

# NEET/JEE 2020

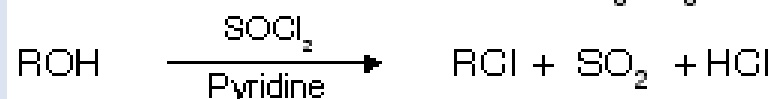
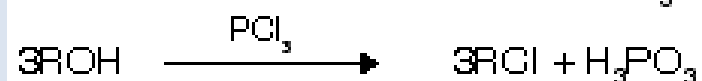


RX AND ArX

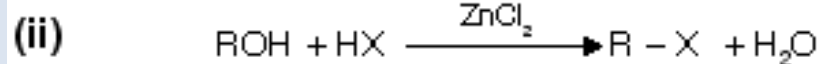
ORG.CHEM.

## Preparation of Mono halogen derivatives (RX)

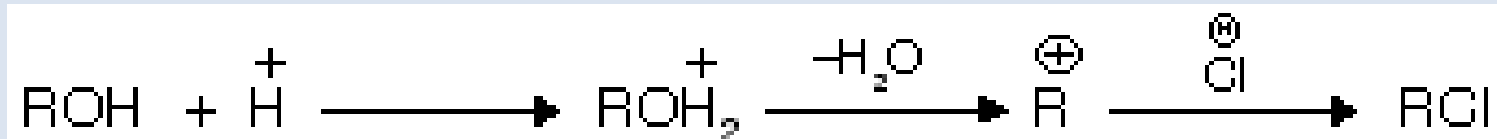
### (i) From alcohol

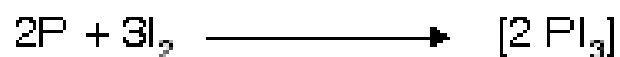
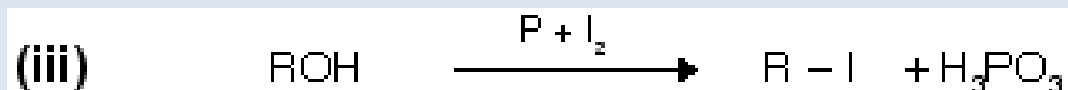


This reaction with  $\text{SOCl}_2$  is known as **Darzon's process**.



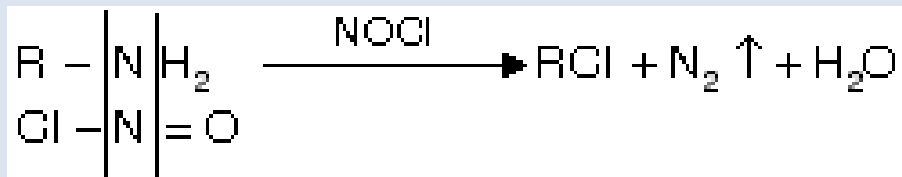
Complex formed which is a stronger acid



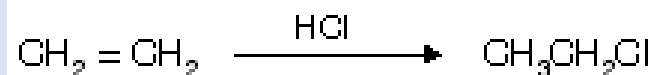
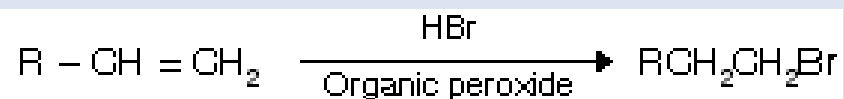
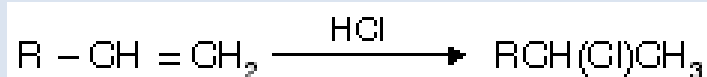


$\text{PI}_3$  is unstable due to large size of iodine, its function is similar as  $\text{PCl}_3$ .

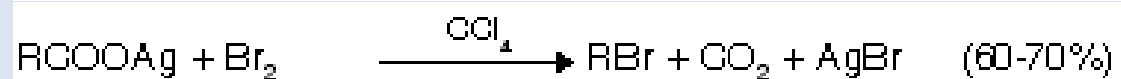
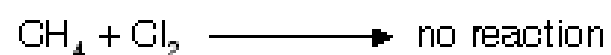
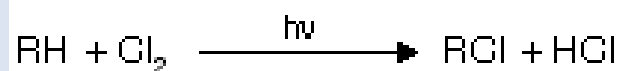
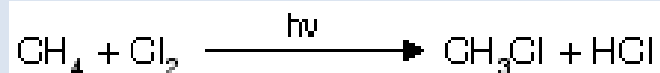
**(iv) From 1° amines with NOCl or Tilden's reagent (nitrosyl chloride)**



**(v) From alkenes**

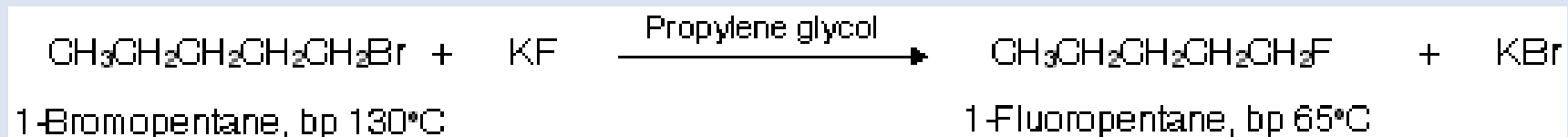
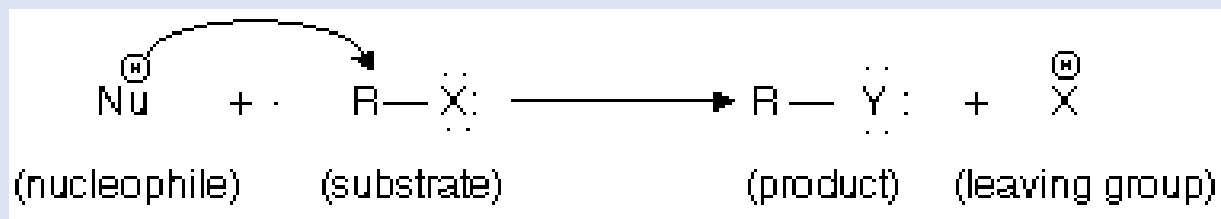


## (vi) Halogenation of alkanes



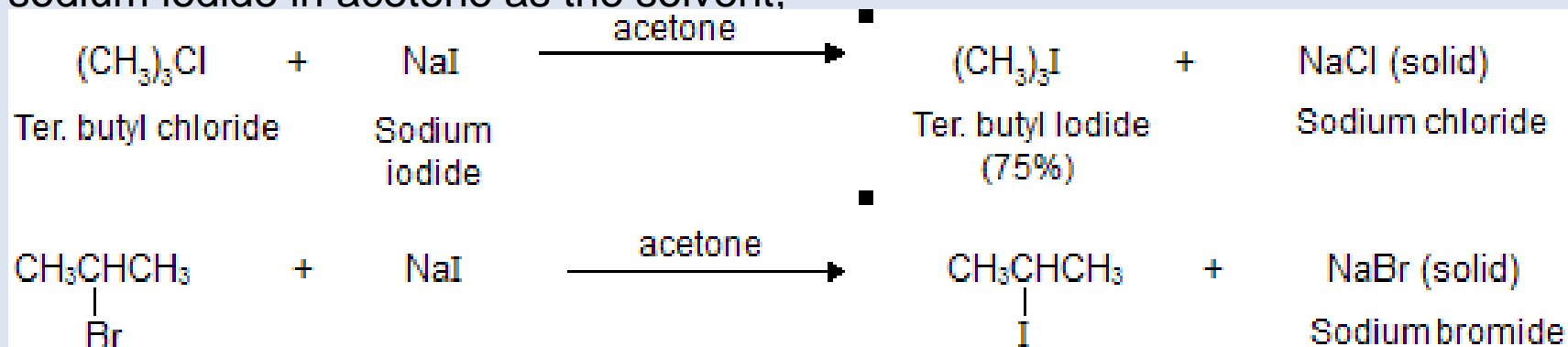
Reaction follows free radical substitution mechanism so that low yields of RBr takes place.

### (viii) Substitution of one halogen by another (Halogen exchange)



**Swart's reaction. N Finkelstein reaction**

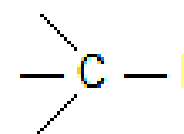
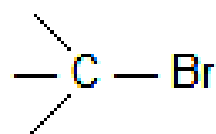
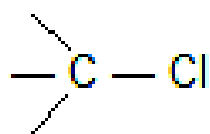
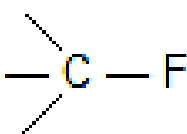
Alkyl iodides may be prepared from alkyl chlorides and bromides by treatment with sodium iodide in acetone as the solvent,



## Physical Properties

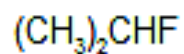
*Bond strength:*

Increasing size of halogen  $p$  orbital and C – X bond length



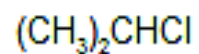
Increasing C – X bond strength

Increasing trend of boiling points $^{\circ}\text{C}$  and densities g/mL (in bracket) of branched chain haloalkanes ( $2^{\circ}$  haloalkanes)



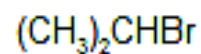
-11

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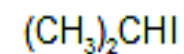
35

(0.863)



59

(1.425)



89

(1.703)

The general characteristics of monohaloalkanes can be enumerated as follows:

(a) Fluoro and chloroalkanes are less dense than water whereas bromo and iodoalkanes are denser than water.

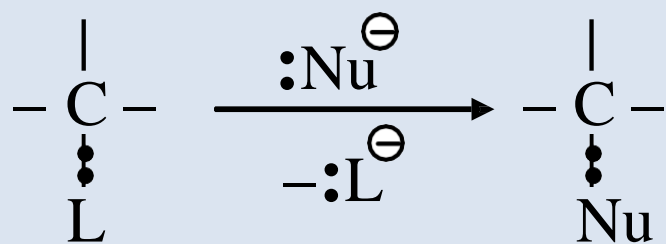
(b) Monofluoroalkanes are unstable and on heating, H-F is eliminated to produce alkene.

(c) Bromo and iodoalkanes are generally photosensitive and are stored in brown opaque bottles. Otherwise, they liberate free bromine and iodine respectively.

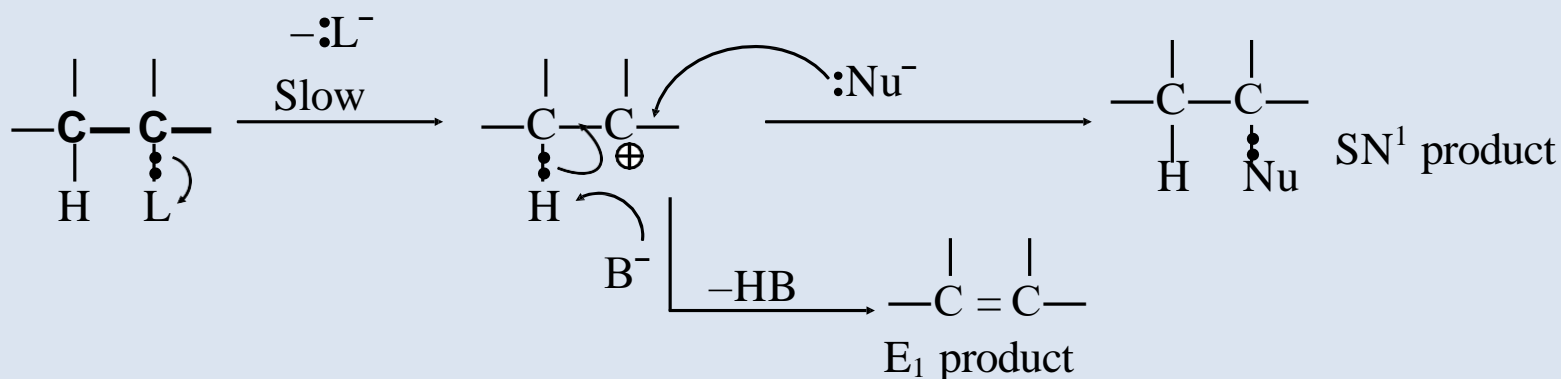


## CHEMICAL Properties of mono halogen derivatives

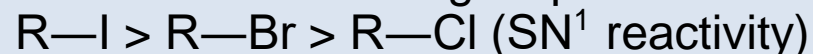
### NUCLEOPHILIC SUBSTITUTION REACTIONS



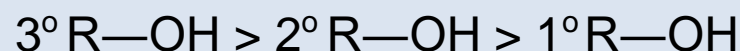
**(a) Unimolecular Nucleophilic Substitution (SN<sup>1</sup> or S<sub>N</sub>1):**



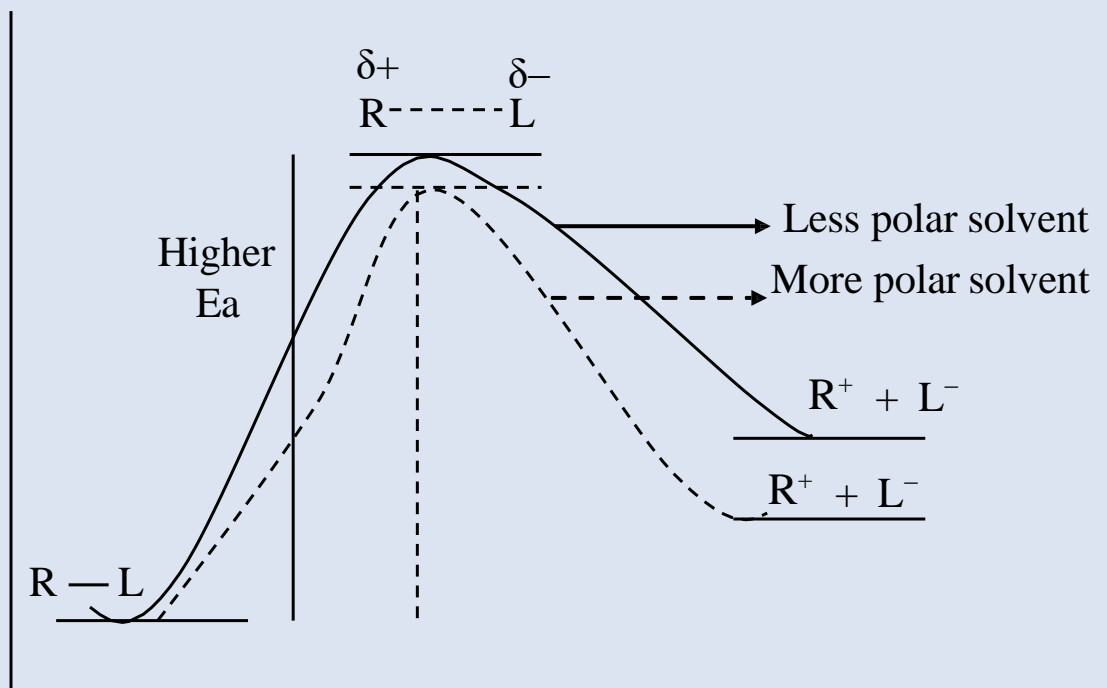
(i) *Better the leaving group, faster will be rate of SN<sup>1</sup> reaction* because leaving group is expelled in rate determining step.



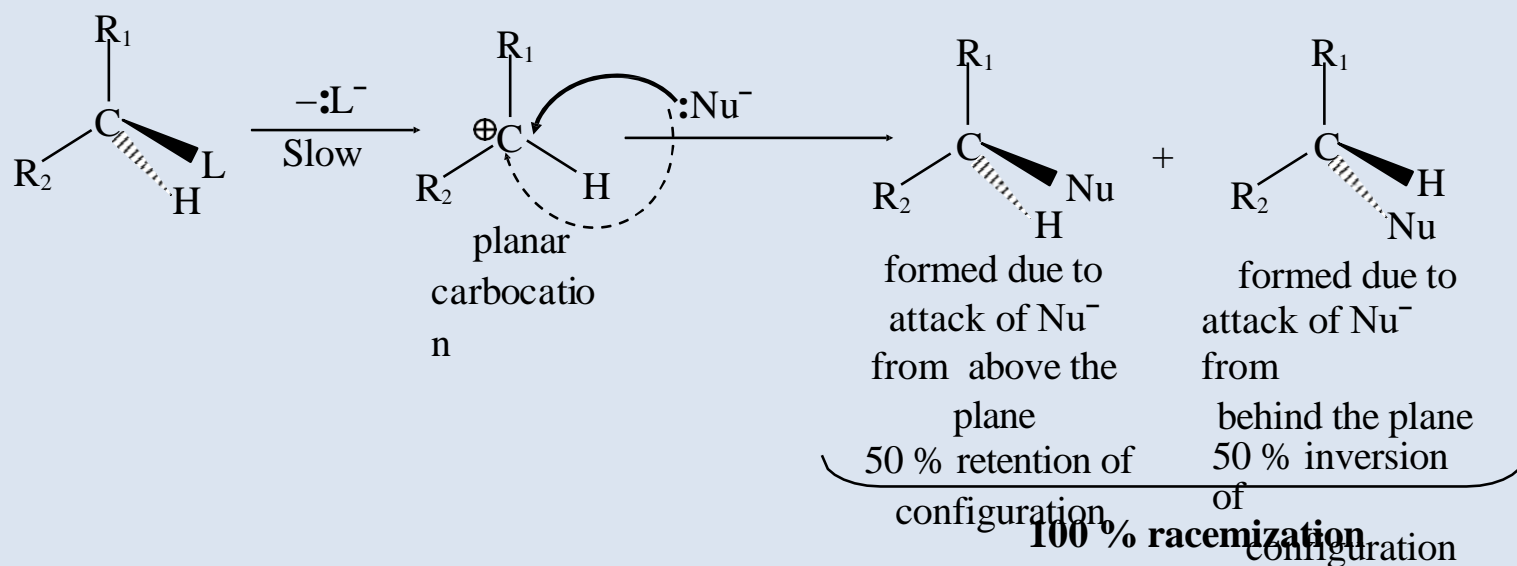
(ii) As the product of rate determining step is carbocation, we can interpret that *more the stability of carbocation, more will be rate of SN<sup>1</sup> reaction*



(iii) When solvent polarity is increased, increase in solvation of neutral reactant is almost unaffected, solvation of partially charged transition state increases slightly but the solvation of charged intermediate increases considerably (as shown in energy profile of rate determining step). Therefore, increase in solvent polarity decreases the activation energy and increases the rate of  $S_N1$  reaction. Hence,  $S_N1$  reaction is highly favoured in polar solvent.



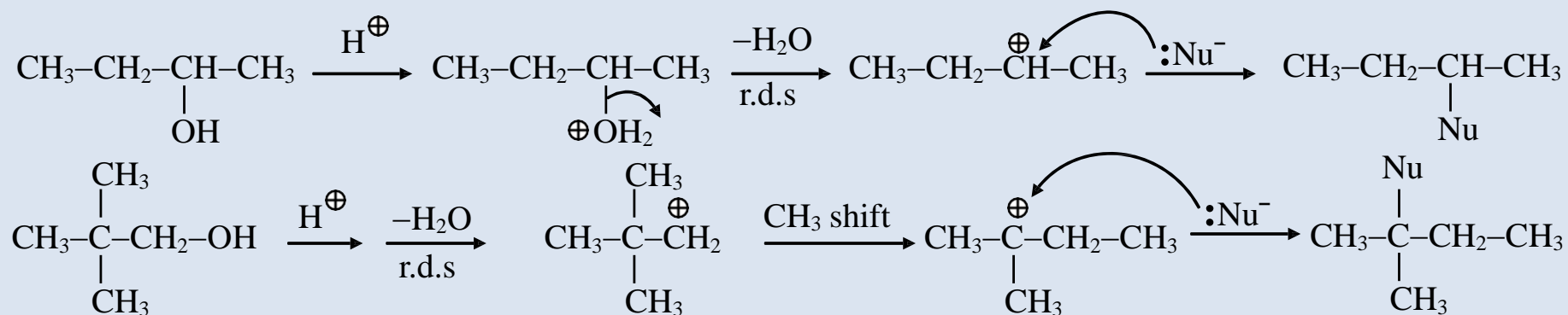
(iv) As a carbocation (containing six valence electrons and a vacant orbital) is formed, rearrangements are possible before the attack of nucleophile.



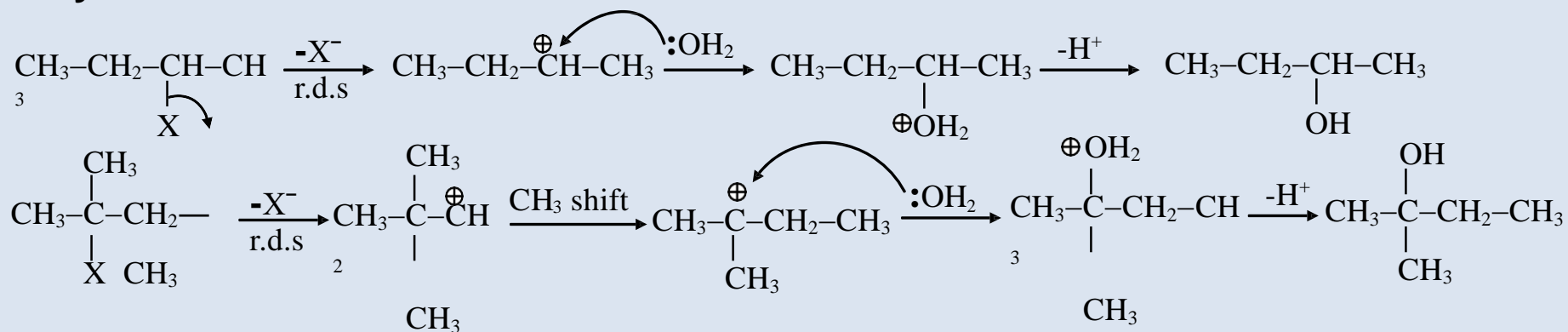
(vii) Unimolecular elimination ( $E_1$ ) will be the competing reaction.

## Examples of SN<sup>1</sup>:

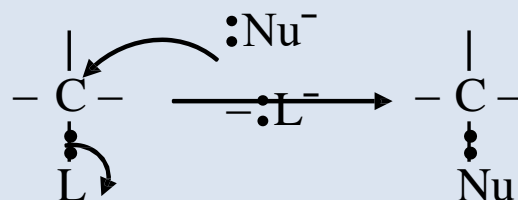
(i) Acid catalyzed nucleophilic substitution on most alcohols except smaller primary alcohols.



**(ii) Solvolysis (hydrolysis & alcoholysis) of most Alkyl halides except smaller 1° Alkyl halides.**

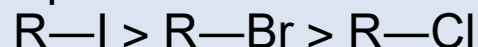


**(b) Bimolecular Nucleophilic Substitution (S<sub>N</sub><sup>2</sup> or S<sub>N</sub>2):**

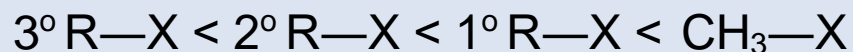


S<sub>N</sub>2 mechanism are:

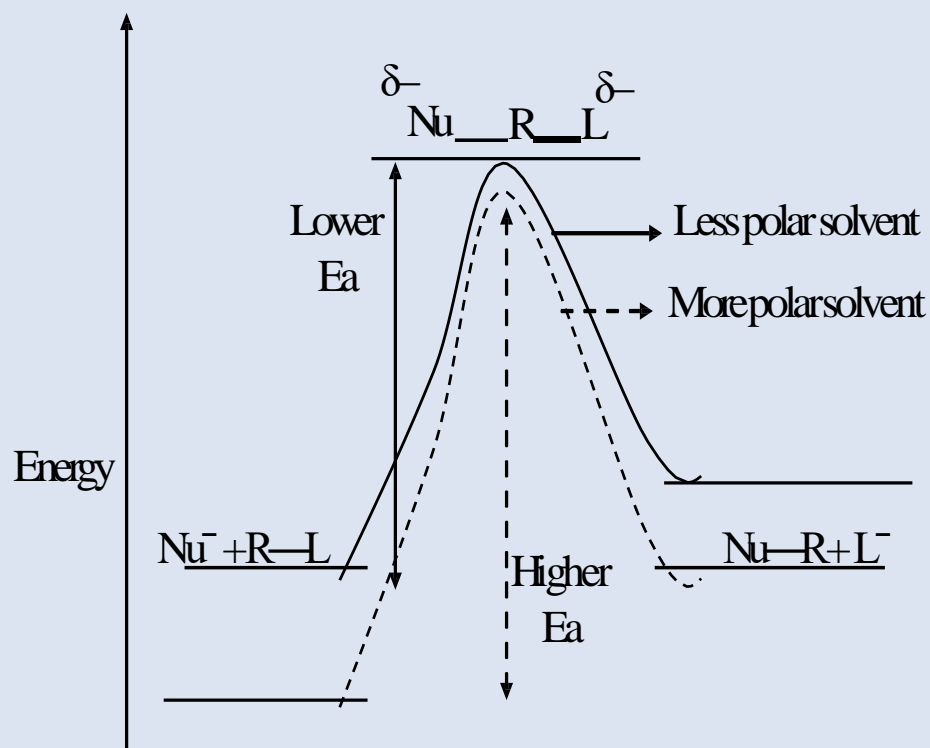
(i) *Better the leaving group, faster will be rate of S<sub>N</sub>2 reaction because leaving group is expelled in rate determining step.*



(ii) As the product of S<sub>N</sub>2 reaction is saturated, stability of the product (highly stable) is of little importance. However, the transition state is highly crowded (five groups attached to carbon), steric hindrance is of large importance. More the steric hindrance, lesser will be the rate of S<sub>N</sub>2 reaction.

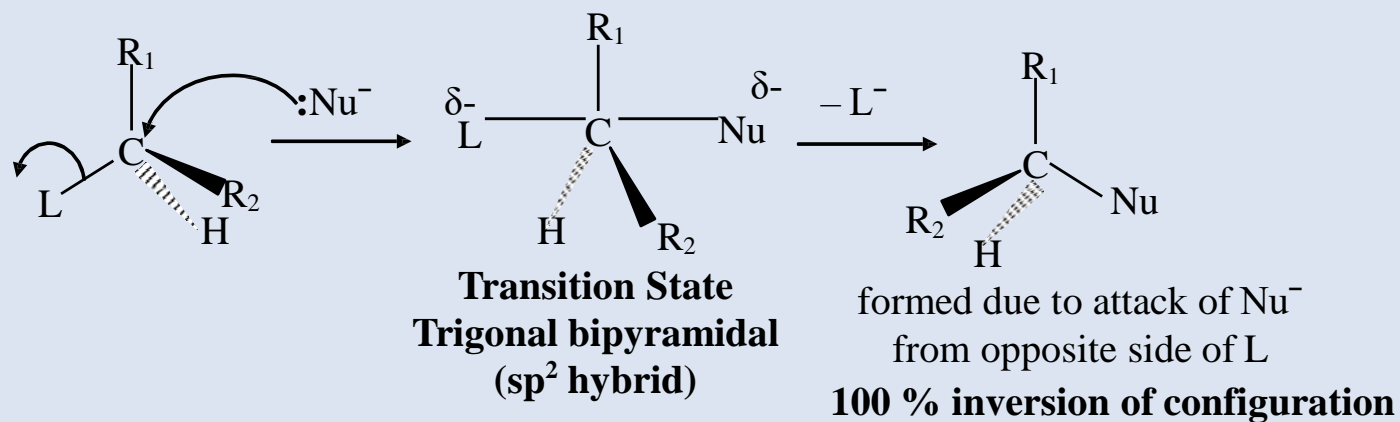


(iii) When solvent polarity is increased, increase in solvation of negatively charged reactant and negatively charged products is considerable, while solvation of partially charged transition state is slight (as shown in energy profile of rate determining step). Therefore, increase in solvent polarity increases the activation energy and decreases the rate of  $S_N2$  reaction. Hence,  $S_N2$  reaction is less favoured in polar solvent.





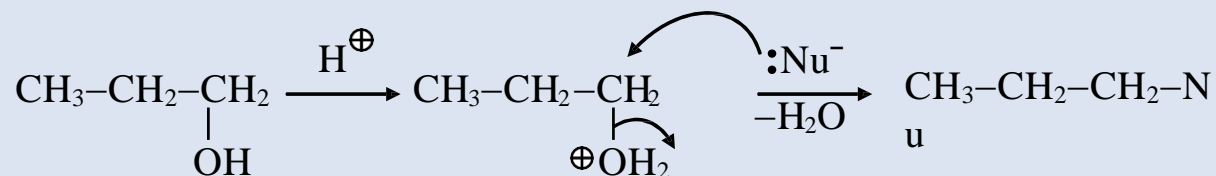
(iv) No rearrangements are observed during  $S_N2$  reaction.



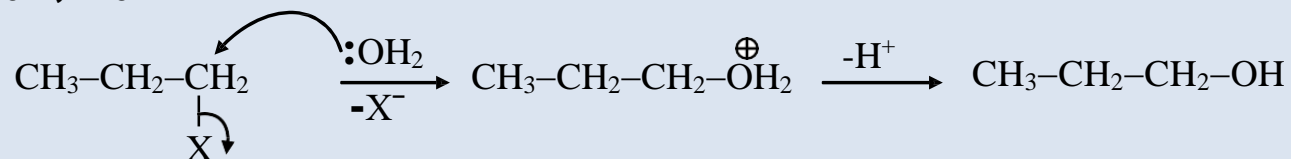
(vii)  $S_N1$  and elimination reactions are the competing reactions because strong nucleophiles are generally strong bases also.

## Examples of S<sub>N</sub>2:

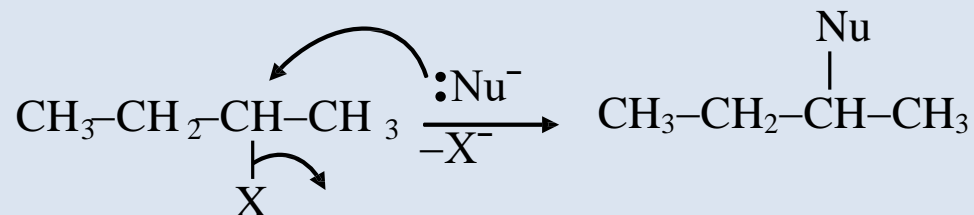
(i) Nucleophilic substitution in lower 1° alcohol (CH<sub>3</sub>OH, EtOH, C<sub>3</sub>H<sub>7</sub>OH etc) in acidic medium.



(ii) Solvolysis (hydrolysis & alcoholysis) of smaller 1° Alkyl halides like CH<sub>3</sub>X, C<sub>2</sub>H<sub>5</sub>X, C<sub>3</sub>H<sub>7</sub>X etc.



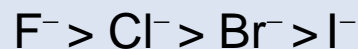
(iii) Most nucleophilic substitution reactions of alkyl halides except 3° alkyl halides.



The order of nucleophilicity of different species depends on the nature of solvent used.

In polar protic solvents, hydrogen bonding or ion–dipole interaction diminishes the reactivity of the anion. Stronger the interaction, lesser is the reactivity of anion.  $F^-$  ion will form strong H–bond with polar protic solvent while weakest ion–dipole interaction will be with  $I^-$  ion. Thus, the nucleophilicity order of  $X^-$  in polar protic solvent would be  $I^- > Br^- > Cl^- > F^-$ .

Polar aprotic solvents have the ability to solvate only cations, thus anions are left free. The reactivity of anions is then governed by their negative charge density (i.e. their basic character). Thus, the order of nucleophilicity of  $X^-$  in polar aprotic solvents would be



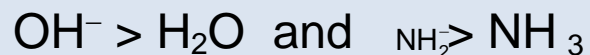
On this basis, certain nucleophilicity orders are

(i) In polar protic solvents,  $HS^- > HO^-$

(ii) In weakly polar aprotic solvents,  $CsF > RbF > KF > NaF > LiF$

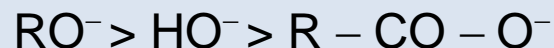
(iii)

Bases are better nucleophiles than their conjugate acids. For example,



(iv) In non-polar solvents,  $\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$

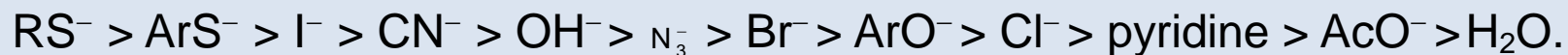
(v) When nucleophilic and basic sites are same, nucleophilicity parallels basicity. For example,



(vi) When the atom bonded to nucleophilic site also has an unshared pair of electrons, nucleophilicity of species increases. For example,

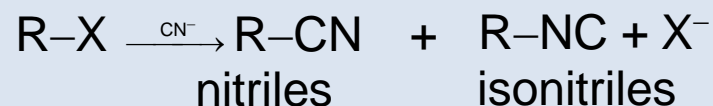


***Edwards and Pearson gave following order of nucleophilicity for  $S_N2$  reactions in protic solvents.***



## AMBIDENT NUCLEOPHILE

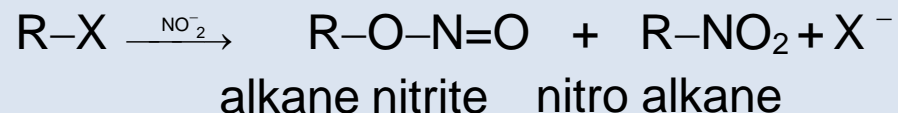
### Attack By $\text{CN}^-$ Nucleophile ( $^-\text{C} \equiv \text{N}:$ )



if the reaction proceeds via  $\text{S}_{\text{N}}2$  mechanism (small positively charged carbon is soft acid) then attack through carbon (soft base) will take place. So, if we want to increase relative yield of nitriles, we can use NaCN or KCN etc in a less polar solvent, which facilitates  $\text{S}_{\text{N}}2$  substitution.

if we want to increase the yield of isonitriles, we can use AgCN.  $\text{Ag}^+$  has very strong affinity for  $\text{X}^-$ , so it favours the formation of  $\text{R}^+$  and the reaction proceeds via  $\text{S}_{\text{N}}1$  mechanism. This will result in attack by hard base giving R-NC.

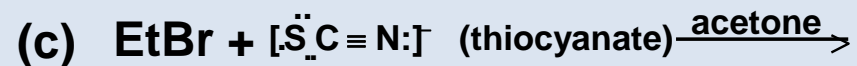
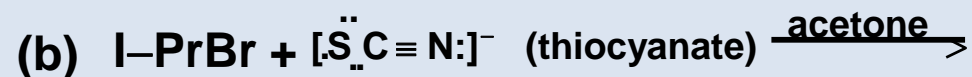
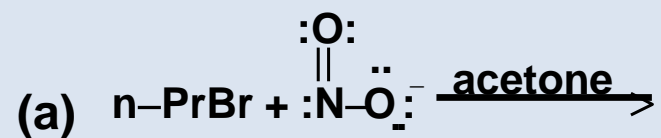
### Attack By $\text{NO}_2^-$ Nucleophile ( $^-\text{O}-\text{N}=\text{O}$ )

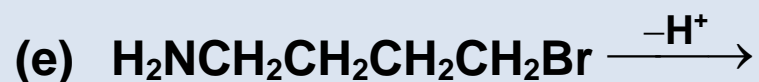


If we want to increase the yield of nitro alkane, the reaction should proceed via  $\text{S}_{\text{N}}2$  mechanism. i.e. we can use  $\text{NaNO}_2$ ,  $\text{KNO}_2$  etc. Moreover, the yield will be best if we use primary alkyl halide and less polar solvent. Formation of nitrite will dominate, if we use tertiary alkyl halide, more polar solvent and  $\text{AgNO}_2$  because  $\text{Ag}^+$  has strong affinity for  $\text{X}^-$  and can form a carbocation to force the reaction to proceed via  $\text{S}_{\text{N}}1$  mechanism. Primary alkyl halide with  $\text{AgNO}_2$  chiefly gives nitro alkane but if secondary and tertiary alkyl halides are used then  $\text{AgNO}_2$  will yield nitrite as the major product.

**Question:**

**Give the organic products of the following reactions.**





**Solution:** The nucleophiles in (a), (b) and (c) are ambident since they each have more than one reactive site. In each case, the more nucleophilic atom reacts even though the other atom may bear a more negative charge.

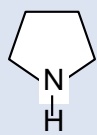
(a) n-PrNO<sub>2</sub>



(b) i-PrSCN

(c) EtSCN

(d) ClCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN (I<sup>-</sup> is a better leaving group than Cl<sup>-</sup>)

(e)  . When the nucleophilic and leaving groups are part of the same molecule,  
molecule,  
an intramolecular displacement occurs if a three-, a five- or a six-membered ring can form.

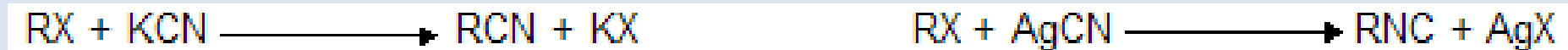
## COMPARISON OF S<sub>N</sub>1 AND S<sub>N</sub>2 REACTIONS

	S <sub>N</sub> 1	S <sub>N</sub> 2
(a) Number of steps	2 steps : (i) $R : L \xrightarrow{\text{slow}} R^+ + :L^-$ (ii) $R^+ + :NuH \xrightarrow{\text{fast}} R:Nu + H^+$	1 step : $R : L + :Nu^- \rightarrow R:Nu + :L^-$ Or $R : L + :NuH \rightarrow R : N^+uH + :L^-$
(b) Reaction rate & order	Rate = $k_1[RL]$ ; first order	Rate = $k_1[RL][:Nu^-]$ ; second order
(c) Molecularity	Unimolecular	Bimolecular

(d) TS of slow step	$\overset{\delta+}{R} \cdots \cdots \overset{\delta-}{L}$	$\overset{\delta-}{Nu} \cdots R \cdots L^{\delta-}$ (with : Nu <sup>-</sup> ) $\overset{\delta+}{H}Nu \cdots R \cdots L^{\delta-}$ (with : HNu)
(e) Stereochemistry	Inversion and retention (Partial racemization)	Inversion of configuration (backside attack)
(f) Reacting nucleophile	Nucleophilic solvent; stable R <sup>+</sup> may react with added nucleophile	Added nucleophile
(g) Structure of R	3° > 2° > 1° > Me	Me > 1° > 2° > 3°
(h) Nature of Leaving group	Weakest base is best leaving group, i.e. I <sup>-</sup> > Br <sup>-</sup> > Cl <sup>-</sup> > F <sup>-</sup>	Weakest base is best leaving group, i.e. I <sup>-</sup> > Br <sup>-</sup> > Cl <sup>-</sup> > F <sup>-</sup>

(i) Nature of nucleophile	For HNu: (solvent), rate $\propto$ basicity of HNu:	In protic solvents, (i) Within a periodic table group, rate $\propto$ polarizability of Nu (ii) For same nucleophilic site, rate $\propto$ basicity of Nu In polaraprotic solvents, rate $\propto$ basicity of Nu
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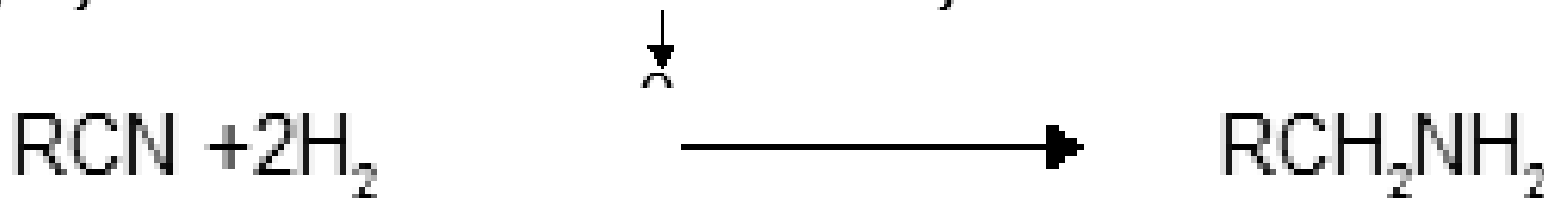
### (i) Synthesis of cyanide and Isocyanide



With KCN, halides mainly form cyanides because in KCN molecule ionic bonding occurs which produces  $CN^-$  with ambident nature where two sites of attachment are

there as negative charge and lone pair of electrons. Attachment prefers at carbon site because negative charge is more active than pure lone pair. Reaction with AgCN

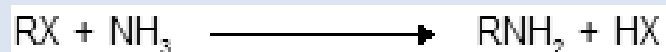
(ii) Synthesis of nitro alkane  $R-N=O$  and alkyl nitrite  $R-O-N=O$



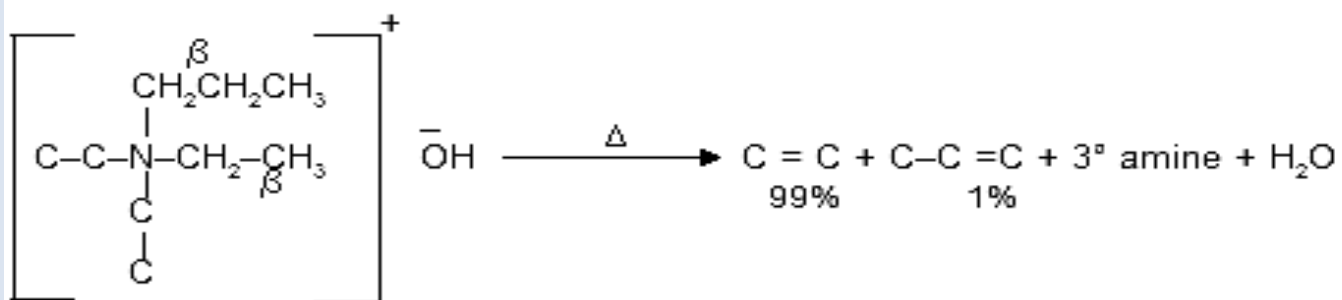
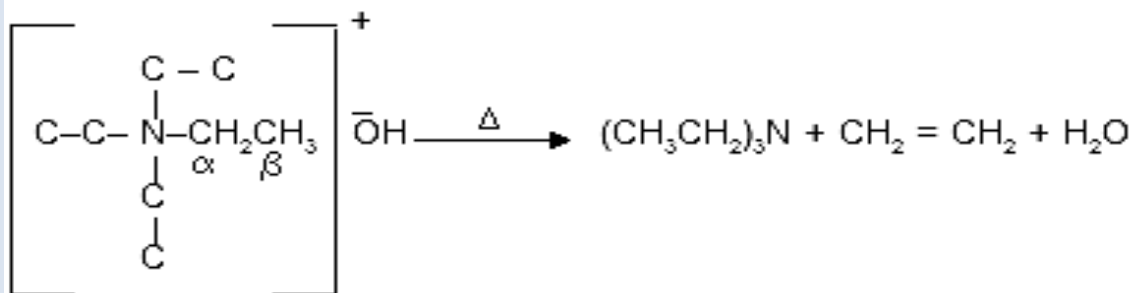
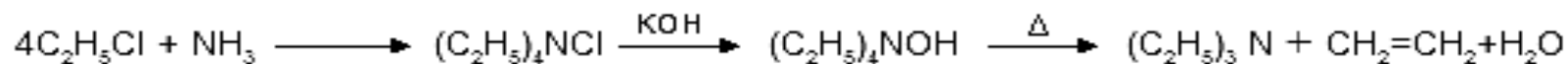
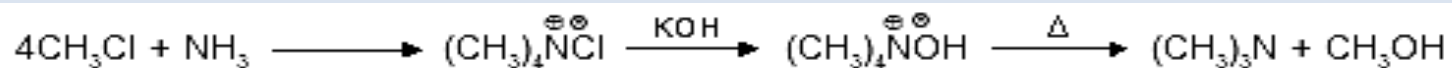
(covalent bonding) produces isoaganimides as major product.

$NO_2$  also works as ambident nucleophile because it has two sites for attachment one is nitrogen lone pair while other is negative charge on oxygen atom. There is ionic bonding in  $KNO_2$  molecule so it produces exclusively alkyl nitrite while with  $AgNO_2$  (covalent) attachment prefer from nitrogen site because lone pair of nitrogen is more reactive than lone pair of oxygen.

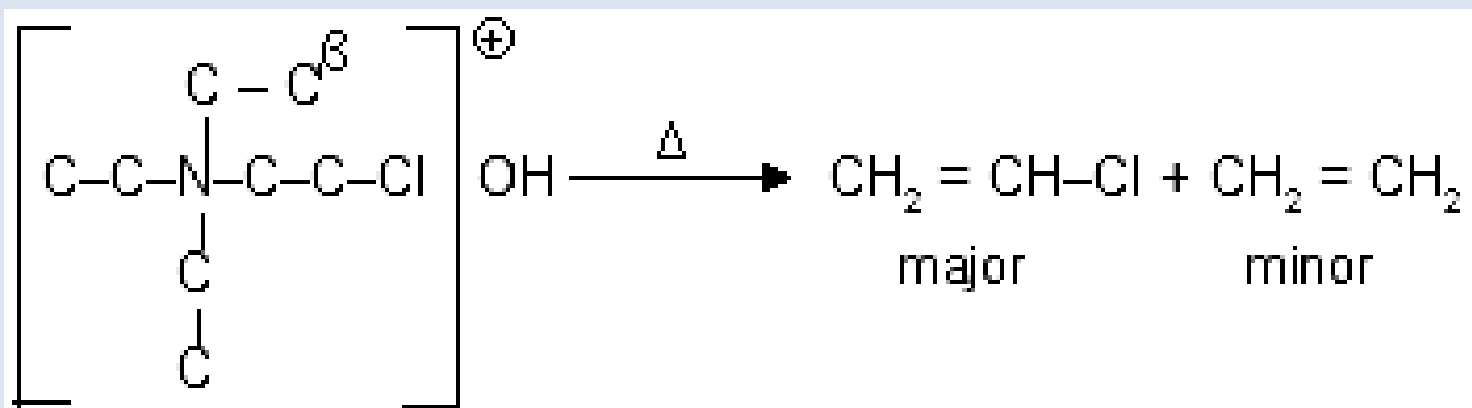
**(iii) Synthesis of quaternary ammonium salt and Hoffmann's  $\beta$ -Elimination.**



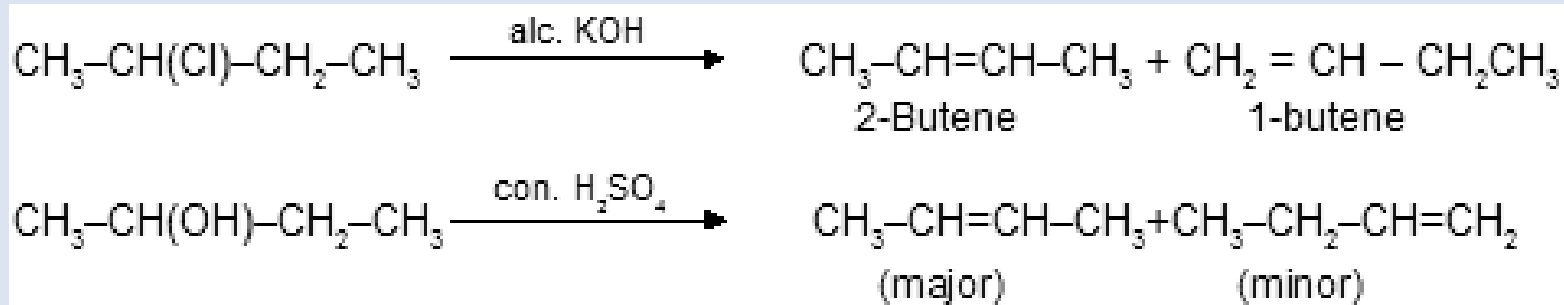
When primary halides reacts with ammonia to form primary amines as major product but when excess of alkyl halides are taken than exhaustive alkylation occurs, where synthesis of quaternary ammonium salts takes place. By heating they undergo  $\beta$ -elimination through Hoffmann's orientation forms less substituted alkenes as major product.



In above cases alkene formation takes place by ethyl group & not by propyl group because  $\beta$ -carbon of propyl is  $2^\circ$  in nature & abstraction of proton order in case of Hoffmann's  $\beta$ -eliminations is  $1^\circ > 2^\circ > 3^\circ$  carbon atom



Other chemical reaction mainly follows E-1 or E-2 reaction for elimination (dehydration and dehydrohalogenation) where sytzeff's rule for stabilization occurs for example.



**(iv) Some other synthetic methods from alkyl halide**



(a)	$RX$	$\xrightarrow{KSH}$	$RSH$	
(b)	$RX$	$\xrightarrow{NaSH}$	$RSH$	
(c)	$RX$	$\xrightarrow{RCOOAg}$	$RCOOR + AgX$	
(d)	$RX$	$\xrightarrow{aq. KOH}$	$ROH + KX$	
(e)	$RX$	$\xrightarrow{alc. KOH}$	Alkene	<b>Elimination reaction</b>
(f)	$RX$	$\xrightarrow{RONa}$	$R-O-R$	<b>Williamson's synthesis</b>
(g)	$RX$	$\xrightarrow{Ag_2O}$	$R-O-R + AgX$	
(h)	$RX$	$\xrightarrow{\text{moist } Ag_2O \text{ or } AgOH}$	$ROH + AgX$	
(i)	$RX$	$\xrightarrow{2Na/THF}$	$R-R$	<b>Wurtz reaction</b>
(j)	$RX$	$\xrightarrow{Zn/ HCl}$	$RH$	
(k)	$RX$	$\xrightarrow{RmgX}$	$R-R$	
(l)	$RX$	$\xrightarrow{R-C \equiv CNa}$	$R-C \equiv C-R + NaX$	
(m)	$RX$	$\xrightarrow[\text{Acetone}]{NaI}$	$RI$	<b>Finkelstein reaction</b>
(n)	$RX$	$\xrightarrow{AgF}$	$RF$	<b>Swart's reaction</b>
(o)	$RCH_2X$	$\xrightarrow{(CH_3)_2SO}$	$RCHO + (CH_3)_2S + HX$	<b>Oxidation</b>
(p)	$R_2CHX$	$\xrightarrow{(CH_3)_2SO}$	$RCOR + (CH_3)_2S + HX$	<b>Oxidation</b>
(q)	$R_3C-X$	$\xrightarrow{DMSO}$	no reaction	
(r)	$RX$	$\xrightarrow[THF]{Mg}$	$RmgX$	

(s)	RX	$\xrightarrow{\text{Na}_2\text{SO}_3}$	$\text{RSO}_3\text{Na}$	Straker's reaction
(t)	RX	$\xrightarrow{\text{R}_2\text{CuLi}}$	R-R	Corey house synthesis
(u)	RX	$\xrightarrow{\text{AgCN}}$	RNC	
(v)	RX	$\xrightarrow{\text{KCN}}$	RCN	
(w)	RX	$\xrightarrow{\text{NaNO}_2}$	R-O-N = O	
(x)	RX	$\xrightarrow{\text{Zn}}$	$\text{R}_2\text{Zn}$ Di alkyl Zinc	Frankland's reagent

## DIHALOGEN DERIVATIVES

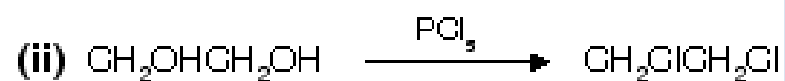
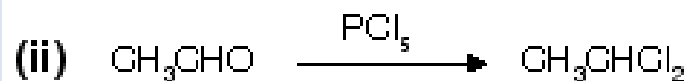
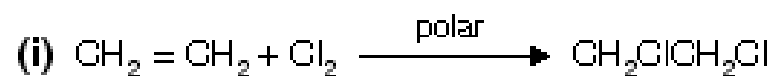
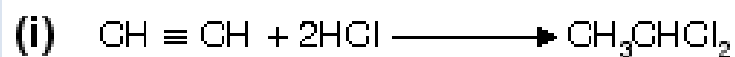


Geminal dihalide (Ethylene chloride)

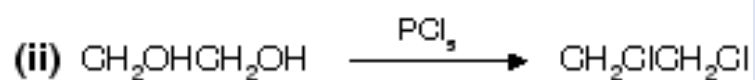
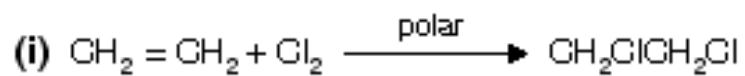
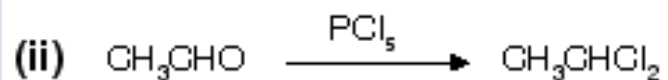
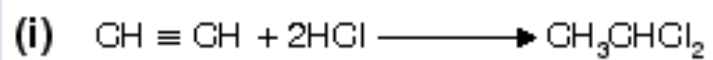


Vicinal dihalide (Ethylene chloride)

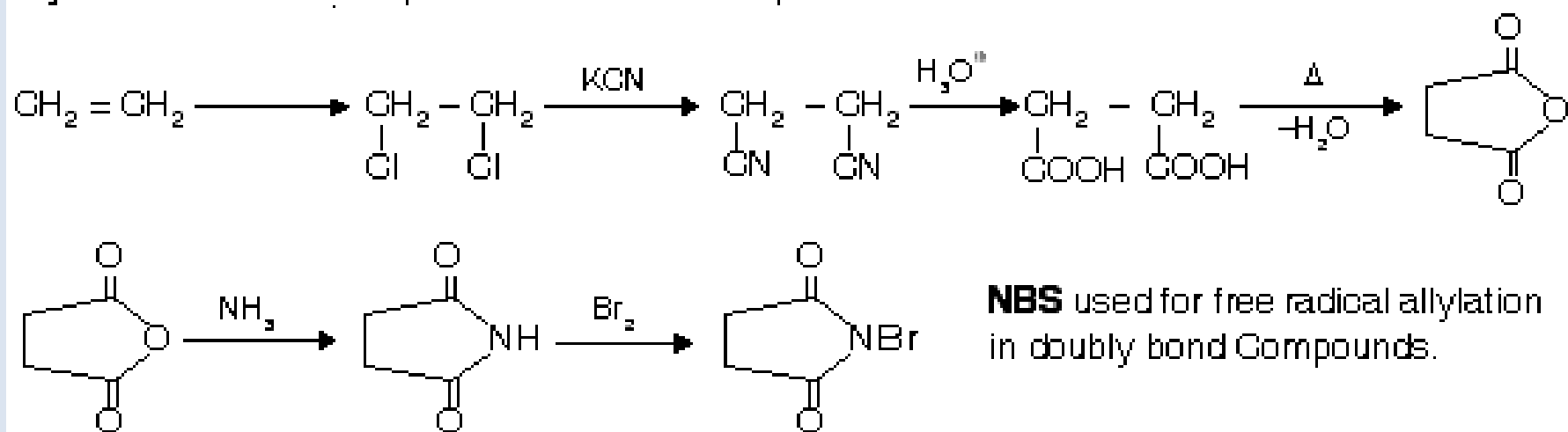
### Preparation



## Properties



## Synthesis of NBS (N-Bromo Succinimide)



## HALOFORMS(Trihalogen Derivatives)

The general formula of trihalogen derivative is  $\text{CHX}_3$

### Preparation

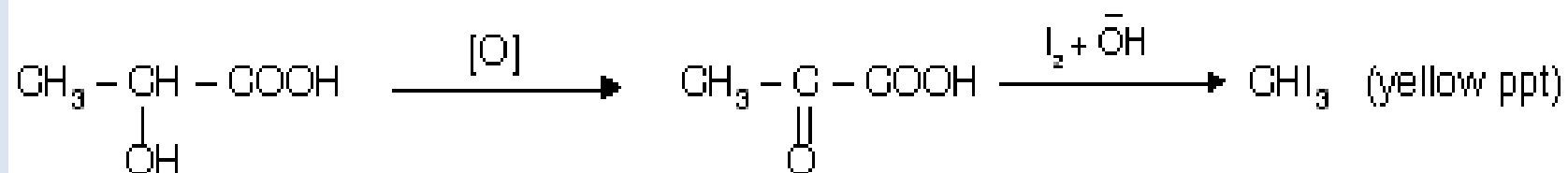
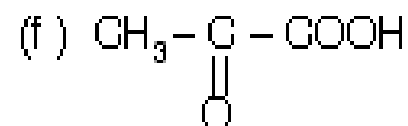
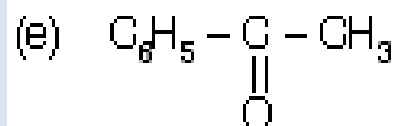
(i) **Haloform test** is given by compounds having  $-\text{COCH}_3$  group.

(a) 2-alkanone

(b) 2-alkanol

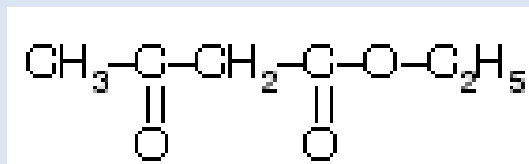
(c)  $\text{CH}_3\text{CHO}$

(d)  $\text{CH}_3\text{CH}_2\text{OH}$



$\text{CH}_3\text{COOH}$  cannot give haloform test due to resonance and does not contain pure  $\text{COCH}_3$  group.

$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$  Benzophenone does not give haloform test due to absence of  $-\text{COCH}_3$  group.

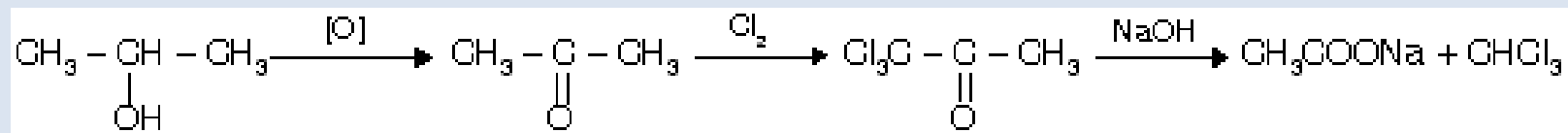


Acetoacetic ester even though contains  $-\text{COCH}_3$  group but does not give haloform test due to active methylene group in the molecule where first halogenation occurs.

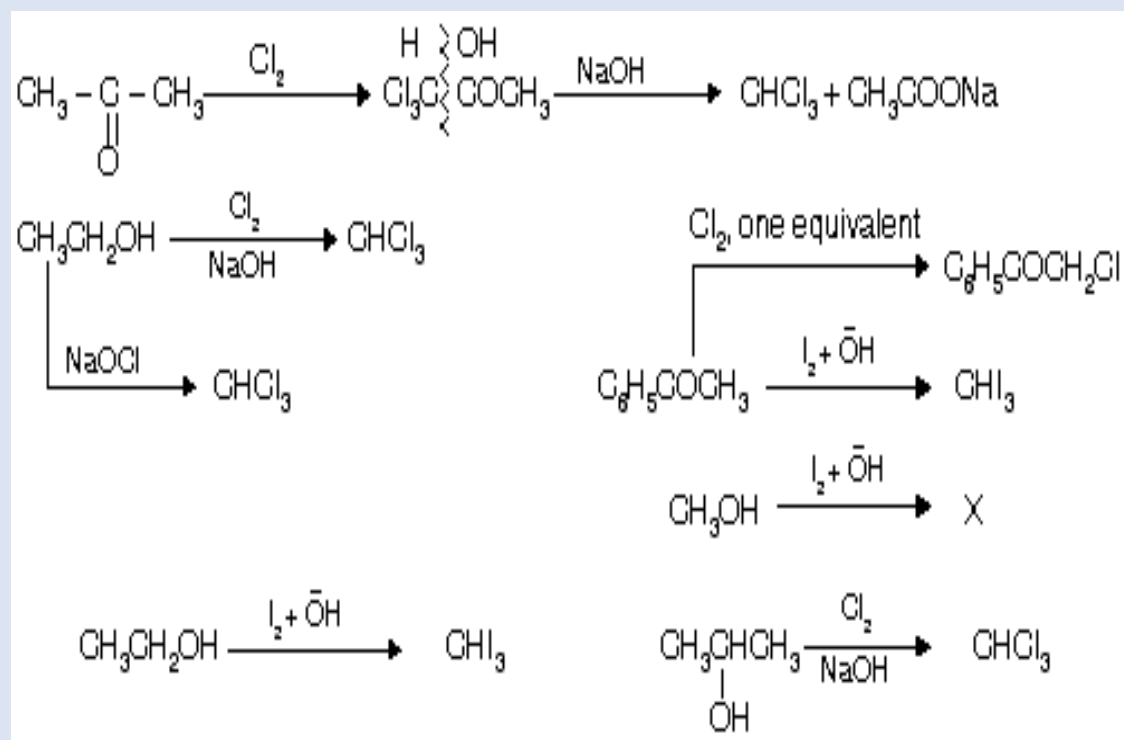
The reacting compounds for haloform test are halogen and alkali which are responsible for halogenation, oxidation and hydrolysis.

Reactions involved in haloform test are :

(a) Oxidation (b) Halogenation (3 equivalent) (c) Hydrolysis in presence of base



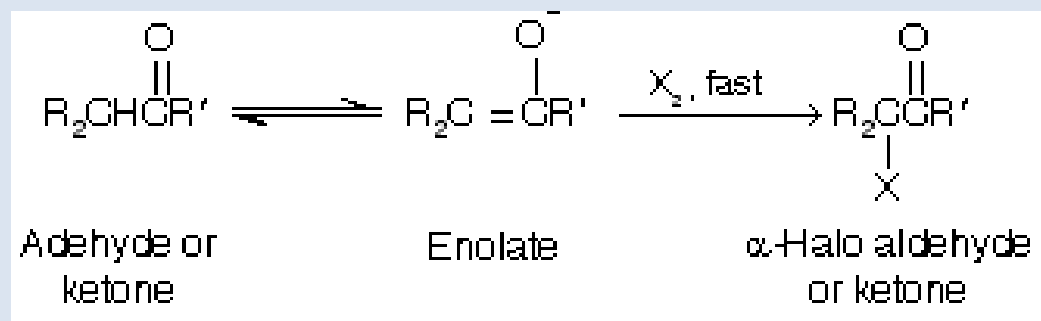
Halogen and alkali are used as they form  $\text{OQCl}$  or hypohalite ion which is a strong base to replace all 3-‘H’



## The haloform reaction

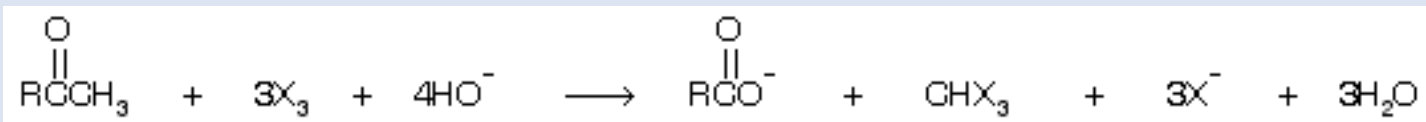
Halogenation of the  $\mu$ - carbon atom takes place when an enolate ion is generated in the presence of chlorine, bromine, or iodine (any halogen).





In the acid-catalyzed halogenation of aldehydes and ketones, rate is independent of the concentration of the halogen; chlorination, bromination, and iodination all at the same rate. Formation of the enolate is rate-determining, and once formed the enolate ion reacts rapidly with the halogen **but remember three equivalents are required for haloforms.**

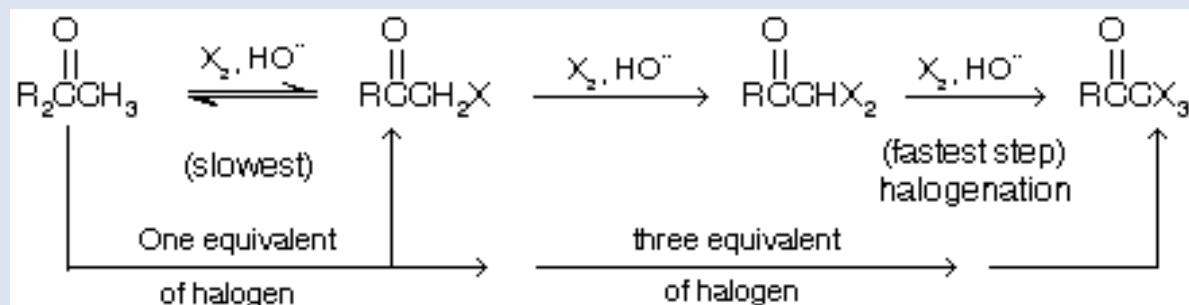
Unlike its acid-catalyzed route,  $\alpha$ -halogenation in base catalysed cannot normally be limited at monohalogenation. Methyl ketones, for example, undergo polyhalogenation and cleavage on treatment with a halogen in aqueous base.



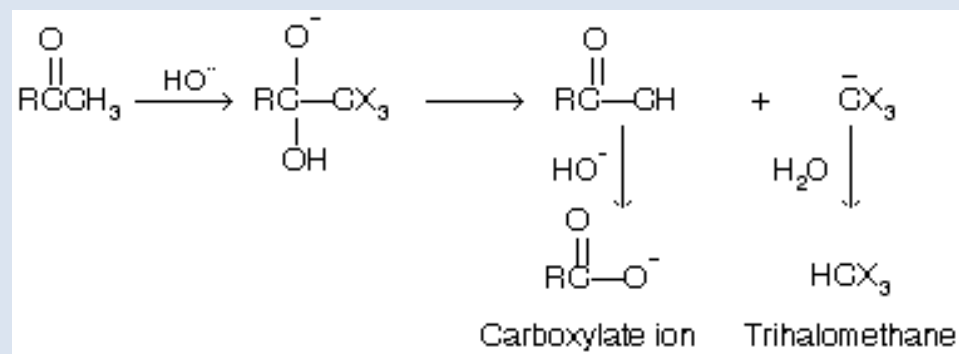
This is called the haloform reaction because the trihalomethane produced is chloroform, bromoform, or iodoform depending, of course, on the halogen used. Remember this reaction is done by three equivalent of halogen but if there is only one equivalent of halogen then mono halo product is formed.

Normally in separation test of 2-alkanol or 2-alkanone with other alkanol or alkanone we prefer  $\text{I}_2$  and alkali for test because formation of yellow ppt of  $\text{CHI}_3$  takes place.

The mechanism of first phase of the haloform reaction begins with  $\alpha$ -halogenation through the enolate. The electron-attracting  $-\text{I}$  effect of an  $\alpha$ -halogen increases the acidity of the protons on the carbon to which it is bonded, making each H active and undergo halogenation at that carbon faster than the preceding one.



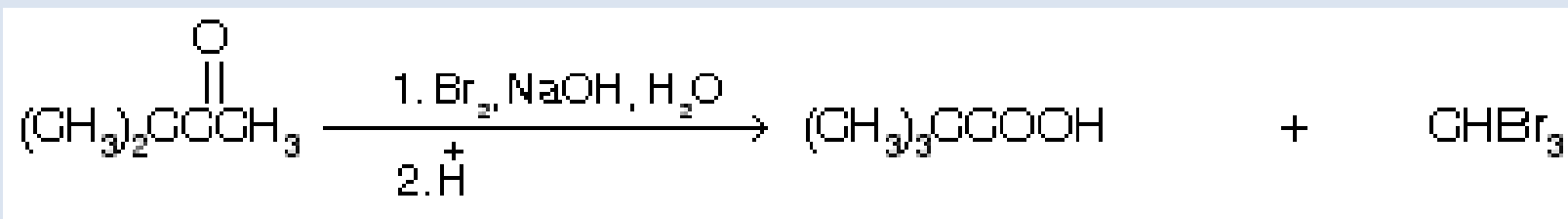
The trihalomethyl ketone (RCOX<sub>3</sub>) so formed when undergoes nucleophilic addition reaction of hydroxide ion to its carbonyl group, and finally its dissociation by cleavage, of the bond to the CX<sub>3</sub> group.



The three –I effect halogen group stabilize the negative charge of the trihalomethide ion (C–X<sub>3</sub>) converting it to weak conjugate acid and permitting it to act as a good leaving

group in the carbon bond-cleavage step or 2-alkanone.

This reaction is also used for the preparation of carboxylic acid from methyl ketones.



### (ii) Haloform test from bleaching powder (CaOCl<sub>2</sub>)

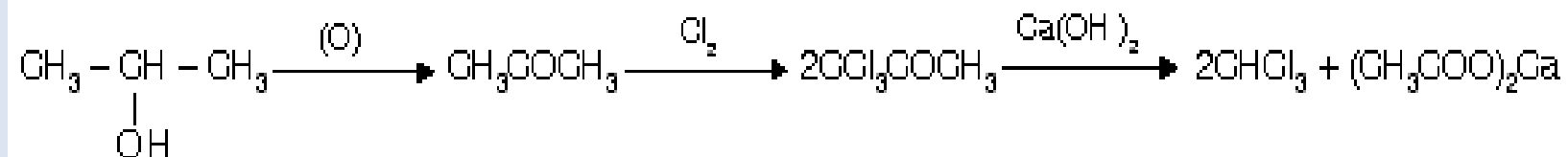
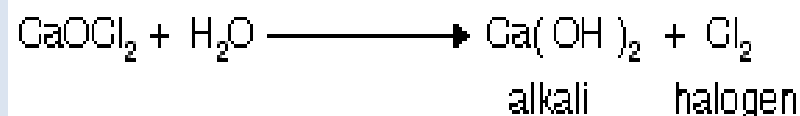
It is also used as reagent for haloform test due to the presence of OQCl which is a strong base.



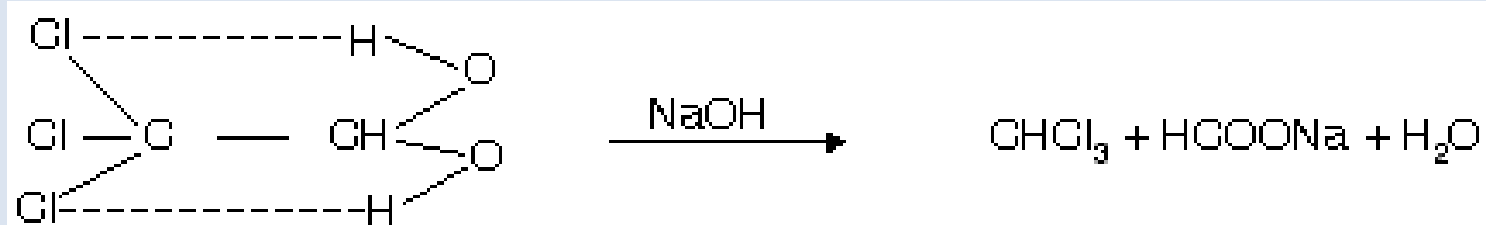
Bleaching powder



Calcium chloro hypochlorite ( IUPAC )

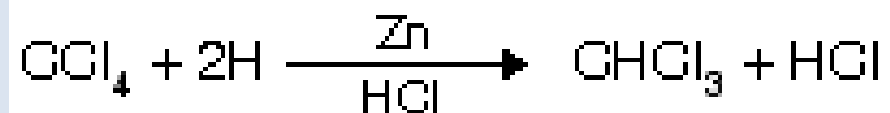


### (iii) From chloral hydrate



It shows intramolecular H-bonding and is thus stable. This method is used to prepare fresh and pure chloroform.

#### (iv) Reduction of $\text{CCl}_4$



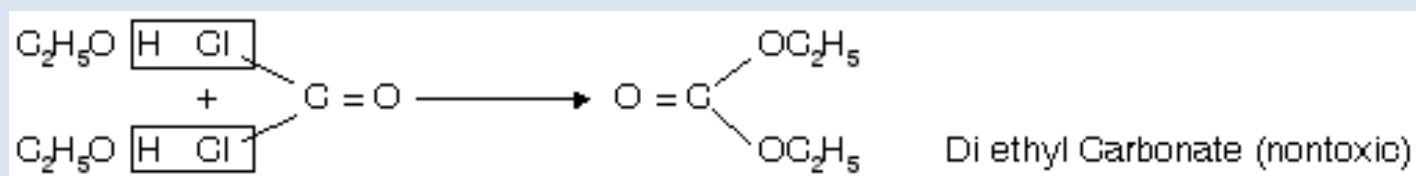
#### Properties of chloroform

##### (i) Oxidation



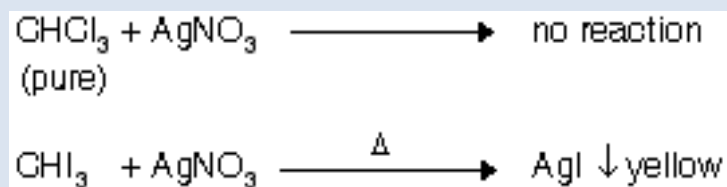
#### Storage of $\text{CHCl}_3$

- It is stored in amber coloured bottles up to the brim in dark.
- Small amount of ethyl alcohol is added which converts poisonous phosgene into nontoxic compound, diethyl carbonate.



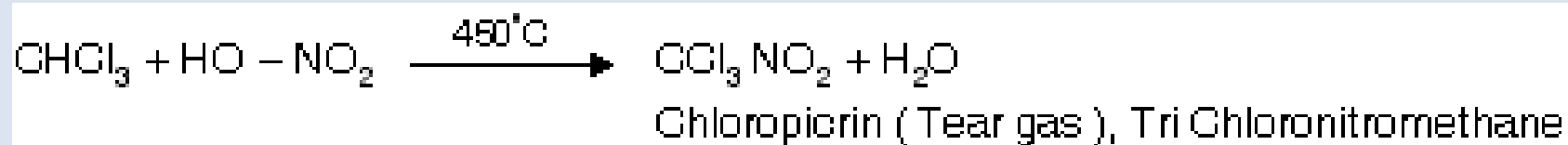
## (ii) Testing of Chloroform

- Pure chloroform does not react with  $\text{AgNO}_3$  due to absence of  $\text{Cl}^-$  ion
- Impure chloroform or oxidised chloroform gives white ppt with  $\text{AgNO}_3$  due to presence of  $\text{HCl}$  which contains  $\text{Cl}^-$  ion.

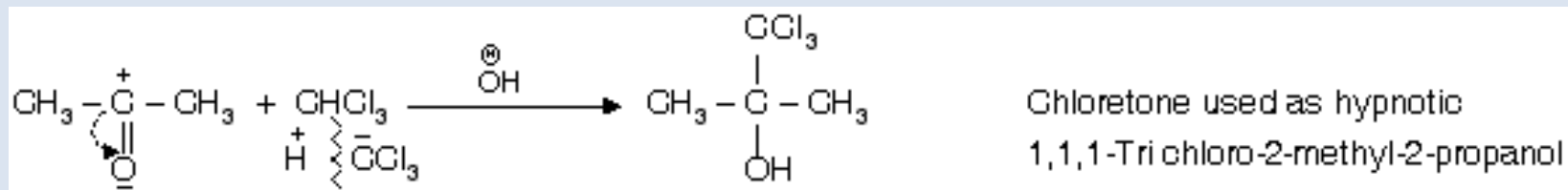


When  $\text{CHCl}_3$  reacts with  $\text{AgNO}_3$  gives no ppt, while  $\text{CHI}_3$  gives yellow ppt of  $\text{AgI}$  with  $\text{AgNO}_3$  due to less bond dissociation energy of  $\text{C} - \text{I}$  bond.

## (iii) Reaction with $\text{HNO}_3$

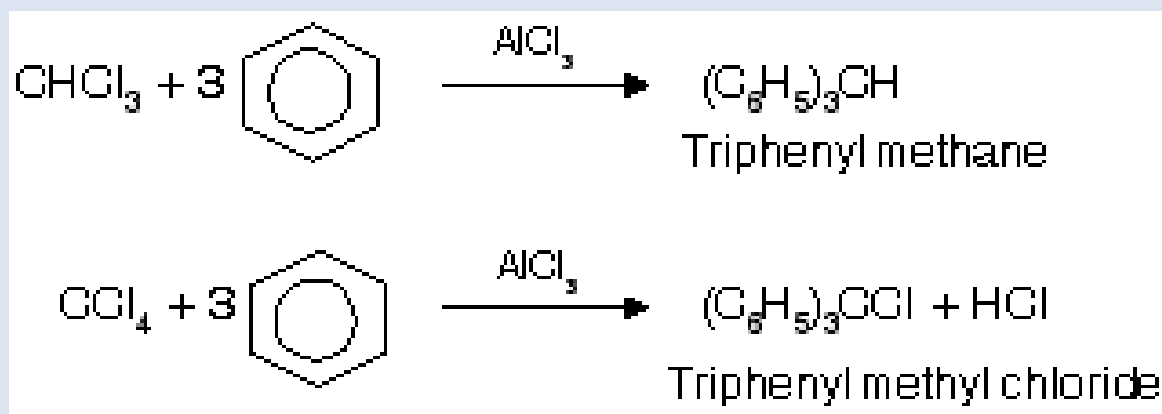


#### (iv) Reaction with acetone



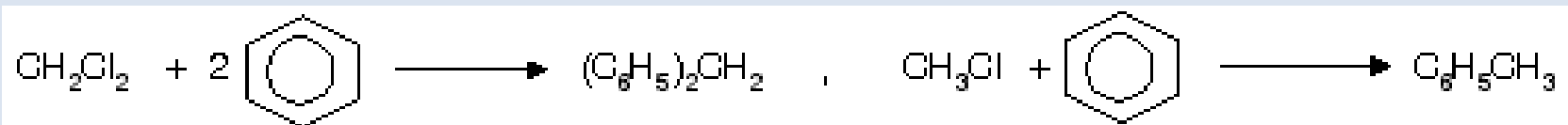
#### (v) Reaction with Benzene

Substitution of halogen by phenyl group occurs in the presence of Lewis acids



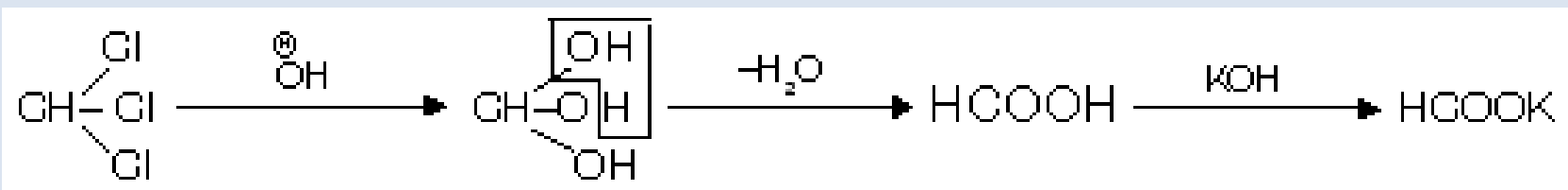
In case of  $\text{CCl}_4$  only 3 'Cl' atoms are replaced by phenyl group, while 4th 'Cl' atom donot undergo replacement by phenyl group due to high stable intermediate triphenyl methyl carbocation.





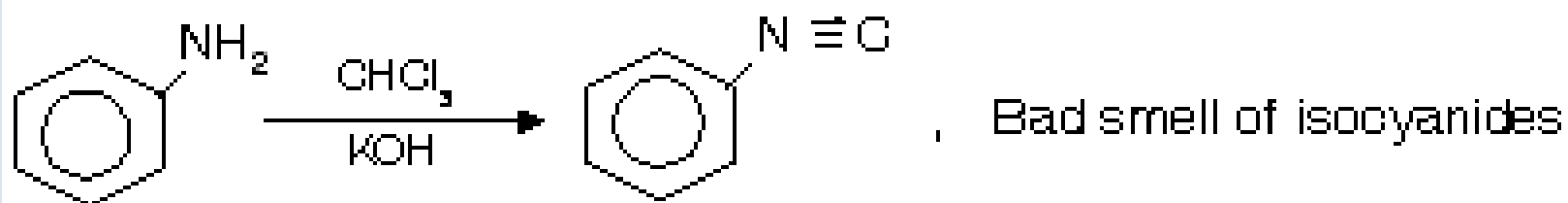
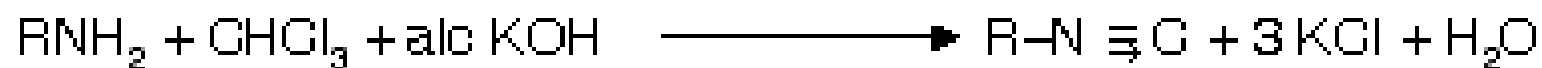
### (vi) Reaction with aq. KOH

Nucleophilic substitution reaction occurs where 'Cl' is substituted by -OH group.

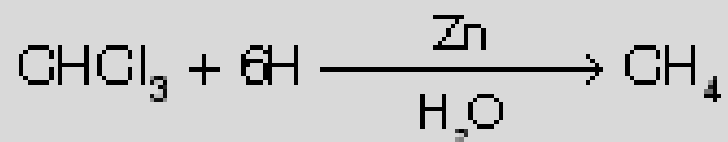


### (vii) Hoffmann's Carbylamine Reaction

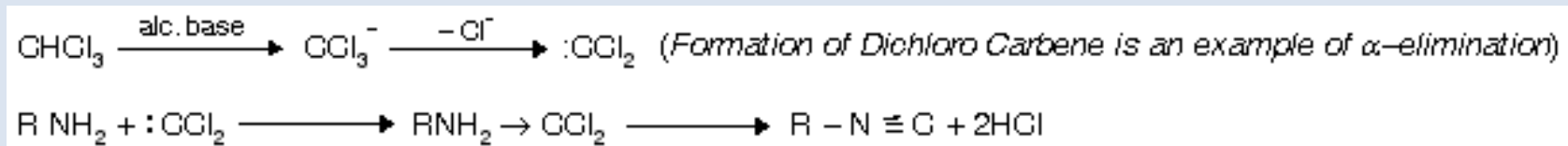
When all primary amines reaction with chloroform and alc. KOH they form isocyanides with bad smell. It is the most versatile test for all primary amines. In this α-elimination occurs.





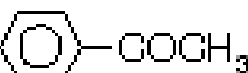
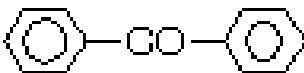

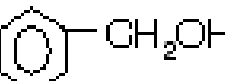
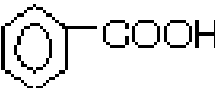

### Reduction of $\text{CHCl}_3$



### Mechanism



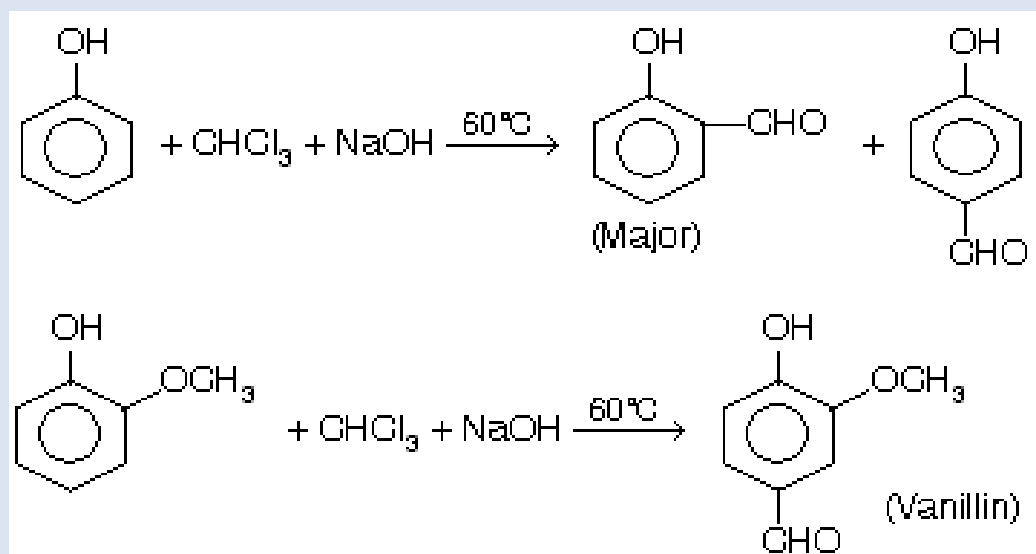
**Separation Tests of some Pairs ?**

Gives	Not gives	Reagent
1. $\text{CH}_3\text{NH}_2$	$(\text{CH}_3)_2\text{NH}$	$\text{CHI}_3 + \text{alc.KOH}$
2. 		$\text{Br}_2$ Water, $\text{KMnO}_4$ (Bayer's reagent)
3. 		Iodoform test
4. $\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{OH}$	Haloform test
5. $\text{CH} \equiv \text{CH}$	$\text{CH}_2 = \text{CH}_2$	$\text{Ag}(\text{NH}_3)_2^+$ or $\text{Cu}(\text{NH}_3)_4^+$
6. $\text{CH} \equiv \text{CH}$	$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	$\text{Ag}(\text{NH}_3)_2^+$ or $\text{Cu}(\text{NH}_3)_4^+$
7. $\text{NH}_4\text{Cl}$	$\text{NH}_4\text{OH}$	$\text{AgNO}_3$
8. Allyl Chloride	Vinyl Chloride	$\text{AgNO}_3$
9. 		$\text{NaOH}$
10. 		$\text{NaHCO}_3$

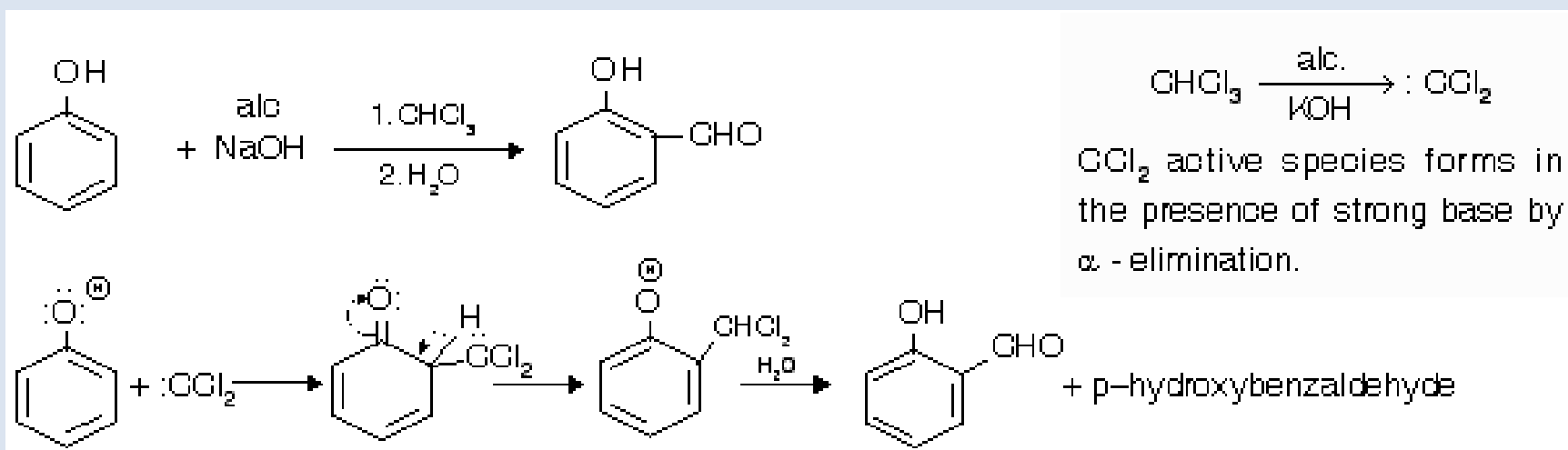
### **(viii) Reimer Tiemann's Reaction**

Process of formylation of phenols with chloroform in alkaline solution is known as **Reimer–Tiemann reaction**.

A mixture of ortho-and para-isomers is obtained in which the ortho isomer predominates due to more thermodynamical stability. If one of the ortho positions is occupied the para-isomer is the major product.



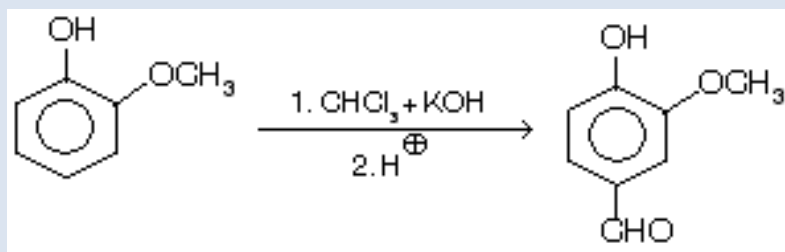
The reaction is carried out by refluxing an alkaline solution of phenol and chloroform at  $60^\circ\text{C}$  for sometime (1/2 h). Excess chloroform is distilled off, the mixture acidified with sulphuric acid and steam distilled. Unreacted phenol and the ortho-isomer distil over leaving behind the para isomer. The two isomers are further purified by sodium bisulphite.



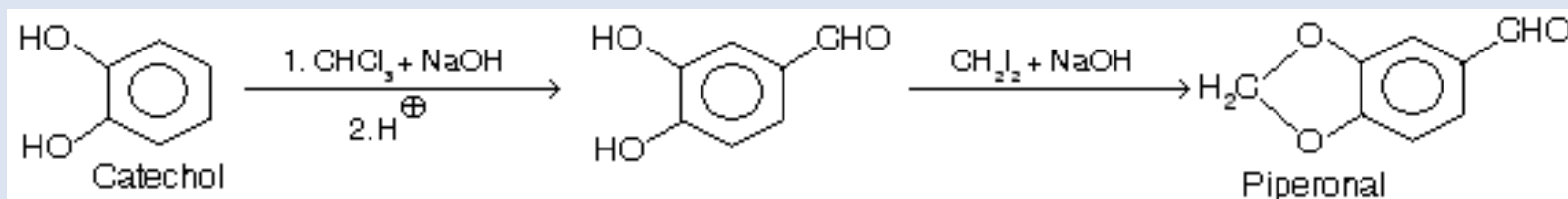
## Applications

The reaction mainly used for introducing aldehyde or carboxyl group in phenols.

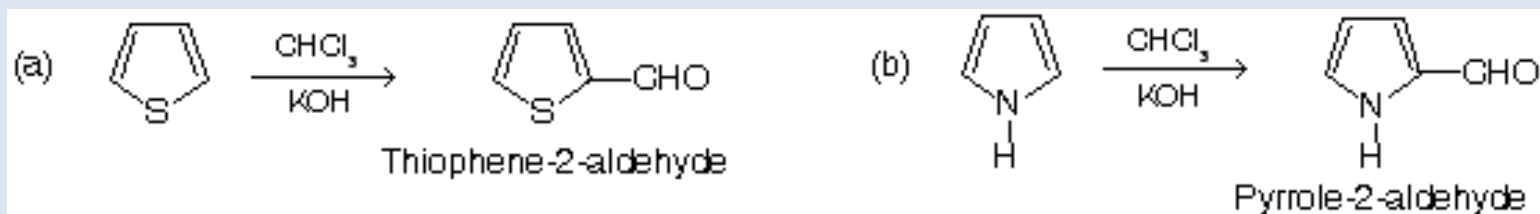
### (i) Preparation of vanillin



## (ii) Preparation of piperonal

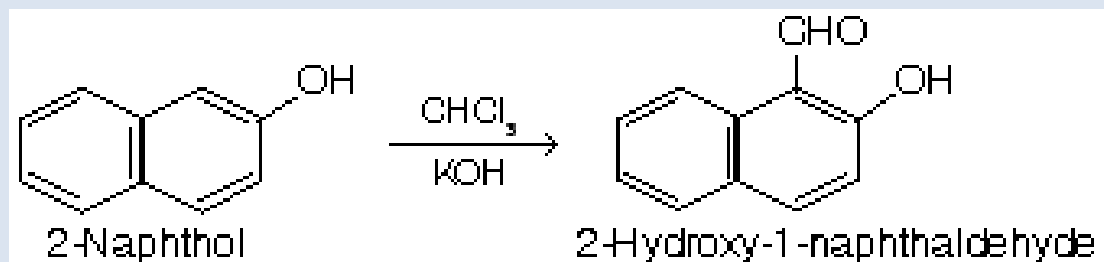


## (iii) Formylation of heterocyclic compounds



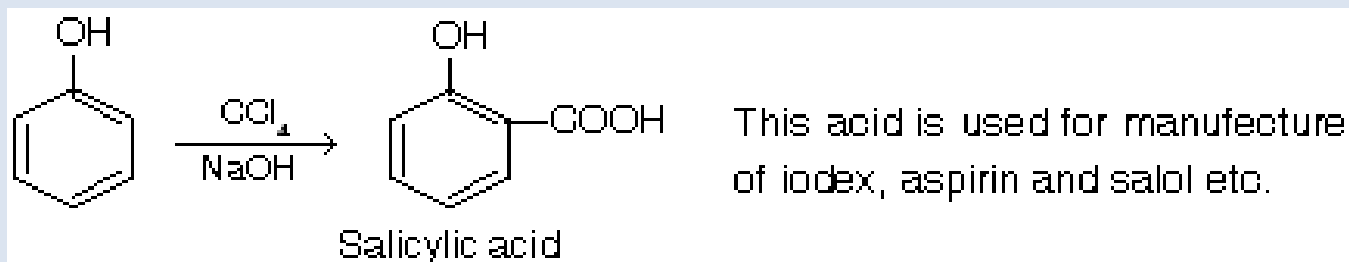


#### (iv) Formylation of $\beta$ -naphthol



#### (v) Preparation of acid (salicylic acid)

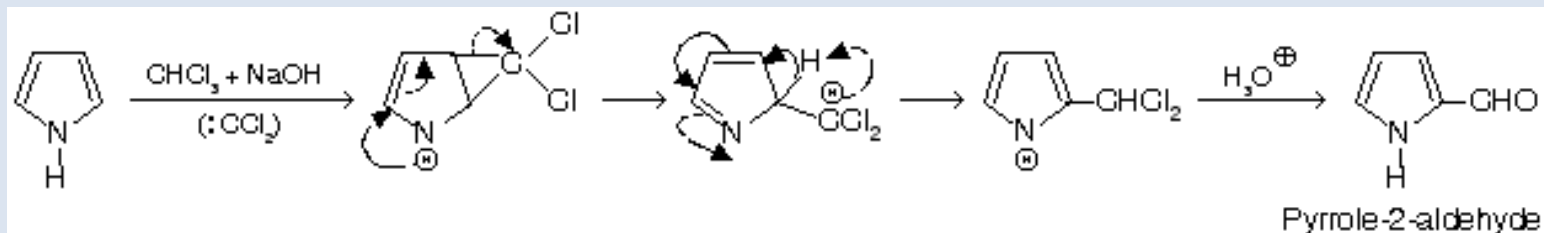
When carbon tetrachloride in place of chloroform is used, a carboxyl group is introduced.



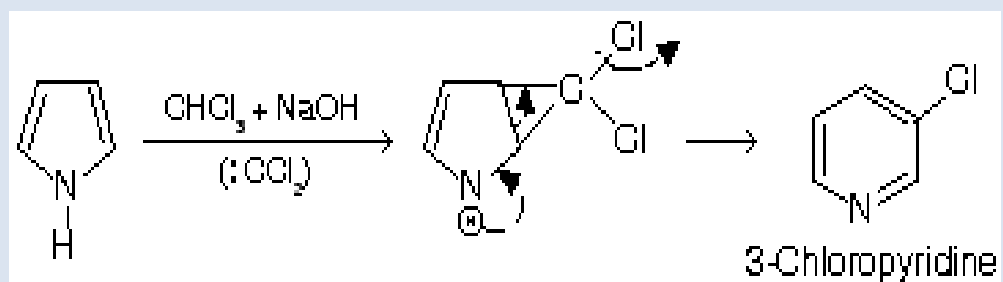
**(vi) Abnormal Reimer–Tiemann reaction** (where ring expansion takes place due to electrocyclic rearrangement)

### 1. Pyrrole undergoes normal and abnormal RTR

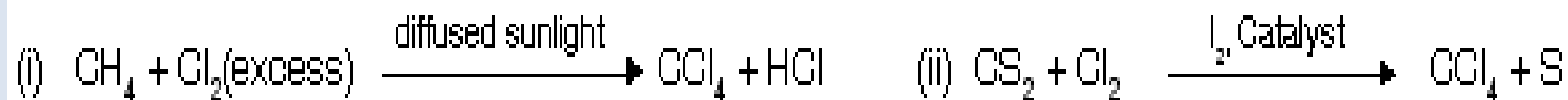
Normal reaction (pyrrole is ortho & para activating compound).



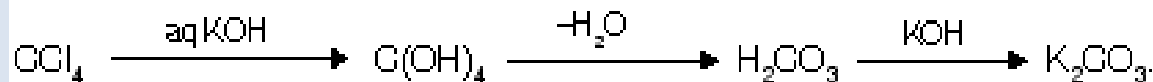
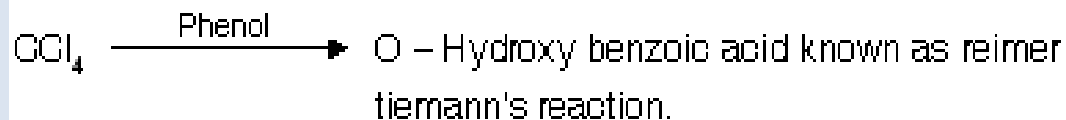
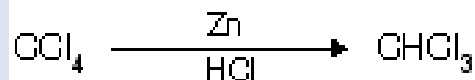
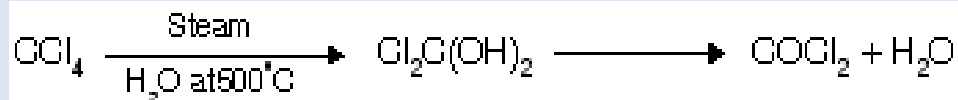
Abnormal reaction (ring expansion)



## Pyrene CCl<sub>4</sub>

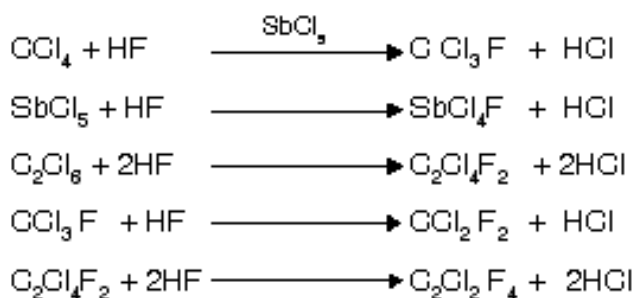
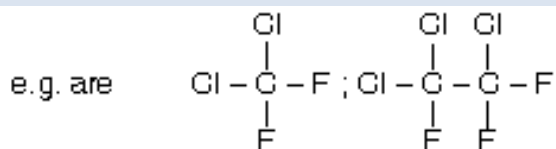


CCl<sub>4</sub> does not react with H<sub>2</sub>O while SiCl<sub>4</sub> reacts due to presence of vacant d-orbital in Si atom used by water molecule as nucleophile. CCl<sub>4</sub> at high temperature reacts with H<sub>2</sub>O where vacant orbital of carbon at high temperature as used by water to form phosgene.



At high temperature Vacant orbitals of carbon atom are used by H<sub>2</sub>O molecule, so partial Hydrolysis occurs.

**Freons** : Poly chloro fluoro alkanes are known as freons. They are colourless, odourless, non toxic, non inflammable liquids with very less chemical reactivity & high stability. They are used in refrigerators and air conditioners for cooling purpose and as propellents in rockets and jets.

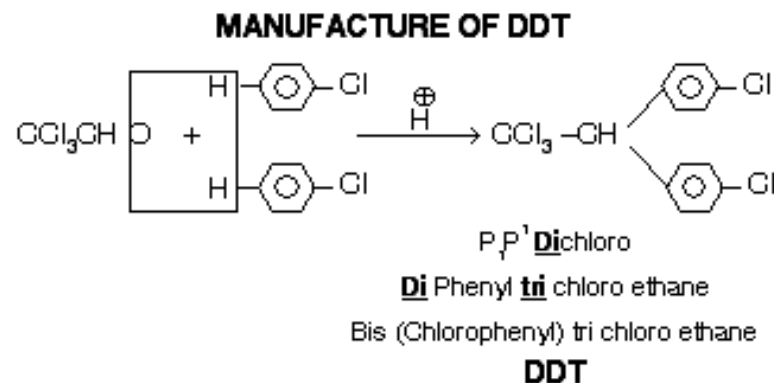


Naming of freons is  $\boxed{\text{F} - \text{ABC}}$

Freon	A	B	C
	no. of 'C' atoms - 1	1	no. of 'F' atoms

For good refrigerant following quality must be fulfilled

- |    |                               |    |                |
|----|-------------------------------|----|----------------|
| 1. | High enthalpy of vaporisation | 2. | non-toxic      |
| 3. | Low cost                      | 4. | High stability |

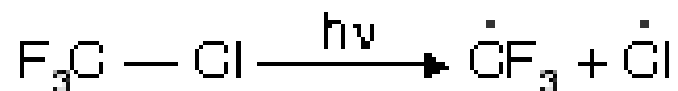


$\text{CCl}_2\text{F}_2$	Freon	-	12
$\text{CCl}_3\text{F}$	Freon	-	11
$\text{C}_2\text{Cl}_4\text{F}_2$	Freon	-	112
$\text{C}_2\text{Cl}_2\text{F}_4$	Freon	-	114

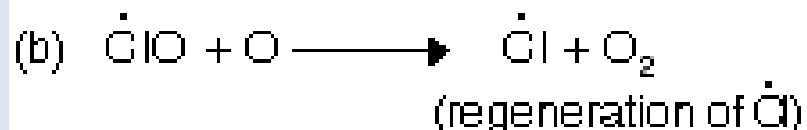
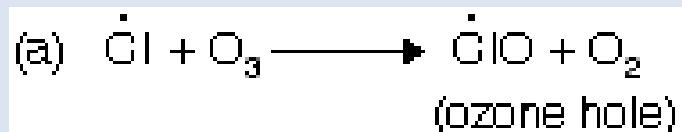
## Ozone hole

Chlorofluorocarbons known as freons, commercially used for refrigeration purpose they are highly volatile and stable in nature (life time is more than 100 years) due to this they

easily move up into the higher zone of atmosphere (stratosphere), and reacts with ozone causing hole resulting in to as ozone depletion.



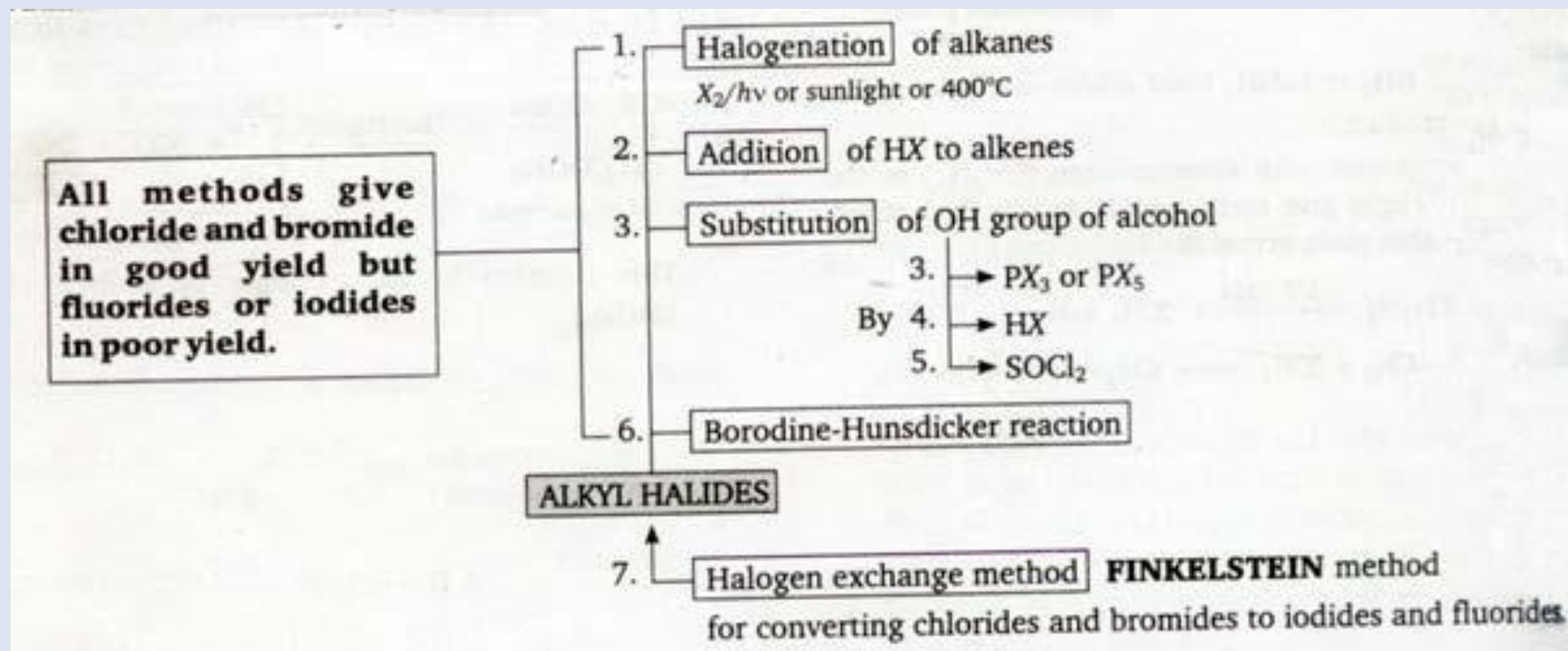
(C - Cl bond break due to weak nature)



The damage of ozone layer in stratosphere clear the path for harmful ultraviolet radiation to come on earth's surface.

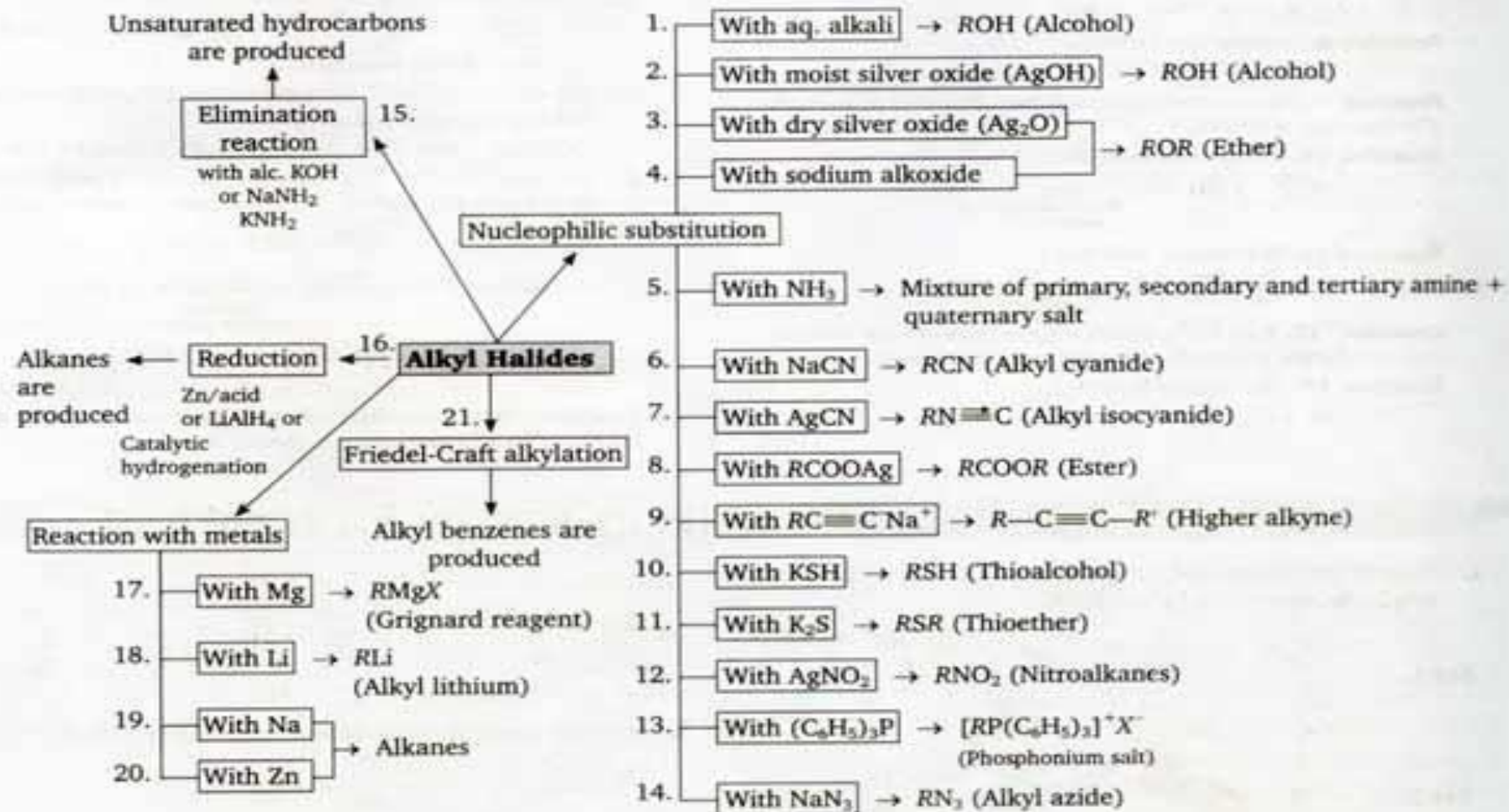
Now a days hydrofluorocarbons (HFC'S) are used as substitutes for CFC'S.

## Methods Of Prepration of Alkyl Halides :

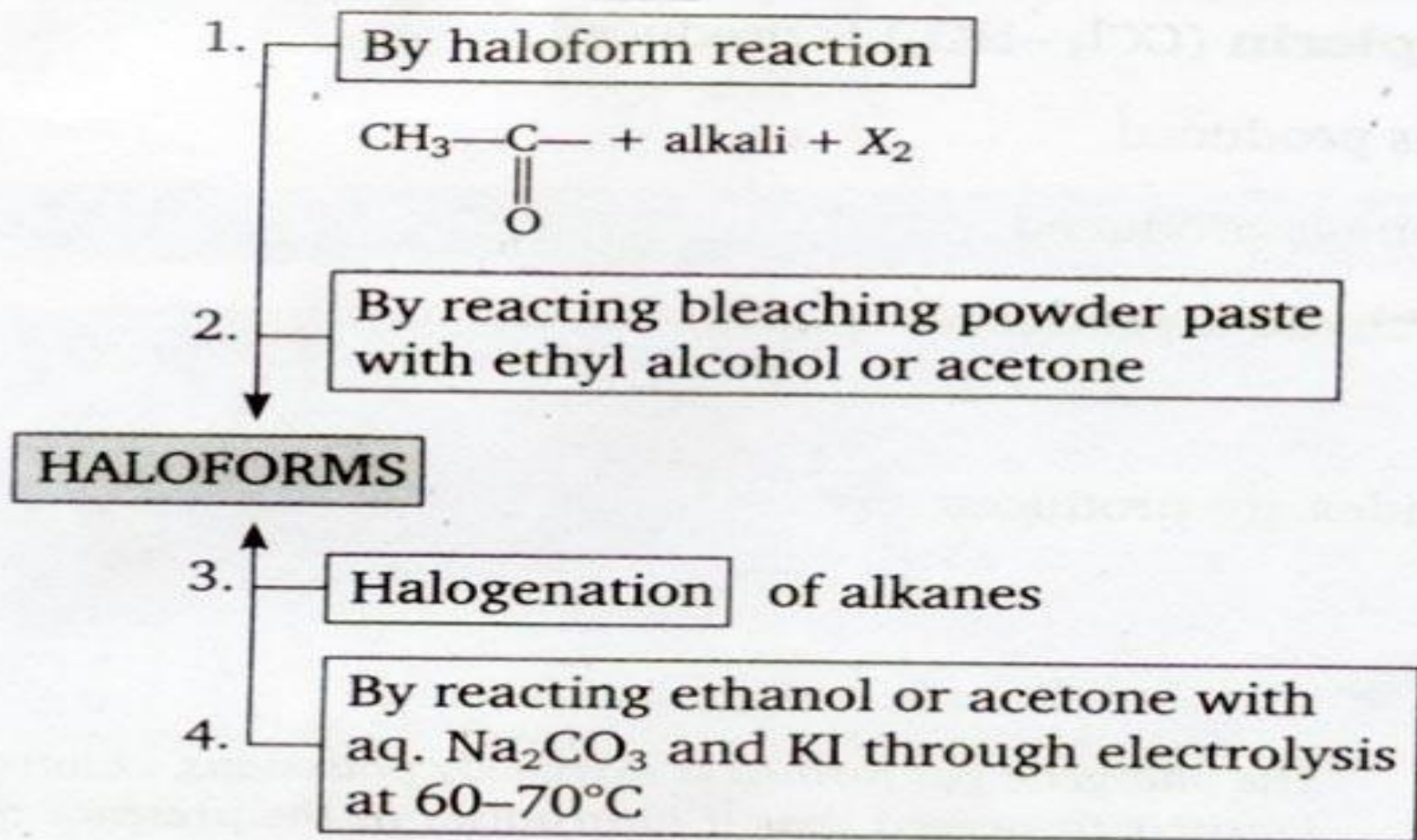




## Properties of Alkyl Halides :



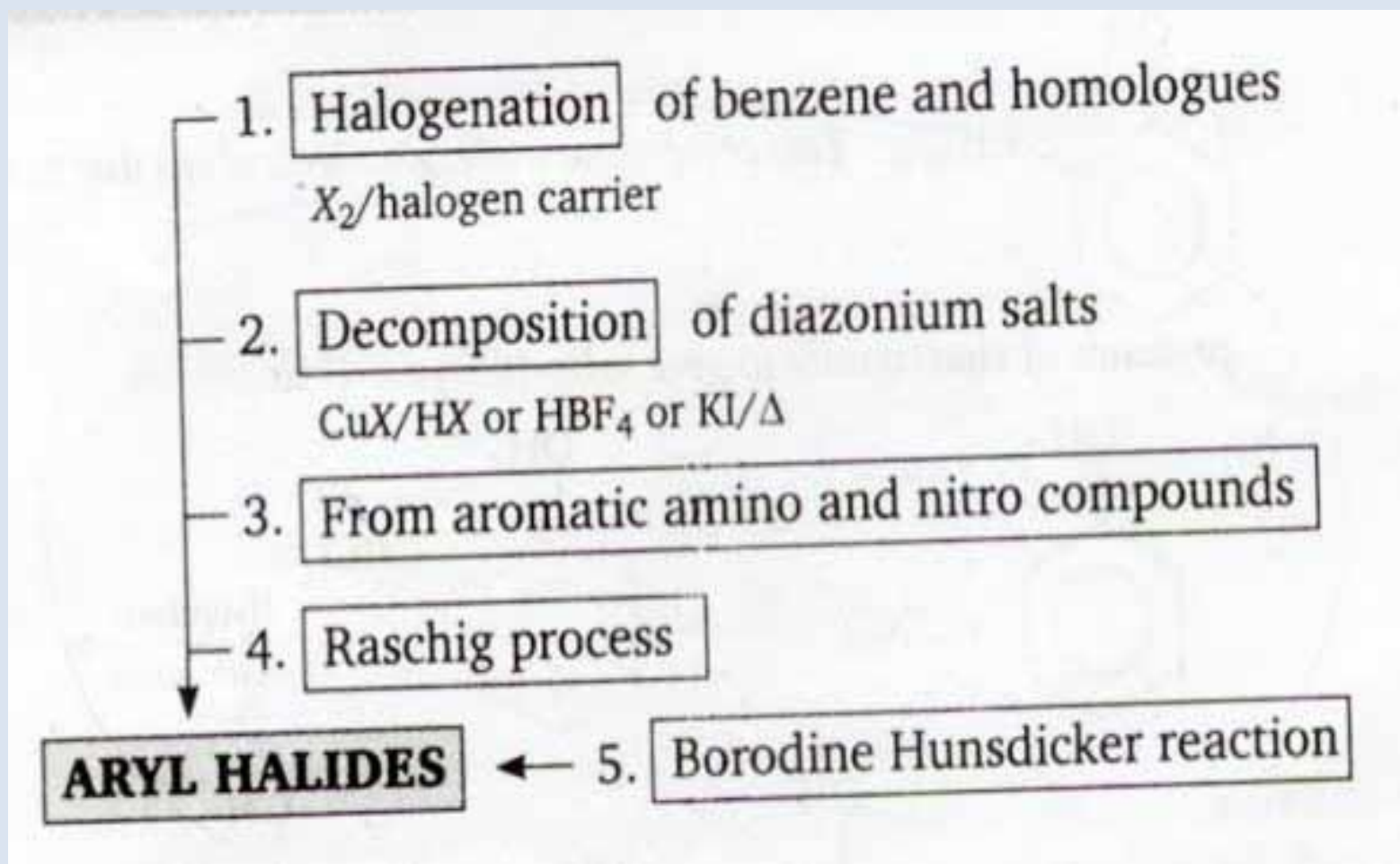


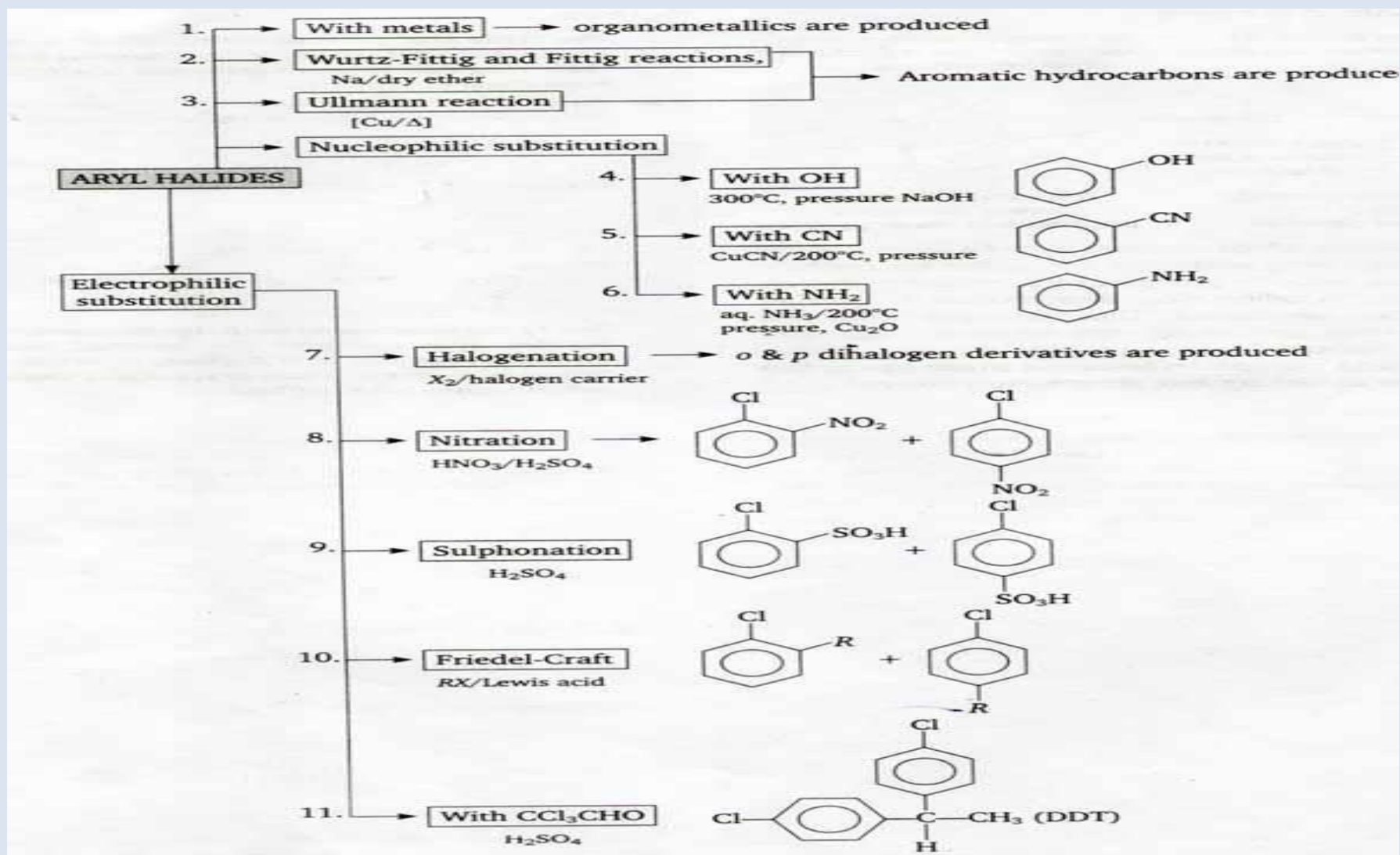


## Properties of Haloforms :

<b>HALOFORMS</b> for $\text{CHCl}_3$	1.	Oxidation	→ $\text{COCl}_2$ is produced (phosgene)
	2.	Reduction	→ Dihalogen, monohalogen derivatives and alkanes are produced.
	3.	Hydrolysis of NaOH/KOH	→ Sod./Pot. formate is produced
	4.	Halogenation	→ $\text{CCl}_4$ is produced
	5.	Nitration	→ <b>Chloropicrin</b> ( $\text{CCl}_3-\text{NO}_2$ ) is produced
	6.	With Ag	→ Alkyne is produced
	7.	With Acetone	→ Chloritone is produced
	8.	Reimer-Tiemann reaction phenol + alkali	→ Salicyldehyde is produced
	9.	Carbylamine reaction or isocyanide reaction Primary amine + alkali	→ Isocyanides are produced

## Methods of Aryl Halides :

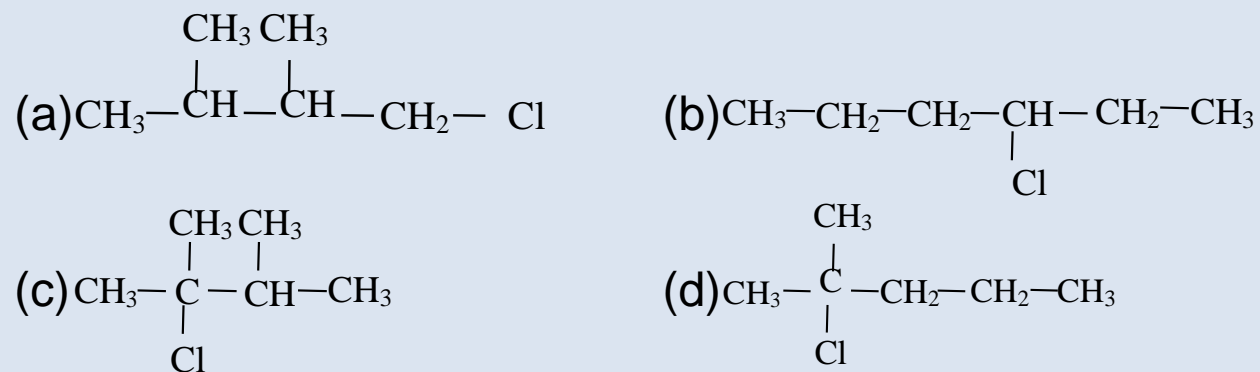




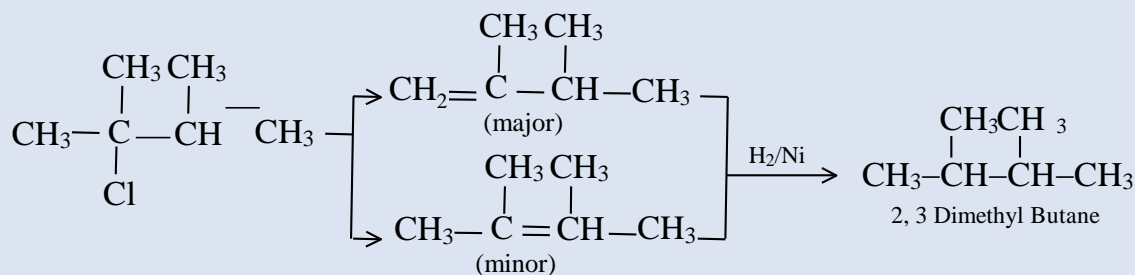


### Example 1:

An alkyl halide (X) having molecular formula  $C_6H_{13}Cl$  reacts with  $(CH_3)_3CO^{\ominus}K^{\oplus}$  to form two isomeric alkenes (Y) and (Z) of molecular formula  $(C_6H_{12})$ . Both the alkenes give 2,3-Dimethyl butane on hydrogenation. The halide (X) is

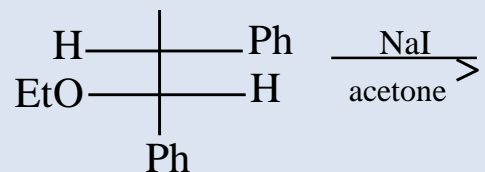


### Solution: (c)

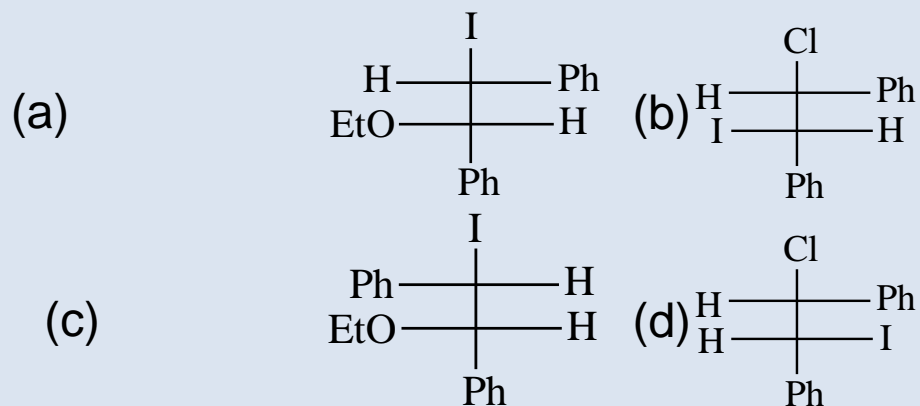




**Example 2.** In the following reaction,  
Cl

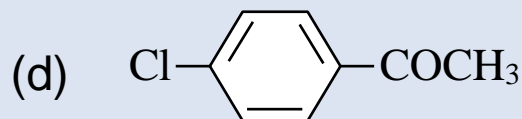
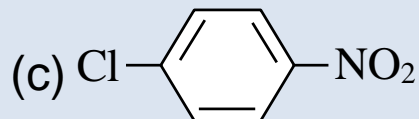
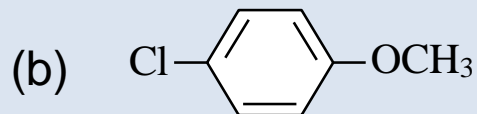
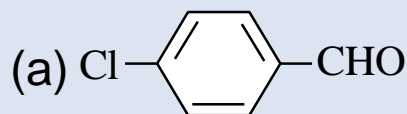


the structure of product is



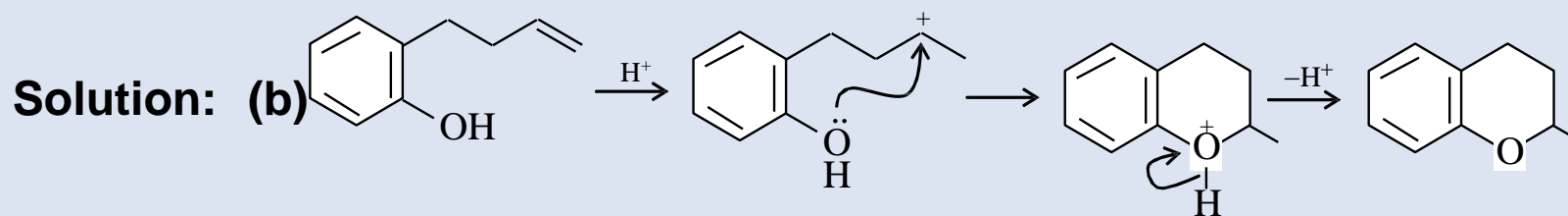
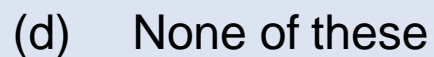
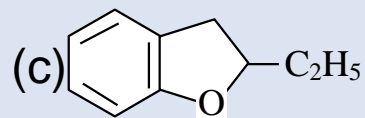
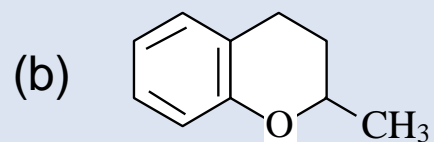
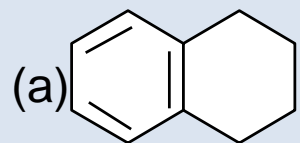
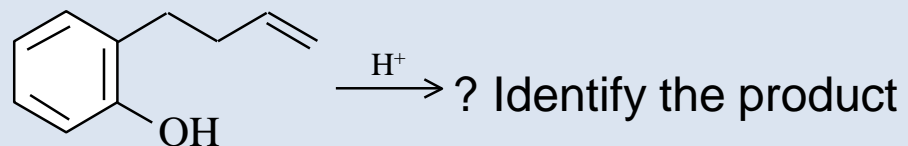
**Solution:** (a) Due to neighbouring group participation of –OEt group retention of configuration is observed.

**Example 3.** Which one of the following form benzyne as intermediate when treated with  $\text{KNH}_2$  in liquid  $\text{NH}_3$ :

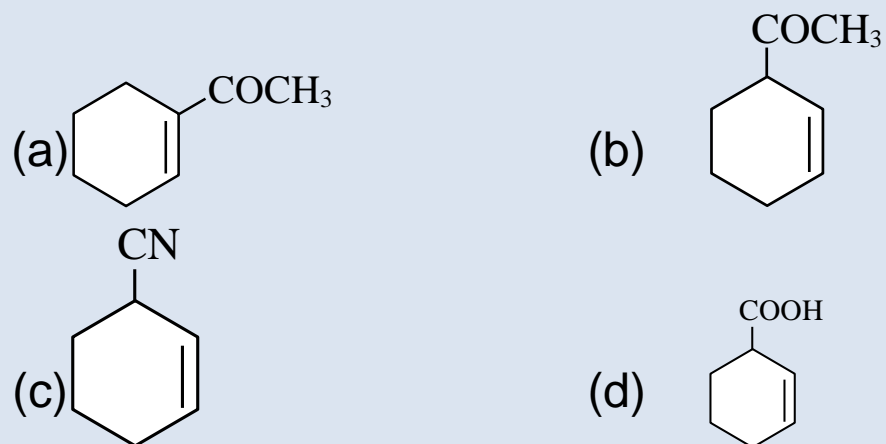
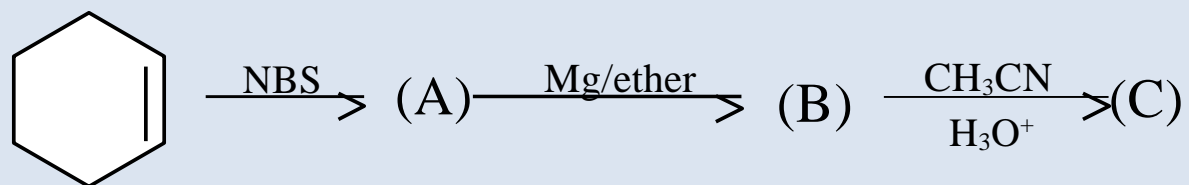


**Solution:** (b) Aryl halides containing electron releasing groups like  $-\text{OCH}_3$  form benzyne as intermediate when treated with  $\text{KNH}_2$  in liquid  $\text{NH}_3$ .

**Example 4.**

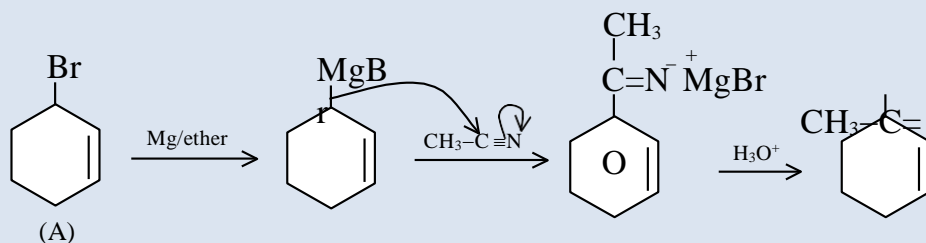


**Example 5.** End product of the following sequence of reaction is:

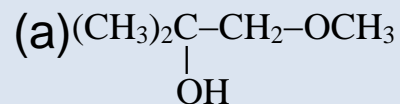
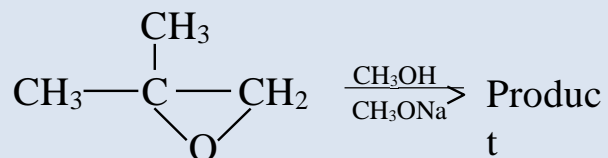


**Solution 5.**

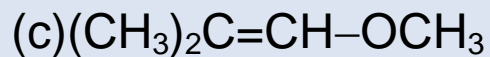
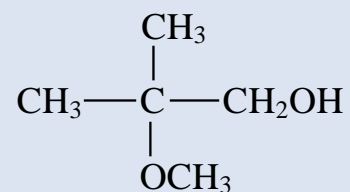
**(b)**



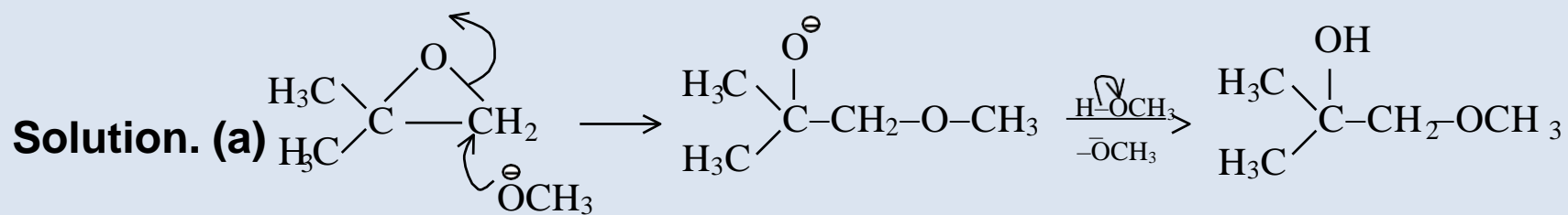
**Example 6.** The product formed in the given reaction is



(b)

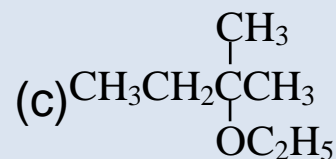
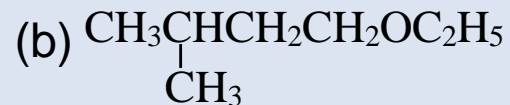
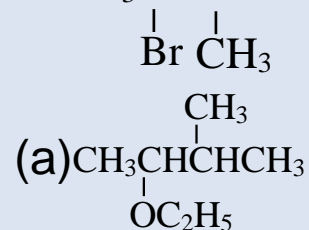
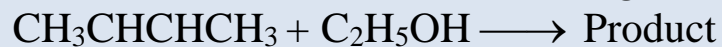


(d) None of these



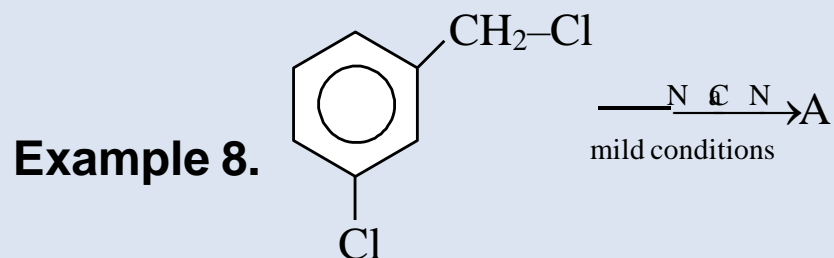
Epoxide cleavage in basic medium proceeds through  $\text{S}_\text{N}^2$  mechanism where nucleophile reacts mainly at less crowded position.

**Example 7.** Which of the following is the major product of the following S<sub>N</sub>1 reaction?

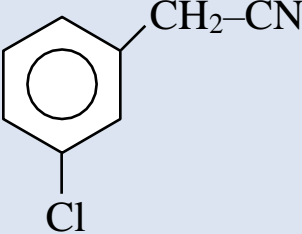
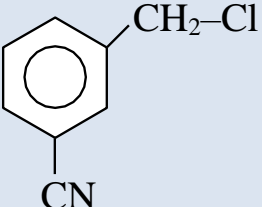
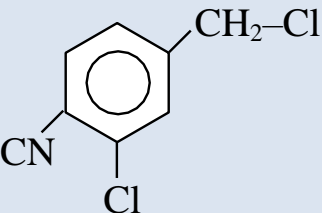
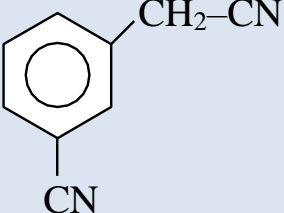


(d) None of these

**Solution.**(c) H<sup>-</sup> shifting takes place to get more stable 3° carbocation.

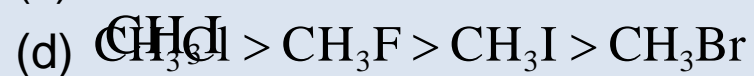
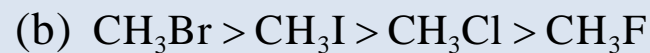


Which of the following is the correct structure of the product 'A'?

- (a)  ClC1=CC=C(C=C1)CCl
- (b)  ClC1=CC=C(C=C1)C#N
- (c)  ClC1=CC=C(C=C1)C#N
- (d)  C#NCC1=CC=C(C=C1)Cl

**Solution.** (a) Due to resonance, 'Cl' attached to benzene ring shows partial double bond character and can not be substituted. However, benzyl halide will undergo nucleophile substitution by  $\text{CN}^-$ .

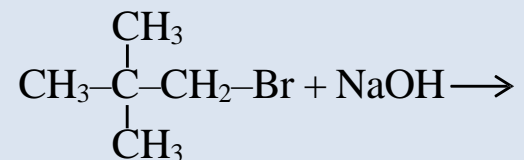
**Example 9.** The correct order of boiling point is



**Solution.** (a) Larger the size of the halogen atom, higher is the B.P.



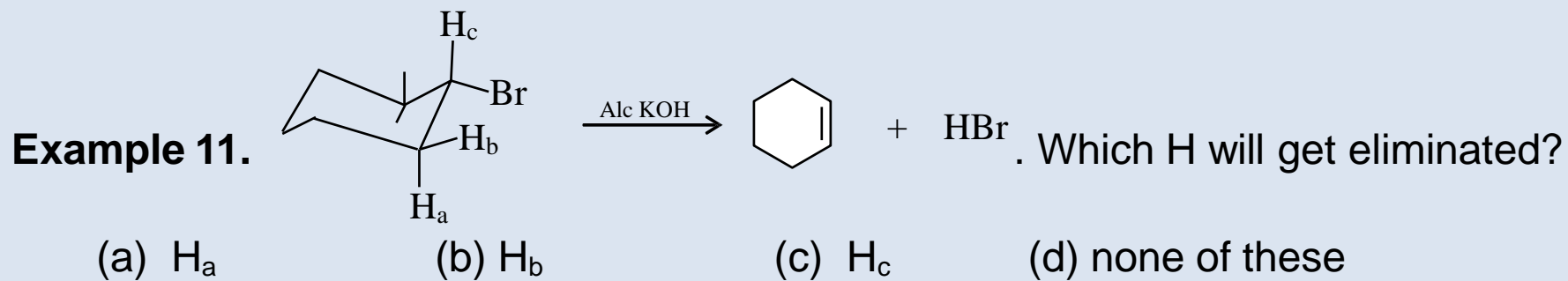
**Example 10.** Consider the following reaction,



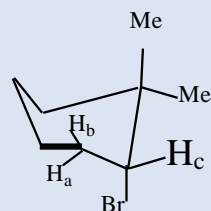
Total number of possible products in this reaction is:

- (a) Two      (b) Four      (c) One      (d) Three

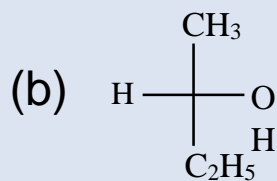
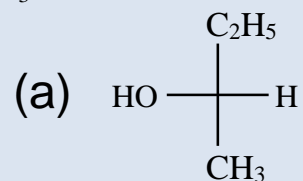
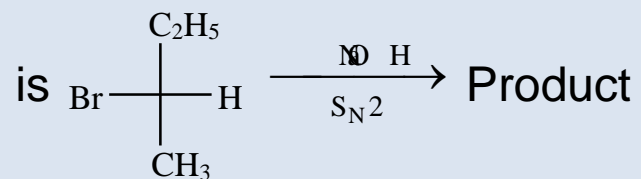
**Solution. (b)** Two substitution and two elimination products.



**Solution (b)** Elimination is favoured when departing groups are anti. Here H<sub>b</sub> is anti to Br when the given chain conformer flips to other chain.



**Example 12.** The product formed in the following reaction

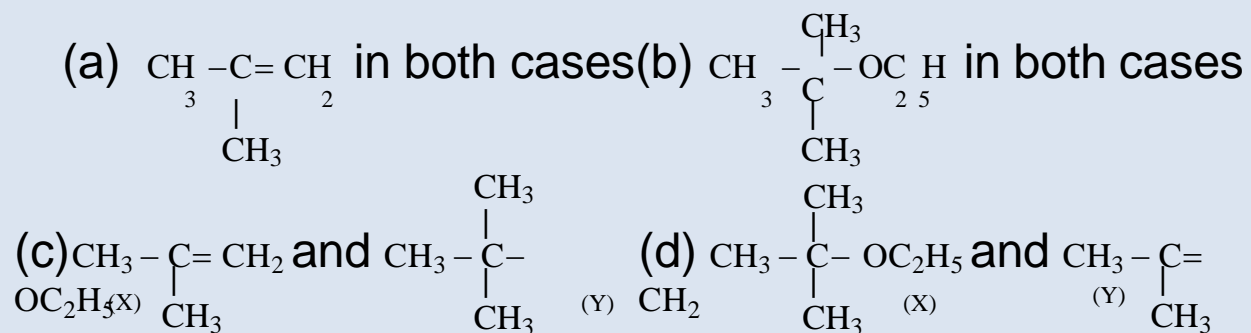
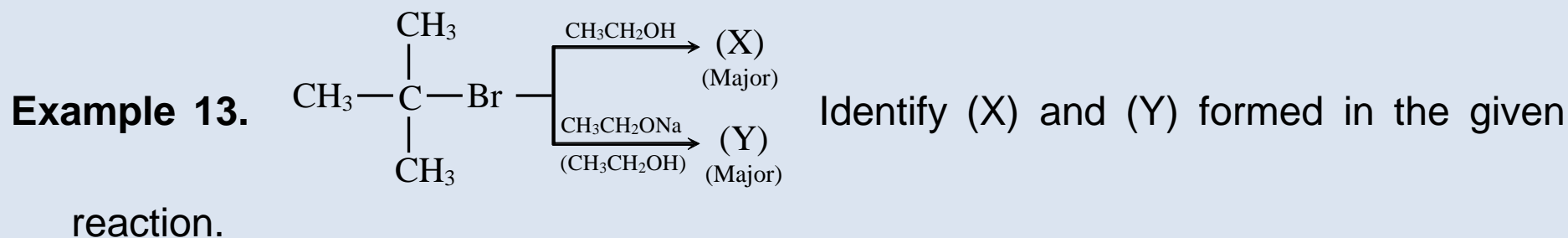


(c) both (a) and (b)

(d) none of these

**Solution(d)** Given reactant has S-configuration, which on  $\text{S}_{\text{N}}2$  reaction will give R-configuration.

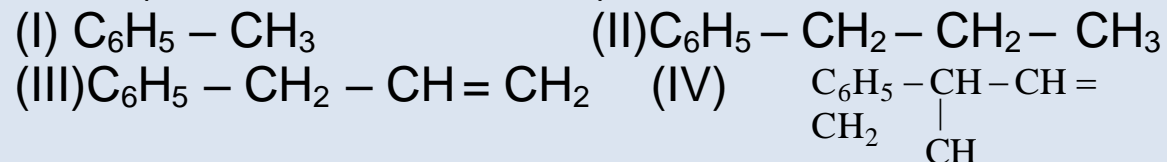
Both (a) and (b) are identical with retention of configuration



**Solution (d)** (X) is formed by ethanolsis through  $\text{SN}^1$  mechanism while (Y) is formed by dehydrohalogenation of tert. butyl bromide through  $\text{E}_2$  mechanism.

**Example 14.** Arrange the following compounds in the decreasing order of reactivity with NBS

(N-bromosuccinimide).

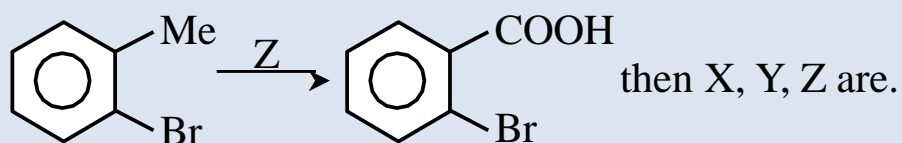
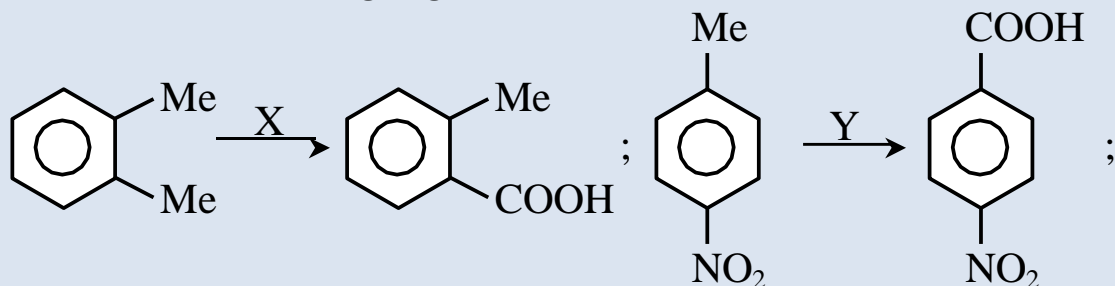


Select the correct answer from the codes given below

- (a)                                      (IV) > (III) > (I) > (II)      (b) (IV) > (III) > (II) > (I)  
 (c)                                      (I) > (II) > (III) > (IV)      (d) (I) > (III) > (II) > (IV)

**Solution (b)** The correct order is decided by the stability of the free radical formed as intermediate.

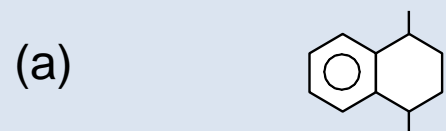
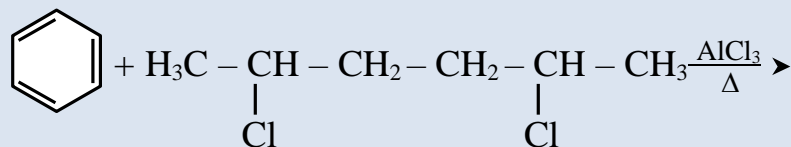
**Example 15.** Oxidizing agent required for these conversions are



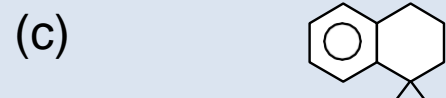
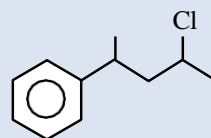
- (a) X =  $\text{KMnO}_4$ ; Y =  $\text{H}_2\text{Cr}_2\text{O}_7$ ; Z =  $\text{H}_2\text{O}_2$       (b) X =  $\text{CrO}_3$ ,  
 Y =  $\text{MnO}_2$ , Z =  $\text{HNO}_3$
- (c) X = Dil  $\text{HNO}_3$  Y =  $\text{Na}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ ; Z = alkaline  $\text{KMnO}_4 / \text{H}^+$
- (d) X, Y, Z = Conc.  $\text{KMnO}_4$

**Solution(c)** Dilute  $\text{HNO}_3$  is a weak oxidising agent as compared to  $\text{KMnO}_4$  and  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Therefore, it oxidises one methyl group among two.

**Example 16.** Product of the following reaction is

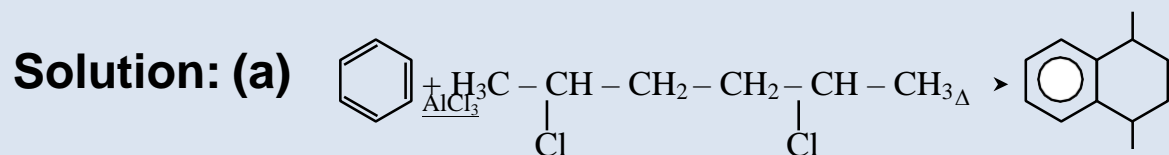


(b)



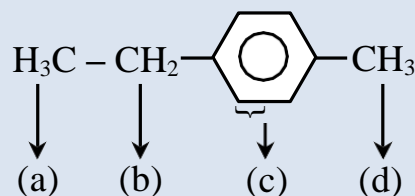
(d)

none of these



No rearrangement occurs. The product is formed due to double F.C. alkylation where second alkylation is intra molecular.

**Example 17.** Which of the following hydrogen is most easily abstracted on reaction with bromine radical  $\text{Br}\cdot$ ?



**Solution(b)**  $\text{Br}\cdot$  radical abstracts hydrogen most easily from that position which gives more stable free radical and that position is (b). It is stabilized by resonance as well as hyper-conjugation.



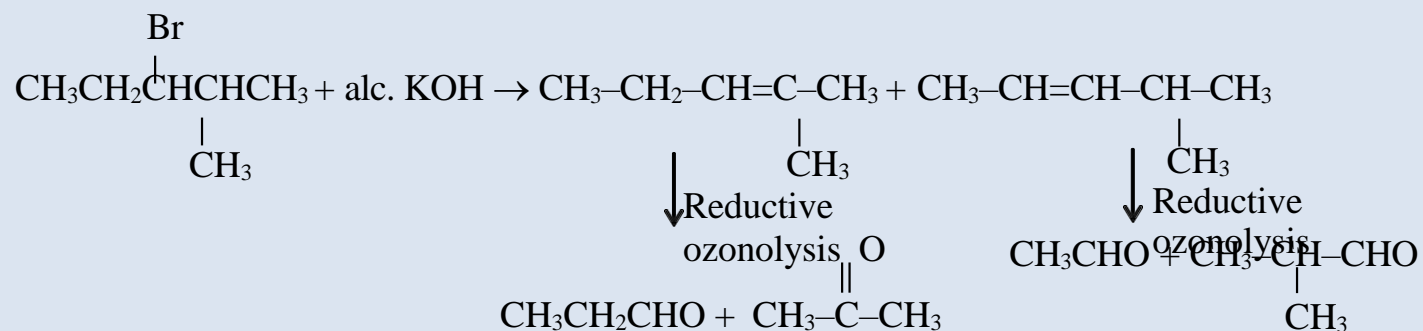
**Example 18.** An alkyl halide with molecular formula,  $C_6H_{13}Br$  on treatment with

alcoholic KOH gave two isomeric alkenes, A and B. Reductive ozonolysis of the mixture gave the following compounds:

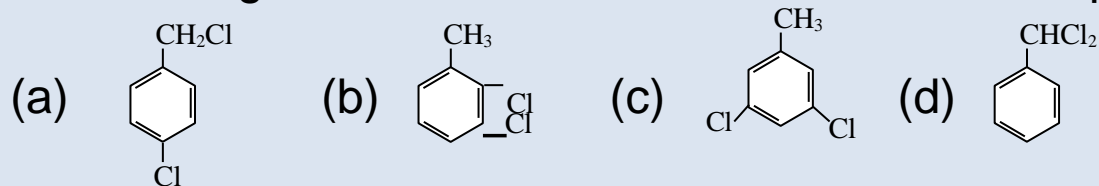
$CH_3COCH_3$ ,  $CH_3CHO$ ,  $CH_3CH_2CHO$  and  $(CH_3)_2CHCHO$  The alkyl halide is

- (a) 2-Bromohexane      (b) 3-Bromo-2-methylpentane  
 (c) 2, 2-Dimethyl-1-bromobutane      (d) 2-Bromo-2, 3-dimethylbutane

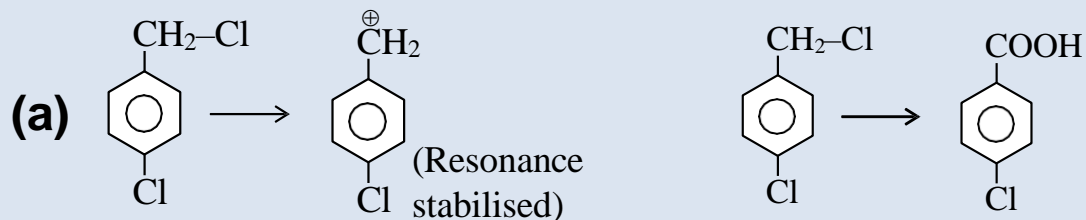
**Solution: (b)**



**Example 19.** An aromatic compound  $C_7H_6Cl_2$  (A), gives  $AgCl$  on boiling with alcoholic  $AgNO_3$  solution and yields  $C_7H_7OCl$  on treatment with sodium hydroxide. (A) on oxidation gives monochlorobenzoic acid. The compound (A) is:



**Solution:**



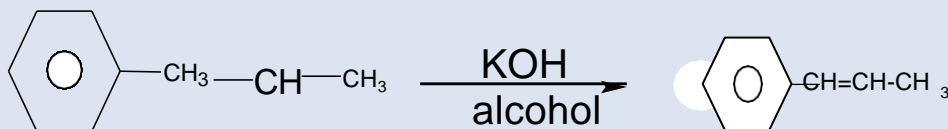
### Example 20.

mainly

1-Phenyl-2 chloropropane on treatment with alcoholic KOH gives

- (a) 2-Phenyl propene.      (b) 1-Phenyl propan-2-ol.  
(c) 1-Phenyl propene.      (d) 1-Phenyl propan-1-ol.

**Solution:(c)** Alcoholic KOH result in dehydrohalogenation of 1-phenyl-2-chloropropane and during dehydrohalogenation that alkene will be formed which is most stable. Here, 1-phenyl propene is formed as the double bond of alkene will be in conjugation with that of phenyl ring.



**Example 21.** The halide, which undergoes nucleophilic substitution (by  $S_NAr$  mechanism) most readily is

- (a)  $p\text{-MeC}_6\text{H}_4\text{Cl}$     (b)  $p\text{-MeOC}_6\text{H}_4\text{Cl}$   
(c)  $p\text{-ClC}_6\text{H}_4\text{Cl}$     (d)  $p\text{-O}_2\text{NC}_6\text{H}_4\text{Cl}$

**Solution:** (d) The reaction proceeds by carbanion formation, which can be stabilized by electron-withdrawing groups present at ortho and/or para positions. The most electron-withdrawing group amongst all is  $-\text{NO}_2$ .

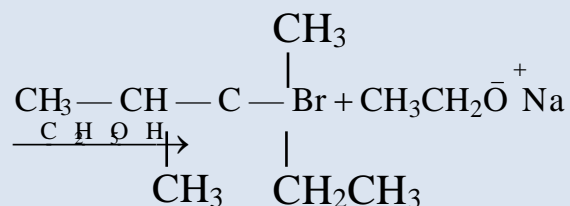
**Example 22.** Identify the set of reagents/ reaction conditions 'X' and 'Y' in the following set of transformations.



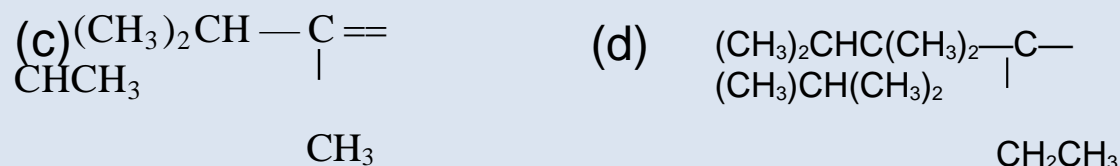
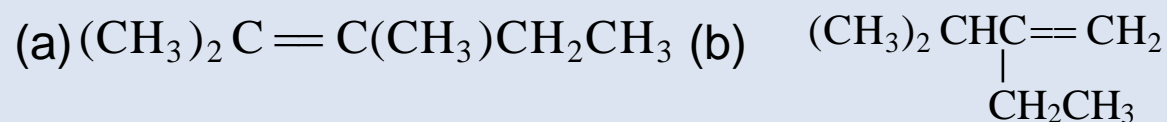
- (a) (X) = dilute aqueous NaOH, 20°C ; (Y) = HBr /acetic acid, 20°C
- (b) (X) = concentrated alcoholic NaOH, 80°C ; (Y) = HBr /acetic acid, 20°C
- (c) (X) = dilute aqueous NaOH, 20°C ; (Y) = Br<sub>2</sub>/CHCl<sub>3</sub>, 0°C
- (d) (X) = concentrated alcoholic NaOH, 80°C ; (Y) = Br<sub>2</sub> / CHCl<sub>3</sub>, 0°C

**Solution (b)** The product obtained in the first reaction can be either CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>3</sub>CH=CH<sub>2</sub>, which is a result of substitution or elimination respectively. If reaction occurs at 20°C, substitution would dominate elimination, as elimination is favoured only at high temperature. At 80°C, the elimination product is predominant and the subsequent reaction of addition of HBr to alkene at low temperature would be greatly favoured.

**Example 23.** The major product in the reaction



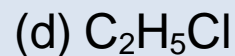
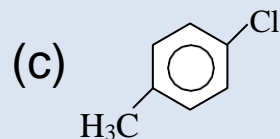
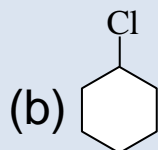
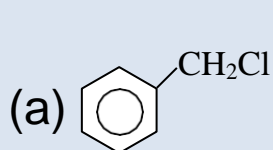
is



**Solution** (a) As a 3° alkyl group is attached to halogen, elimination occurs instead of substitution.

More substituted alkene will be major product in presence of 1°R – O<sup>-</sup> according to saytzeff's rule.

**Example 24.** Which of the following will be the least reactive towards nucleophilic substitution?



**Solution.** (c) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction due to partial double bond character between halogen atom and C-atom involving resonance.

**Example 25:** An optically active 3-bromo-3-methyl hexane on hydrolysis gives

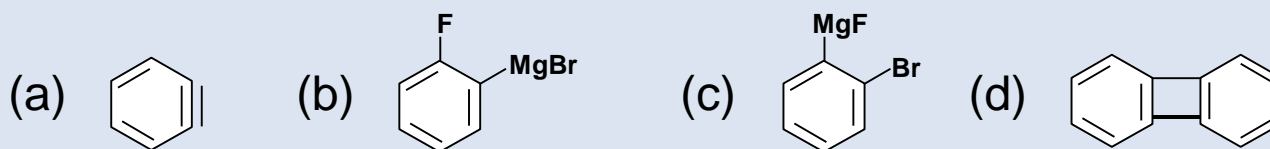
- (a) 3-methyl-3-hexanol with retention of configuration
- (b) 3-methyl-3-hexanol with inversion of configuration
- (c) a mixture of optically active 3-methyl-3-hexanol and 3-methyl-3-hexene
- (d) optically inactive 3-methyl-3-hexanol.

**Solution:** 3-bromo-3-methyl hexane, on ionization gives a  $3^\circ$  carbocation, which can be attacked by nucleophile ( $\text{H}_2\text{O}$ ) to give 3-methyl-3-hexanol. But the products will be optically inactive due to racemic mixture.



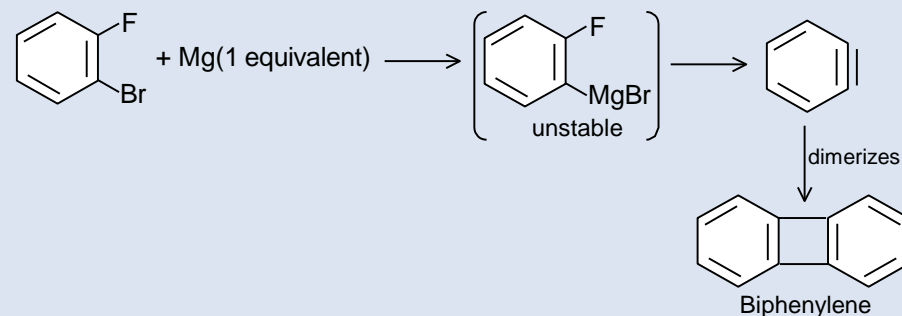
### Example 26:

Treatment of o-bromofluorobenzene with one equivalent of Mg in presence of ether generates



### Solution:

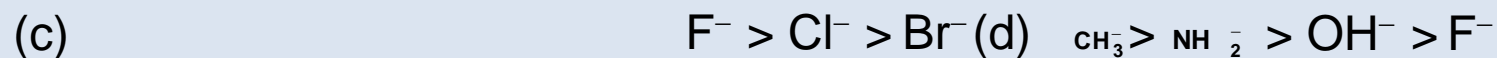
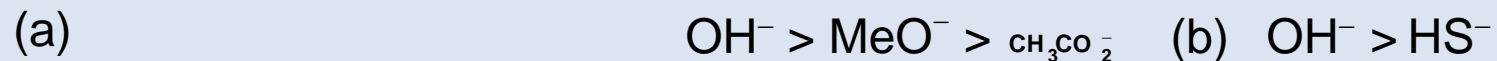
The reaction proceeds as



∴ (d)

### Example 27:

In non-polar solvents, which of the following represents correct order of decreasing nucleophilicity?



### Solution:

In non-polar solvents, the salts of nucleophile are present as ion-pairs in which nearby cations diminish the reactivity of the anion. Smaller the anion more will be -ve charge density, stronger will be ion pairing and lesser will be nucleophilicity.

**Example 28:**

Successful  $S_N2$  reactions

- (a) are endothermic      (b) proceeds with retention of configuration  
(c) are stereospecific      (d) occur rapidly in polar protic solvents

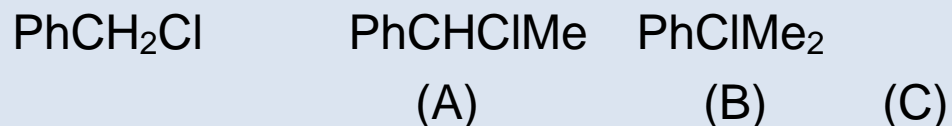
**Solution:**

Successful  $S_N2$  displacements are exothermic, proceeds with inversion of configuration, are favoured in a protic solvents and are stereospecific (because stereoisomeric reactants gives stereochemically different products).

∴ (c)

**Example 29:**

Arrange following compounds in the decreasing order of their reactivity towards  $S_N2$  reaction.



- |     |                 |                     |
|-----|-----------------|---------------------|
| (a) | (C) > (B) > (A) | (b) (A) > (B) > (C) |
| (c) | (B) > (A) > (C) | (d) (B) > (C) > (A) |

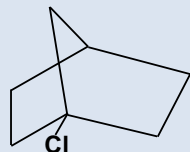
**Solution:**

The rate of  $S_N2$  reaction depends on steric crowding in the transition state. More is the steric crowding, less stable the transition state is, less will be the rate of  $S_N2$  reaction. Thus, the reactivity order of  $S_N2$  reaction would be (A) > (B) > (C).

∴ (b)

**Example 30:**

For the given compound



, the nucleophilic substitution by  $C_2H_5OH$  occurs

by

- |     |                      |     |                        |
|-----|----------------------|-----|------------------------|
| (a) | $S_N1$ mechanism     | (b) | $S_N2$ mechanism       |
| (c) | $S_N1$ & $S_N2$ both | (d) | no reaction will occur |

**Solution:**

In the given compound,  $S_N2$  reaction do not occur due to impossibility of attack of nucleophile from rear side while  $S_N1$  reaction is also not possible because the carbocation formed after ionization is not stable as the bridge head carbon having one carbon bridge cannot be  $sp^2$  hybridized.

**$\therefore$  (d)**

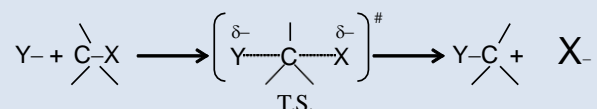
### Example 31:

$S_N2$  reaction at an asymmetric carbon of a compound always gives

- (a) an enantiomer of the substrate (b) a product with opposite rotation
- (c) a mixture of diastereomers (d) a single stereoisomer

### Solution:

A typical  $S_N2$  reaction is shown as

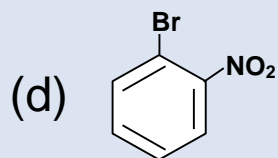
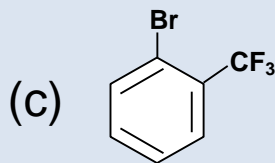
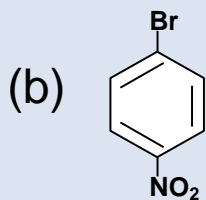
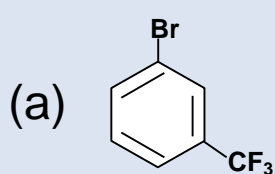


It is evident that only one product is formed, which is not the enantiomer of the substrate. Moreover, it is not necessary that the product have opposite optical rotation than that of the substrate, they differ in configuration only. When the reactant is a stereoisomer, product will also be a single stereoisomer.

$\therefore$  (d)

### Example 32:

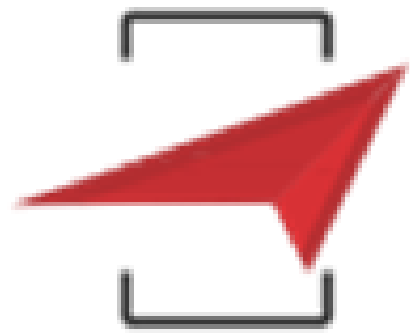
Which of the aryl halide undergoes nucleophilic substitution by benzyne mechanism?



### Solution:

Unactivated and deactivated aryl halides undergo reaction by benzyne mechanism. Activated aryl halides are the one in which strongly electron-withdrawing groups are present at ortho/para to halogen atoms.

∴ (a)



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