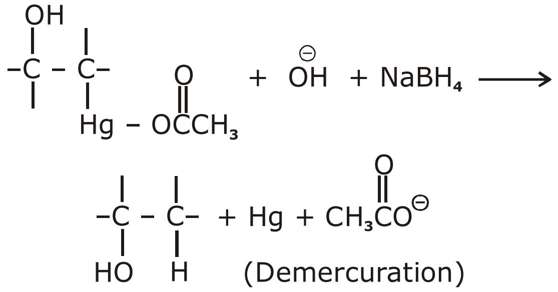
Alkenes react with mercuric acetate in a mixture of water and tetrahydrofuran (THF) to produce (hydroxyalkyl) mercury compounds. These can be reduced to alcohols with sodium borohydride and water.

Oxymercuration



General Reaction :



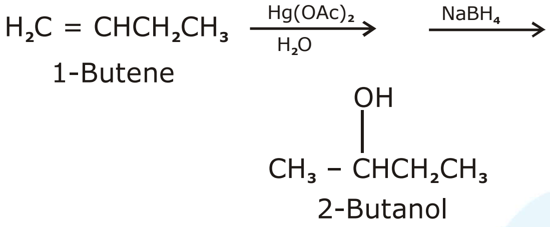


$$\underset{\text{Hg}-\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3}{\overset{\text{OH}}{-\text{C}-\text{C}-}} + \overset{\ominus}{\text{OH}} + \text{NaBH}_4 \longrightarrow \underset{\text{HO}\quad\text{H}}{-\text{C}-\text{C}-} + \text{Hg} + \text{CH}_3\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}^{\ominus}$$

(Demercuration)

In the oxymercuration step, water and mercuric acetate add to the double bond; in the demercuration step, sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen. Then net addition of H –and –OH takes place with Markovnikov's rule and generally takes place without the complication of rearrangements.

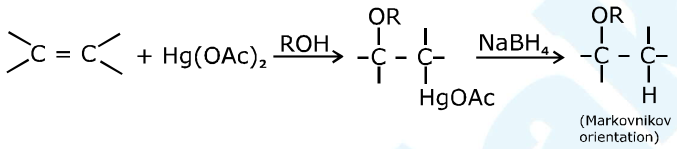
e.g.



$$\underset{\text{1-Butene}}{H_2C = CHCH_2CH_3} \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} \underset{\text{2-Butanol}}{CH_3-\overset{\text{OH}}{\overset{|}{C}}HCH_2CH_3}$$

(b) Alkoxymercuration - Demercuration :

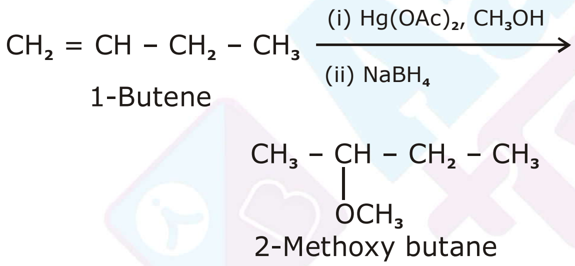
General reaction :



$$\rangle C = C\langle + Hg(OAc)_2 \xrightarrow{ROH} \underset{\text{HgOAc}}{\overset{\text{OR}}{-C-C-}} \xrightarrow{NaBH_4} \underset{\text{H}}{\overset{\text{OR}}{-C-C-}}$$

(Markovnikov orientation)

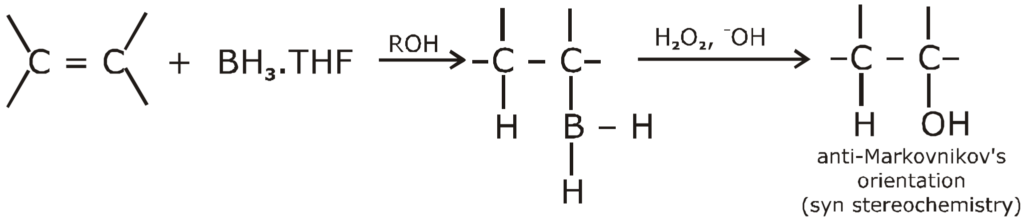
e.g.



$$\underset{\text{1-Butene}}{CH_2 = CH - CH_2 - CH_3} \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2\text{, CH}_3\text{OH}} \underset{\text{2-Methoxy butane}}{CH_3 - \underset{OCH_3}{\underset{|}{CH}} - CH_2 - CH_3}$$

(iii) Hydroboration-Oxidation (SYN ADDITION)

General Reaction

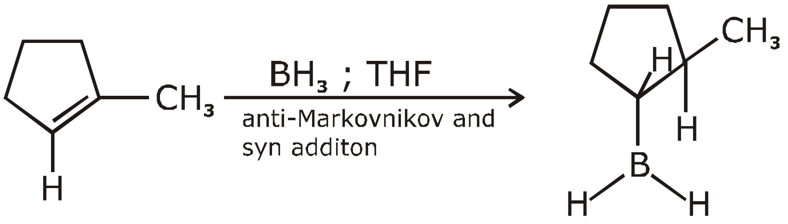


$$\rangle C = C\langle + BH_3.THF \xrightarrow{ROH} \underset{\text{H}\quad \text{B}-\text{H}\atop \quad\ \ |\ \text{H}}{-C-C-} \xrightarrow{H_2O_2,\ ^{-}OH} \underset{\text{H}\quad\text{OH}}{-C-C-}$$

anti-Markovnikov's orientation (syn stereochemistry)

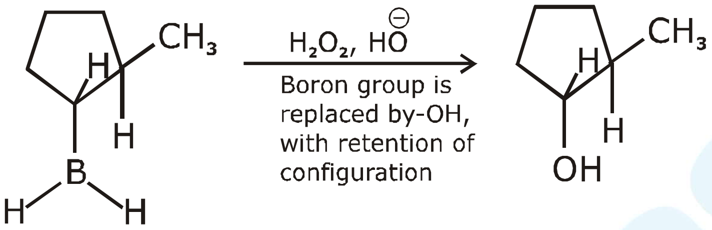
An alkene reacts with BH_3 in THF or diborane to produce an alkylborane. Oxidation and hydrolysis of the alkylborane with hydrogen peroxide and base yields an alcohol.

e.g.



+ other enantiomer + dialkyl-and trialkylborane

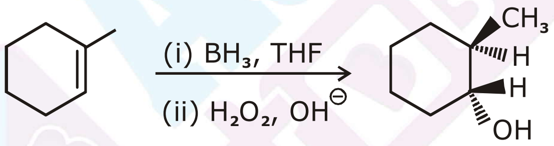
Oxidation



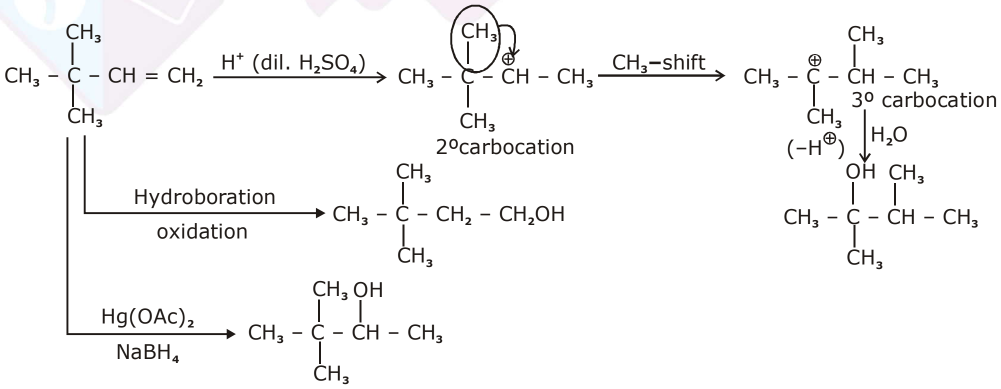
+ other enantiomer

In the first step, boron and hydrogen undergo syn addition with the alkene in the second step, treatment with hydrogen peroxide and base replaces the boron with –OH with retention of configuration. The net addition of –H and –OH occurs with anti Markovnikov's rule and syn stereoselectivity. Hydroboration –oxidation therefore, serves as a useful regiochemical complement to oxymercuration demercuration.

e.g.



e.g.



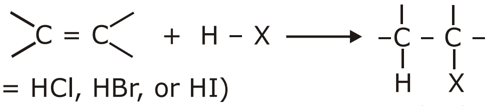
(i) Hydration with dil. H_2SO_4 proceeds via carbocation rearrangement.

(ii) Hydration with $Hg(OAc)_2$, H_2O, followed by $NaBH_4$ proceeds via Markovnikov's rule.

(iii) Hydration with $(BH_3)_2$ followed by H_2O_2 / OH^- proceeds via Anti Markovnikov's rule.

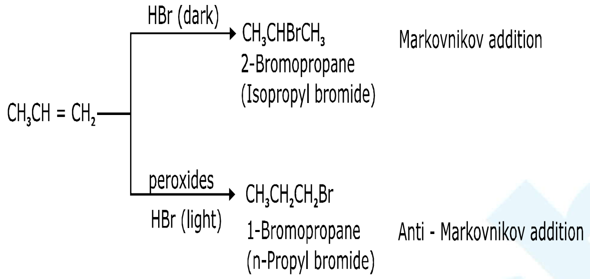
(iv) Addition of Hydrogen Halides:

General Reaction



(HX = HCl, HBr, or HI)

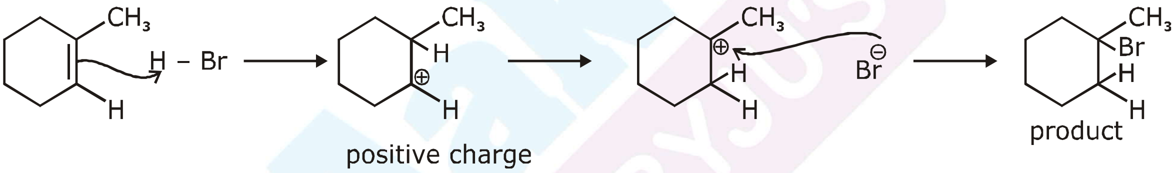
Markovnikov orientation (anti-Markovnikov with HBr and peroxide)



Note : (1) Anti Markovnikov addition is valid only for HBr in presence of peroxide and light only.
(2) HF, HCl and HI give only polar addition and give Markovnikov product only.

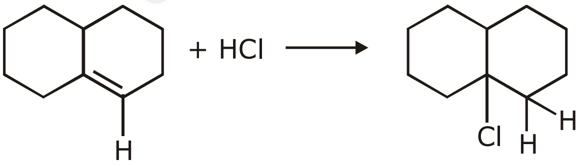
e.g. $CH_3CH = CH_2 \xrightarrow{HI} CH_3CHICH_3$

Propene — 2-Iodopropane (Isopropyl iodide)



positive charge
on less substituted carbon
less stable ; not formed

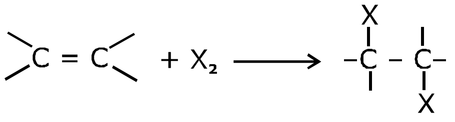
e.g.



(v) Addition of Halogen :

Halogen add to alkenes to form vicinal dihalides.

General Reaction


usually anti addition

$(X_2 = Cl_2, Br_2)$

The electron rich double bond induces a dipole in an approching halogen molecule making one halogen electron deficient and another electron rich.

Note :

(i) F_2 is not added because F^+ is never generated. Morever reaction is explosive giving CO_2 & H_2O

(ii) I_2 is not added because reaction is reversible with equilibrium in backward direction.

(iii) Reaction with bromine is basis for test of alkenes.

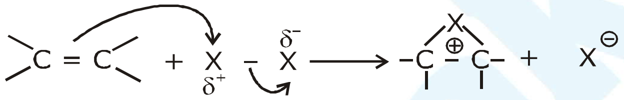
(iv) Halogen addition is stereospecific anti addition.

(v) Halogens can also be added in presence of sunlight and give free radical addition.

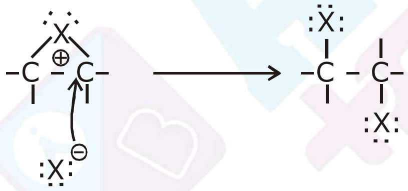
(Reactivity of halogen addition in sunlight is F_2 (explosive) $> Cl_2 > Br_2 > I_2$)

Mechanism

Step-1 Formation of a halonium ion


Halonium ion

Step-2 Opening of the halonium ion



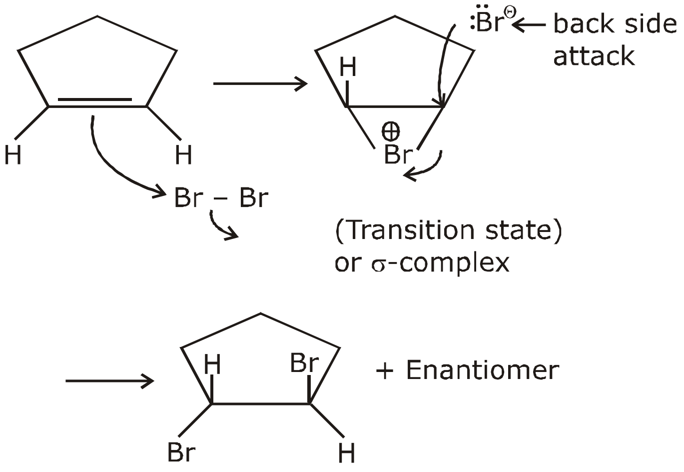
$X^\ominus$ attacks from the back side of halonium ion.

e.g.

$$CH_3CH = CH_2 \xrightarrow{Br_2 \text{ in } CCl_4} CH_3CHBrCH_2Br$$

Propene (Propylene) 1,2-Dibromopropane (Propylene bromide)

e.g.

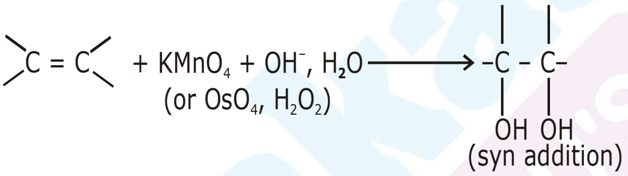


trans-1,2-Dibromocylopentane

(vi) Hydroxylation of Alkenes:

(a) Syn Hydroxylation : (Reaction with Beayer's reagent, (cold dilute alkaline $KMnO_4$ solution). Both OH groups are added from same face of alkene. This addition is example of syn addition.

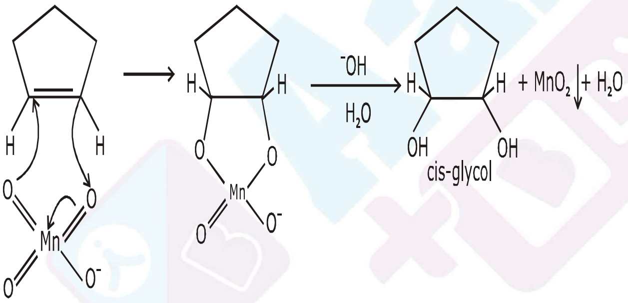
General Reaction



$$>C=C< \; + KMnO_4 + OH^-, H_2O \xrightarrow[\text{(or } OsO_4,\ H_2O_2)]{} -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

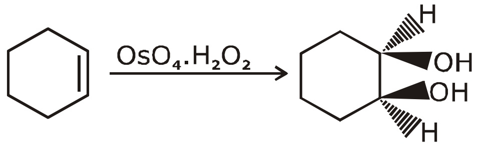
(syn addition)

e.g.



The same function of syn addition of 2 - OH groups is performed by OsO_4 / H_2O_2

e.g.



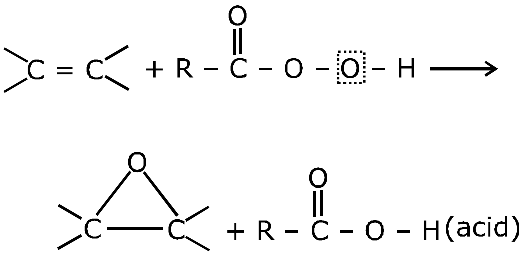
Cyclohexene

cis-Cyclohexane-1,2-diol

(III) EPOXIDATION OF ALKENES :

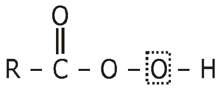
An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a –O – O – (peroxy) linkage.

General Reaction :



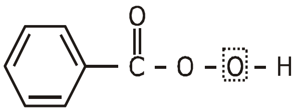
Epoxide (Oxirane)

The epoxidation of an alkene is clearly an oxidation, since in oxidation, an oxygen atom is added. Peroxyacids are highly selective oxidizing agents. Some simple peroxyacids (sometimes called per acids) and their corresponding carboxylic acids are shown below :



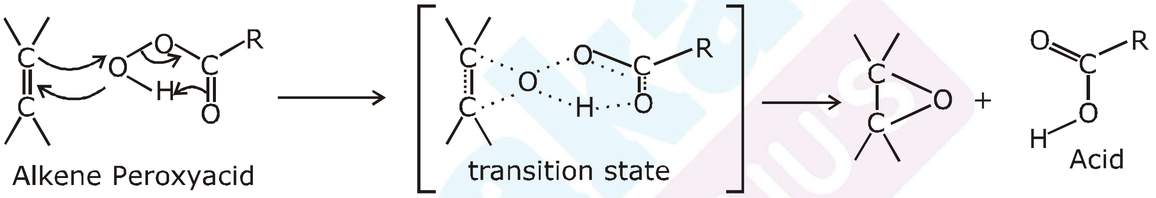
$R-\overset{O}{\overset{\|}{C}}-O-\boxed{O}-H$

a peroxyacetic acid

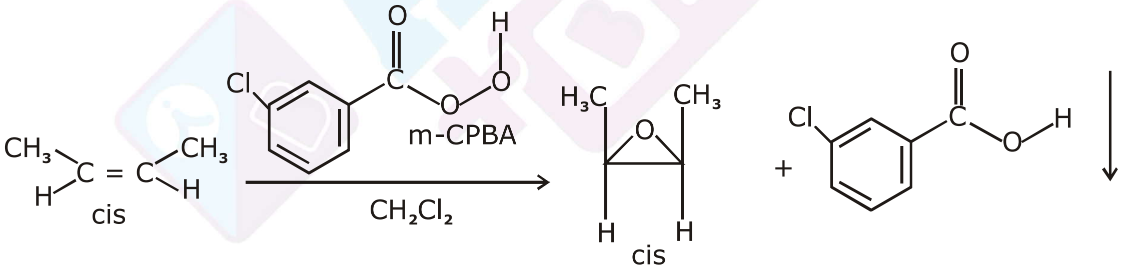


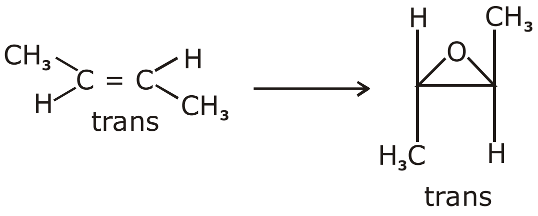
Peroxybenzoic acid

Mech.

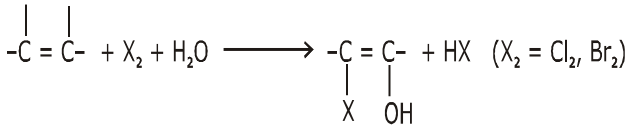


e.g.





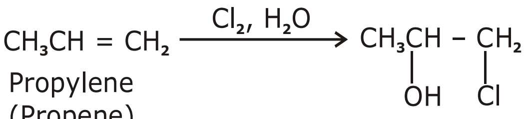
(IV) HALOHYDRIN FORMATION:

General Reaction 

$$-\overset{|}{C}=\overset{|}{C}- + X_2 + H_2O \longrightarrow -\underset{X}{\underset{|}{C}}=\underset{OH}{\underset{|}{C}}- + HX \quad (X_2 = Cl_2, Br_2)$$

Addition of the electrohpile X^+ (from X_2) to form a bridged halonium ion, followed by Nu attack by H_2O

Halohydrin formation commences when the π electrons of the alkene react with electrophilic bromine to form a bridge intermediate called a bromonium ion. Water, acting as a nucleophile, uses a lone pair of electron to open the three-membered bromonium ion ring and forms a bond with the carbon in an S_N2 process.

e.g. 

$$CH_3CH=CH_2 \xrightarrow{Cl_2,\ H_2O} CH_3\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$$

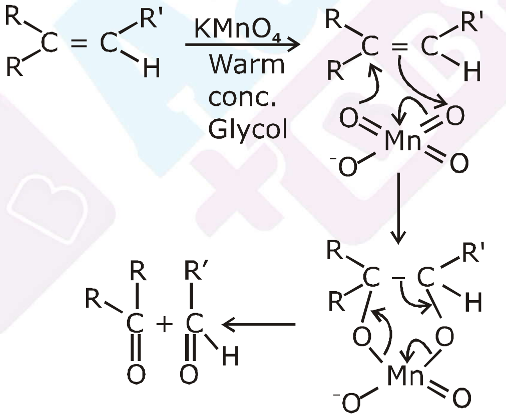
Propylene
(Propene)

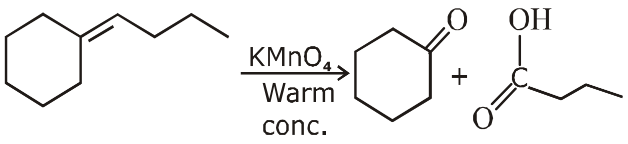
Propylene chlorohydrin
(1-Chloro-2-propanol)

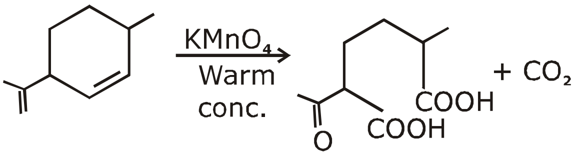
(V) OXIDATIVE CLEAVAGE OF ALKENES:

(i)Cleavage by permanganate

In a $KMnO_4$ hydroxylation, if the solution is warm or acidic or too concentrated, oxidative cleavage by $KMnO_4$ starts with an addition to the π bond forming a cyclic intermediate which eventually breaks down to an aldehyde or a ketone. The aldehyde is further oxidzed to a carboxylic acid by the $KMnO_4$. The mechanism of this transformation is covered in the oxidation of alcohols.

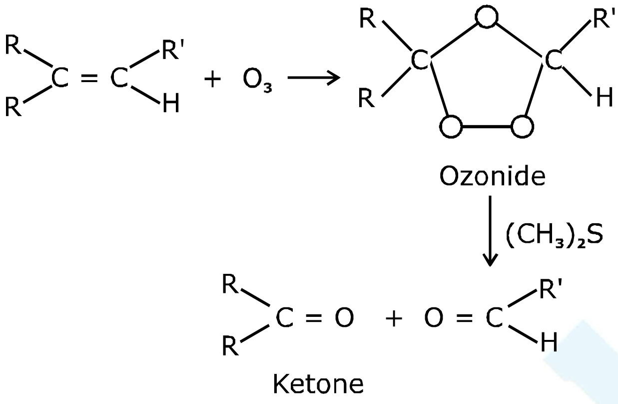
General Reaction 

e.g. 

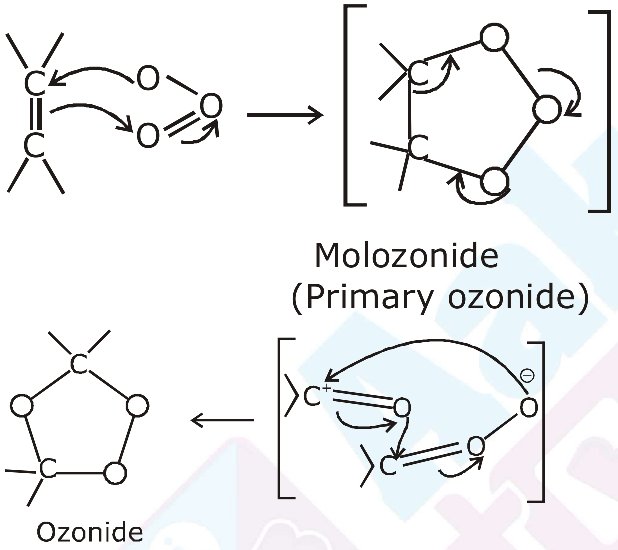
e.g. 

(ii) Ozonolysis : Like permanganate, ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.

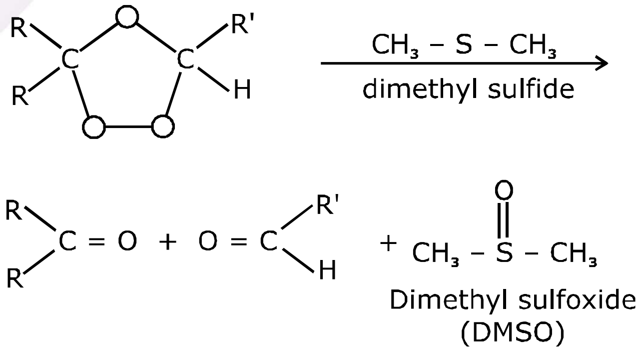
General Reaction



Mechanism



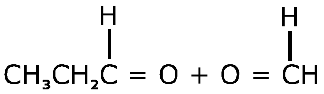
e.g.



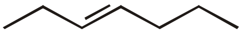
e.g.

$CH_3CH_2CH = CH_2 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn}$

1-Butene

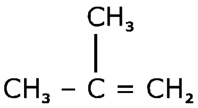


$CH_3CH_2\overset{H}{C} = O + O = \overset{H}{C}H$

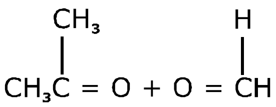
e.g. 

3 - Heptene $\xrightarrow[(ii)\ (CH_3)_2\ S]{(i)\ O_3} CH_3CH_2CHO$

$+ CH_3(CH_2)_2CHO$ (65%)

e.g. 

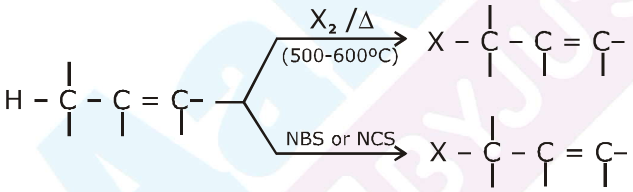
$CH_3 - \overset{CH_3}{C} = CH_2 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn}$



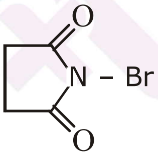
$CH_3\overset{CH_3}{C} = O + O = \overset{H}{C}H$

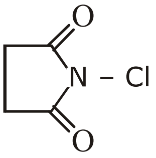
(VI) HALOGENATION, ALLYLIC SUBSTITUTION

General Reaction



$X_2 = Cl_2, Br_2$ (allylic halide)

NBS = N-Bromosuccinimide 

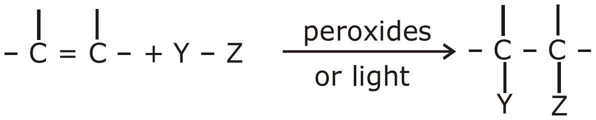
NCS = N-Chlorosuccinimide 

e.g. $CH_3CH = CH_2 \xrightarrow{Cl_2,\ 600^\circ C} Cl - CH_2CH = CH_2$

Propylene (Propene) Allyl Chloride (3-Chloro-1-propene)

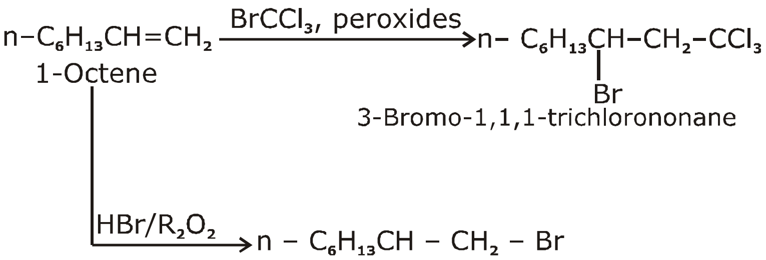
(VII) ADDITION OF FREE RADICALS:

General Reaction



$$-\overset{|}{C}=\overset{|}{C}- + Y-Z \xrightarrow[\text{or light}]{\text{peroxides}} -\underset{Y}{\overset{|}{\underset{|}{C}}}-\underset{Z}{\overset{|}{\underset{|}{C}}}-$$

e.g.



$$n-C_6H_{13}CH=CH_2 \xrightarrow{BrCCl_3,\ peroxides} n-C_6H_{13}\underset{Br}{\underset{|}{C}}H-CH_2-CCl_3$$

$$n-C_6H_{13}CH=CH_2 \xrightarrow{HBr/R_2O_2} n-C_6H_{13}CH-CH_2-Br$$

HYDROCARBON
(ALKYNES)

ALKYNES

Introduction

A triple bond gives an alkyne with four fewer hydrogen atoms than the corresponding alkane. Therefore the triple bond contributes two degree of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene as far as we know, is the the most important commercial alkyne. Acetylene is an important industrial feedstock but its largest use is as the fuel for the oxyacetylene welding torch.

Structure and bonding in Alkynes

(1) Alkynes are hydrocarbons that contain carbon -carbon triple bond.

(2) Alkynes are also called acetylenes because they are derivatives of acetylene.

(3) The general formula is : C_nH_{2n-2}. (one triple bond)

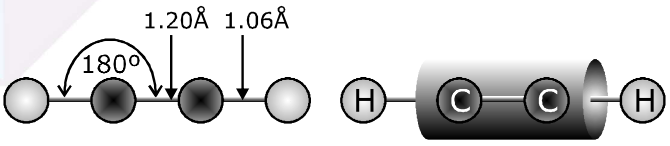
(4) In alkyne $C \equiv C$ bond length is 1.20 Å.

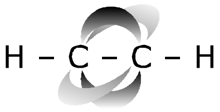
(5) Its bond energy is 192 kcal mol^{-1}

(6) The hybridization of carbon atoms having triple bond ($C \equiv C$) in alkynes is sp.

(7) Overlapping of these sp hybrid orbitals with each other and with the hydrogen orbitals gives the sigma bond framework which is linear (180º) structure.

(8) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90º) to each other, forming one π bond with electron density above and below the C – C sigma bond, and the other with electron density in front and in back of the sigma bond. This results in a cylindrical π electron cloud around σ bonded structure.





Note :

Any type of stereochemistry does not arise in acetylenic bond due to linearity of $C \equiv C$ bond.

Physical Properties of Alkynes

(1) Alkynes are relatively nonpolar (w.r.t. alkyl halides and alcohols) and are nearly insoluble in water (but they are more polar than alkenes and alkanes). They are quite soluble in most organic solvents, (acetone, ether, methylene chloride, chloroform and alcohols).

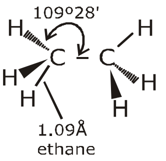
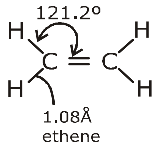
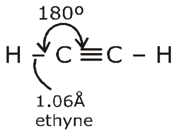
(2) Acetylene, propyne, and butynes are gases at room temperature, just like the corresponding alkanes and alkenes. In fact, the boiling point of alkynes are nearly the same as those of alkanes and alkenes with same number of carbon atoms.

Table

Name	Formula	M.p., °C	B.P., °C	Relative density (at 20°C)
Acetylene	$HC\equiv CH$	– 82	– 75	
Propyne	$HC\equiv CCH_3$	– 101.5	– 23	
1-Butyne	$HC\equiv CCH_2CH_3$	– 122	9	
1-Pentyne	$HC\equiv C(CH_2)_2CH_3$	– 98	40	0.695
2-Butyne	$CH_3C\equiv CCH_3$	– 24	27	0.694
2-Pentyne	$CH_3C\equiv CCH_2CH_3$	– 101	55	0.714
3-Methyl-1-butyne	$HC\equiv CCH(CH_3)_2$		29	665

TABLE - COMPARATIVE STUDY OF ALKANES, ALKENES, ALKYNES

S.No.	Properties	Alkanes	Alkenes	Alkynes
1.	Bond length (angstrom)	1.54 (C – C)	1.32 (C = C)	1.20 ($C\equiv C$)
2.	Bond energy ($kJmol^{-1}$)	415 (C – C)	615 (C = C)	835 ($C\equiv C$)
3.	Hybridization	sp^3	sp^2	sp
4.	% s character	25%	33%	50%
5.	pK_a	50	44	25
6.	Electronegativity of 'C'		Increases →	
7.	Polarity		Increases →	
8.	Rate of hydrogenation		less	more
9.	Rate of electrophilic addition reaction		more	less
10.	Heat of combustion	C_2H_6(-373 kcal)	C_2H_4(-337 kcal)	C_2H_2(-317 kcal)

S.No.	Properties	Alkanes	Alkenes	Alkynes
11.	Density (g/cm^3)	C_3H_8(0.49)	C_3H_6(0.52)	C_3H_4(0.67)
12.	Structure	 1.09Å ethane	 1.08Å ethene	 1.06Å ethyne
13.	Shape	Tetrahedral	Planar	Linear

Laboratory Test of Alkyne :

Functional Group	Reagent	Observation	Reaction	Remarks
– C ≡ C –	(1) Baeyer's Reagent alk.dil. cold $KMnO_4$	Pink colour disappears	$HC \equiv CH + H_2O + O \xrightarrow{alk.\ KMnO_4} OHC - CHO$	Hydroxylation
	(2) Br_2/H_2O	Red colour decolourises	$Br_2 + HC \equiv CH \rightarrow CHBr_2 - CHBr_2$ White ppt	Bromination
	(3) O_3 (ozone)	Acid Formed	$R - C \equiv C - R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis

Laboratory Test of Terminal Alkynes :

When triple bond comes at the end of a carbon chain, the alkyne is called a terminal alkyne.

acetylenic hydrogen

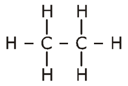
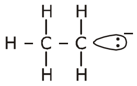
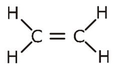
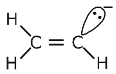
$H - C \equiv C - CH_2CH_3$

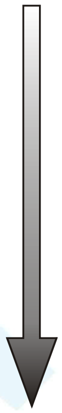
1-Butyne, terminal alkyne

Functional Group	**Reagent**	**Observation**	**Reaction**
R–C≡C–H	(1) Cuprous chloride +NH_4OH	Red ppt	$R - C \equiv CH + CuCl \xrightarrow{NH_4OH} R - C \equiv C\ Cu\downarrow$(red)
	(2) $AgNO_3$ + NH_4OH	White ppt	$R - C \equiv CH + Ag^+ \longrightarrow R - C \equiv C\ Ag\downarrow$(white)
	(3) Na in ether	Colourless gas	$HC \equiv CH + 2Na \longrightarrow Na - C \equiv C - Na + H_2\uparrow$

Acidity of Terminal Alkynes :

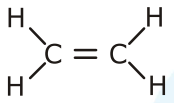
Terminal alkynes are much acidic than other hydrocarbons due to more electronegative sp hybridised carbon. The polarity (acidity) of a C – H bond varies with its hydridization, increases with the increase in precentage of s character of the orbitals. $sp^3 < sp^2 < sp$

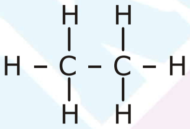
S.No.	Compound	Conjugate Base	Hybridization of C	% s-Character	pK_a
1.	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$		sp^3	25%	50
2.			sp^2	33%	44
3.	$:NH_3$	$:\ddot{N}H_2^-$			
4.	$H-C\equiv C-H$	$H-C\equiv\ddot{C}^{\ominus}$	sp	50%	25
5.	$R-OH$	$R-\ddot{\underset{\cdot\cdot}{O}}^-$			16-18



The hydrogen bonded to the carbon of a terminal alkyne is considerably more acidic than those bonded to carbons of an alkene and alkane (see section). The pK_a values for ethyne, ethene & ethane illustrate this point.

$H-C\equiv C-H$





$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

$pK_a = 25$ $pK_a = 44$ $pK_a = 50$

The order of basicity of their anions is opposite to that of their relative acidity:

Relative Basicity

$CH_3CH^{\ominus}_2 > H_2C=CH^{\ominus} > HC\equiv C^{\ominus}$

Relative acidity

$$H-\underset{\cdot\cdot}{\ddot{O}}H > H-\underset{\cdot\cdot}{\ddot{O}}R > H-C\equiv CR > H-\ddot{N}H_2 > H-CH=CH_2 > H-CH_2CH_3$$

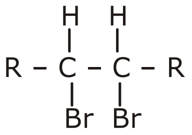
pK_a 15.7 16-17 25 38 44 50

Relative Basicity

$$\overset{\ominus}{:}\underset{\cdot\cdot}{\ddot{O}}H < \overset{\ominus}{:}\underset{\cdot\cdot}{\ddot{O}}R < \overset{\ominus}{:}C\equiv CR < \overset{\ominus}{:}\ddot{N}H_2 < \overset{\ominus}{:}CH=CH_2 < \overset{\ominus}{:}CH_2CH_3$$

Preparation methods of Alkyne :

(I) By dehydrohalogenation of gem and vic dihalide:

General Reaction: $RCH=CHR + Br_2 \rightarrow$  $\xrightarrow{2NaNH_2} R-C\equiv C-R + 2NaBr$

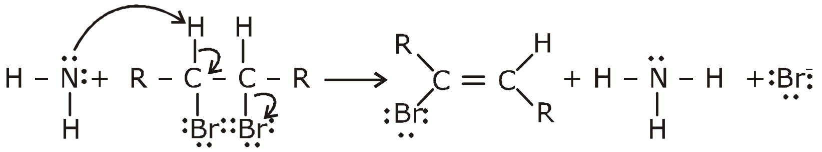
$$RCH=CHR + Br_2 \rightarrow R-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-R \xrightarrow{2NaNH_2} R-C\equiv C-R + 2NaBr$$

vic - Dibromide

The dehydrohalogenations occur in two steps, the first yielding a bromoalkene and the second alkyne.

Mechanism :

Step 1



Amide ion (The strongly basic amide ion brings about an E2 reaction.)

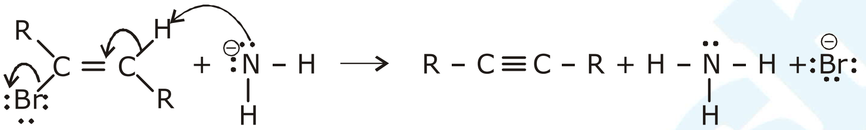
vic-Dibromide

Bromoalkene

Ammonia

Bromide ion

Step 2



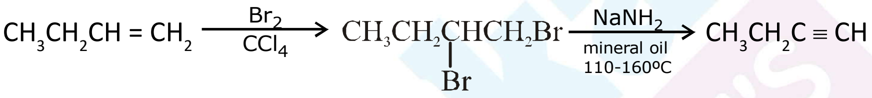
Bromoalkene (A second E2 reation produces the alkyne)

Amide ion

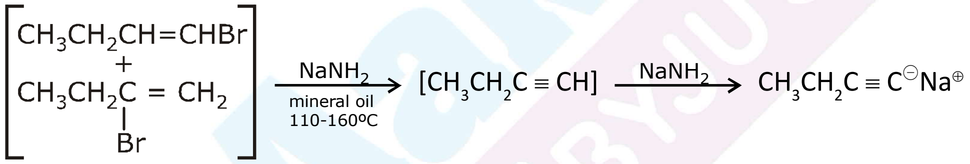
Alkyne

Ammonia

Bromide ion

e.g. 

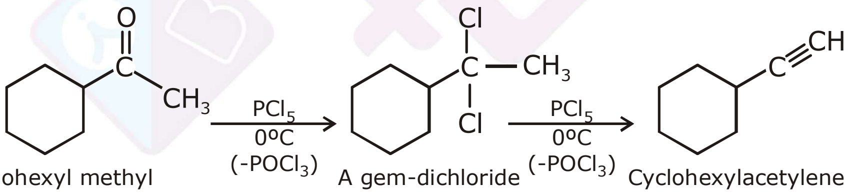
$$CH_3CH_2CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[\text{mineral oil } 110\text{-}160^oC]{NaNH_2} CH_3CH_2C\equiv CH$$

e.g. 

$$\left[\begin{array}{c} CH_3CH_2CH=CHBr \\ + \\ CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}} = CH_2 \end{array}\right] \xrightarrow[\text{mineral oil } 110\text{-}160^oC]{NaNH_2} [CH_3CH_2C\equiv CH] \xrightarrow{NaNH_2} CH_3CH_2C\equiv C^{\ominus}Na^{\oplus}$$

$CH_3CH_2C\equiv C^-Na^+ \xrightarrow{NaNH_2} CH_3CH_2C\equiv CH$

General Reaction



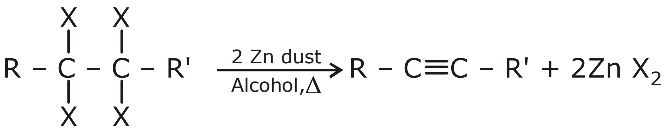
Cyclohexyl methyl Ketone

A gem-dichloride (70-80%)

Cyclohexylacetylene (46%)

(II) By dehalogenation of tetrahaloalkane:

General Reaction



$$R-\overset{\displaystyle X}{\underset{\displaystyle X}{C}}-\overset{\displaystyle X}{\underset{\displaystyle X}{C}}-R' \xrightarrow[\text{Alcohol},\Delta]{2\text{ Zn dust}} R-C\equiv C-R' + 2Zn\ X_2$$

(III) Replacement of The acetylenic hydrogen atom of terminal alkynes:

General Reaction $R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv\overset{\ominus}{C}: + R'-X \longrightarrow R-C\equiv C-R'$

Sodium ethynide and other sodium alkynides can be prepared by treating terminal alkynes with sodium amide in liquid ammonia.

$$H-C\equiv CH-H + NaNH_2 \xrightarrow{liq.\ NH_3} H-C\equiv\overset{\ominus}{C}\!:Na^{\oplus} + NH_3$$

$$CH_3-C\equiv C-H + NaNH_2 \xrightarrow{liq.\ NH_3} CH_3C\equiv\overset{\ominus}{C}\!:Na^{\oplus} + NH_3$$

$$\underset{\substack{\text{Sodium}\\\text{alkynide}}}{R-C\equiv C^{\ominus}\,Na^{\oplus}} + \underset{\substack{\text{Primary}\\\text{alkyl halide}}}{R'CH_2-Br} \longrightarrow \underset{\substack{\text{Mono or disubstituted}\\\text{acetylene}}}{R-C\equiv C-CH_2R'} + NaBr$$

(R or R' or both may be hydrogen)
The following example illustrates this synthesis of higher alkyne homologues.

$$CH_3CH_2C\equiv C:^{\ominus}\,Na^{\oplus} + CH_3CH_2-Br \xrightarrow[6\ hours]{liq.\ NH_3} \underset{\substack{\text{3-Hexyne}\\(75\%)}}{CH_3CH_2C\equiv CCH_2CH_3} + NaBr$$

$$R-C\equiv\overset{\ominus}{C}: + R'-X \xrightarrow{S_N2} R-C\equiv C-R' + X^{\ominus}$$

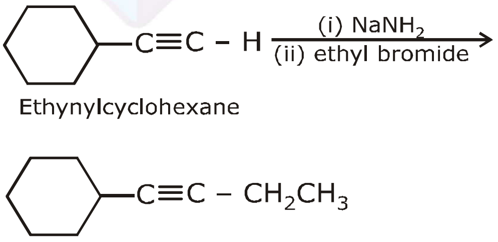
(R'–X must be an unhindered primary halide or tosylate)
The unshared electron pair of the alkynide ion attacks the back side of the carbon atom that bears the halogen atom and forms a bond to it. The halogen atom departs as a halide ion.
e.g.

$$H-C\equiv C-H \xrightarrow[NaNH_2]{2\ eq.} Na^+C^- \equiv C^-Na^+ \xrightarrow{\substack{2\ moles\\(CH_3X)}} CH_3-C\equiv C-CH_3$$

e.g. $R-C\equiv C-H \xrightarrow{R'\,MgX} \underset{+\,R'\,H}{R-C\equiv C\,Mg\,X} \xrightarrow{R'\,X}$

$R-C\equiv C-R' + MgX_2$

e.g.

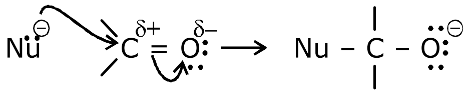


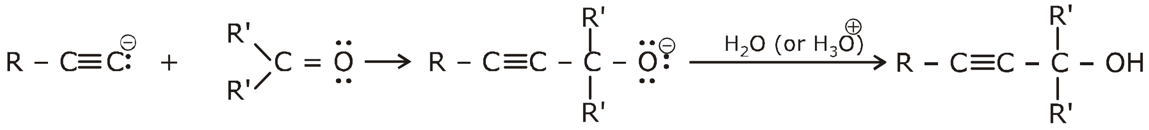
Ethynylcyclohexane

(i) $NaNH_2$
(ii) ethyl bromide

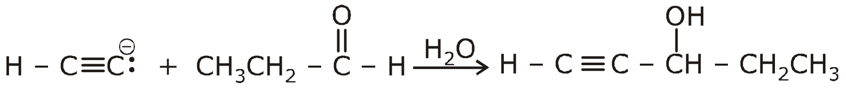
1-Cyclohexyl-1-butyne
(ethylcyclohexyl acetylene)

Addition of acetylide ions to carbonyl groups :





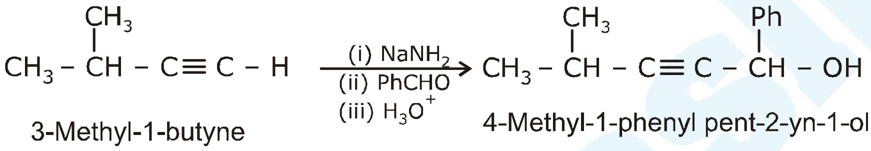
e.g.



$$H-C\equiv C^{\ominus} + CH_3CH_2-\overset{O}{\overset{||}{C}}-H \xrightarrow{H_2O} H-C\equiv C-\overset{OH}{\overset{|}{CH}}-CH_2CH_3$$

sodium acetylide Propanal 1-Pentyn-3-ol

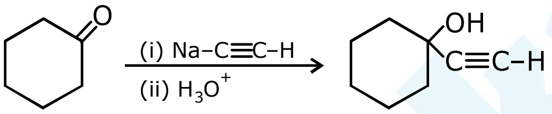
e.g.



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-C\equiv C-H \xrightarrow[\text{(ii) PhCHO (iii) } H_3O^+]{\text{(i) } NaNH_2} CH_3-\overset{CH_3}{\overset{|}{CH}}-C\equiv C-\overset{Ph}{\overset{|}{CH}}-OH$$

3-Methyl-1-butyne 4-Methyl-1-phenyl pent-2-yn-1-ol

e.g.



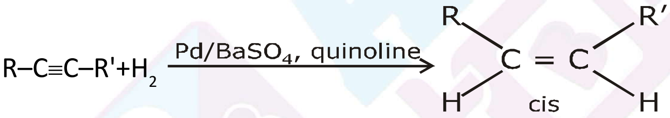
Cyclohexanone 1-Ethynylcyclohexanol(3º)

Chemical reaction of Alkyne

(I) Reduction to alkenes

(a) By Lindlar's reagent

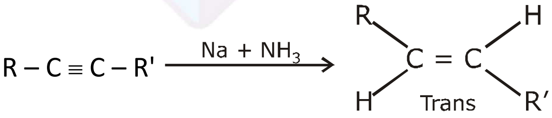
General Reaction



(syn addition)

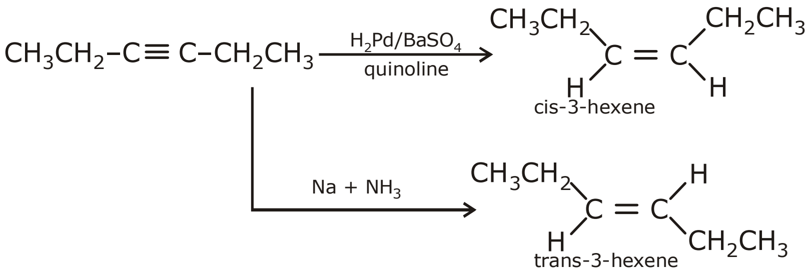
(b) By Birch reduction

General Reaction



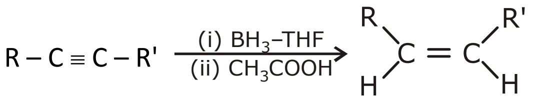
(anti addition)

e.g.



(c) By hydroboration reduction

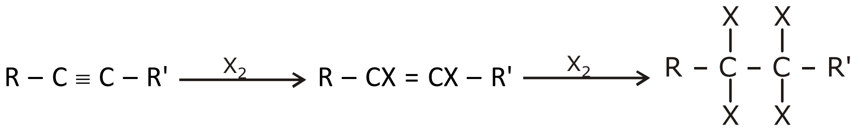
General Reaction



$$R-C\equiv C-R' \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } BH_3\text{–THF}} (R)(H)C=C(R')(H)$$

(II) Addition of halogen (X_2=Cl_2, Br_2)

General Reaction

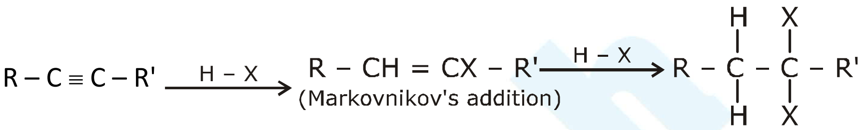


$$R-C\equiv C-R' \xrightarrow{X_2} R-CX=CX-R' \xrightarrow{X_2} R-CX_2-CX_2-R'$$

(Anti-addition)

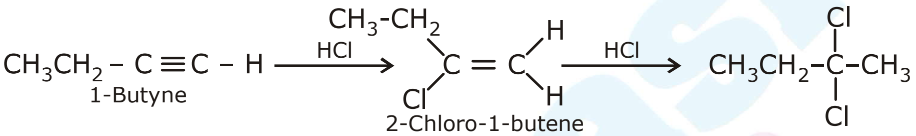
(III) Addition of hydrogen halides (Were HX = HCl, HBr, HI)

General Reaction



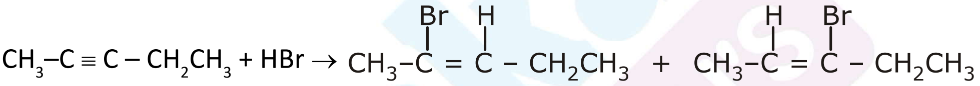
$$R-C\equiv C-R' \xrightarrow{H-X} \underset{\text{(Markovnikov's addition)}}{R-CH=CX-R'} \xrightarrow{H-X} R-CH_2-CX_2-R'$$

e.g.



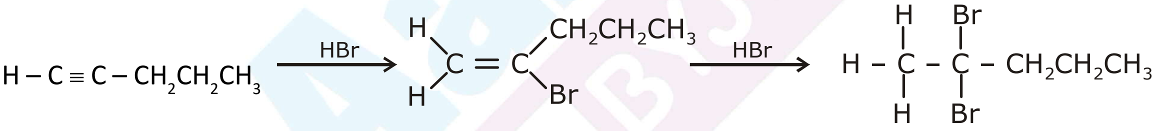
$$\underset{\text{1-Butyne}}{CH_3CH_2-C\equiv C-H} \xrightarrow{HCl} \underset{\text{2-Chloro-1-butene}}{(CH_3\text{-}CH_2)(Cl)C=CH_2} \xrightarrow{HCl} \underset{\text{2,2-Dichlorobutane}}{CH_3CH_2\text{-}CCl_2\text{-}CH_3}$$

e.g.



$$CH_3\text{–}C\equiv C-CH_2CH_3 + HBr \rightarrow CH_3\text{–}C(Br)=C(H)-CH_2CH_3 + CH_3\text{–}C(H)=C(Br)-CH_2CH_3$$

e.g.

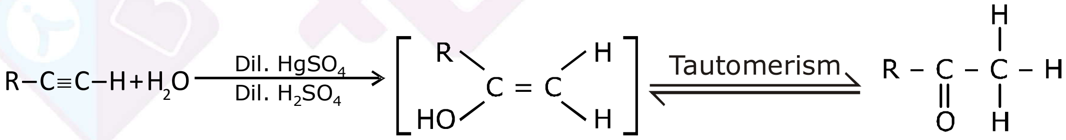


$$H-C\equiv C-CH_2CH_2CH_3 \xrightarrow{HBr} (H)(H)C=C(CH_2CH_2CH_3)(Br) \xrightarrow{HBr} H-CH_2-CBr_2-CH_2CH_2CH_3$$

(IV) Addition of water

(a) Mercuric ion catalyzed hydration:

General Reaction

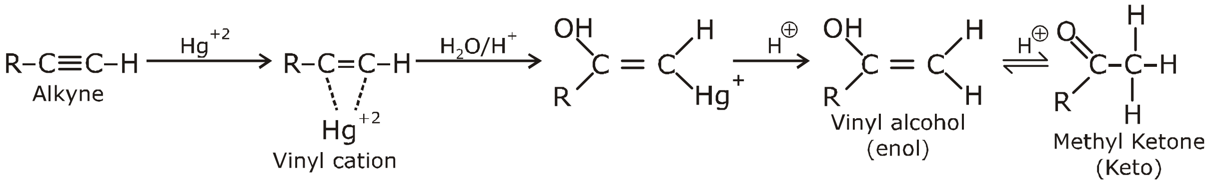


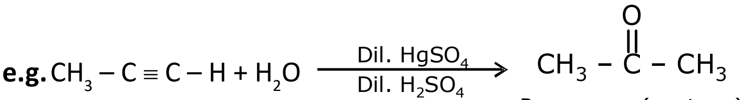
$$R-C\equiv C-H+H_2O \xrightarrow[\text{Dil. } H_2SO_4]{\text{Dil. } HgSO_4} \left[(R)(HO)C=C(H)(H)\right] \xrightleftharpoons{\text{Tautomerism}} R-\underset{\|}{C}(O)-CH_3$$

(Markovnikov rule) Vinyl alcohol (unstable) Ketone (stable)

Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercuri alcohol. Under the acidic reaction condition, Hg is replaced by hydrogen to give a vinyl alcohol, called an enol.

Mech.



e.g. 

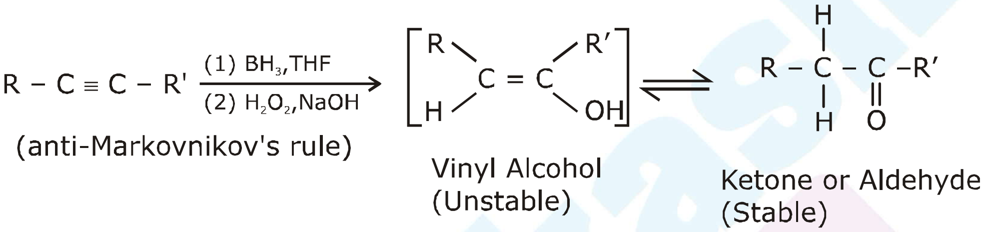
$CH_3-C\equiv C-H+H_2O \xrightarrow[\text{Dil. } H_2SO_4]{\text{Dil. } HgSO_4} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

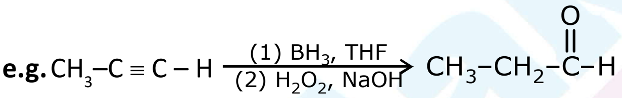
Propanone (acetone)

(b) Hydroboration-oxidation:

In alkyne, except that a hindered dialkylborane must be used to prevent addition of two molecules of borane across the triple bond.

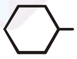
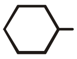
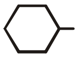
General Reaction



e.g. 

$CH_3-C\equiv C-H \xrightarrow[(2)\ H_2O_2,\ NaOH]{(1)\ BH_3,\ THF} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

Propanal

Reactant	Product obtained by	
	Hydroboration oxidation	Hg^{2+} ion-catalysed hydration
(a) $CH_3C\equiv CCH_3$	$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$	$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$
(b)  C≡CH	 CH_2CHO	 $\overset{\overset{O}{\|}}{C}CH_3$

(V) Formation of alkylide anions (Alkynides)

Sodium, lithium and magnesium alkynide

General Reaction

$R-C\equiv C-H+NaNH_2 \rightarrow R-C\equiv C^{-}\ {}^{+}Na+NH_3$

$R-C\equiv C-H+R'-Li \rightarrow R-C\equiv CLi+R'H$

$R-C\equiv C-H+R'MgX \rightarrow R-C\equiv CMgX+R'H$

(VI) Alkylation of alkylide ions

General Reaction

$R-C\equiv C^{-} + R'-X \rightarrow R-C\equiv C-R'$

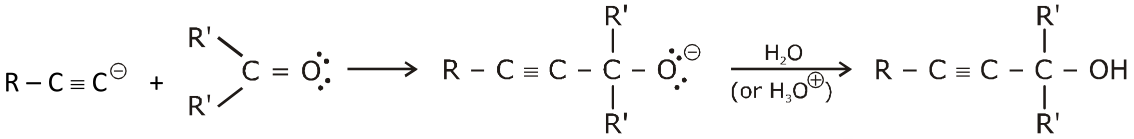
($R'-X$ must be an unhindered primary halide or tosylate)

e.g. $CH_3CH_2\,C\equiv C^{\ominus}Na^{\oplus} + CH_3CH_2CH_2-Br \rightarrow CH_3CH_2-C\equiv C-CH_2CH_2CH_3$

Sodium butynide 1-Bromopropane Hept-3-yne

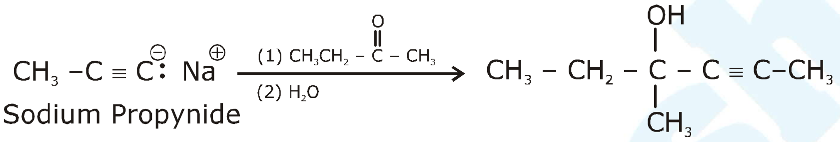
(VII) Reactions with carbonyl groups

General Reaction



$$R-C\equiv C^{\ominus} + \begin{matrix}R'\\ \\R'\end{matrix}\!\!>C=\ddot{O}\!: \longrightarrow R-C\equiv C-\underset{R'}{\overset{R'}{C}}-\ddot{O}\!:^{\ominus} \xrightarrow[\text{(or } H_3O^{\oplus})]{H_2O} R-C\equiv C-\underset{R'}{\overset{R'}{C}}-OH$$

e.g.



$$CH_3-C\equiv C\!:^{\ominus}\,Na^{\oplus} \xrightarrow[(2)\ H_2O]{(1)\ CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3} CH_3-CH_2-\underset{CH_3}{\overset{OH}{C}}-C\equiv C-CH_3$$

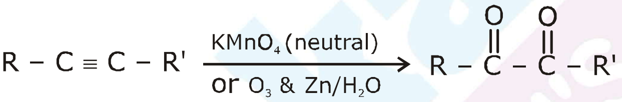
Sodium Propynide

3-Methylhex-4-yn-3-ol

(VIII) Oxidation of alkyne

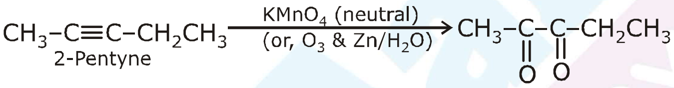
If an alkyne is treated with aqueous $KMnO_4$ under nearly neutral conditions, an α-diketone results.

General Reaction



$$R-C\equiv C-R' \xrightarrow[\text{or } O_3\ \&\ Zn/H_2O]{KMnO_4\,(\text{neutral})} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R'$$

e.g.



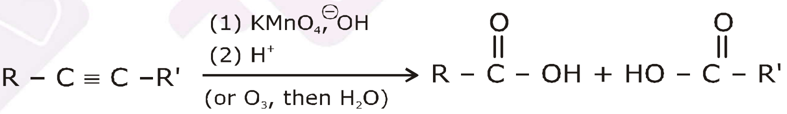
$$\underset{\text{2-Pentyne}}{CH_3-C\equiv C-CH_2CH_3} \xrightarrow[(\text{or, } O_3\ \&\ Zn/H_2O)]{KMnO_4\ (\text{neutral})} CH_3-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-CH_2CH_3$$

Pentane-2,3-dione

(IX) Oxidative cleavage

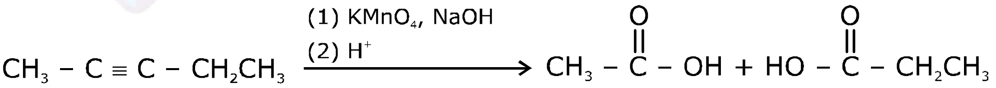
If the reaction mixture becomes warm or too basic the diketone undergoes oxidative cleavage. The products are the salts of carboxylic acids, which can be converted to the free acids by adding dilute acid.

General Reaction



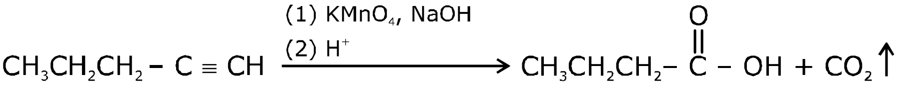
$$R-C\equiv C-R' \xrightarrow[(\text{or } O_3,\ \text{then } H_2O)]{(1)\ KMnO_4,\,^{\ominus}OH\quad (2)\ H^{+}} R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R'$$

e.g.



$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{(1)\ KMnO_4,\ NaOH\quad (2)\ H^{+}} CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

e.g.



$$CH_3CH_2CH_2-C\equiv CH \xrightarrow{(1)\ KMnO_4,\ NaOH\quad (2)\ H^{+}} CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH + CO_2\uparrow$$

Ozonolysis :

General reaction $R-C\equiv C-R' \xrightarrow[(ii)\ H_2O]{(i)\ O_3} R-COOH + R'-COOH$

e.g. $CH_3-C\equiv C-CH_2CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3-COOH + CH_3CH_2-COOH$

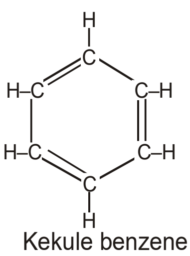
AROMATIC COMPOUNDS

BENZENE

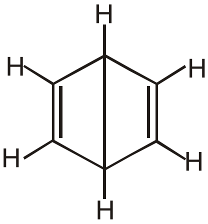
Introduction :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.

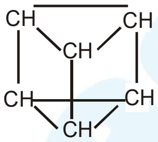
Proposed structure of benzene :



Kekule benzene



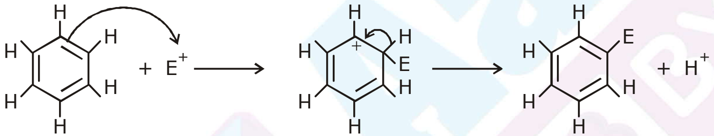
Dewar's benzene



[Prism like structure proposed by Albert Ladenberg]

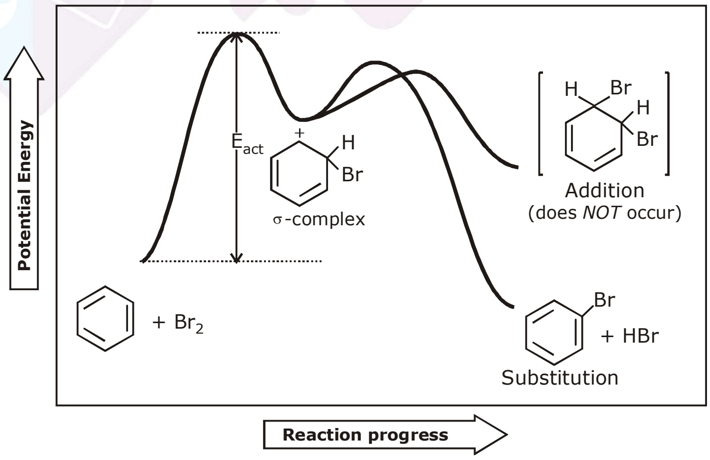
* Benzene mostly represents by Kekule structure.

Electrophilic aromatic substitution reaction (AR_sE reaction)

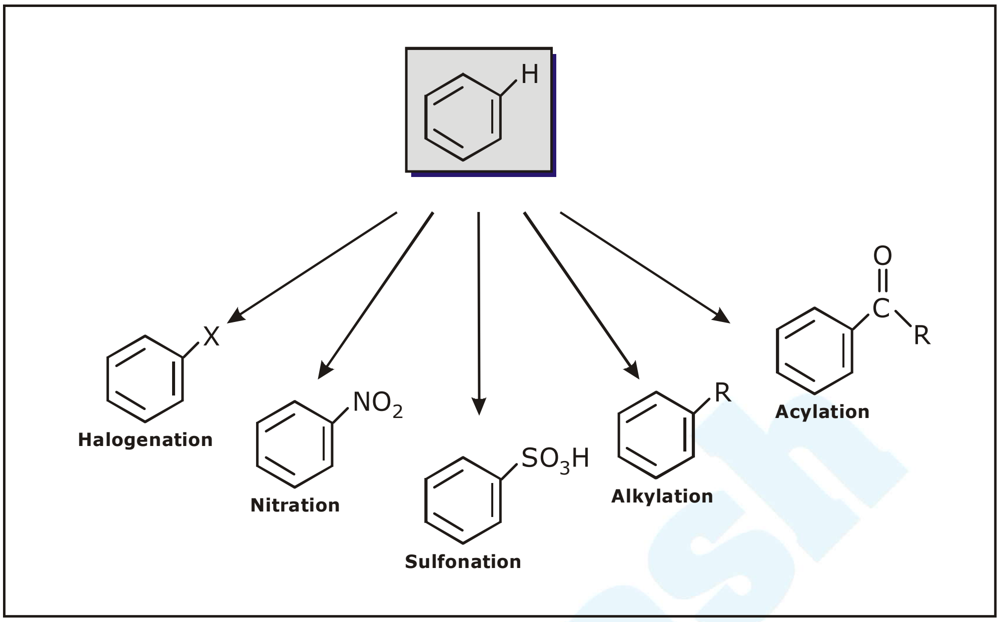


σ-complex

A reaction energy diagram for the electrophilic bromination of benzene
The reaction occurs in two steps and releases energy



Some Electrophilic Aromatic substitution Reactions of Benzene :



(i) Ortho- and para-directing activators : Groups like –OH and $–NH_2$ present on a ring direct an electrophile, E^+, to ortho or para position and they react faster than benzene.

(ii) Ortho- and para-directing deactivators : Halogens present on a ring direct an electrophile, E^+, to ortho or para positions, and they react slower than benzene.

(iii) Meta-directing deactivators : Groups containing a carbonyl (>C = O) or a –CN group direct an electrophile, E^+, to the meta positions, but they react slower than benzene.

No meta-directing activators are known. Figure 5.8 shows how the directing effects of the groups correlate with their reactivities. All meta directing grops are deactivating and most ortho - and para - directing groups are activating. The halogens are unique in being ortho and para directing and deactivating.

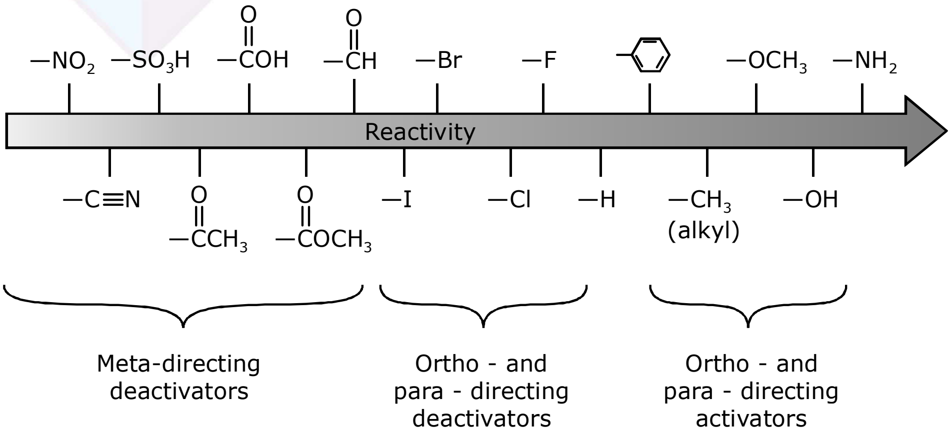
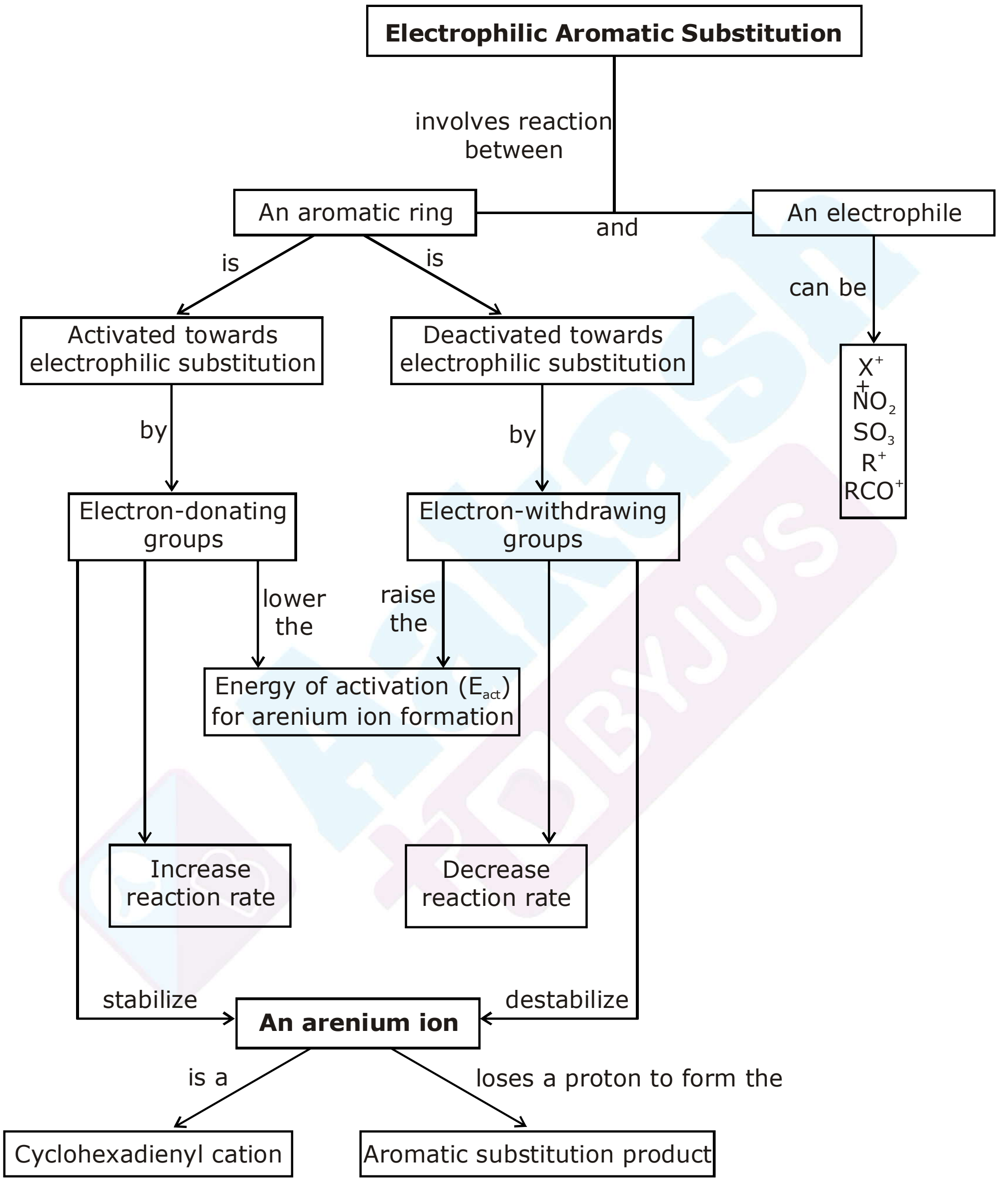


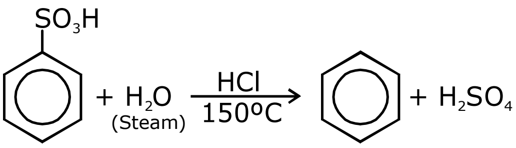
Figure: Effects of Substituents in electrophilic aromatic substitutions. All activating groups are ortho - and para - directing, and all deactivating groups other than halogen are meta-directing. The halogens are ortho and para-directing deactivators.

Concept Map :

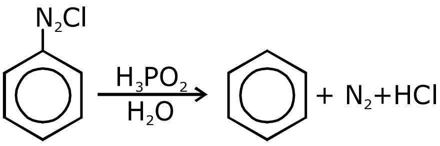


Method of Preparation of Benzene :

(I) From Sulphonic Acid: When benzene sulphonic acid is heated with steam under pressure benzene is formed.

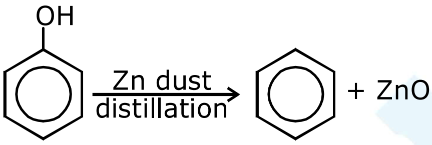


(II) From Diazonium Salts:

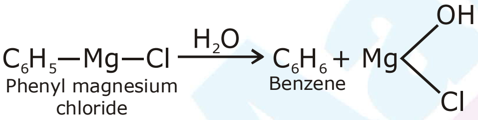


When benzene diazonium chloride undergoes reduction with H_3PO_2 in presence of H_2O, benzene is formed.

(III) From phenol: When phenol is distilled with zinc dust, benzene is formed.



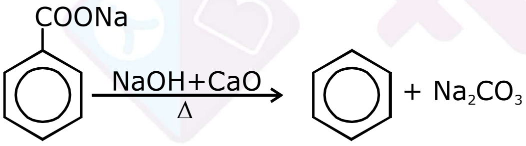
(IV) From Grignard Reagent:



$$\underset{\text{Phenyl magnesium chloride}}{C_6H_5-Mg-Cl} \xrightarrow{H_2O} \underset{\text{Benzene}}{C_6H_6} + Mg\begin{matrix} OH \\ Cl \end{matrix}$$

Note: $C_6H_5-Cl \xrightarrow[\text{dry ether}]{Mg} C_6H_5-MgCl$

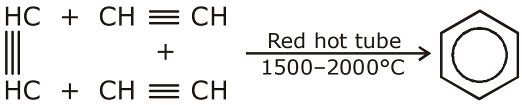
(V) From Decarboxylation of Sodium Benzoate:



Note: Benzene is prepared in the laboratory by heating the mixture of sodalime and sodium benzoate. This reaction is called decarboxylation.

(VI) From Acetylene: [Synthesis] Acetylene polymerizes to give benzene when passed through a heated metallic tube.

ie.



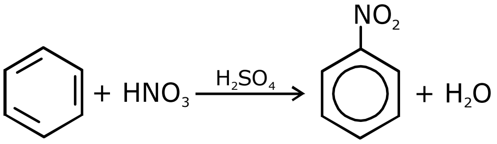
Note: (i) This reaction is called cyclic polymerisation.

(ii) Red hot tube or a tube containing a complex organo-nickel catalyst at 70°C.

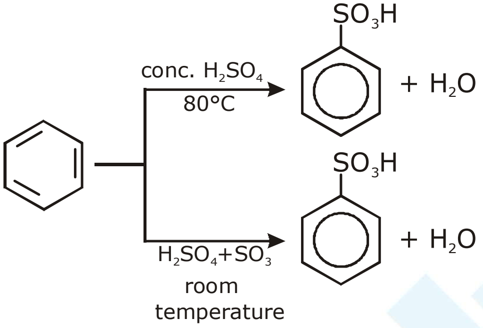
Chemical reactions of Benzene

The characteristic reaction of benzene are aromatic substitution. In these reaction one of the ring hydrogen is replaced by some other group.

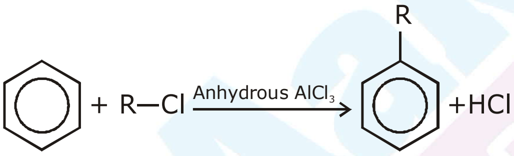
(I) Nitration: The treatment of benzene with conc. HNO_3 in the presence of concentrated H_2SO_4. Then nitrobenzene is formed.



(II) Sulphonation: The treatment of benzene with conc. H_2SO_4 at 80°C or fuming sulphuric acid (i.e conc. H_2SO_4 + SO_3) at room temperature.

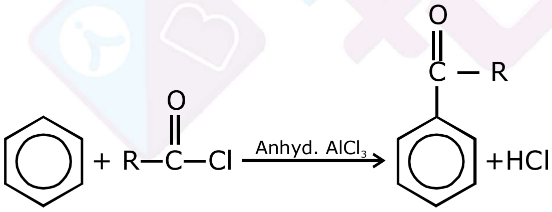


(III) Friedel-Crafts Alkylation:



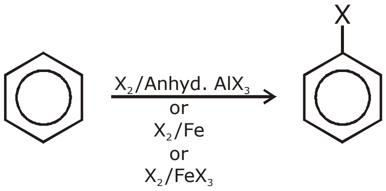
This involves the treatment of benzene with alkyl chlorides in the presence of anhydrous $AlCl_3$.

(IV) Friedel-Crafts Acylation:



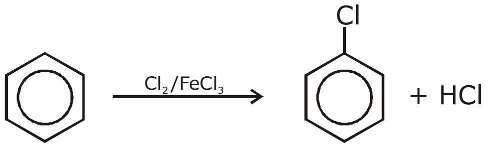
The treatment of benzene with acyl chlorides in the presence of anhydrous $AlCl_3$.

(V) Halogenation:

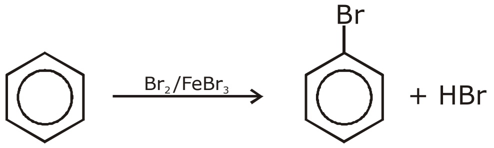


Example:

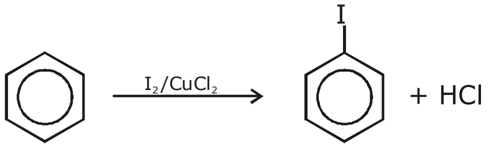
(i) Chlorination:



(ii) Bromination:



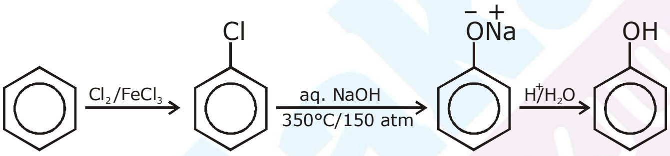
(iii) Iodination:



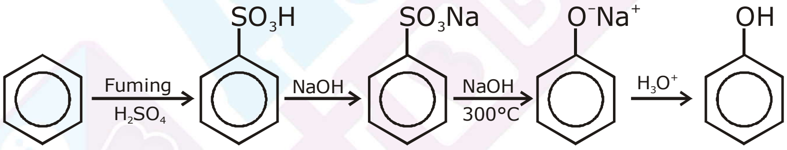
Note: Fluorobenzene cannot be prepared by a direct method.

(VI) Phenol From Benzene:

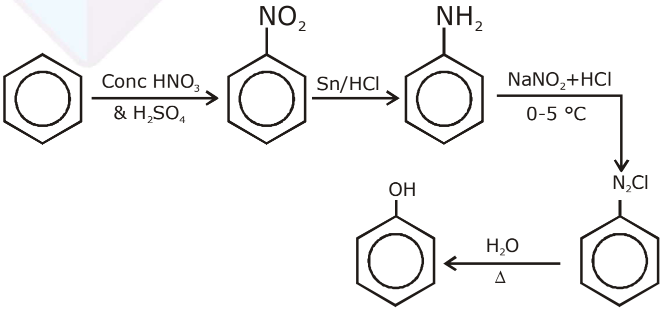
(i) From Chlorobenzene: [Dow Process]



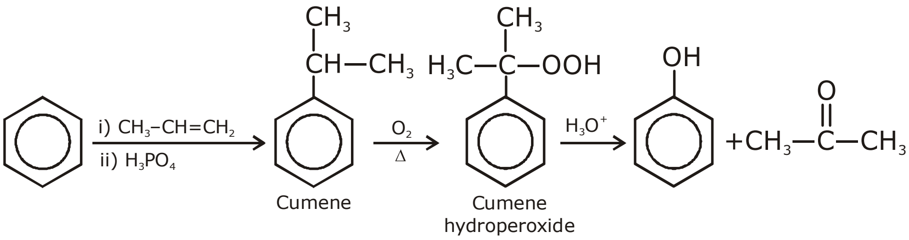
(ii) From Benzene Sulphonic Acid:



(iii) From Benzene Diazonium Chloride:

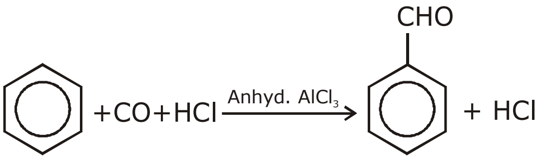


(iv) From Cumene Hydroperoxide: [Cumene Process]



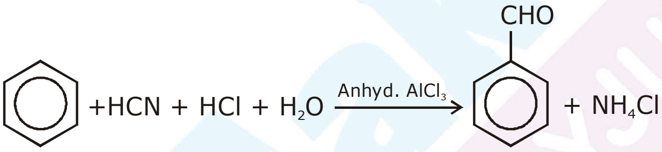
(VII) Benzaldehyde From benzene:

1. Method:- Gattermann-Koch Synthesis:



This reaction involves the treatment of benzene with carbon monoxide and hydrogen chloride (CO + HCl) in the presence of anhydrous $AlCl_3$ catalyst.

2. Method: Gattermann-Aldehyde Synthesis:



This reaction involves the treatment of benzene with (HCN + HCl + H_2O) in the presence of anhydrous $AlCl_3$ catalyst.

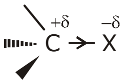
ALKYL HALIDE (HALOALKANES)

Aliphatic Halogen Derivatives :

Compounds obtained by the replacement of one or more hydrogen atom(s) from hydrocarbons are known as halogen derivatives. The halogen derivatives of alkanes, alkenes, alkynes and arenes are known as alkyl halide (haloalkane), alkenyl halide (haloalkenes), alkynyl halides (haloalkynes) and aryl halides (halobenzenes) respectively.

Alkyl halides : Monohalogen derivatives of alkanes are known as alkyl halides.

Structure of alkyl halides:



Classification of alkyl halides :

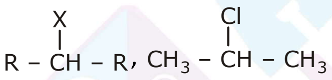
(i) Primary halide : The halogen bearing carbon is bonded to one carbon atom or with no carbon atom.

Example :

$CH_3 - X$, $R - CH_2 - X$

(ii) Secondary halide : If two carbon atoms are bonded to the halogen bearing carbon.

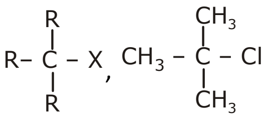
Example :



$$R - \overset{\overset{X}{|}}{C}H - R, \; CH_3 - \overset{\overset{Cl}{|}}{C}H - CH_3$$

(ii) Tertiary halide : Three other carbon atoms bonded to the halogen bearing carbon atom.

Example :



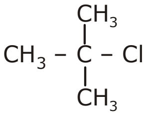
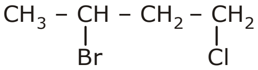
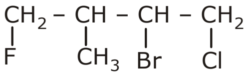
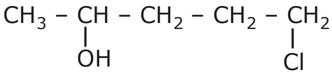
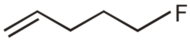
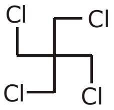
$$R - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}} - X, \; CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Cl$$

Haloalkanes can be classified into following three categories.

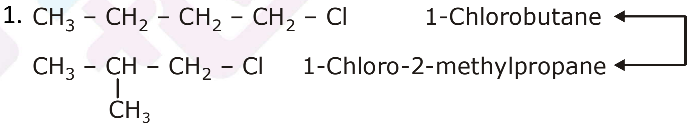
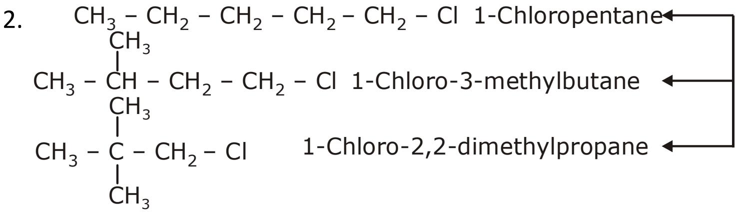
(i) Monohaloalkanes (ii) Dihaloalkanes (iii) Polyhaloalkanes

ALKYL HALIDE

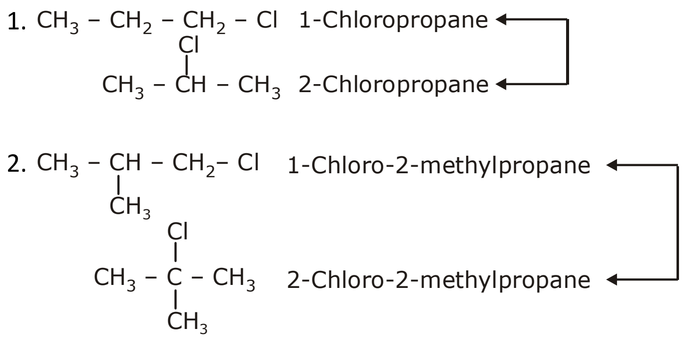
IUPAC nomenclature of alkyl halides

S.N.	Compound	IUPAC name
1.	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$	2–Chloro-2-methylpropane
2.	 $CH_3-\underset{Br}{CH}-CH_2-\underset{Cl}{CH_2}$	3-Bromo-1-chlorobutane
3.	 $\underset{F}{CH_2}-\underset{CH_3}{CH}-\underset{Br}{CH}-\underset{Cl}{CH_2}$	2-Bromo-1-chloro-4-fluoro-3-methylbutane
4.	 $CH_3-\underset{OH}{CH}-CH_2-CH_2-\underset{Cl}{CH_2}$	5-Chloropentan-2-ol
5.		5-Fluoropent-1-ene
6.		2,2-Bis(chloromethyl)-1,3-dichloropropane

Isomerism in haloalkanes :

S.N.	Compound	IUPAC name
1.	Structural Isomerism	
(a)	Chain	 1. $CH_3-CH_2-CH_2-CH_2-Cl$ 1-Chlorobutane $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ 1-Chloro-2-methylpropane  2. $CH_3-CH_2-CH_2-CH_2-CH_2-Cl$ 1-Chloropentane $CH_3-\overset{CH_3}{CH}-CH_2-CH_2-Cl$ 1-Chloro-3-methylbutane $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Cl$ 1-Chloro-2,2-dimethylpropane

(b) Position



1. $CH_3 - CH_2 - CH_2 - Cl$ 1-Chloropropane

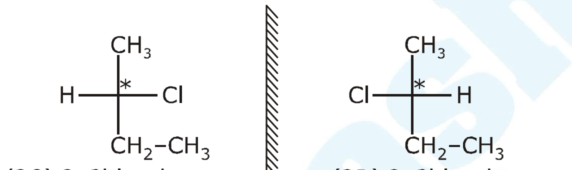
$CH_3 - CH(Cl) - CH_3$ 2-Chloropropane

2. $CH_3 - CH(CH_3) - CH_2 - Cl$ 1-Chloro-2-methylpropane

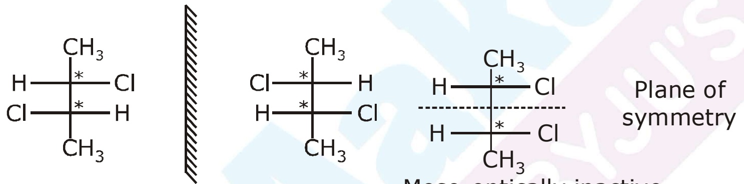
$CH_3 - C(Cl)(CH_3) - CH_3$ 2-Chloro-2-methylpropane

2. Stereoisomerism

` (a) Optical isomerism

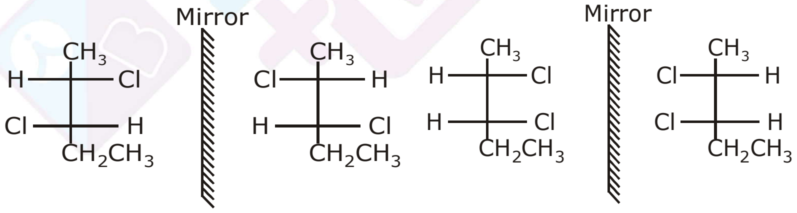


(2S)-2-Chlorobutane (2R)-2-Chlorobutane



Enantiomers of
2,3-Dichlorobutane

Meso-optically inactive



Enantiomers
2,3-Dichloropentane

Enantiomers

Bonding in alkyl halide

Table : 1 Carbon halogen bond lengths

Bond	**Bond length(Å)**
$CH_3 - F$	1.39
$CH_3 - Cl$	1.78
$CH_3 - Br$	1.93
$CH_3 - I$	2.14

Physical properties of alkyl halide

Dipole moment of the halogen derivatives:

$\mu = 4.8 \times \delta \times d$

Where δ is the charge and d is the bond length

These two effects e.g. charge and distance oppose each other, with the larger halogens having longer bond but lesser value of electronegativity. The overall result is that the bond dipole moment increase in the order.

$$\begin{array}{lcccc} & C-I < & C-Br < & C-F < & C-Cl \\ \mu: & 1.29\ D & 1.48\ D & 1.51\ D & 1.56\ D \end{array}$$

The electronegativities of the halogen increase in the order:

I < Br < Cl < F

Table : 2 Molecular dipole moments of methylhalides

X	**CH_3X**	**CH_2X_2**	**CHX_3**	**CX_4**
F	1.82 D	1.97 D	1.65 D	0
Cl	1.94 D	1.60 D	1.03 D	0
Br	1.79 D	1.45 D	1.02 D	0
I	1.64 D	1.11 D	1.00 D	0

Boiling point :

(a) With respect to the halogen in a group of alkyl halides, the boiling point increases as one descends in the periodic table. Alkyl fluorides have the lowest boiling points and alkyl iodides have the highest boiling point. This trend matches the order of increasing polarizability of the halogens (Polarizability is the ease with which the electrons distribution around an atom is distorted by a nearby electric field and is a significant factor in determining the strength of induced-dipole/induced-dipole and dipole/induced-dipole attractions). Forces that depend on induced dipoles are strongest when the halogen is a highly polarizable iodine, and weakest when the halogen is a non-polarizable fluorine.

Table : 3 Boiling points of some alkyl halide in °C (1 atm)

Formula	**X = F**	**X = Cl**	**X = Br**	**X = I**
$CH_3- X$	– 78	– 24	3	42
$CH_3- CH_2X$	– 32	12	38	72
$CH_3- CH_2- CH_2X$	– 3	47	71	103
$CH_3- (CH_2)_3- CH_2X$	65	108	129	157
$CH_3- (CH_2)_4- CH_2X$	92	134	155	180

Fluorine is unique among the halogens is that increasing the number of fluorines does not lead to higher and higher boiling point (B.P.).

Density :

Alkyl fluorides and chlorides are less dense and alkyl bromides and iodides more dense than water.

Table : 5

	$CH_3-(CH_2)_6-CH_2F$	$CH_3-(CH_2)_6-CH_2Cl$	$CH_3-(CH_2)_6-CH_2Br$	$CH_3-(CH_2)_6-CH_2I$
Density (20ºC)	0.80 g/mL	0.89 g/mL	1.12 g/mL	1.34 g/mL

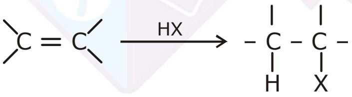
Because alkyl halides are insoluble in water, mixture of an alkyl halide and water separates into two layers. When the alkyl halide is a fluoride or chloride, it is on the upper layer and water is in the lower. The situation is reversed when the alkyl halide is a bromide or an iodide. In these cases the alkyl halide is in the lower layer. Polyhalogenation increases the density. The compounds CH_2Cl_2, $CHCl_3$ and CCl_4 for example, are all more dense than water.

Preparation of alkyl halide :

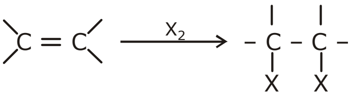
From alkane :

$R - H \xrightarrow{X_2/hv} R - X + HX$

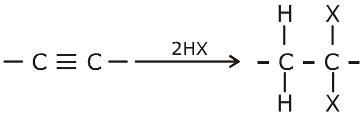
From alkenes and alkynes

(a) 

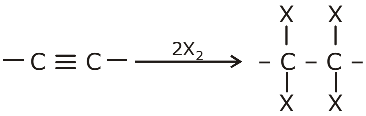
$$>C=C< \xrightarrow{HX} -\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-$$

(b) 

$$>C=C< \xrightarrow{X_2} -\underset{X}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-$$

(c) 

$$-C\equiv C- \xrightarrow{2HX} -\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-$$

(d) 

$$-C\equiv C- \xrightarrow{2X_2} -\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-$$

From alcohol

$R-OH \xrightarrow{HX,\ PX_3, PX_5,\ SOX_2} R-X$

From other halides

$R-X + I^- \xrightarrow{\text{acetone}} R-I + X^-$

$R-Cl\ + KF \xrightarrow{\text{18-crown-6}} R-F$

Finkelstein Reaction

1. $CH_3-CH_2-Cl \xrightarrow{NaI/acetone} CH_3-CH_2-I$

   Nucleophilicity in polar protic solvent

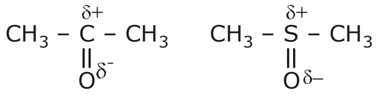
   $-\ F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$

   Polar aprotic solvent

   $-\ F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

   Covalent Nature : NaF < NaCl < NaBr < NaI

   Solubility in polar solvent decreases.



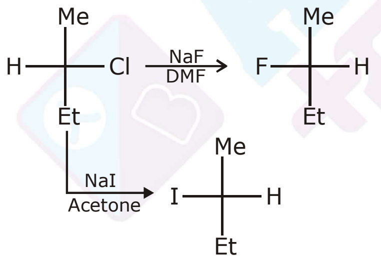
$CH_3-\overset{\delta+}{\underset{\underset{O^{\delta-}}{\|}}{C}}-CH_3 \qquad CH_3-\overset{\delta+}{\underset{\underset{O^{\delta-}}{\|}}{S}}-CH_3$

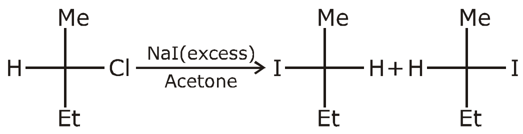
   Acetone → Solubility order in acetone

   NaF < NaCl < NaBr < NaI

2. $CH_3-CH_2-Br \xrightarrow[\text{Acetone}]{NaBr} CH_3-CH_2-Br$
3. $CH_3-CH_2-Cl \xrightarrow[\text{Acetone}]{NaCl} CH_3-CH_2-Cl$
4. $CH_3-CH_2-Cl \xrightarrow[\text{Acetone}]{NaF} CH_3-CH_2-F$
5. $CH_3-CH_2-Cl \xrightarrow[\substack{DMF\\ \text{or DMSO}}]{KF} CH_3-CH_2-F$

   (Swart's reaction)

6. 

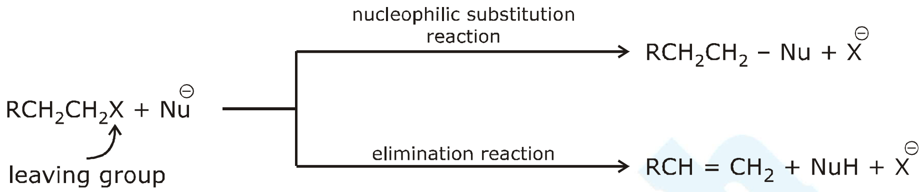
7. 

(Racemisation)

Chemical reactions of alkyl halide

Nucleophilic substitution reaction:

Those organic compounds in which a sp^3 hybridized carbon is bonded to an electronegative atom or group, can undergo two types of reactions e.g. substitution reaction in which the electronegative atom or group is replaced by another atom or group. Second is elimination reaction in which the electronegative atom or group is eliminated along with hydrogen from an adjacent carbon. The electronegative atom or group which is substituted or eliminated is known as leaving group.



Because of more electronegativity of halogen atom it has partial negative charge and partial positive charge develops on carbon atom.

$R\overset{\delta+}{C}H_2 - \overset{\delta-}{X}$

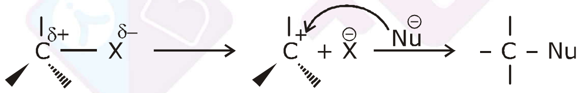
X = F, Cl, Br, I

Due to this polar carbon - halogen bonded alkyl halides shows nucleophilic substitution and elimination reaction.

There are two important mechanisms for the substitution reaction

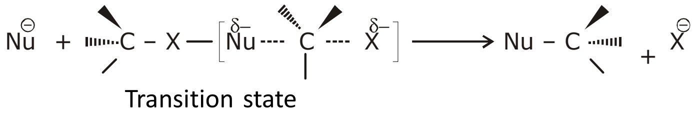
(1) A nucleophile is attracted to the partially positively charged carbon. As the nucleophile approaches the carbon, it causes the carbon - halogen bond to break heterolytically (the halogen keeps both of the bonding electrons.)

(2) The carbon-halogen bond breaks heterolytically without any assistance from the nucleophile, by the help of polar protic solvent and carbocation is formed (solvolysis). Formed carbocation then reacts with the nucleophile to form the substitution product.



(A) Bimolecular nucleophilic substitution reaction (S_N2)

The mechanism of S_N2 reaction



Characteristic of S_N2

(1) It is bimolecular, unistep process.

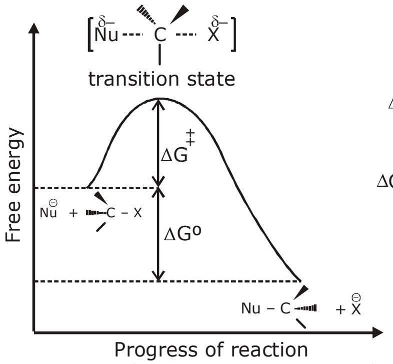
(2) It is second order reaction because in the rate determining step two species are involved.

(3) Kinetics of the reaction → rate ∝ [alkyl halide] [nucleophile]

rate ∝ [alkyl halide] [nucleophile]

If the concentration of alkyl halide in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction is double. If the concentration of nucleophile is doubled the rate of reaction is also double. If the concentration of both are doubled then the rate of the reaction becomes four times.

(4) Energetics of the reaction →



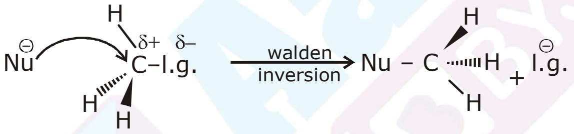
$\Delta G^{\ddagger}$ → The difference in free energy between the reactant and the transition state.

ΔG^{o} → The difference in free energy between the reactant and product.

Figure : A free energy diagrams for a hypothetical S_N2 reaction that takes place with a negative $\Delta G°$

(5) No intermediates are formed in the S_N2 reaction, the reaction proceeds through the formation of an unstable arrangement of atoms or group called transition state.

(6) The stereochemistry of S_N2 reaction → As we have seen earlier, in an S_N2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as walden inversion.



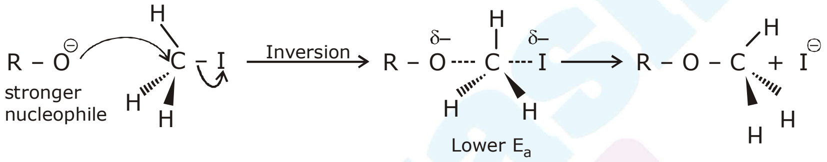
(7) Factors affecting the rate of S_N2 reaction → Number of factors affect the relative rate of S_N2 reaction, the most important factors are:
(i) Structure of the substrate
(ii) Concentration and reactivity of the nucleophile
(iii) Effect of the solvent
(iv) Nature of the leaving group

(i) Effect of the structure of the substrate →
Order of reactivity in S_N2 reaction : – CH_3 > 1º > 2º >> 3º (unreactive)
The important factor behind this order of reactivity is a steric effect. Very large and bulky groups can often hinder the formation of the required transition state and crowding raises the energy of the transition state and slows down reaction.

Table : 6 Relative rates of reactions of alkyl halide in $S_N{}^2$ reaction.

Substituent	**Compound**	**Relative rate**
Methyl	CH_3X	30
1º	CH_3CH_2X	1
2º	$(CH_3)_2CHX$	0.02
Neopentyl	$(CH_3)_3CCH_2X$	0.00001
3º	$(CH_3)_3CX$	~0

(ii) According to kinetics of S_N2 increasing the concentration of the nucleophile increases the rate of an S_N2 reaction. The nature of nucleophile strongly affect the rate of S_N2 reaction. A stronger nucleophile is much more effective than a weaker. For example we know that a negatively charged nucleophile is more reactive than its conjugate acid e.g. $HO^{\ominus} > H_2O$, $RO^{\ominus} > ROH$.



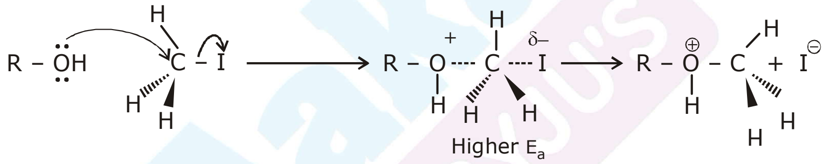
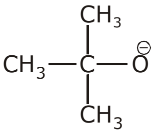


Table : 7

Some common nucleophiles listed in decreasing order of nucleophilicity in hydroxylic solvent	
Strong nucleophiles $(CH_3CH_2)_3\ddot{P}$	Moderate nucleophile : $\overset{\ominus}{Br}$
$\overset{\ominus}{\ddot{S}H}$	$\ddot{N}H_3$
$\overset{\ominus}{I}$	$(CH_3)_2\ddot{S}$
$(CH_3-CH_2)_2\ddot{N}H$	$\overset{\ominus}{Cl}$
$-\overset{\ominus}{CN}$	$Ac\overset{\ominus}{O}$
$(CH_3-CH_2)_3\ddot{N}$	Weak nucleophile $\overset{\ominus}{F}$
$H\overset{\ominus}{O}$	H_2O
$CH_3\overset{\ominus}{O}$	CH_3OH

Steric effects on nucleophilicity



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O^{\ominus}$$

$CH_3 - CH_2 - O^{\ominus}$

t-Butoxide
Stronger base, yet weaker nucleophile cannot approach the carbon atom so easily.

Ethoxide is weaker base, yet stronger nucleophile

(iii) The effect of the solvent ⤚ In polar protic solvent large nucleophiles are good, and the halide ions show the following order:

$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ (in polar protic solvent)

This effect is related to the strength of the interaction between nucleophile and solvent molecules of polar protic solvent forms hydrogen bond to nucleophiles in the following manner.

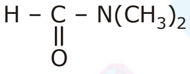
Because small nucleophile is solvated more by the polar protic solvent thus its nucleophilicity decreases and rate of S_N2 decreases.

Relative nucleophilicity in polar protic solvent:

$SH^{\ominus} > CN^{\ominus} > I^{\ominus} > OH^{\ominus} > N_3^{\ominus} > Br^{\ominus} > AcO^{\ominus} > Cl^{\ominus} > F^{\ominus} > H_2O$

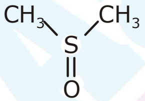
So, polar protic solvents are not useful for rate of S_N2, if nucleophile is anionic. But polar aprotic solvent does not have any active hydrogen atom so they cannot forms H bond with nucleophiles. Polar aprotic solvent have crowded positive centre, so they do not solvate the anion appreciably therefore the rate of S_N2 reactions increased when they are carried out in polar aprotic solvent.

Examples of polar aprotic solvent.



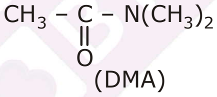
$$H-\underset{\underset{\displaystyle O}{\|}}{C}-N(CH_3)_2$$

(DMF)



$$CH_3-\underset{\underset{\displaystyle O}{\|}}{S}-CH_3$$

(DMSO)



$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-N(CH_3)_2$$

(DMA)

In DMSO, the relative order of reactivity of halide ions is

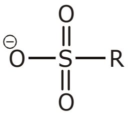
$F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

(iv) The nature of the leaving group ⤚ The best leaving groups are those that become the most stable ion after they leave, because leaving group generally leave as a negative ion, so those leaving group are good, which stabilise negative charge most effectively and weak base do this best, so weaker bases are good leaving groups. A good leaving group always stabilize the transition state and lowers its free energy of activation and thereby increases the rate of the reaction.

Order of leaving ability of halide ion

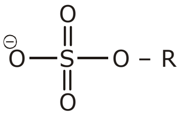
$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

Other leaving groups are



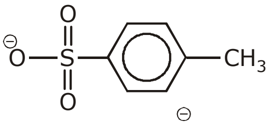
$$^{\ominus}O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-R$$

Alkane sulphonate ion



$$^{\ominus}O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-R$$

Alkyl sulphate ion



Tosylate ion ($\overset{\ominus}{O}$Ts)

$CF_3S\overset{\ominus}{O}_3$

Triflate ion

(Best leaving group)

Strongly basic ions rarely act as leaving group →

$\overset{\ominus}{Br} + R - OH \not\longrightarrow R - X + \overset{\ominus}{O}H$ (strong base and bad leaving group)

$\overset{\ominus}{Nu} + CH_3 - CH_3 \not\longrightarrow CH_3 - Nu + \overset{\ominus}{C}H_3$ ($\overset{\ominus}{C}H_3$ is a strong base)

Table : 8 Examples of S_N2 reactions of alkyl halide →

$\overset{\ominus}{\ddot{N}u} + CH_3 - X \xrightarrow{S_N2} \ddot{N}u - R + \overset{\ominus}{X}$ ($\overset{\ominus}{X}$ is not $\overset{\ominus}{F}$)

Nucleophile		**Product**	**Class of Product**
$R - X + {}^{-}\ddot{I}:$	$\longrightarrow$	$R - \ddot{I}:$	Alkyl halide
$R - X + {}^{-}:\ddot{O}H$	$\longrightarrow$	$R - \ddot{O}H$	Alcohol
$R - X + {}^{-}:\ddot{O}R'$	$\longrightarrow$	$R - \ddot{O}R'$	Ether
$R - X + {}^{-}:\ddot{S}H$	$\longrightarrow$	$R - :\ddot{S}H$	Thiol(mercaptan)
$R - X + {}^{-}:\ddot{S}R'$	$\longrightarrow$	$R - :\ddot{S}R'$	Thioether (sulphide)
$R - X + :NH_3$	$\longrightarrow$	$[R - :NH_3]^{+}X^{-}$	Amine
$R - X + {}^{-}:\ddot{N} = \overset{+}{N} = \ddot{N}:^{-}$	$\longrightarrow$	$R - \ddot{N} = \overset{+}{N} = \ddot{N}:^{-}$	Azide
$R - X + {}^{-}:C \equiv C - R'$	$\longrightarrow$	$R - C \equiv C - R'$	Alkyne
$R - X + {}^{-}:C \equiv N:$	$\longrightarrow$	$R - C \equiv N:$	Nitrile
$R - X + R' - CO\ddot{O}:^{-}$	$\longrightarrow$	$R - COO - R$	Ester
$R - X + :P(Ph)_3$	$\longrightarrow$	$[R - PPh_3]^{+}X^{-}$	Phosphonium salt

(B) Unimolecular nucleophilic substitution reaction (S_N1) :

$$(CH_3)_3C - Cl + \overset{\ominus}{O}H \xrightarrow[H_2O]{Acetone} (CH_3)_3C - OH + \overset{\ominus}{Cl}$$

Mechanism of S_N1 reaction :

Step - 1 Formation of a carbocation (Rate determining step)

$$R - X \rightleftharpoons \overset{\oplus}{R} + \overset{\ominus}{X}$$

Step - 2 Nucleophilic attack on the carbocation (fast)

$$\overset{\oplus}{R} + \overset{\ominus}{Nu} \longrightarrow R - Nu$$

Characteristics of S_N1 reactions :

1. It is unimolecular, two step process and intermediate is formed (intermediate is carbocation).
2. It is first order reaction.
3. Kinetics of the reaction
   Rate $\propto$ [Alkyl halide]
   Rate = $k[(CH_3)_3C–X]$
   Rate of S_N1 reaction is independent of concentration and reactivity of nucleophile.
4. Energetics of the S_N1

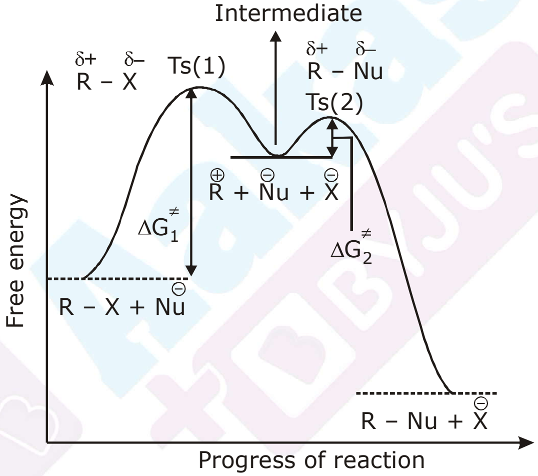


Figure : Free energy diagram for the S_N1 reaction.

5. **Factors affecting the rate of S_N1:**

(i) The structure of the substrate ⤚

The rate determining step of the S_N1 reaction is ionisation step, in this step carbocation is formed. This ionisation is strongly endothermic process, rate of S_N1 reaction depends strongly on carbocation stability because carbocation is the intermediate of S_N1 reaction which determines the energy of activation of the reaction.

S_N1 reactivity : 3º > 2º > 1º > $CH_3 - X$

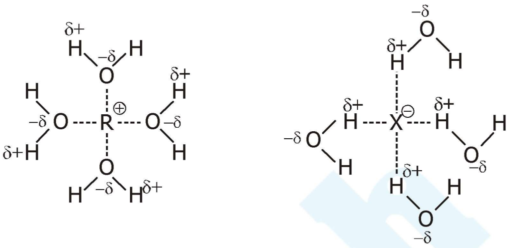
(ii) Concentration and reactivity of the nucleophile :

The rate of S_N1 reactions are unaffected by the concentration and nature of the nucleophile.

(iii) Effect of the solvent → the ionizing ability of the solvent:

To solvate cations and anions effectively the use of polar protic solvent will greatly increase the rate of ionization of an alkyl halide in any S_N1 reaction. It does this because solvation stabilizes the transition state leading to the stabilization of intermediate carbocation and halide ion more than it does the reactant, thus the energy of activation is lower.

$R - X \rightleftharpoons \overset{\oplus}{R} + \overset{\ominus}{X}$ (Solvolysis)



Solvated ions

Table : 9 Dielectric constants (∈) and ionization rates of t-Butylchloride in common solvents

Solvent	∈	Relative rate
H_2O	80	8000
CH_3OH	33	1000
C_2H_5OH	24	200
$(CH_3)_2CO$	21	1
CH_3CO_2H	6	-

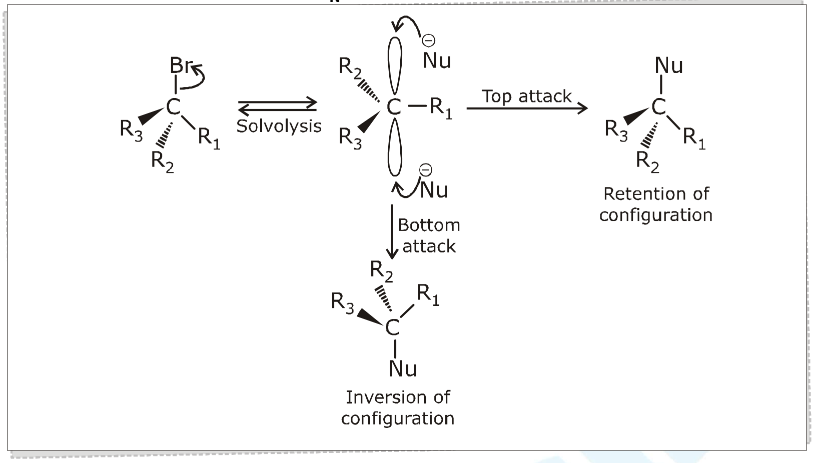
(iv) The nature of the leaving group ⟶

In the S_N1 reaction the leaving group begins to acquire a negative charge as the transition state is reached stabilisation of this developing negative charge at the leaving group stabilizes the transition state and this lowers the free energy of activation and thereby increases the rate of reaction.

Leaving ability of halogen is $\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} >> \overset{\ominus}{F}$

6. Stereochemistry of S_N1 reactions → In the S_N1 mechanism, the carbocation intermediate is sp^2 hybridized and planar. A nucleophile can attack on the carbocation from either face, if reactant is chiral than after attack of nucleophile from both faces gives both enantiomers of the product, which is called racemization.

Mechanism of racemization (S_N1) →



Comparison of S_N1 and S_N2 reactions

		S_N1	S_N2
(i)	Effect of the nucleophile	Nucleophile strength is not important	Stronger nucleophile is required
(ii)	Effect of the substrate	$3^o > 2^o > 1^o > CH_3X$	$CH_3X > 1^o > 2^o$
(iii)	Effect of solvent	Good ionizing solvent required	It goes faster in less polar solvent, if $Nu^{\ominus}$ is present
(iv)	Kinetics	Rate = k [R-X]	Rate = k[R-X] [$Nu^{\ominus}$]
(v)	Stereochemistry	Racemisation	walden inversion
(vi)	Rearrangement	Common	Impossible

Some Nucleophilic reaction of R – X :–

$$Me{-}Cl \xrightarrow{RMgX} R{-}Me$$

$$Me{-}Cl \xrightarrow{RNa} R{-}Me \text{ (Wurtz Reaction)}$$

$$Me{-}Cl \xrightarrow{R_2Zn} R{-}Me \text{ (}R_2Zn\text{ is Frankland Reagent)}$$

$$Me{-}Cl \xrightarrow{R_2CuLi} R - Me \text{ (}R_2CuLi\text{ is Gilman's Reagent)}$$

$$Me{-}Cl \xrightarrow{R{-}C{\equiv}\overset{\ominus}{C}\overset{\oplus}{Na}} R - C{\equiv}C - Me$$

$$Me{-}Cl \xrightarrow{NH_3} H_3\ddot{N}\ \ Me{-}Cl \longrightarrow Me{-}NH_2{+}HCl$$

$$Me{-}Cl \xrightarrow{MeNH_2} Me{-}NH{-}Me$$

$$Me{-}Cl \xrightarrow{Me_2NH} Me_3\ddot{N}$$

$$Me{-}Cl \xrightarrow{Me_3N} Me_3\ddot{N}\ \ Me{-}Cl \longrightarrow Me_4\overset{\oplus}{N}\ \overset{\ominus}{Cl}$$

$$Me{-}Cl \xrightarrow{H_2S/heat} MeSH + HCl$$

$$Me{-}Cl \xrightarrow{KCN\ (\overset{\oplus}{K}\overset{\ominus}{C}{\equiv}N)} \underset{\text{(Major product)}}{Me{-}CN} + \underset{\text{(Minor product)}}{Me - N{\equiv}C\ )}$$

$$Me{-}Cl \xrightarrow{AgCN} Me{-}NC \text{ (Methyl isocyanide)}$$

$$Me{-}Cl \xrightarrow{KNO_2} (\underset{\text{(Major product)}}{CH_3{-}\ O - N = O} + \underset{\text{(Minor product)}}{CH_3 - NO_2})$$

$$Me{-}Cl \xrightarrow[(Ag{-}O{-}N{=}O)]{AgNO_2} Me{-}NO_2$$

$$Me{-}Cl \xrightarrow{RONa} ROMe \text{ (Williamson's ether synthesis)}$$

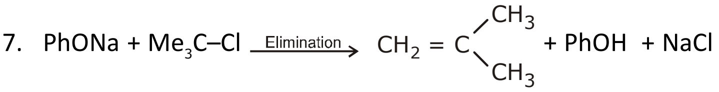
$$Me{-}Cl \xrightarrow{RSNa} RSMe \text{ (Thioether)}$$

Williamson's Ether Synthesis: (S_N2)

1. $R\overset{\ddot{}}{\overset{\ominus}{O}}\overset{\oplus}{Na} + R - Cl \longrightarrow R - O - R + NaCl$
2. $EtONa + Me - Cl \longrightarrow EtOMe$
3. $Me\overset{\ominus}{O}\overset{\oplus}{Na} + Et - Cl \longrightarrow EtOMe$

   Rate (2) > (3), 2 is better method. (Due to less steric hindrance)
4. $PhONa + MeCl \longrightarrow PhOMe + NaCl$
5. $Me_3CO^{\ominus}Na^{\oplus} + MeCl \longrightarrow Me_3COMe + NaCl$
6. $MeO^{\ominus}Na^{\oplus} + Me_3C - Cl \xrightarrow{\text{Elimination}} CH_2 = \overset{CH_3}{\underset{CH_3}{C}} + MeOH + NaCl$

   Major

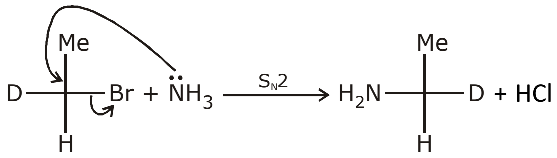


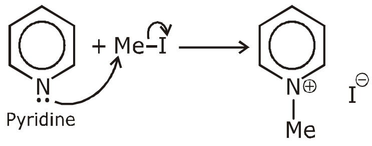
7. $PhONa + Me_3C{-}Cl \xrightarrow{\text{Elimination}} CH_2 = C(CH_3)_2 + PhOH + NaCl$

Reaction of RX with NH_3

1. $EtCl + \ddot{N}H_3 \xrightarrow{S_N2} EtNH_2 + HCl$

2. $CH_3{-}CH_2{-}CH_2{-}Cl \xrightarrow[S_N2]{\ddot{N}H_3} CH_3{-}CH_2{-}CH_2{-}NH_2 + HCl$

3. 

4. 

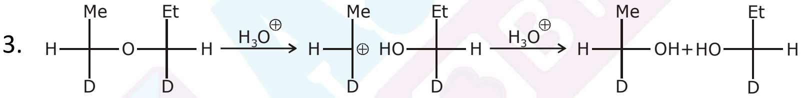
(Pyridinium salt)

Some other reactions

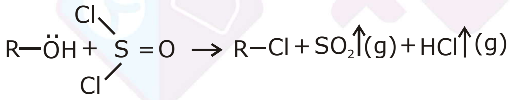
Hydrolysis of Ether

1. $Me\overset{18}{O}Et \xrightarrow{H_3O^{\oplus}} Et - OH + Me\overset{18}{O}H$

2. $MeOEt \xrightarrow{H_3\overset{18}{O}^{\oplus}} Et - \overset{18}{O}H + Me - OH$

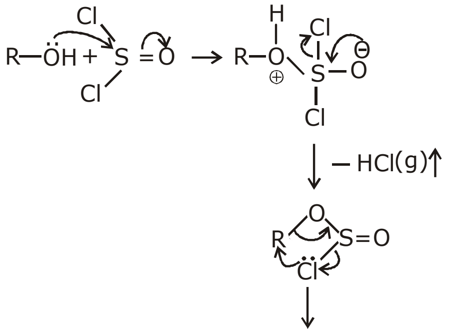
3. 

S_Ni (Nucleophilic substitution intramolecular) (Darzen's process)



$R{-}\ddot{O}H + SOCl_2 \rightarrow R{-}Cl + SO_2\uparrow(g) + HCl\uparrow(g)$

Mechanism



$R - Cl + O = S = O \uparrow (g)$

Note : (1) In S_Ni retention of configuration takes place.

Note : (2) In presence of pyridine above reaction follow the S_N2 reaction mechanism.

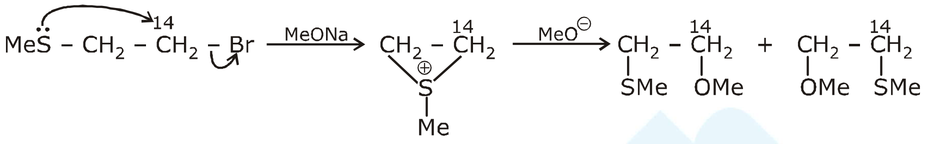
S_N^{NGP}(Neighbouring group participation)

Increase in rate of S_N reaction due to attack of internal nucleophile is called as S_N^{NGP} is also known as anchimeric assistance.

For S_N^{NGP} :–

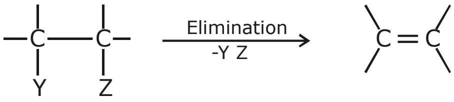
1. Internal nucleophile must be present.
2. Internal nucleophile must be anti to leaving group.

Example



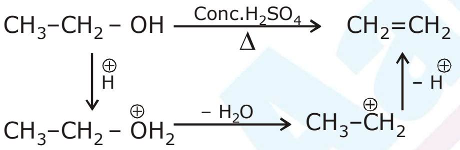
Elimination reactions:

In an elimination reaction two atoms or groups (YZ) are removed from the substrate with formation of pi bond.



Depending on the reagents and conditions involved, an elimination may be a first order (E_1) or second order (E_2).

Dehydration of Alcohol (E1)



Characteristics of E_1 reaction :

(i) It is unimolecular, two step process.

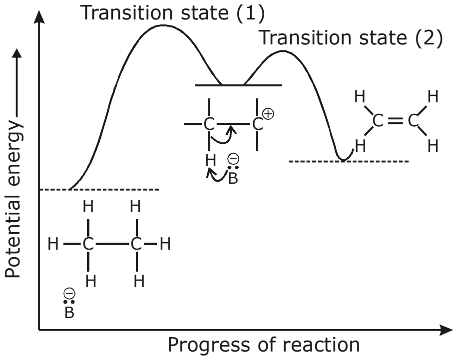
(ii) It is first order reaction.

(iii) Reaction intermediate is carbocation, so rearrangement is possible.

(iv) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.

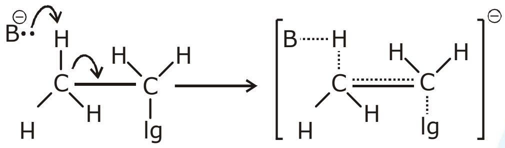
(v) Kinetics ⟶ Rate $\propto$ [Substrate]

Rate = k[Substrate]



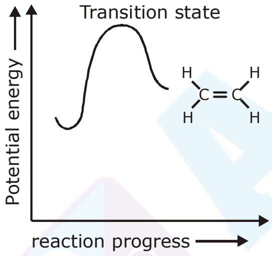
E_2- elimination :

$$H–CH_2 – CH_2 – Ig \longrightarrow CH_2 = CH_2 + \overset{\ominus}{Ig}$$



Rate α [R-Ig]

α $[B^{\ominus}]$



Bimolecular reaction, second order kinetic.

1. Leaving group leads when base is taking proton from adjacent carbon.
2. It is a single step reaction
3. Rate ∝ Leaving group tendency
4. It shows elemental as well as kinetic isotopic effect with leaving group as well as at β-position.
5. Normally saytzeff product is major.
6. Transition state mechanism therefore rearrangement is not possible.
7. The orientation of proton & leaving group should be antiperiplanar for E_2.
8. **Positional orientation of elimination** ↣ In most E_1 and E_2 eliminations gives two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule (i.e., most stable alkene will be the major product)

9. E_2–elimination is favoured by :
   (1) Moderate leaving group.
   (2) Strong base ($RO^{\ominus}$, Alc. KOH).
   (3) Polar aprotic solvent.
   (4) High concentration of base.
   (5) High temperature.

Reactivity towards

E_2 $\rightarrow R-I > R-Br > R-Cl > R-F$

Comparison of E_1 and E_2 elimination:

Promoting factors	**E_1**	**E_2**
(i) Base	Weak base	Strong base required
(ii) Solvent	Good ionizing solvent	Wide variety of solvent
(iii) Substrate	3° > 2° > 1°	3° > 2° > 1°
(iv) Leaving group	Better one required	Better one required

Characteristics		
(i) Kinetics	K[R– X], I order	K[R – X] [Base], II order
(ii) Orientation	Saytzeff alkene	Saytzeff alkene
(iii) Stereochemistry	No special geometry is required	transition state must be co-planar

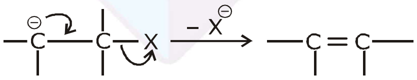
(C) Mechanism of E_1CB reaction (Unimolecular conjugate base reaction) :

The E_1CB or carbanion mechanism : In the E_1CB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism:

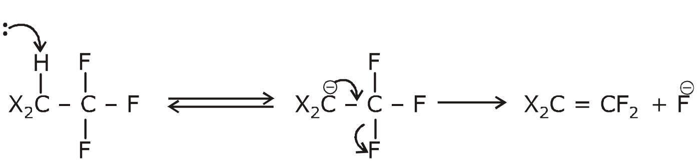
Step-1 : Consists of the removal of a proton, $H^{\oplus}$ by a base generating a carbanion

Step-2 : Carbanion loses a leaving group to form alkene



Condition: For the E_1 CB, substrate must be containing acidic hydrogens and poor leaving groups (i.e., bad l.g.)

Ex.



In case of ethanol, the reaction occurs as follows

$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

$CH_3CH_2OH + Cl_2 \xrightarrow{\text{Oxidation}} CH_3CHO + 2HCl$

$$CH_3CHO + 3Cl_2 \xrightarrow{\text{Chlorination}} CCl_3CHO + 3HCl$$

Chloral

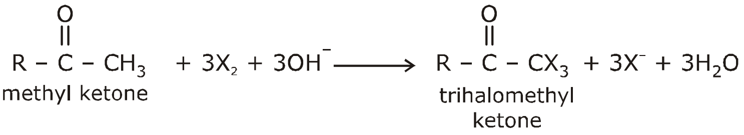
$$Ca(OH)_2 + 2CCl_3\ CHO \xrightarrow{\text{Hydrolysis}} 2CHCl_3 + (HCOO)_2Ca$$

Chloroform Calcium formate

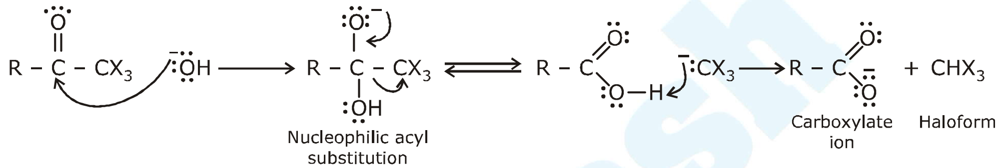
1. From carbontetrachloride

$$CCl_4 + 2[H] \xrightarrow[\text{Heat}]{Fe/H_2O} CHCl_3 + HCl \text{ (partial reduction)}$$

2. Haloform reaction



$$\underset{\text{methyl ketone}}{R-\overset{\overset{O}{\|}}{C}-CH_3} + 3X_2 + 3OH^- \longrightarrow \underset{\text{trihalomethyl ketone}}{R-\overset{\overset{O}{\|}}{C}-CX_3} + 3X^- + 3H_2O$$



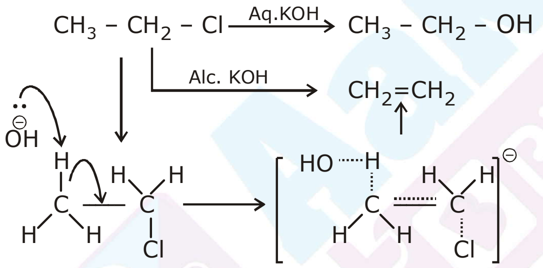
(Haloform)

Step 1 : Attack of the nucleophile

Step 2 : Elimination of the leaving group

Step 3 : Proton transfer

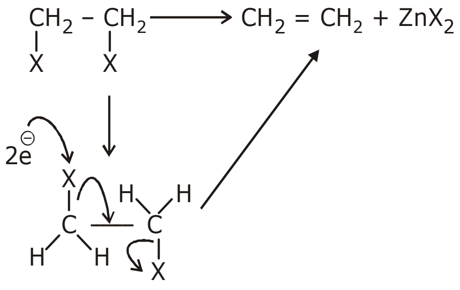
Dehydrohalogenation (−HX) E_2



Anti elimination

Dehalogenation : − (−X_2) E_2

$$Zn \longrightarrow Zn^{+2} + 2e^-$$



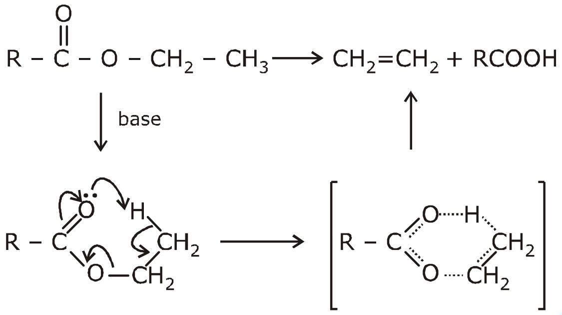
Anti elimination

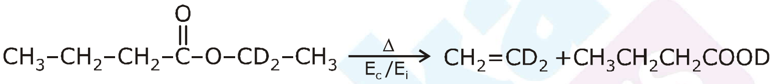
E_c or E_i (Intramolecular or cyclic elimination mechanism):

(1) Leaving group and Base present in same molecule.
(2) It proceeds by cyclic transition state.
(3) Overall it is syn elimination.
(4) Hoffmann is major product as it is obtained by least hindered site/cyclic transition state.
(5) No rearrangement.

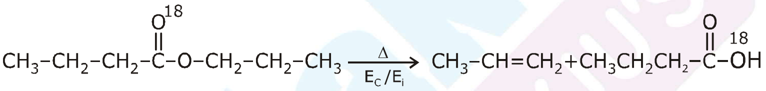
Example of E_c/E_i

Pyrolysis of Ester :



1.


$$CH_3{-}CH_2{-}CH_2{-}\overset{\overset{O}{||}}{C}{-}O{-}CD_2{-}CH_3 \xrightarrow[E_c/E_i]{\Delta} CH_2{=}CD_2 + CH_3CH_2CH_2COOD$$

2.


$$CH_3{-}CH_2{-}CH_2{-}\overset{\overset{O^{18}}{||}}{C}{-}O{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[E_c/E_i]{\Delta} CH_3{-}CH{=}CH_2 + CH_3CH_2CH_2{-}\overset{\overset{O}{||}\ 18}{C}{-}OH$$

Chemical properties of chloroform

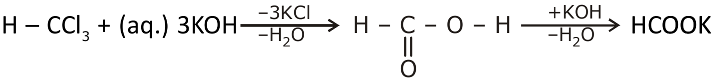
1. Action of sunlight and air

$$2\ CHCl_3 + O_2 \xrightarrow{\text{Sunlight}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

As chloroform is used for anaesthetic purposes, we need to maintain a high purity of chloroform, this reaction can be avoided by storing it in dark bottles, completely filled upto brim. The use of dark bottles (brown or blue) cuts off active light radiations and filling upto brim, keeps out air. Apart from this a small amount of ethanol (1%) is usually added to bottles of chloroform. Addition of a little ethanol fixes the toxic $COCl_2$ as non-poisonous Diethyl carbonate.

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Diethyl carbonate}}{O = C(OC_2H_5)_2} + 2HCl$$

2. Hydrolysis :



$$H - CCl_3 + (aq.)\ 3KOH \xrightarrow[-H_2O]{-3KCl} H - \underset{\underset{O}{||}}{C} - O - H \xrightarrow[-H_2O]{+KOH} HCOOK$$

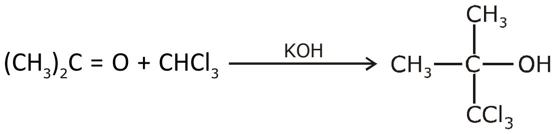
3. Reduction :

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$CHCl_3 + 2[H] \longrightarrow \underset{\substack{\text{Dichloromethane}\\ \text{(Methylene chloride)}}}{CH_2Cl_2} + HCl$$

$$CHCl_3 \xrightarrow{Zn\ +\ H_2O} CH_4 + 3HCl$$

4. **Reaction with acetone :**



$$(CH_3)_2C = O + CHCl_3 \xrightarrow{KOH} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CCl_3}{|}}{C}}-OH$$

Chloretone

Use : Chloretone is used as hypnotic (a sleep inducing) drug.

5. **Reaction with nitric acid**

$2CHCl_3 + HONO_2 \longrightarrow CCl_3.\ NO_2 + H_2O$
(chloropicrin)

Use : Chloropicrin is used as an insecticide and war gas.

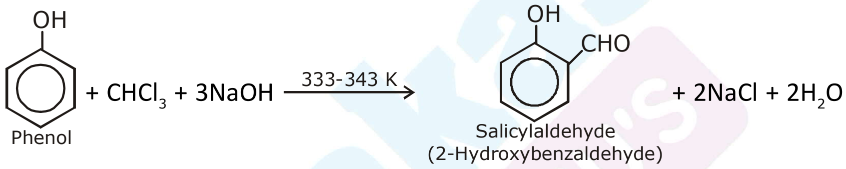
6. **Reaction with silver powder :**

$2CHCl_3 + 6\ Ag \xrightarrow{Heat} CH \equiv CH + 6\ AgCl$
(Acetylene)

7. **Chlorination :**

$CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$

8. **Reimer-Tiemann reaction:**



Uses of chloroform

1. As solvent in oils and varnishes
2. As preservative for anatomical specimens
3. As laboratory reagent
4. As an anaesthetic

ARYL HALIDE (HALOARENES)

Aliphatic Halogen Derivatives :

Compounds obtained by the replacement of one or more hydrogen atom(s) from hydrocarbons are known as halogen derivatives. The halogen derivatives of alkanes, alkenes, alkynes and arenes are known as alkyl halide (haloalkane), alkenyl halide (haloalkenes), alkynyl halides (haloalkynes) and aryl halides (halobenzenes) respectively.

Electrophilic aromatic substitution (EAS) :

Based on its structure and properties, what kind of reaction should benzene undergo ? Are any of its bond particularly weak does it have electron rich or electron deficient atom.

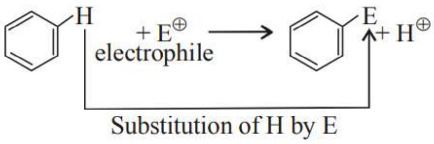
* Benzene has six p-electron delocalized in six p-orbitals that overlap above and below the plane of ring.

These loosely held π-electron make the benzene ring electron rich, and so it reacts with electrophile.

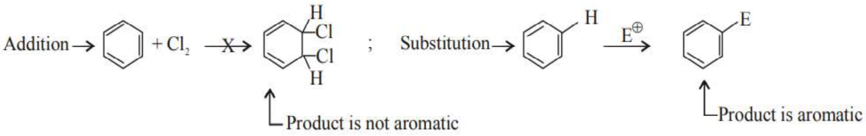
* Because benzene six π-electron satisfyHuckel's rule, benzene is especiallystable. Reactions that keep the aromatic ring intact are therefore, favoured.

* Electron cloud above and below the plane of benzene shields the ring carbon from the attack of a nucleophile.

As a result, the characteristic reaction of benzene is electrophilic aromatic substitution - a hydrogen atom is replaced by an electrophile.

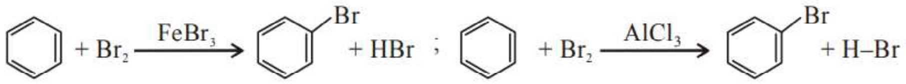


Benzene does not undergo addition reaction like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic . Substitution of a hydrogen on the other hand, keeps the aromatic ring intact.



Preparation of haloarene

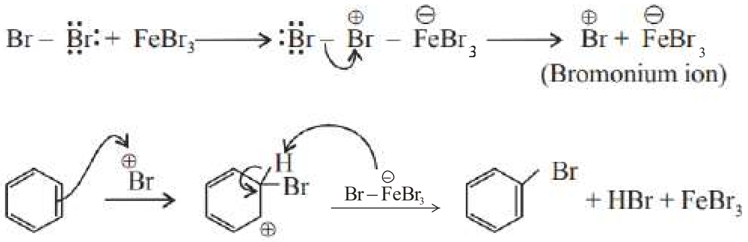
1. The introduction of halo (–X) group on benzene known as halogenation of benzene



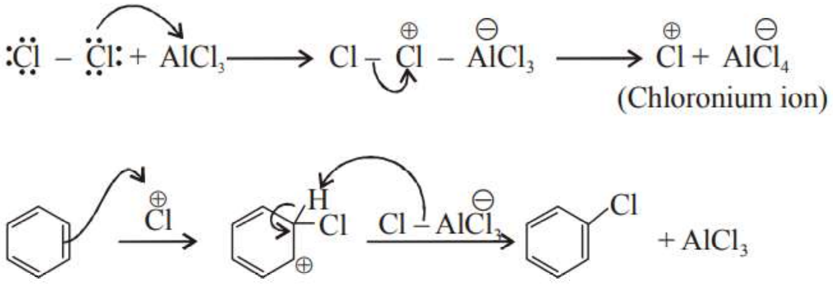
The bromination or chlorination of benzene requires a Lewis acid catalyst such as $FeBr_3$,$AlBr_3$, $FeCl_3$ or $AlCl_3$.

Sometime Fe orAl is used but real catalyst is not Fe orAl itself but FeX_3 orAlX_3 is formed from the reaction between halogen and Fe orAl.

Mechanisms for Bromination



Mechanisms for Chlorination



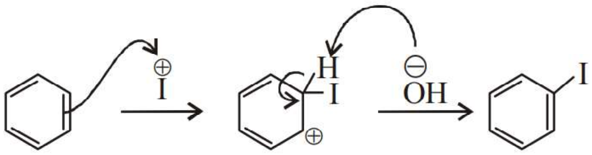
Bromination and chlorination also occur by $H\overset{-}{O}\overset{+}{Br}$ and $H\overset{-}{O}\overset{+}{Cl}$, obtained by reaction between H_2O and X_2.

$H_2O + X_2 \rightarrow 2HOX$ (X = Cl, Br)

Iodination of benzene requires an acidic oxidizing agent such as nitric acid. Nitric acid is consumed in the reaction, so it is a reagent rather a catalyst.

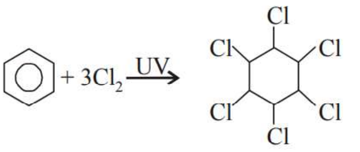
Mechanisms for Iodination

$$HNO_3 + \frac{1}{2}I_2 \rightarrow I^{\oplus} + NO_2 + \overset{\ominus}{O}H$$



The electrophile required for halogenation reaction is halonium ion (X^+)

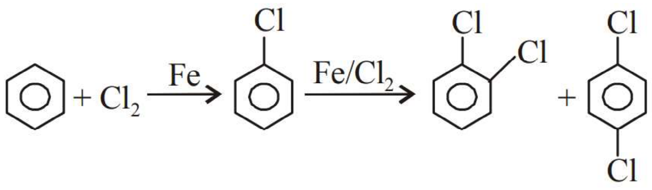
2. Addition of Halogen



benzenehexachloride, B.H.C, 666

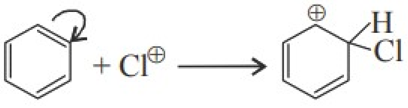
Benzenehexachloride (BHC, $C_6H_6Cl_6$) is also called Lindane or Gammaxene (γ-isomer) and is used insecticide.

3. Direct halogenation :

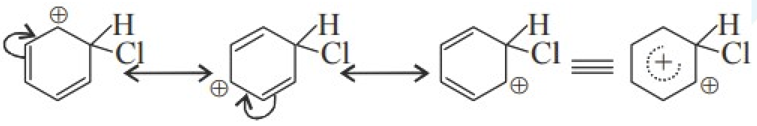


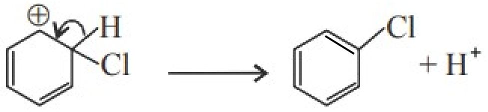
Low temperature and the presence of a halogen carrier favour nuclear substitution. The chlorides or bromides ofAl, Fe, Sb may use used :

$$Fe \xrightarrow{Cl_2} FeCl_2 \underset{}{\overset{Cl_2}{\rightleftharpoons}} FeCl_4^{-} + Cl^{+}$$



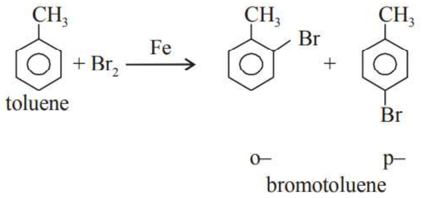
σ-complex
(stable by resonance)



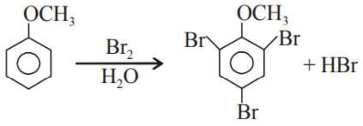


$$FeCl_4^{-} + H^{+} \longrightarrow FeCl_3 + HCl$$

Iron is most commonly used being converted to Lewis acid $FeCl_3$ as shown above.
It is again S_E reaction and without halogen-carrier (Lewis acid), Cl^+ (halonium) is not formed and hence, reaction is not possible :

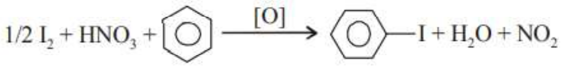


A methoxy group is so strongly activating that anisole quickly bromines in water without a catalyst :



Direction iodination is not possible since, iodine is least reactive and HI formed makes reaction reversible.

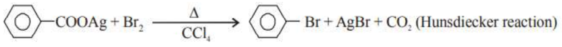
In presence of oxidising agents like HNO_3 or HIO_3 , iodination of benzene is possible and HI formed is converted to I_2 :



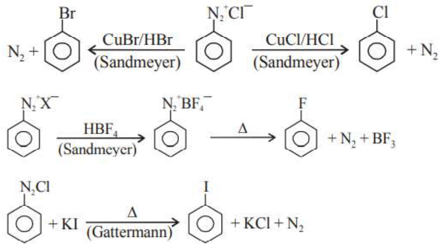
$$5\ HI + HIO_3 \longrightarrow 3\ I_2 + 3H_2O$$

Iodination probably involves an electrophilic aromatic subtitution with iodonium (I^+) acting as the electrophile. I^+ is formed from iodine byoxidation with HNO_3.

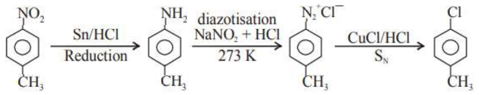
$$H^+ + HNO_3 + 1/2\ I_2 \longrightarrow I^+ + NO_2 + H_2O$$

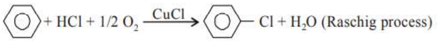


Diazonium salts are converted to halogen compounds :

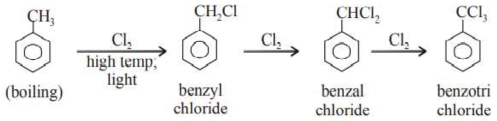


Diazonium salts are obtained by diazotisation of amino compounds and this provides a better route to convert amino compounds into halogen compounds :





Side-Chain Derivatives

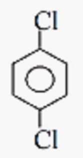


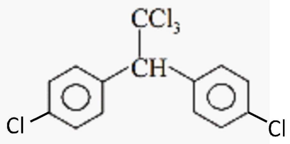
Side-chain halogenation involves free radical mechanisms due to lower bond energyof the benzyl C–H bond.

Physical Properties

- Less polar, insoluble in water but soluble in organic solvents like ethanol and ether.
- They show physiological activity and are used as insecticides.

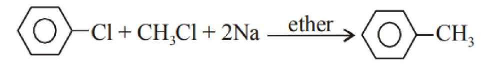
  Examples are :

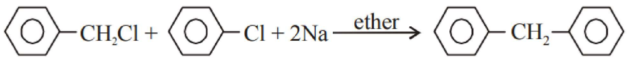

(dichlorobenzene)


(DDT)

Chemical Properties

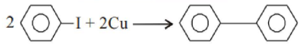
(a) Wurtz-Fitting Reaction





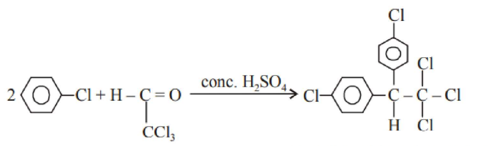
Only aryl halide is involved, diphenyl is formed (Fitting reaction)

(b) Ullman synthesis



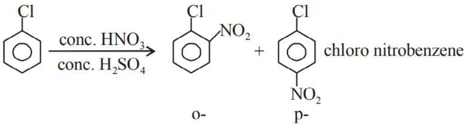
(c) Reaction with Chloral

DDT is formed when chloral reacts with chlorobenzene in presence of concentrated H_2SO_4.

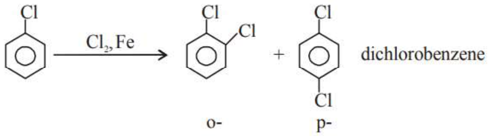

2, 2-di (p-chlorophenyl)-1, 1 1-trichloroethane (DDT)

DDT is causing ecological problems, its use as insecticides is being banned.

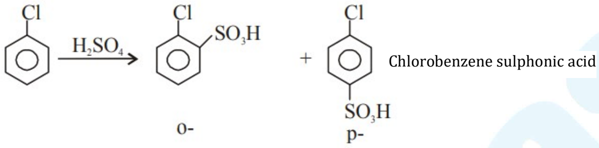
Nitration



Chlorination

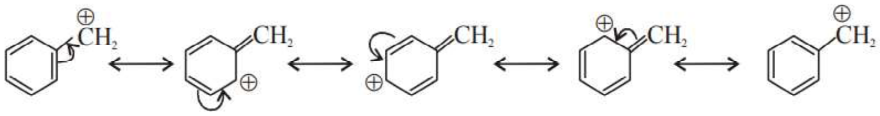


Sulphonation

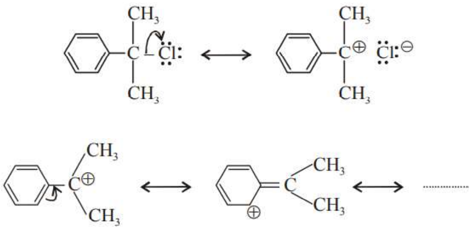


- Chlorine is not a good donor of electrons by resonance due to its high electronegativity. Thus, the inductive effect of the Cl atom overcomes the resonance effect, and thus, it deactivates the benzene ring.

(d) Substitution on benzyl carbon (S) : The greater reactivities of benzylic halides result from the stabilities of the carbocation intermediates that are formed when they react.

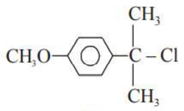


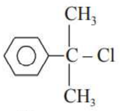
Tertiarycumyl chloride ionises to a carbocation with four important resonance structure :



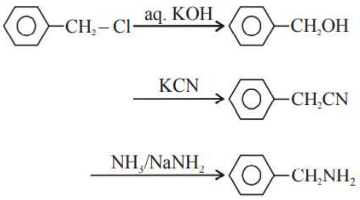
(resonance-stablised)

Because of the possibilitie of resonance, ortho and para substituent group on the benzene ring that activate electrophilic aromaticsubstitution further accelerate S_N1 reaction at the benzylic position. Thus p-methoxytert-cumyl chloride (I) undergoes hydrolysisabout 3400 times fasterthan tert-cumyl chloride II.


I


II

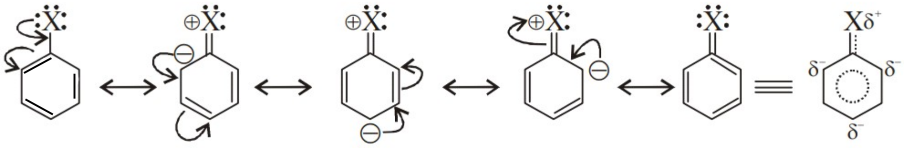
Benzylic halides undergo S_N reactions like aliphatic halides.



This provides a path of converting toluence into so many other compounds benzyl chloride.

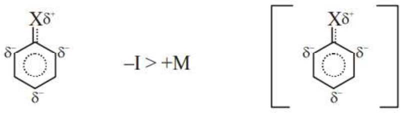
Anamalous behaviour of halogen substituent :

– X(F, Cl, Br, I) is o–, p-directing but is deactivating group.



Rate ∝ single step reaction

This deactivating nature is attributed to high electronegativity of the halogen atom due to which they withdraw electrons; resonance effect explains its electron-donating behaviour.



electron displacement due to inductive effect not compensated by resonance effect

overall result; o–, p-directing but deactivating