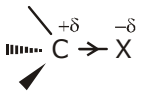
HALOGEN DERIVATIVES

1.1 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 (haloalkene), 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 :

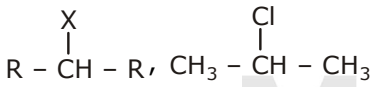
(i) Primary halide : If the halogen bearing carbon is bonded to one carbon atom or with no carbon atom

Example :

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

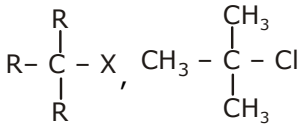
(ii) Secondary halide : If two carbon atoms are bonded to the halogen bearing carbon.

Example :



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

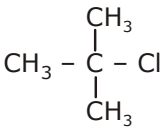
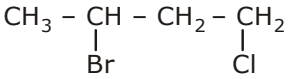
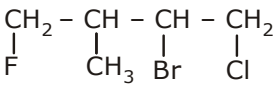
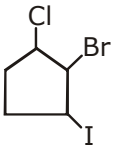
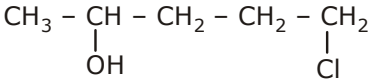
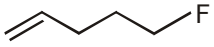
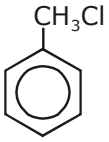
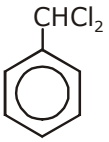
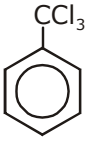
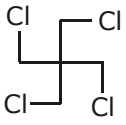
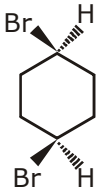
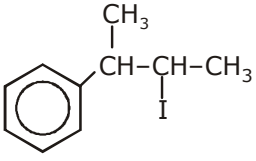
Example :



Halolkanes can be classified into following three categories.

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

1.2 IUPAC NOMENCLATURE OF ALKYL HALIDES

S.N.	Compound	IUPAC name
1.		2 – Chloro-2-methylpropane
2.		3-Bromo-1-chlorobutane
3.		2-Bromo-1-chloro-4-fluoro-3-methylbutane
4.		2-Bromo-1-chloro-3-iodocyclopentane
5.		5-chloropentan-2-ol
6.		5-Fluoropent-1-ene
7.		Chlorophenylmethane
8.		Dichlorophenylmethane
9.		Trichlorophenylmethane
10.		2,2-Bis(chloromethyl)-1,3-dichloropropane
11.		Cis-1,4-dibromocyclohexane
12.		2-iodo-3-phenylbutane

1.3 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

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

2. $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - Cl$ 1-Chloropentane

   $CH_3 - CH(CH_3) - CH_2 - CH_2 - Cl$ 1-Chloro-3-methylbutane

   $CH_3 - CH(CH_3) - CH_2 - Cl$ 1-Chloro-2,2-dimethylpropane

(b) Position

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

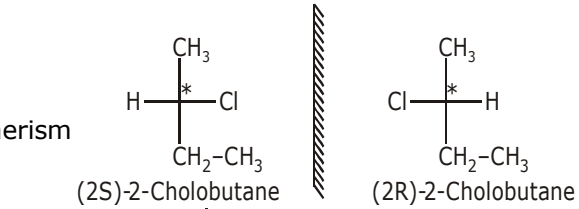
   $CH_3 - CH(Cl) - CH_3$ 2-Chloropropane

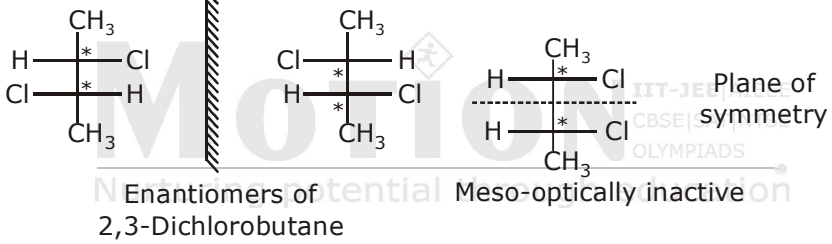
2. $CH_3 - CH(CH_3) - CH_2 - Cl$ 1-Chloro-2-methylpropane

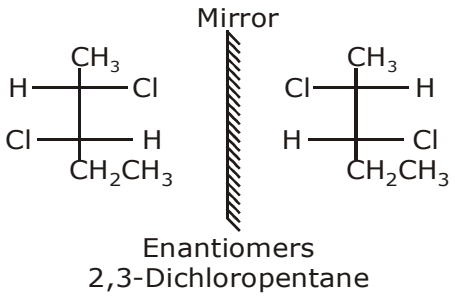
   $CH_3 - C(Cl)(CH_3) - CH_3$ 2-Chloro-2-methylpropane

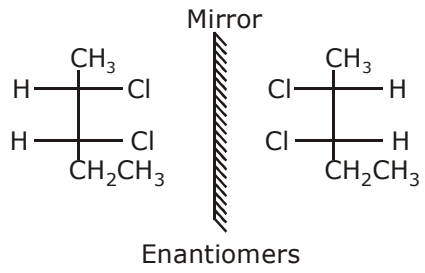
2. Stereoisomerism

(a) Optical isomerism







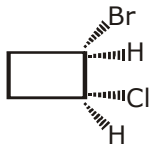
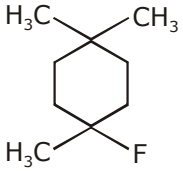


1.4 BONDING IN ALKYL HALIDE:

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

Ex.1 Classify the compound as a primary, secondary and tertiary halide

(a) $(CH_3)_2CH–CH_2Cl$ (b)  (c) 

(d) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2Cl$ (e) Isopentyl bromide (f) Neopentyl iodide

Sol. (a) Primary (b) Secondary (c) Tertiary (d) Primary
(e) Primary (f) Primary

1.5 PHYSICAL PROPERTIES OF ALKYL HALIDE:

1.5.1 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 weaker electronegativity. The overall result is that the bond dipole moment increase in the order.

C – I < C – Br < C – F < C – Cl
μ : 1.29 D 1.48 D 1.51 D 1.56 D
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

1.5.2 Boiling point :

(a) With respect to the halogen in a group of alkyl halides, the boiling point increases as one descends 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 nonpolarizable fluorine.

Table : 3 Boiling points of some alkyl halide in ºC (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) The boiling points of the chlorinated derivatives of methane increase with the number of chlorine atoms because of an increase in the induced-dipole/dipole attractive forces.
Compound CH_3Cl CH_2Cl_2 $CHCl_3$ CCl_4
B.P. –24ºC 40ºC 61ºC 77ºC

Table : 4

	CH_3-CH_2F	CH_3-CHF_2	CH_3-CF_3	CF_3-CF_3
B.P.	-32ºC	– 25ºC	– 47ºC	– 78ºC

1.5.3 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 halides in a fluoride or chloride, it is on the upper layer and water is 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.

1.6 PREPARATION OF ALKYL HALIDE :

1.6.1 From alkane :

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

1.6.2 From alkenes and alkynes (Detail in alkene and alkyne)

(a) $>C=C< \xrightarrow{HX} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$ (b) $>C=C< \xrightarrow{X_2} -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-$

(c) $-C\equiv C- \xrightarrow{2HX} -\overset{H}{\overset{|}{C}}-\overset{X}{\overset{|}{C}}-$ (d) $-C\equiv C- \xrightarrow{2X_2} -\overset{X}{\overset{|}{C}}-\overset{X}{\overset{|}{C}}-$

1.6.3 From alcohol (Detail in the alcohol)

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

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

   Nucleophility – 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 ↓

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

   Acetone → Solubility in acetone is soluble

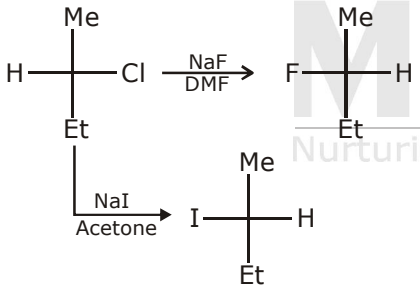
   NaF < NaCl < NaBr < NaI

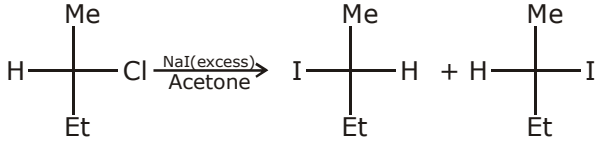
2. $C - C - Br \xrightarrow[\text{Acetone}]{NaBr} C - C - Br$

3. $C - C - Cl \xrightarrow[\text{Acetone}]{NaCl} C - C - Cl$

4. $C - C - Cl \xrightarrow[\text{Acetone}]{NaF} C - C - F$

5. $C - C - Cl \xrightarrow[\text{DMF or DMSO}]{KF} C - C - F$ (swart reaction)

6. 

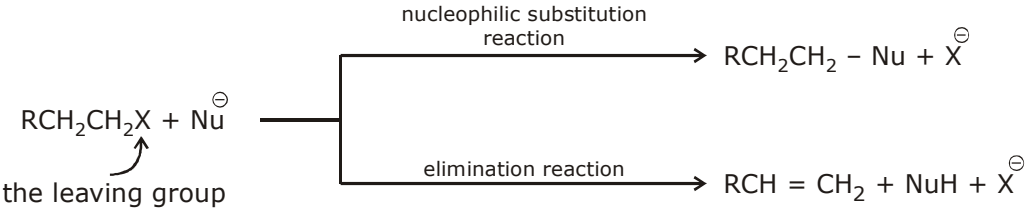
7. 

(racemisation)

1.7 CHEMICAL REACTIONS OF ALKYL HALIDE:

1.6.4 Nucleophilic substitution reaction:

Those organic compounds in which an sp^3 hybridized carbon is bonded to an electronegative atom or group can undergo two type of reaction e.g. substitution reactions 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 cha develops on carbon atom.

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

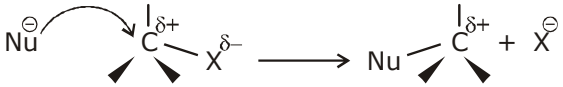
X = F, Cl, Br, I

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

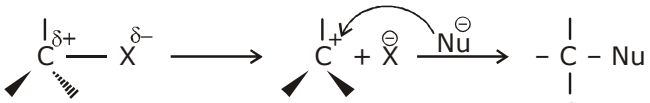
There are two important mechanisms for the substitution reaction

(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_N^2)

The mechanism of S_N^2 reaction

transition state

Characteristic of S_N^2

(1) It is bimolecular, unistep process

(2) It is second order reaction because in the Rds two species are involved

(3) Kinetics of the reaction $\rightarrow$ rate $\propto$ [alkyl halide] [nucleophile]

rate $\propto$ k[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 quadriples.

(4) Energetics of the reaction →

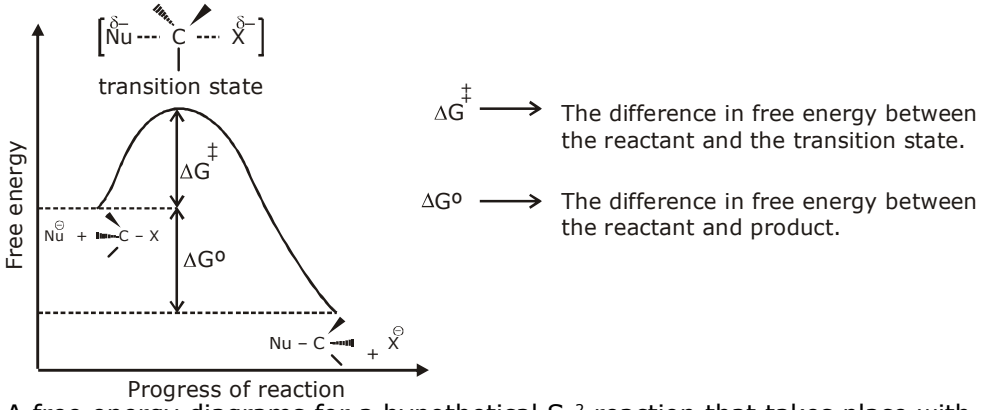
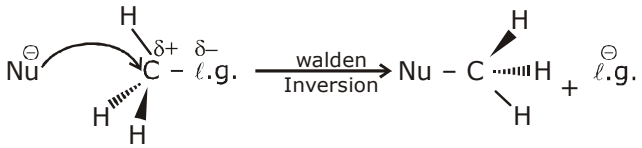


Figure : A free energy diagrams for a hypothetical S_N^2 reaction that takes place with a negative ΔG^o

(5) No intermediates are formed in the S_N^2 reaction, the reaction proceeds through the formation of an unstable arrangement of atoms or group called transition state.

(6) The stereochemistry of S_N^2 reaction → As we seen earlier, in an S_N^2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. this mode of attack causes a inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as walden inversion.



(7) Factor's affecting the rate of S_N^2 reaction → Number of factors affect the relative rate of S_N^2 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_N^2 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_N^2 increasing the concentration of the nucleophile increases the rate of an S_N^2 reaction. The nature of nucleophile strongly affect the rate of S_N^2 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.

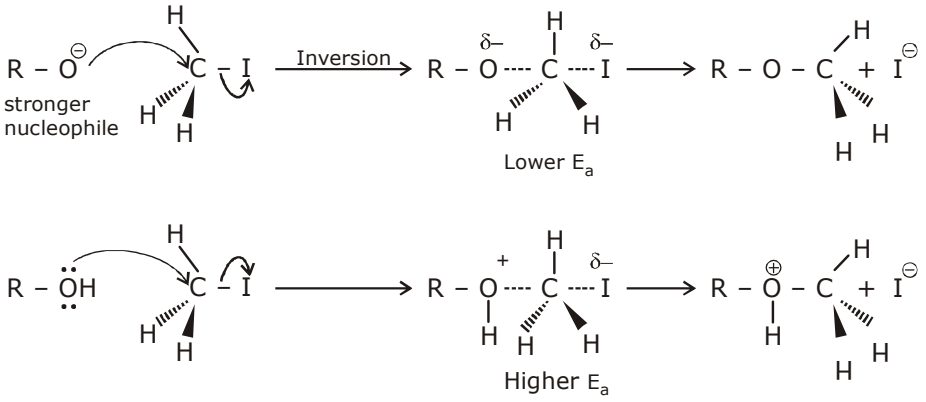
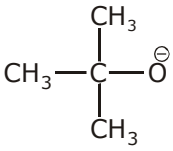


Table : 7

some common nucleophiles listed in decreasing order of nucleophilicity in hydroxylic solvent	
Strong nucleophiles $(CH_3CH_2)_3\ddot{P}$	Moderate nucleophile : $Br^{\ominus}$
$-\ddot{S}H$	$\ddot{N}H_3$
$I^{\ominus}$	$(CH_3)_2\ddot{S}$
$(CH_3-CH_2)_2\ddot{N}H$	$Cl^{\ominus}$
$-CN^{\ominus}$	$ACO^{\ominus}$
$(CH_3-CH_2)_3\ddot{N}$	Weak nucleophile $F^{\ominus}$
$HO^{\ominus}$	H_2O
$CH_3O^{\ominus}$	CH_3OH

Steric effects on nucleophilicity



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

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

ethoxide 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.

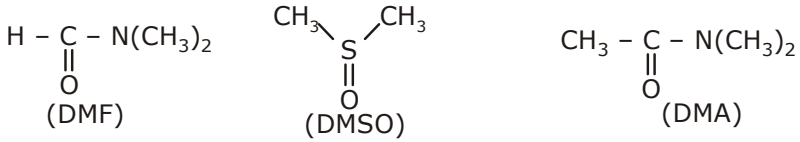
Because small nucleophile is solvated more by the polar protic solvent thus its nucleophilicity decreases and rate of SN^2 decreases

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_N^2, if nucleophile is anionic. But polar aprotic

solvent does not have any active hydrogen atom so they can not 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_N^2 reactions increased when they are carried out in polar aprotic solvent.
Examples of polar aprotic solvent.



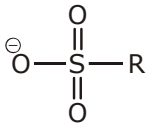
In DMSO, the relative order of reactivity of halide ions is

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

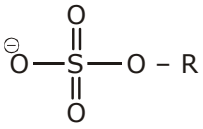
(iv) The nature of the leaving group ⟼ The best leaving groups are those that become the most stable ion after they leave, because leaving group generally leave as a negative ion, so those leaving group are good, which stabilise negative charge most effectively and weak base do this best, so weaker bases 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

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

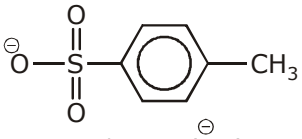
Other leaving groups are



Alkanesulphonate ion



Alkyl sulphate ion



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

$CF_3\overset{\ominus}{S}O_3$

Triflate ion
(a super leaving group)

Strongly basic ions rarely act as leaving group →

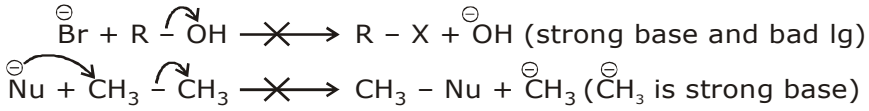
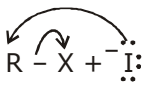
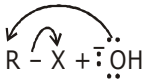
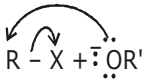
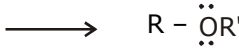
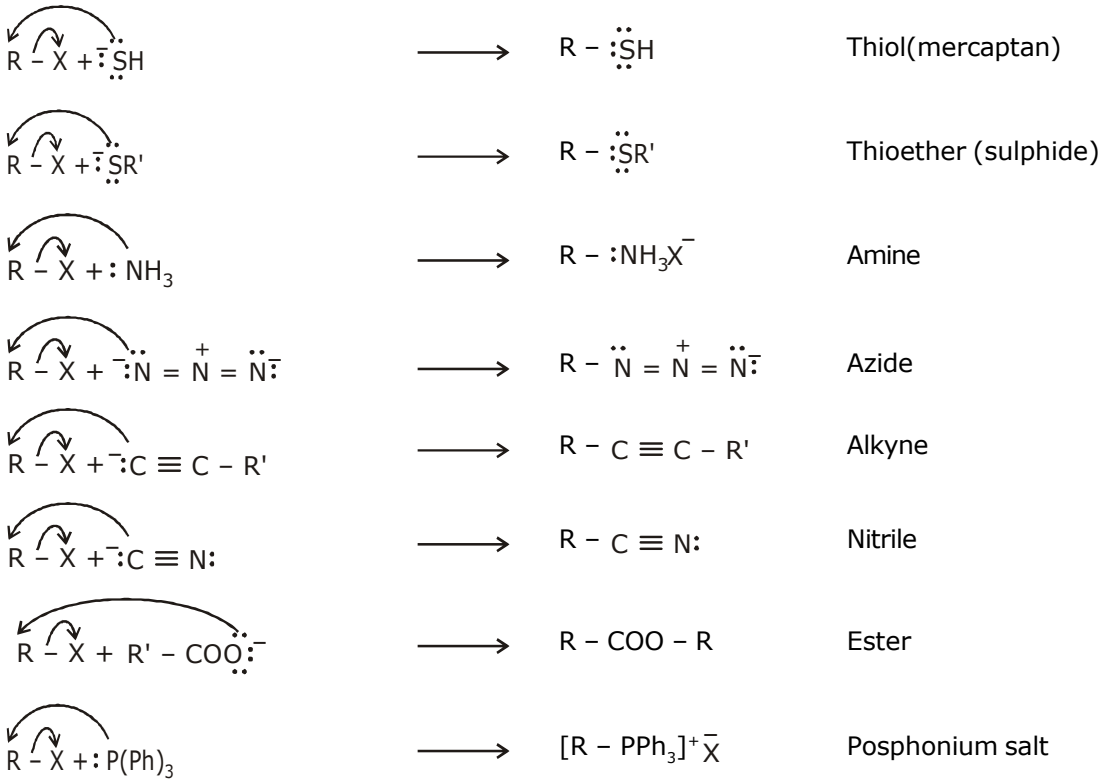
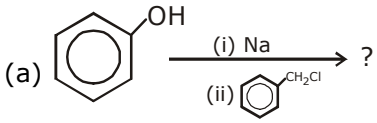


Table : 8 Examples of SN² reactions of alkyl halide →

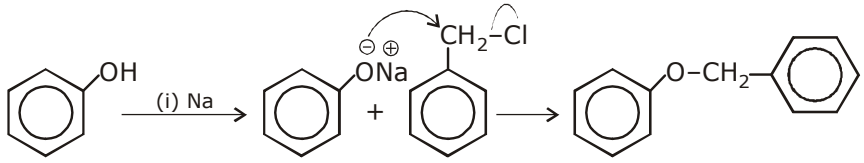
Nucleophile	Product	Class of Product
		Alkyl halide
		Alcohol
		Ether

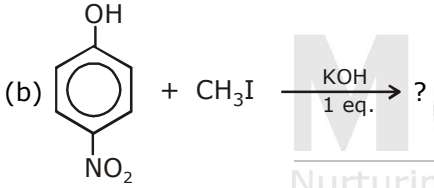


Ex. Complete the following reactions with mechanism

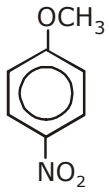


Sol.

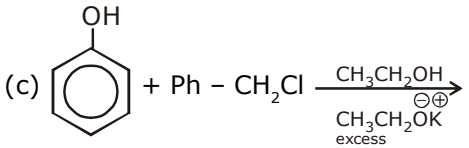




Sol.



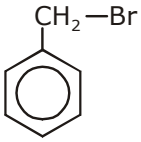
(p-Nitroanisole)

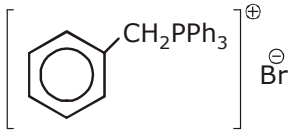


Sol. $CH_3–CH_2–O^{\ominus}$ is present in excess and it is stronger nucleophile than Ph – $O^{\ominus}$ so product is Ph–CH_2 – OEt

(d) $CH_3 - C \equiv CH \xrightarrow{Na} X \xrightarrow{CH_3–CH_2–I} Y$

Sol. $CH_3 - C \equiv C^{\ominus} + CH_3 - CH_2 - I \longrightarrow CH_3 - C \equiv C - CH_2 - CH_3$

(e)  + $Ph_3\ddot{P} \rightarrow$ Salt

Sol. 

Ex. **When the concentration of alkyl halide is tripled and the concentration of OH^- ion is reduced to half, the rate of S_N2 reaction increases by :**
(A) 3 times (B) 2 times (C) 1.5 times (D) 6 times

Ans. **C**

Ex. **In the given reaction, $CH_3CH_2 – X + CH_3SNa \rightarrowtail$**
The fastest reaction occurs when 'X' is –
(A) – OH (B) – F (C) – $OCOCF_3$ (D) $OCOCH_3$

Ans. **C**

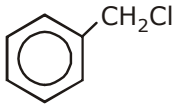
Ex. **Correct decreasing order of reactivity towards S_N2 reaction**

(I) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl$ (II) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2Cl$ (III) $CH_3CH_2CH_2CH_2Cl$ (IV) $CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCl$

(A) IV > I > II > III (B) III > II > I > IV (C) IV > I > III > II (D) II > I > IV > III

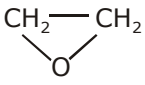
Ans. **B**

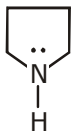
Q.1 $CH_3 - \underset{\displaystyle Et}{\underset{|}{N}}(CH_2)(CH_2)(CH_2-Cl) \xrightarrow[C_2H_5OH]{C_2H_5O^{\ominus}} ?$

Q.2  + KF $\xrightarrow{18\text{-crown-6}}$ Products.

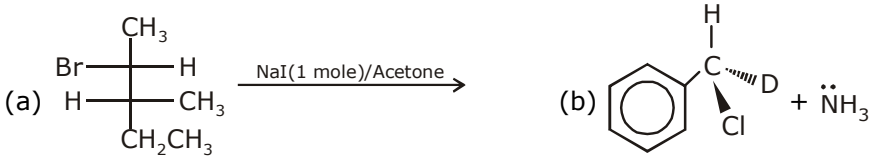
What is the function of 8 corwn-6?

Q.3 Write mechanisms that account for the product of the following reactions:

(a) $HOCH_2CH_2Br \xrightarrow[H_2O]{^{\ominus}OH}$ 

(b) $NH_2–CH_2–CH_2–CH_2–CH_2–Br \xrightarrow[H_2O]{^{\ominus}OH}$ 

Q.4 Draw a flscher projection for the product of the following S_N^2 reaction



(B) Unimolecular nucleophillic substitution reaction (S_N^1) :

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

Mechanism of S_N^1 reaction :

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

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

Step - 2 Nucleophillic attack on the carbocation (fast)

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

Characteristics of S_N^1 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 SN^1 reaction is independent of concentration and reactivity of nucleophile.

4. Energetics of the S_N^1

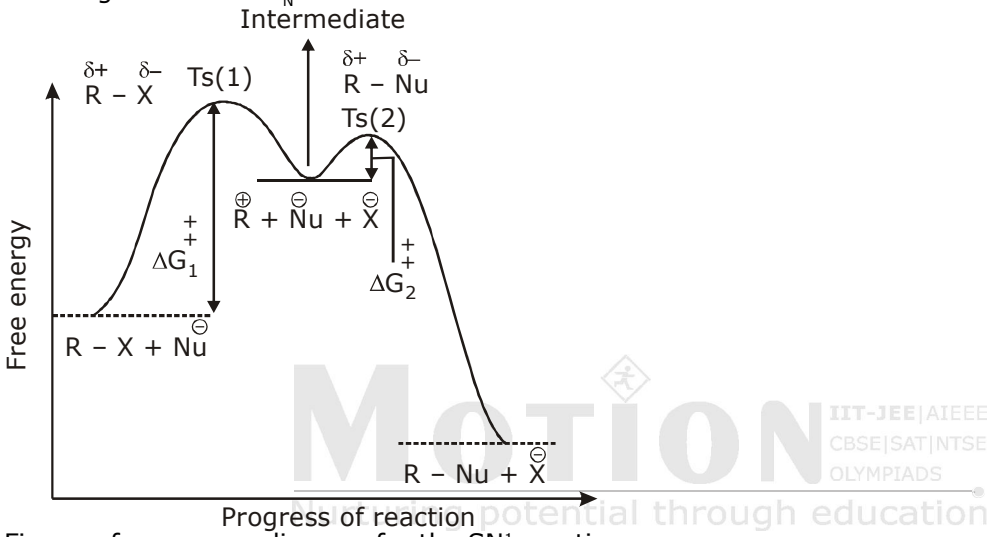


Figure : free energy diagram for the SN^1 reaction.

5 Factor's affecting the rates of S_N^1

5.(i) The structure of the substrate ⟼

The Rds of the S_N^1 reaction is ionization step, in this step form a carbocation. This ionisation is strongly endothermic process, rate of S_N^1 reaction depends strongly on carbocation stability because carbocation is the intermediate of S_N^1 reaction which determines the energy of activation of the reaction.

S_N^1 reactivity : $3^o > 2^o > 1^o > CH_3 - X$

5.(ii) Concentration and reactivity of the nucleophile ⟼

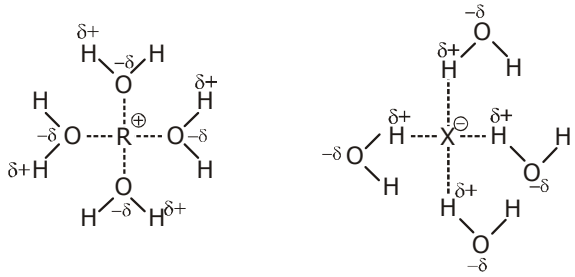
The rate of S_N^1 reactions are unaffected by the concentration and nature of the nucleophile

5.(iii) Effect of the solvent ⟼ the ioizing ability of the solvent:

Because to solvate cations and anions so effectively the use of polar protic solvent will greatly

increase the rate of ionization of an alkyl halide in any S_N^1 reaction. It does this because solvation stabilizes the transition state leading to the 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

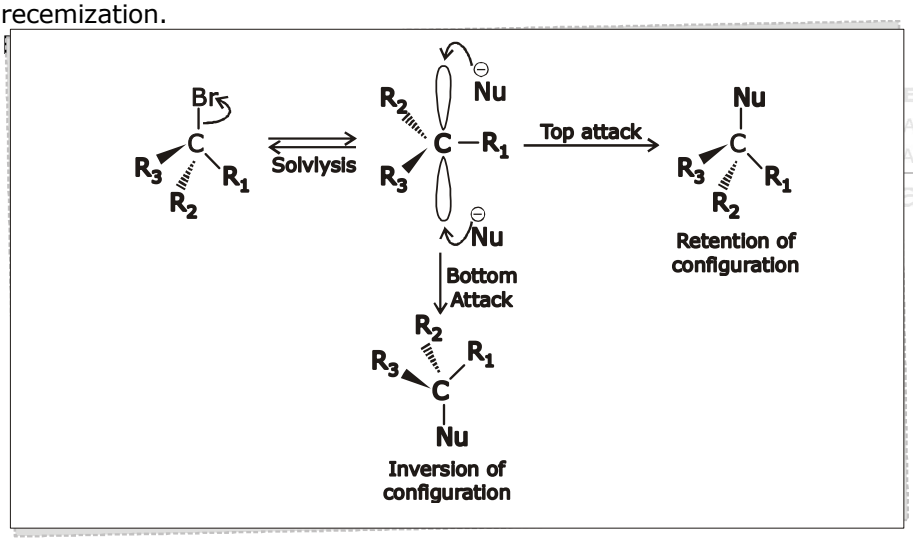
Table : 9 Dielectric constants ($\in$) and ionization rates of t-Butylchloride in common solvents

5.(iV) The nature of the leaving group $\rightarrowtail$

In the S_N^1 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.

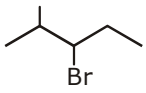
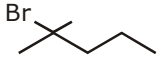
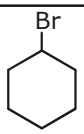
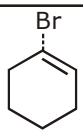
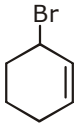
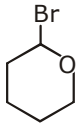
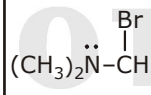
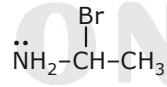
leaving ability of halogen is $\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} >> \overset{\ominus}{F}$

6. Stereochemistry of S_N^1 reactions $\rightarrow$ In the S_N^1 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 recemization.



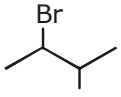
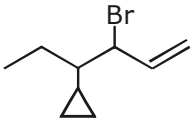
Comparison of SN^1 and SN^2 reactions :

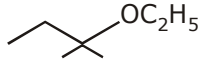
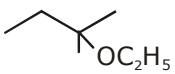
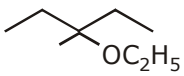
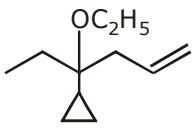
Ex. 6 Predict the compound in each pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

	I	II
(a)	$(CH_3CH_2)_2CH-Cl$	$(CH_3)_3CCl$
(b)		
(c)		
(d)		
(e)		

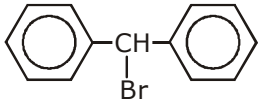
Sol. (a) II > I (b) II > I (c) I > II (d) II > I (e) II > I

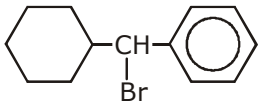
Ex. 7 Give the solvolysis products expected when each compound is heated in ethanol

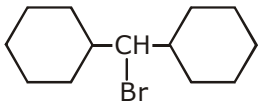
(a)  (b)  (c)  (d) 

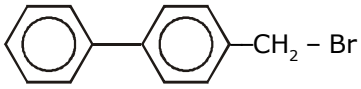
Sol. (a)  (b)  (c)  (d) 

Ex.8 The rate of SN^1 reaction is fastest with

(A) 

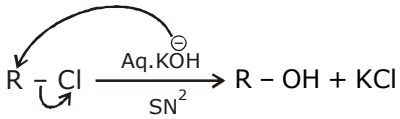
(B) 

(C) 

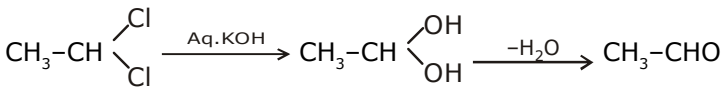
(D) 

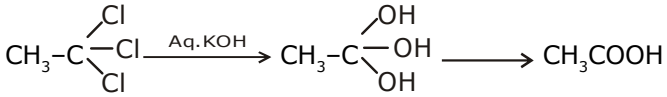
Ans. (A)

Reaction of RX with aq. KOH

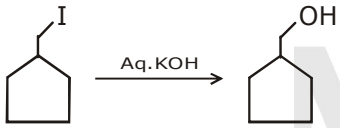
1. 

2. $CH_3–CH_2–Cl \xrightarrow{Aq.KOH} CH_3–CH_2–OH$

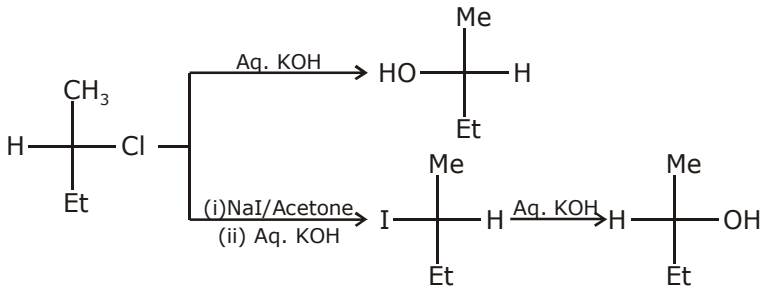
3. 

4. 

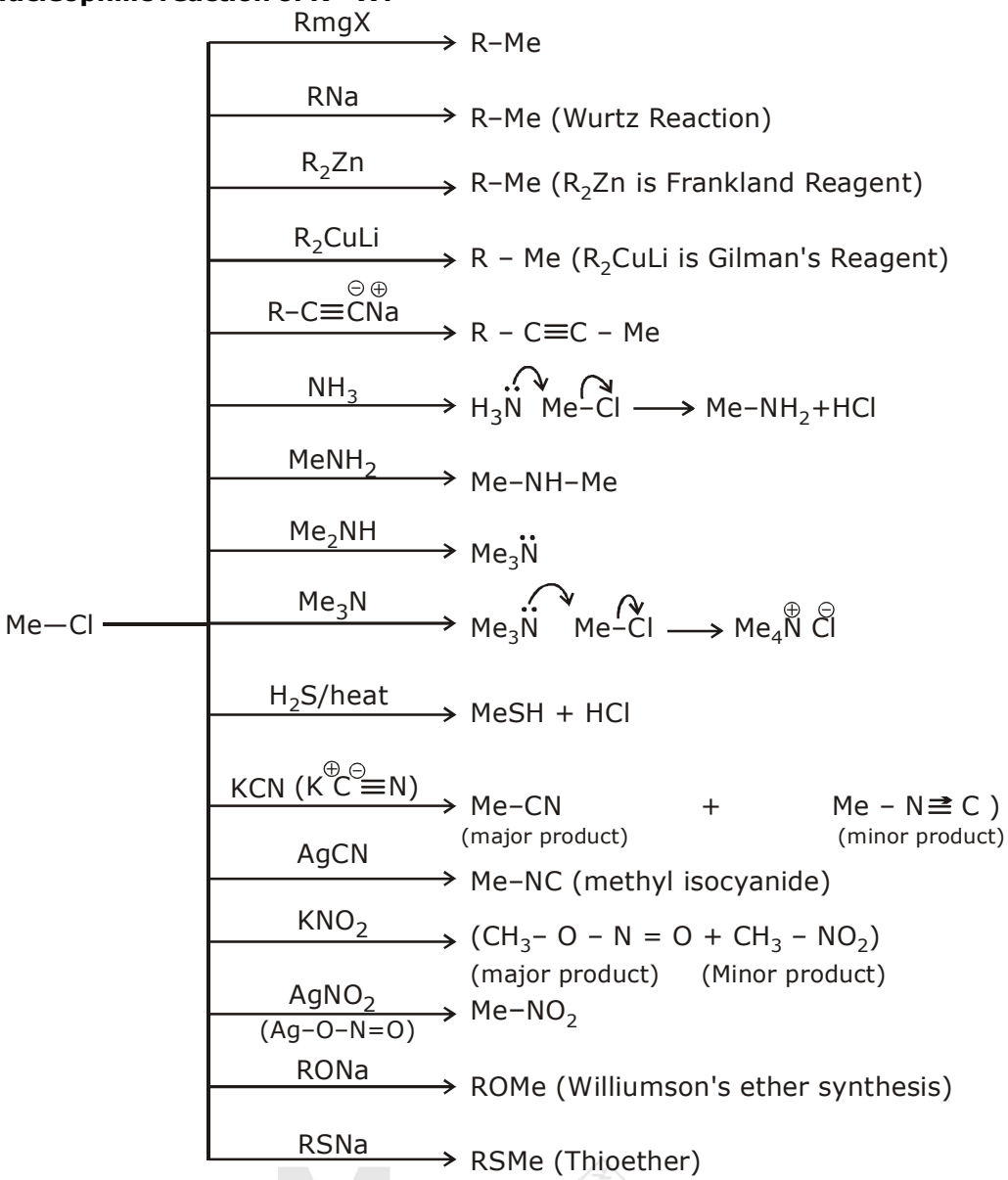
5. $C – C – C – C – Br \xrightarrow{Aq.KOH} C – C – C – C – OH$

6. 

7. $^{14}C = C – C – I \longrightarrow {}^{14}C = C – C – OH + C = C – C^{14} – OH$

8. 

Other Nucleophilic reaction of R – X :–



WillionSon's Ether Synthesis: (SN^2)

1. $R\ddot{O}Na + R - Cl \longrightarrow R - O - R + NaCl$

2. $EtONa + Me - Cl \longrightarrow EtOMe$

3. $MeONa + Et - Cl \longrightarrow EtOMe$

   Rate (2) > (3) 2 is better method. (Due to less steric hindrence)

4. $MeONa + PhCl \xrightarrow{\text{(lone pair is in resonance)}} \text{No reaction}$

5. $PhONa + MeCl \longrightarrow PhOMe + NaCl$

6. $Me_3CO^{\ominus}Na^{\oplus} + MeCl \longrightarrow Me_3COMe + NaCl$

7. $MeO^{\ominus}Na^{\oplus} + Me_3C - Cl \xrightarrow{\text{Elimination}} CH_2 = C(CH_3)_2 + MeOH + NaCl$

Major

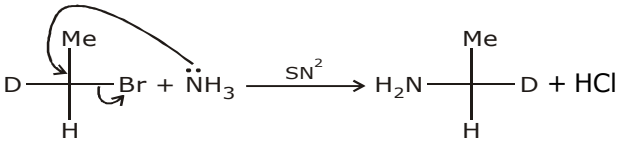
8. $PhONa + Me_3C{-}Cl \xrightarrow{\text{Elimination}} CH_2 = C(CH_3)_2 + PhOH + NaCl$

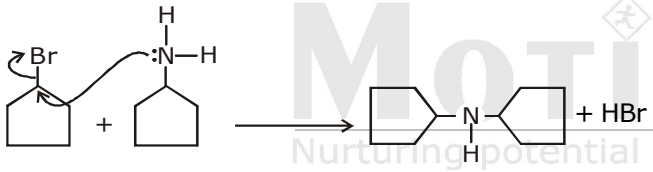
9. $Me_3CONa + Ph{-}Cl \longrightarrow$ No. reaction

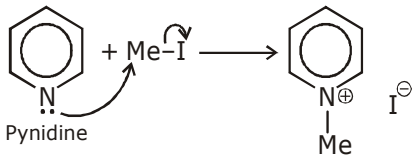
$Me_3CO{-}Ph$ can not prepared by willionson's ether synthesis.

1. $EtCl + NH_3 \xrightarrow{SN^2} EtNH_2 + HCl$

2. $C - C - C - Cl \xrightarrow[SN^2]{NH_3} C - C - C - NH_2 + HCl$

3. 

4. 

5. 

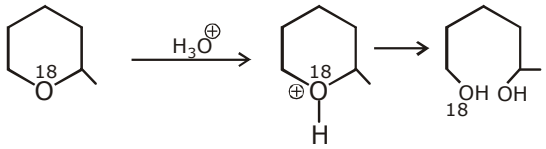
(Pyridinium salt)

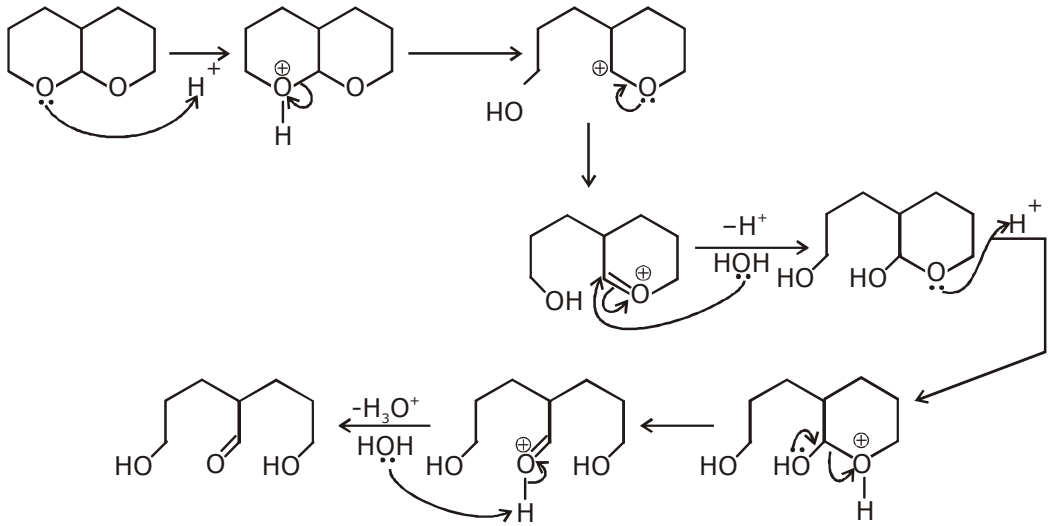
Some Other reactions

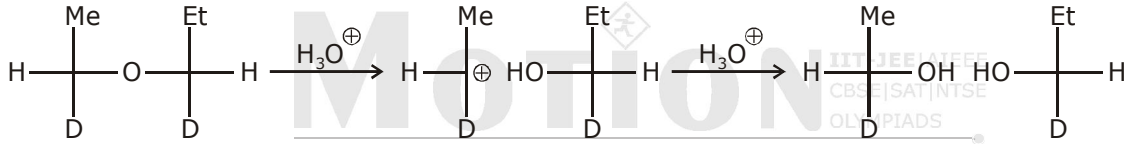
Hydrolysis of Ether

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

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

3. 

4. 

5. 

Reaction of ether with HI :

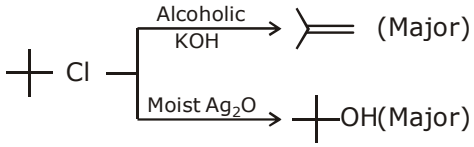
1. $Me - O - Et \xrightarrow[SN^2]{HI(anhydrous)A} MeI + EtOH$

2. $Me_3C-O-Me \xrightarrow[\text{conc.HI(excess)}]{\text{anhydrous HI}} Me_3CI + MeOH$ (Due to formation of more stable carbocation)

$Me_3C-O-Me \xrightarrow{\text{Conc.HI}} Me_3CI + MeOH$

$Me_3C-O-Me \xrightarrow[\text{conc.HI(excess)}]{\Delta} Me_3CI + MeOH$

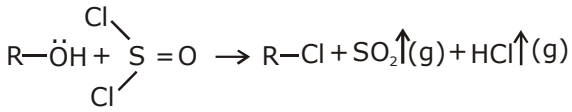
With moist and dry Ag_2O :

1. 

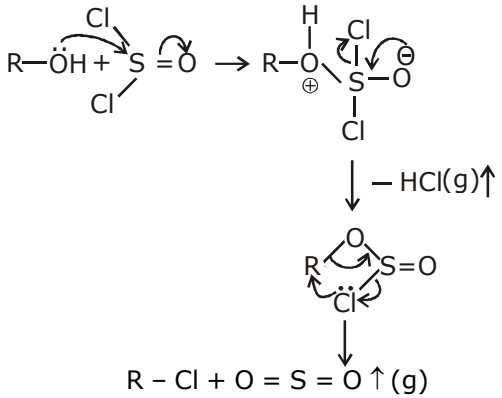
2. $2Me - Cl \xrightarrow[dry]{Ag_2O} Me - O - Me + 2AgCl$

3. $Me - Cl + EtCl \xrightarrow[dry]{Ag_2O} Me - O - Et + Me - O - Me + EtOEt$

SN_i (Nucleophilic substitution intramolecular) (Darzon's process)



Mech.



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

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

Note : (2) In presence of pyridene above reaction follow the SN^2 reaction mechanism.

SN^{NGP}(Neighbouring group participation)

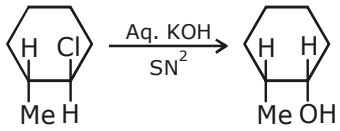
Increase in rate of SN reaction due to attack of internal nucleophie is called as SN_{NGP} is also known as Anchimeric assistence.

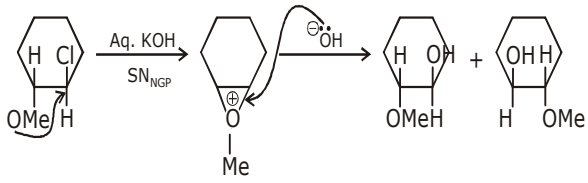
For SN^{NGP}:–

1. Internal nucleophile must be present

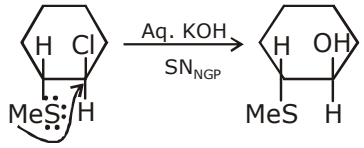
2. Internal nucleophile must be anti to lg.

During NGP :–

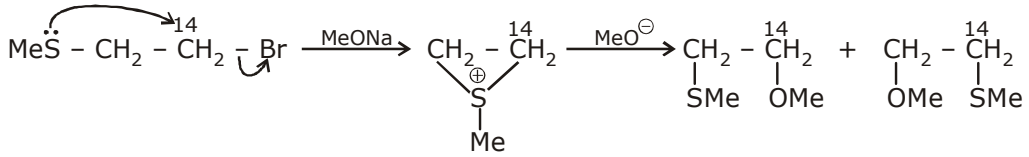
1. 

2. 

(enantiomers)

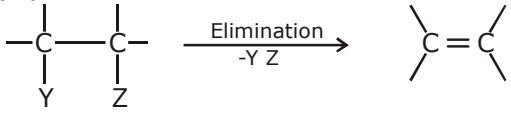
3. 

+ (enantiomer) ∴ Rate 3 > 2 > 1

4. 

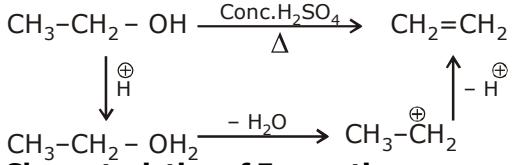
1.7.2 Elimination reactions:

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 Alohol (E1)



Characteristics of E_1 reaction :

(i) It is unimolecular, two step process

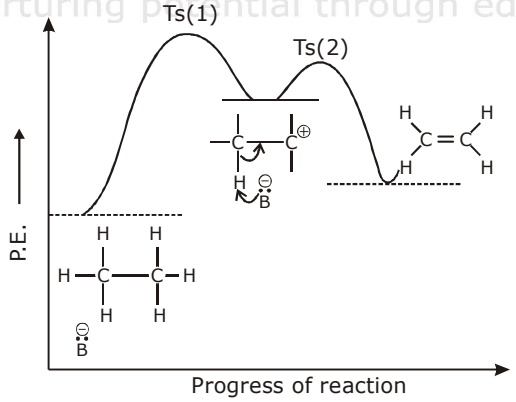
(ii) It is first order reaction

(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.

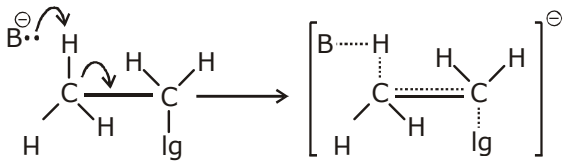
(v) Kinetics ⟶ Rate ∝ [Substrate]

Rate = k[Substrate]



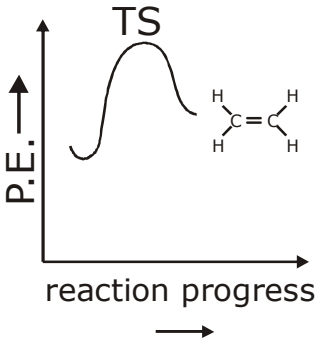
E_2- elimination :

$$B^{\ominus} \quad H{-}CH_2{-}CH_2{-}lg \longrightarrow CH_2{=}CH_2 + lg^{\ominus}$$



Rate α [R-lg] α [$B^{\ominus}$]

T.S.



Bimolecular reaction, second order kinetic.

1. Leaving group leads when base is taking proton from adjecent carbon.
2. It is a single step reaction
3. Rate α single step reaction
   Rate α Leaving group tendency
4. It shows elimental as well as kinetic isotopic effect with lg as well as at β-position.
5. Normally saytzaff product is major.
6. Transition state machenism therefor rearrangement is not possible.
7. The orientation of proton & leaving group should be antiperiplanar for E2.
8. **Positional orientation of elimination** $\rightarrowtail$ 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 favour by :
   (1) Moderate lg
   (2) Strong base ($RO^{\ominus}$, Alc. KOH)
   (3) Polar aprotic solvent.
   (4) High conc. of base.
   (5) High temperature

Reactivity towards E_2 $\rightarrowtail$ R – I > R – Br > R – Cl > R – F

Ex. Predict the elimination products of the following reactions.

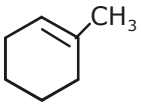
(a) Sec. butyl bromide + $\overset{\oplus}{Na}O\overset{\ominus}{E}t \xrightarrow{\Delta}$ (b) 3-Bromo-3-ethylpentane + $CH_3OH \longrightarrow$

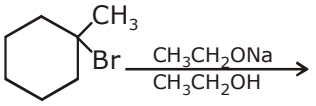
(c) 2–Bromo-3-ethylpentane + $MeONa \xrightarrow{\Delta}$ (d) 1-Bromo-2-methylcyclohexane + $EtONa \xrightarrow{\Delta}$

Sol. (a) $CH_3 - CH = CH - CH_3$

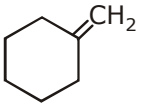
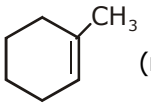
(b) $CH_3 - CH_2 - \underset{\displaystyle OCH_3}{\overset{\displaystyle CH_2-CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2 - CH_3$

(c) $CH_3 - CH_2 = \underset{\displaystyle CH_2-CH_3}{\overset{\displaystyle CH_2-CH_3}{C}}$

(d) 

Ex.11  major + minor

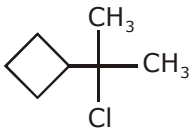
Write the structure of major and minor product.

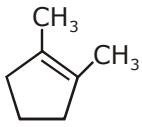
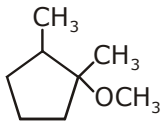
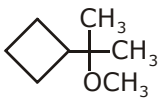
Sol.  (minor)  (major)

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	$3^o > 2^o > 1^o$	$3^o > 2^o > 1^o$
(iv) Leaving group	Better one required	Better one required

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

Ex.12  $\xrightarrow{CH_3OH,\ \Delta}$ P + Q + R

Sol. P is  , Q is  , R 

Q.6 Arrange the compounds of each set in order of reactivity towards dehydrohalogenation by strong base

(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(b) 1-Bromo-3-methylbutane, 2-bromo-2-methylbutane-2-Bromo-3-methylbutane

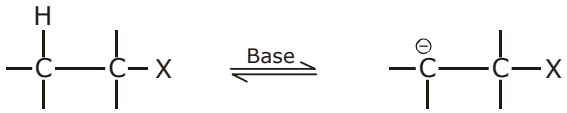
(c) 1-Bromobutane,1-Bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-Bromo-3-methylbutane

(C) mechanism of E_1 CB reaction (Unimolecular conjugate base reaction) :

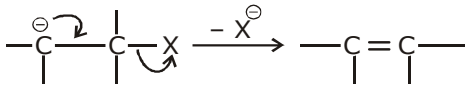
The E_1 CB or carbanion mechanism : In the E_1 CB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism:

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

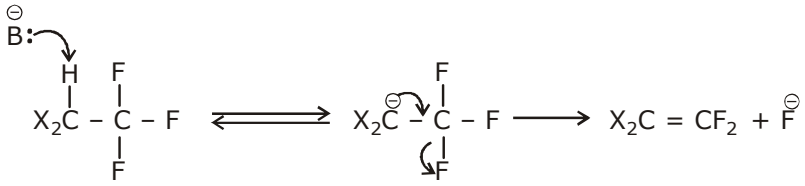


Step-2 : Carbanion loses a leaving group to form alkene



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

Ex.



1.8 Polyhalogen derivatives
Trichloromethane (Chloroform), $CHCl_3$

1.8.1 Preparation

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

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

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

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

The mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 can be separated by fractional distillation.

2. From chloral hydrate, Pure chloroform can prepare.

$NaOH + CCl_3CHO \rightarrowtail HCOONa + CHCl_3$
chloral

$NaOH + CCl_3CH(OH)_2 \rightarrowtail HCOONa + CHCl_3 + H_2O$
Chloral hydrate sodium formate Chloroform

3. Laboratory Method : From ethanol or acetone by reaction with a paste of bleaching powder and water.

In case of ethanol, the reaction occurs as follows

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

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

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

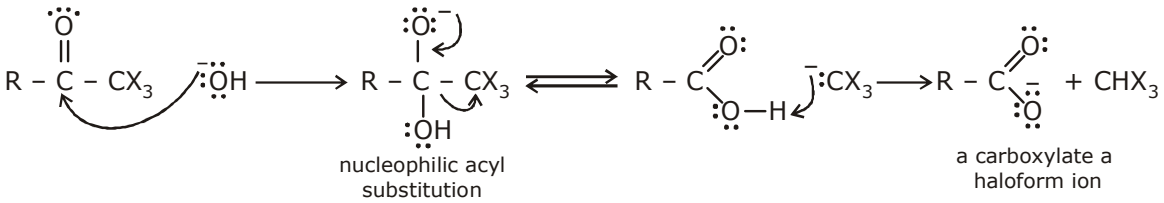
$Ca(OH)_2 + 2CCl_3CHO \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$

4. From carbontetrachloride

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

5. Haloform reaction

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



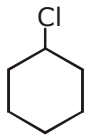
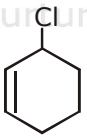
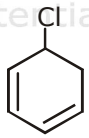
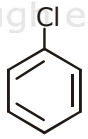
(Haloform)

Step 1 : Attack of the nucleophile

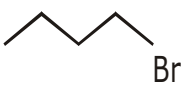
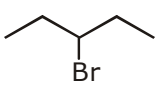
Step 2 : Elimination of the leaving group

Step 3 : Proton transfer

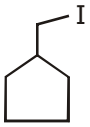
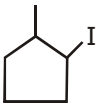
Prob. Compare rate of elimination (Dehydro halogenation in presence of alcoholic KOH) i.e., E2 :

1. (a)  (b)  (c)  (d) 

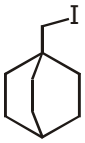
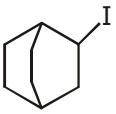
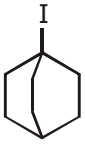
c > b > a > d

2. (a)  (b)  (c) 

c > b > a

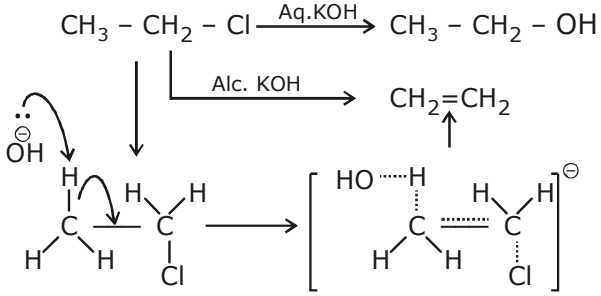
3. (a)  (b)  (c) 

c > b > a

4. (a)  (b)  (c) 

b > a > c

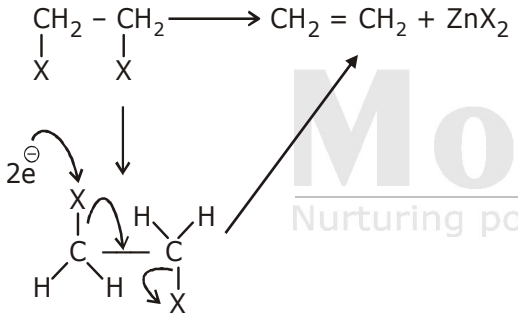
Dehyodro halegenation (–HX) E2



Anti elimination

Dehalogenation : – ($-X_2$) E2

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



Anti elimination

E_c or E_i (Intramolecular or cyclic elimination mechanism):

(1) Lg and Base present in same molecule

(2) It proceed by cyclic transition state.

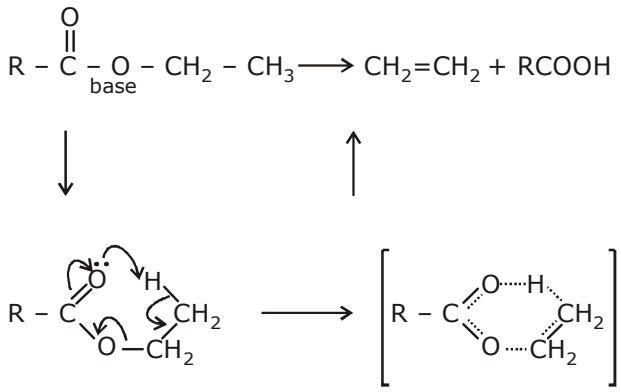
(3) Overall it is syn ellimination.

(4) Hoffmann is major product as it is obtain by least hinberd site/cyclic transition state.

(5) No rearrangement.

Example of E_c/E_i

Pyrolysis of Ester :



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

2. $CH_3-CH_2-CH_2-\overset{O^{18}}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3 \xrightarrow[E_C/E_i]{\Delta} CH_3-CH=CH_2 + CH_3CH_2-\overset{O}{\overset{\|}{C}}-\overset{18}{O}H$

1.8.2 Physical properties of chloroform

Chloroform is a colourless, heavy liquid which has sweetish, sickly odour and taste. It boils at 334º K and is slightly soluble in water. It is heavier than water. As inhaling of the vapours of chloroform induces unconsciousness therefore it can be used as an anaesthetic agent for surgery.

1.8.3 Chemical properties of chloroform

1. Action of sun light and air

$$2\,CHCl_3 + O_2 \xrightarrow{\text{Sun light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

As chloroform is used for anaesthetic purposes, therefore in order 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 enthanol (1%) is usually added to bottles of chloroform. Addition of a little ethanol fixes the toxic $COCl_2$ as non-poisonous diethyl carbonate.

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

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 :

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

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

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

4. Reaction with acetone :

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

Chlroetone

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

5. Reaction with nitric acid

$$2CHCl_3 + HONO_2 \longrightarrow \underset{\text{(chloropicrin)}}{CCl_3.NO_2} + H_2O$$

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

6. Reaction with silver powder :

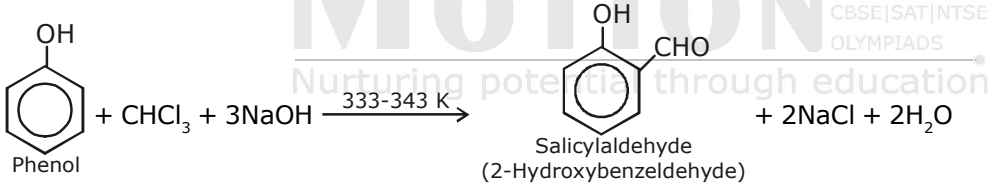
$$2CHCl_3 + 6\ Ag \xrightarrow{Heat} CH \equiv CH + 6\ AgCl$$

(Acetylene)

7. Chlorination :

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

8. Reimer-Tiemann reaction:



Phenol

Salicylaldehyde
(2-Hydroxybenzeldehyde)

1.8.4 Uses of chloroform

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