



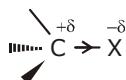
ALKYL HALIDE (HALOALKANES)

Aliphatic Halogen Derivatives :

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

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

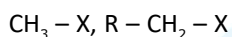
Structure of alkyl halides:



Classification of alkyl halides :

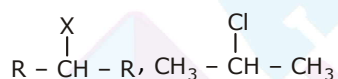
(i) Primary halide : The halogen bearing carbon is bonded to one carbon atom or with no carbon atom.

Example :



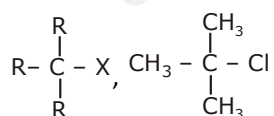
(ii) Secondary halide : If two carbon atoms are bonded to the halogen bearing carbon.

Example :



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

Example :



Haloalkanes can be classified into following three categories.

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

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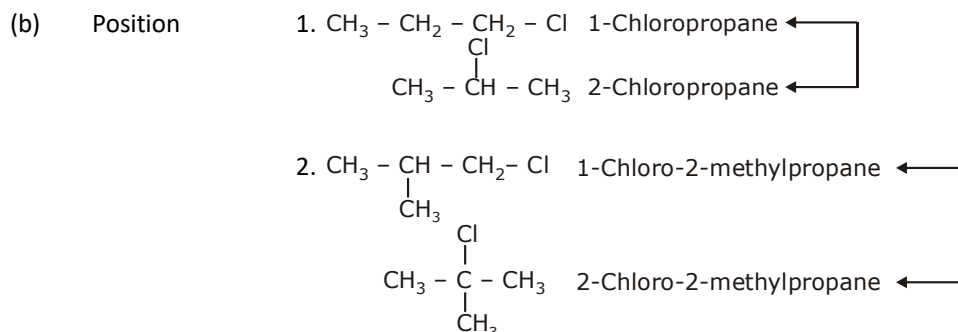
IUPAC nomenclature of alkyl halides

S.N.	Compound	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	2-Chloro-2-methylpropane
2.	$\begin{array}{cccc} \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 \\ & & & & \\ & & \text{Br} & & \text{Cl} \end{array}$	3-Bromo-1-chlorobutane
3.	$\begin{array}{cccc} \text{CH}_2 & - & \text{CH} & - & \text{CH} & - & \text{CH}_2 \\ & & & & & & \\ \text{F} & & \text{CH}_3 & & \text{Br} & & \text{Cl} \end{array}$	2-Bromo-1-chloro-4-fluoro-3-methylbutane
4.	$\begin{array}{ccccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 \\ & & & & & & \\ & & \text{OH} & & & & \text{Cl} \end{array}$	5-Chloropentan-2-ol
5.		5-Fluoropent-1-ene
6.		2,2-Bis(chloromethyl)-1,3-dichloropropane

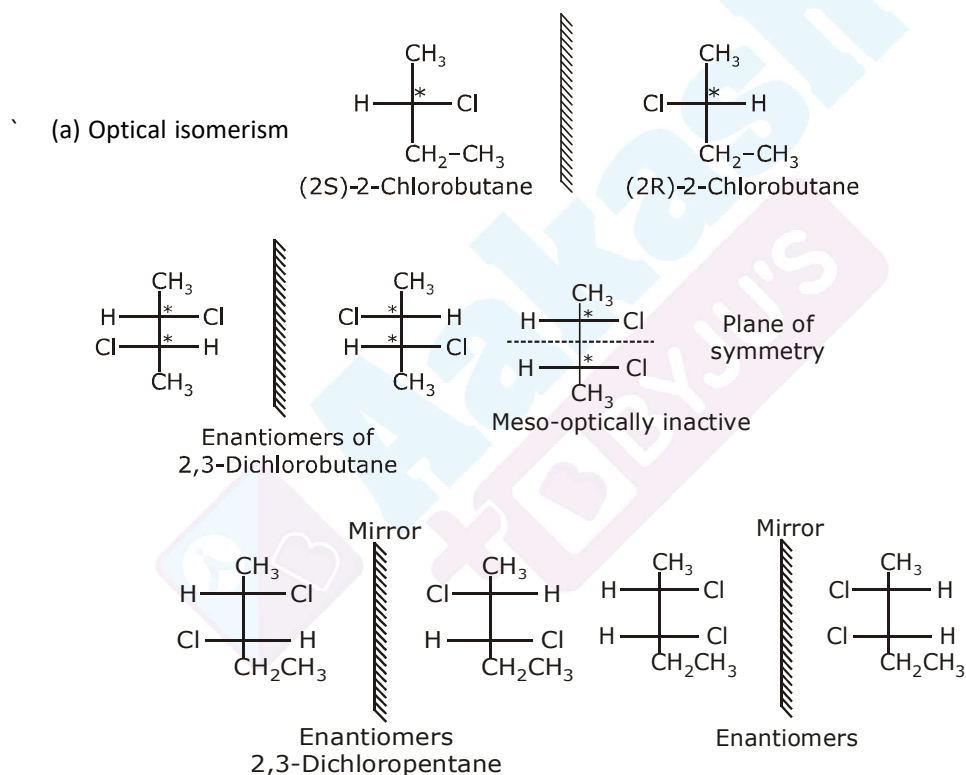
Isomerism in haloalkanes :

S.N.	Compound	IUPAC name
1.	Structural Isomerism	
(a)	Chain	
	1. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	1-Chlorobutane
	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro-2-methylpropane
	2. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	1-Chloropentane
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro-3-methylbutane
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro-2,2-dimethylpropane

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2. Stereoisomerism



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Bonding in alkyl halide

Table : 1 Carbon halogen bond lengths

Bond	Bond length(Å)
CH ₃ – F	1.39
CH ₃ – Cl	1.78
CH ₃ – Br	1.93
CH ₃ – I	2.14

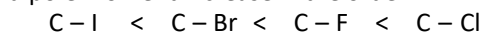
Physical properties of alkyl halide

Dipole moment of the halogen derivatives:

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

Where δ is the charge and d is the bond length

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



$$\mu : 1.29 \text{ D} \quad 1.48 \text{ D} \quad 1.51 \text{ D} \quad 1.56 \text{ D}$$

The electronegativities of the halogen increase in the order:

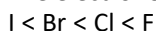


Table : 2 Molecular dipole moments of methylhalides

X	CH ₃ X	CH ₂ X ₂	CHX ₃	CX ₄
F	1.82 D	1.97 D	1.65 D	0
Cl	1.94 D	1.60 D	1.03 D	0
Br	1.79 D	1.45 D	1.02 D	0
I	1.64 D	1.11 D	1.00 D	0

Boiling point :

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

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

Formula	X = F	X = Cl	X = Br	X = I
CH ₃ - X	- 78	- 24	3	42
CH ₃ - CH ₂ X	- 32	12	38	72
CH ₃ - CH ₂ - CH ₂ X	- 3	47	71	103
CH ₃ - (CH ₂) ₃ - CH ₂ X	65	108	129	157
CH ₃ - (CH ₂) ₄ - CH ₂ X	92	134	155	180

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

Density :

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

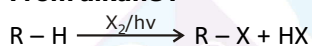
Table : 5

	CH ₃ -(CH ₂) ₆ -CH ₂ F	CH ₃ -(CH ₂) ₆ -CH ₂ Cl	CH ₃ -(CH ₂) ₆ -CH ₂ Br	CH ₃ -(CH ₂) ₆ -CH ₂ I
Density (20°C)	0.80 g/mL	0.89 g/mL	1.12 g/mL	1.34 g/mL

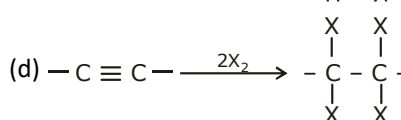
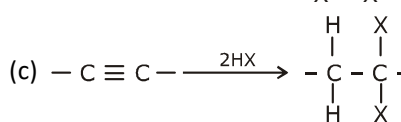
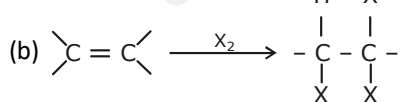
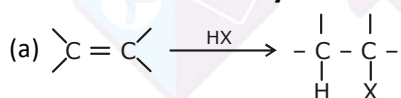
Because alkyl halides are insoluble in water, mixture of an alkyl halide and water separates into two layers. When the alkyl halide is a fluoride or chloride, it is on the upper layer and water is in the lower. The situation is reversed when the alkyl halide is a bromide or an iodide. In these cases the alkyl halide is in the lower layer. Polyhalogenation increases the density. The compounds CH₂Cl₂, CHCl₃ and CCl₄ for example, are all more dense than water.

Preparation of alkyl halide :

From alkane :



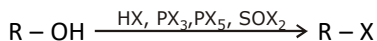
From alkenes and alkynes



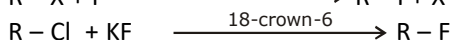
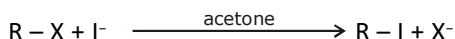
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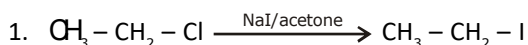
From alcohol



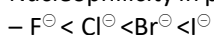
From other halides



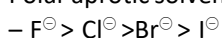
Finkelstein Reaction



Nucleophilicity in polar protic solvent

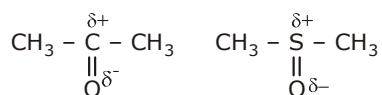


Polar aprotic solvent



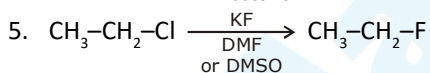
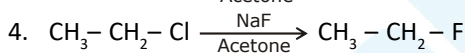
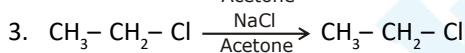
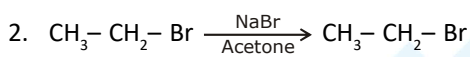
Covalent Nature : $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$

Solubility in polar solvent decreases.

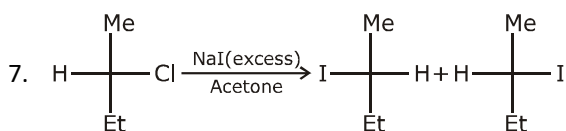
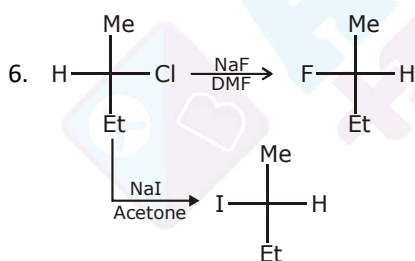


Acetone \rightarrow Solubility order in acetone

$\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$



(Swart's reaction)



(Racemisation)



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

(4) Energetics of the reaction →

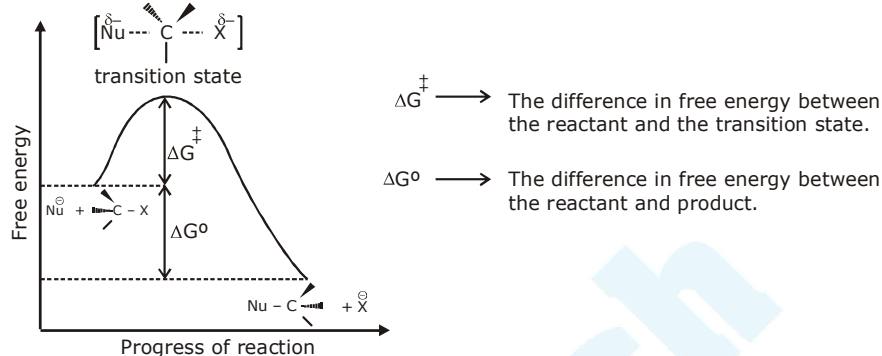
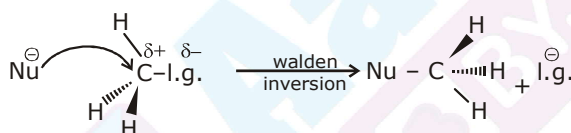


Figure : A free energy diagrams for a hypothetical S_N2 reaction that takes place with a negative ΔG°

- (5) No intermediates are formed in the S_N2 reaction, the reaction proceeds through the formation of an unstable arrangement of atoms or group called transition state.
- (6) The stereochemistry of S_N2 reaction → As we have seen earlier, in an S_N2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as walden inversion.



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

(i) Effect of the structure of the substrate →

Order of reactivity in S_N2 reaction : $-CH_3 > 1^\circ > 2^\circ \gg 3^\circ$ (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.

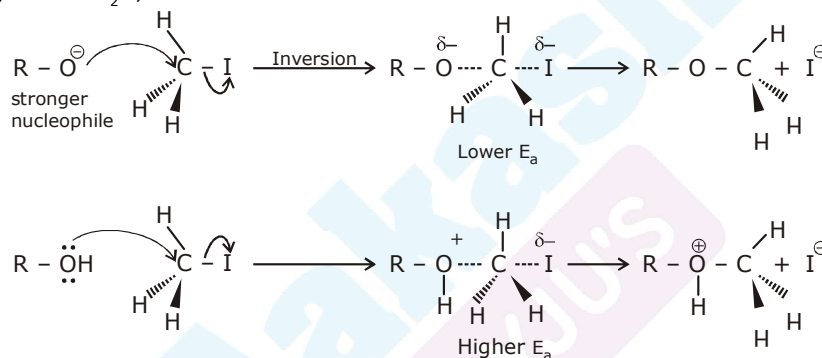
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Table : 6 Relative rates of reactions of alkyl halide in S_N2 reaction.

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

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

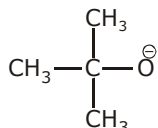


Some common nucleophiles listed in decreasing order of nucleophilicity in hydroxylic solvent	
Strong nucleophiles	Moderate nucleophile : Br^\ominus
$(CH_3CH_2)_3P^\ominus$	NH_3
SH^\ominus	$(CH_3)_2S^\ominus$
I^\ominus	Cl^\ominus
$(CH_3-CH_2)_2NH$	AcO^\ominus
CN^\ominus	Weak nucleophile F^\ominus
$(CH_3-CH_2)_3N^\ominus$	H_2O
HO^\ominus	CH_3OH
CH_3O^\ominus	

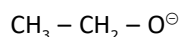
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Steric effects on nucleophilicity

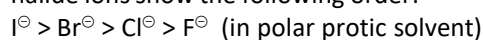


t-Butoxide
Stronger base, yet weaker nucleophile cannot approach the carbon atom so easily.



Ethoxide is weaker base, yet stronger nucleophile

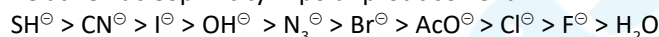
(iii) The effect of the solvent \rightarrow In polar protic solvent large nucleophiles are good, and the halide ions show the following order:



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.

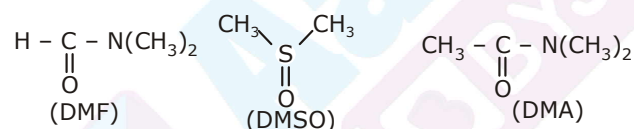
Because small nucleophile is solvated more by the polar protic solvent thus its nucleophilicity decreases and rate of $\text{S}_{\text{N}}2$ decreases.

Relative nucleophilicity in polar protic solvent:



So, polar protic solvents are not useful for rate of $\text{S}_{\text{N}}2$, if nucleophile is anionic. But polar aprotic solvent does not have any active hydrogen atom so they cannot form H bond with nucleophiles. Polar aprotic solvent has a crowded positive centre, so they do not solvate the anion appreciably therefore the rate of $\text{S}_{\text{N}}2$ reactions increased when they are carried out in polar aprotic solvent.

Examples of polar aprotic solvent.

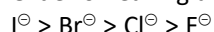


In DMSO, the relative order of reactivity of halide ions is

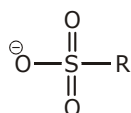


(iv) The nature of the leaving group \rightarrow The best leaving groups are those that become the most stable ion after they leave, because leaving groups generally leave as a negative ion, so those leaving groups are good, which stabilise negative charge most effectively and weak bases do this best,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

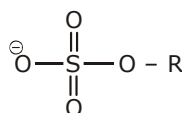
Order of leaving ability of halide ion



Other leaving groups are

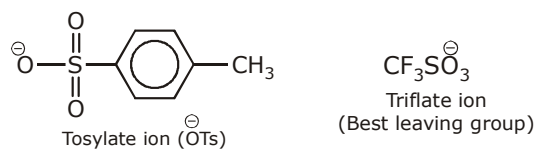


Alkane sulphonate ion



Alkyl sulphate ion

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Strongly basic ions rarely act as leaving group →

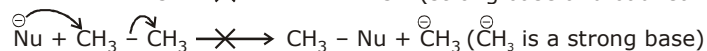
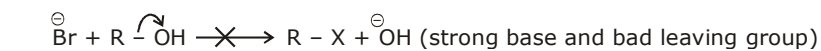
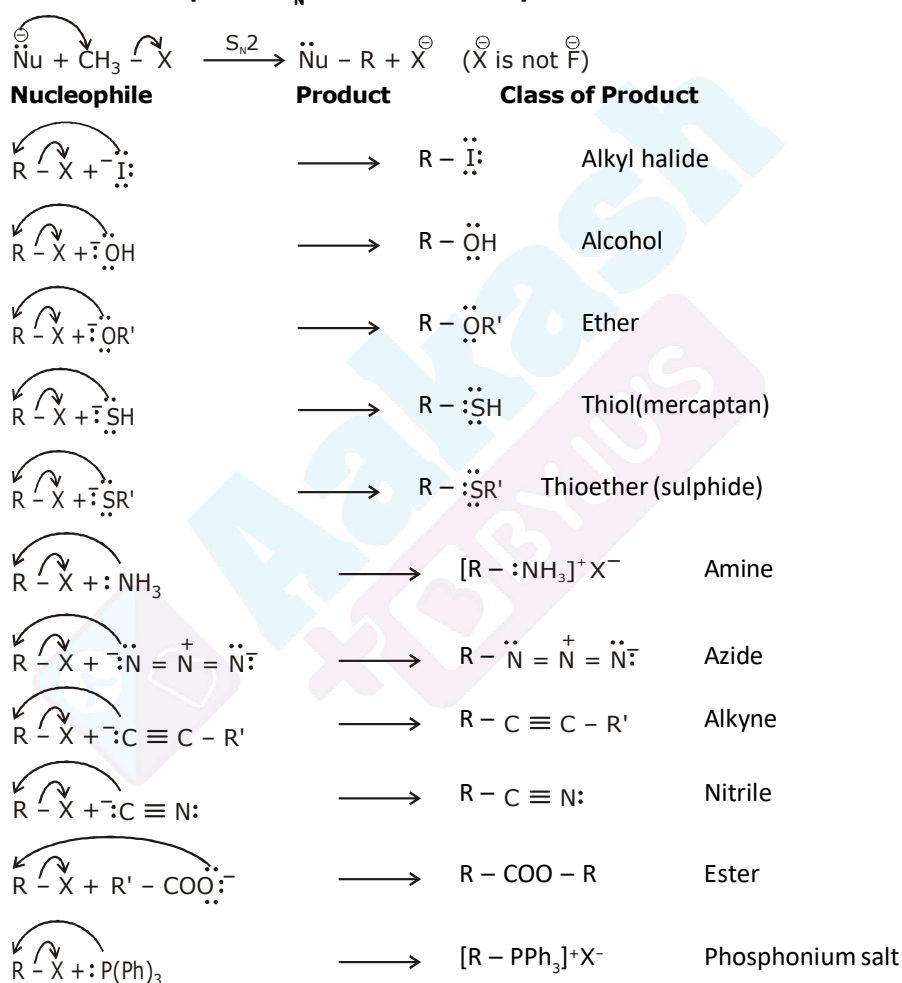


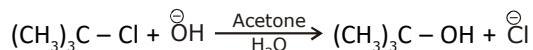
Table : 8 Examples of S_N2 reactions of alkyl halide →



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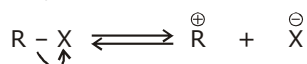


(B) Unimolecular nucleophilic substitution reaction (S_N1):

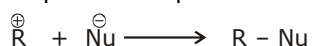


Mechanism of S_N1 reaction:

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



Step - 2 Nucleophilic attack on the carbocation (fast)



Characteristics of S_N1 reactions:

1. It is unimolecular, two step process and intermediate is formed (intermediate is carbocation).
2. It is first order reaction.
3. Kinetics of the reaction
Rate \propto [Alkyl halide]
Rate = $k[(\text{CH}_3)_3\text{C}-\text{X}]$
Rate of S_N1 reaction is independent of concentration and reactivity of nucleophile.
4. Energetics of the S_N1

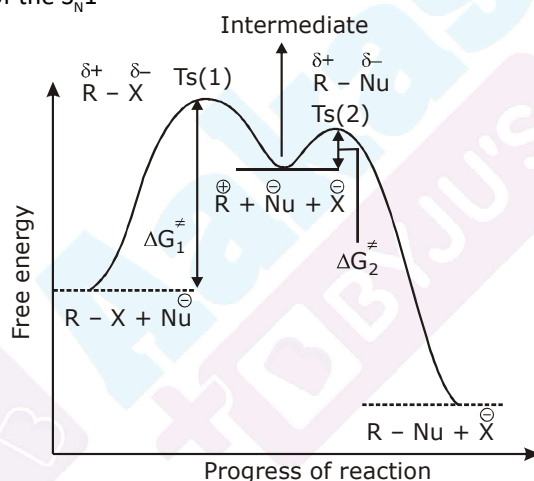


Figure: Free energy diagram for the S_N1 reaction.

5. Factors affecting the rate of S_N1 :

(i) The structure of the substrate \rightarrow

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

S_N1 reactivity: $3^\circ > 2^\circ > 1^\circ > \text{CH}_3 - \text{X}$

(ii) Concentration and reactivity of the nucleophile:

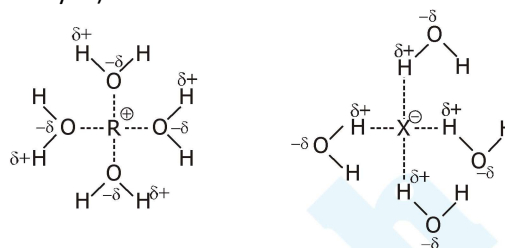
The rate of S_N1 reactions are unaffected by the concentration and nature of the nucleophile.

ALKYL HALIDE



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

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



Solvated ions

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

Solvent	ϵ	Relative rate
H ₂ O	80	8000
CH ₃ OH	33	1000
C ₂ H ₅ OH	24	200
(CH ₃) ₂ CO	21	1
CH ₃ CO ₂ H	6	-

(iv) The nature of the leaving group →

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

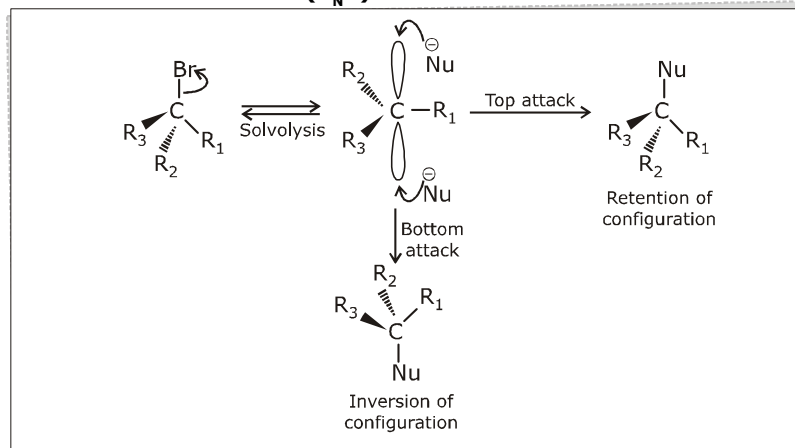
Leaving ability of halogen is $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} \gg F^{\ominus}$

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

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Mechanism of racemization (S_N1) →



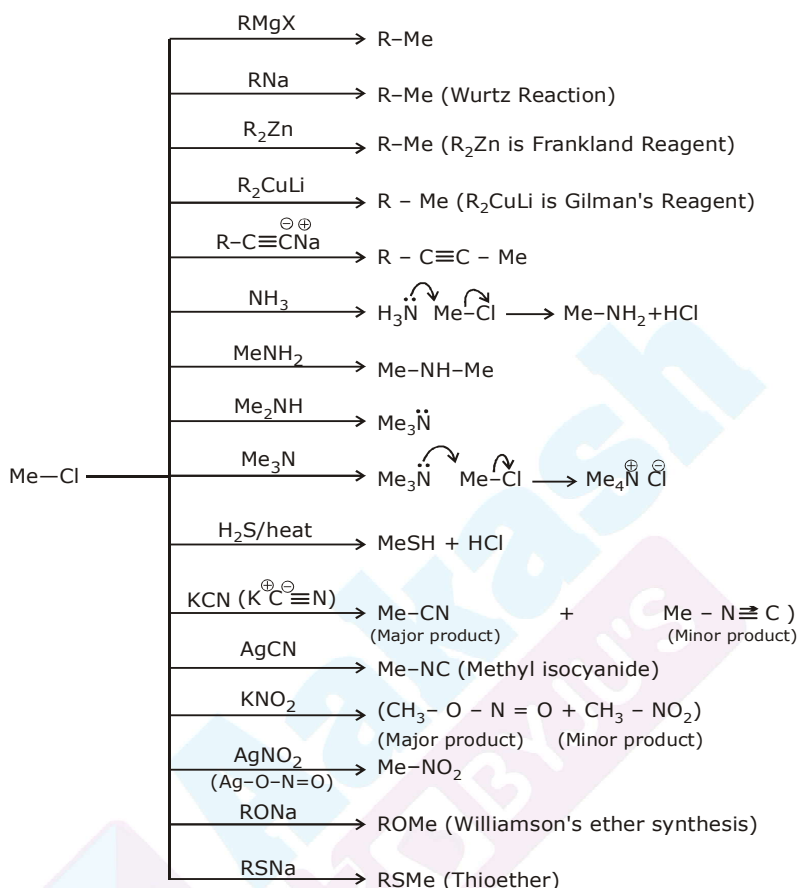
Comparison of S_N1 and S_N2 reactions

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

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Some Nucleophilic reaction of R - X :-

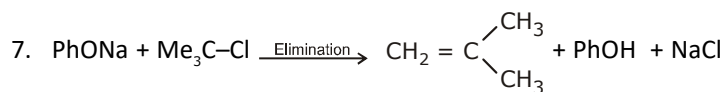


Williamson's Ether Synthesis: (S_N2)

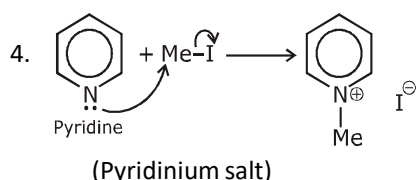
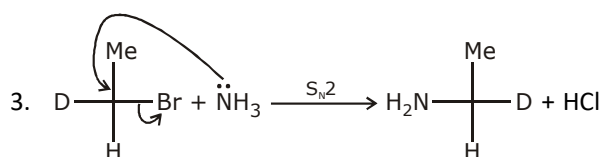
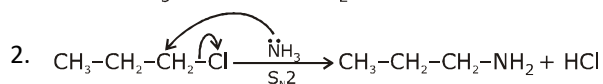
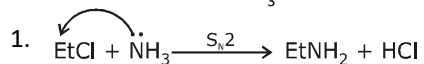
- $\text{R}-\ddot{\text{O}}^{\ominus}\text{Na}^{\oplus} + \text{R}-\text{Cl} \longrightarrow \text{R}-\text{O}-\text{R} + \text{NaCl}$
- $\text{EtONa} + \text{Me}-\text{Cl} \longrightarrow \text{EtOMe}$
- $\text{MeO}^{\ominus}\text{Na}^{\oplus} + \text{Et}-\text{Cl} \longrightarrow \text{EtOMe}$
Rate (2) > (3), 2 is better method. (Due to less steric hindrance)
- $\text{PhONa} + \text{MeCl} \longrightarrow \text{PhOMe} + \text{NaCl}$
- $\text{Me}_3\text{CO}^{\ominus}\text{Na}^{\oplus} + \text{MeCl} \longrightarrow \text{Me}_3\text{COMe} + \text{NaCl}$
- $\text{MeO}^{\ominus}\text{Na}^{\oplus} + \text{Me}_3\text{C}-\text{Cl} \xrightarrow{\text{Elimination}} \text{CH}_2 = \text{C} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} + \text{MeOH} + \text{NaCl}$
Major



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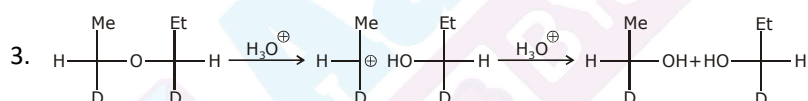
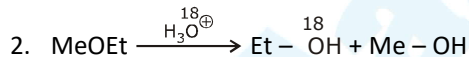
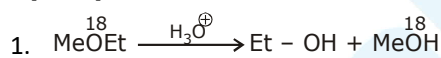


Reaction of RX with NH_3

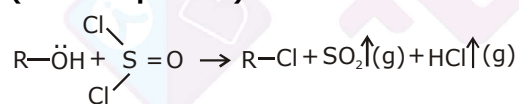


Some other reactions

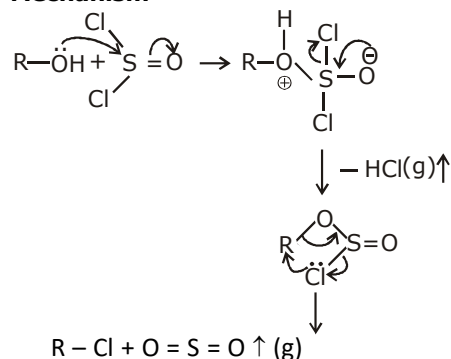
Hydrolysis of Ether



$\text{S}_\text{N}1$ (Nucleophilic substitution intramolecular) (Darzen's process)



Mechanism



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Note : (1) In S_N1 retention of configuration takes place.

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

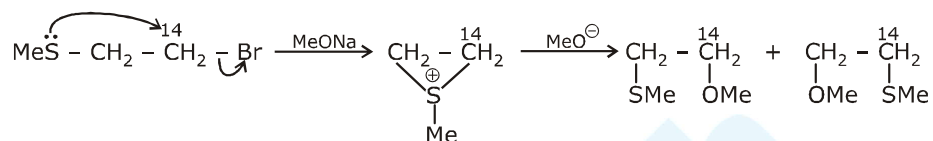
S_N^{NGP} (Neighbouring group participation)

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

For S_N^{NGP} :-

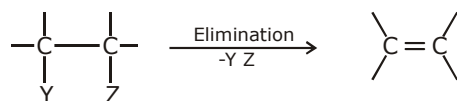
1. Internal nucleophile must be present.
2. Internal nucleophile must be anti to leaving group.

Example



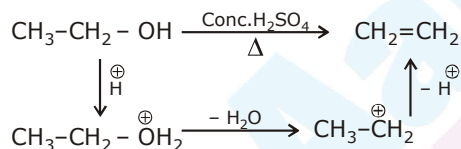
Elimination reactions:

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



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

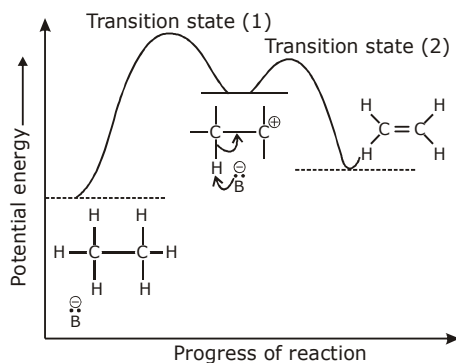
Dehydration of Alcohol (E_1)



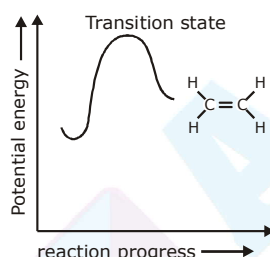
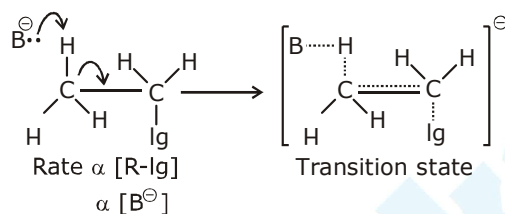
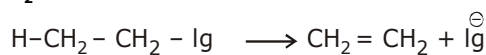
Characteristics of E_1 reaction :

- (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 \rightarrow Rate \propto [Substrate]
Rate = k[Substrate]

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E₂- elimination :



Bimolecular reaction, second order kinetic.

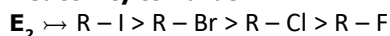
1. Leaving group leaves when base is taking proton from adjacent carbon.
2. It is a single step reaction
3. Rate \propto Leaving group tendency
4. It shows elemental as well as kinetic isotopic effect with leaving group as well as at β -position.
5. Normally saytzeff product is major.
6. Transition state mechanism therefore rearrangement is not possible.
7. The orientation of proton & leaving group should be antiperiplanar for E₂.
8. **Positional orientation of elimination** \rightarrow In most E₁ and E₂ 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)

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

Reactivity towards



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

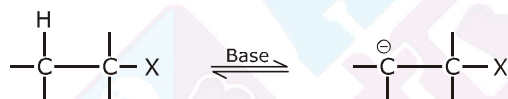
Characteristics	E_1	E_2
(i) Kinetics	$k[R-X]$, I order	$k[R-X][Base]$, II order
(ii) Orientation	Saytzeff alkene	Saytzeff alkene
(iii) Stereochemistry	No special geometry is required	transition state must be co-planar

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

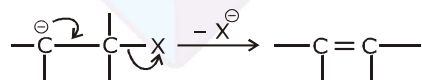
The E_1CB or carbanion mechanism : In the E_1CB , H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism:

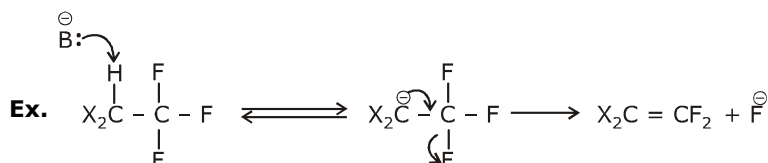
Step-1 : Consists of the removal of a proton, H^\oplus by a base generating a carbanion



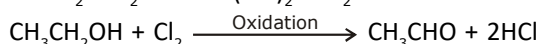
Step-2 : Carbanion loses a leaving group to form alkene



Condition: For the E_1CB , substrate must be containing acidic hydrogens and poor leaving groups (i.e., bad l.g.)

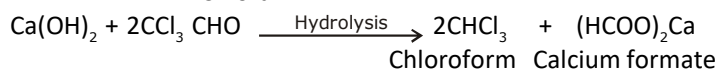
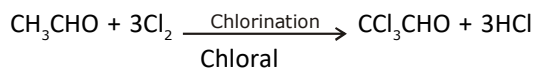


In case of ethanol, the reaction occurs as follows

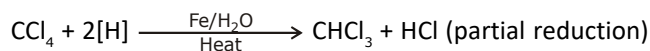




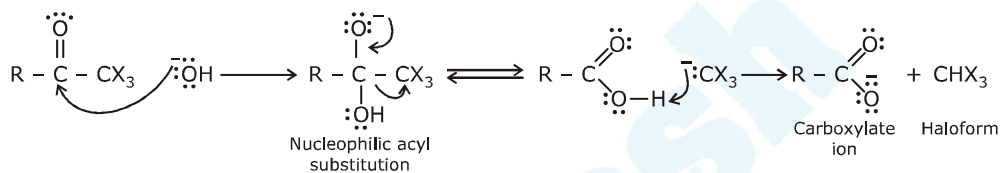
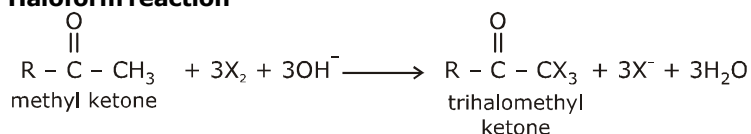
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1. From carbontetrachloride

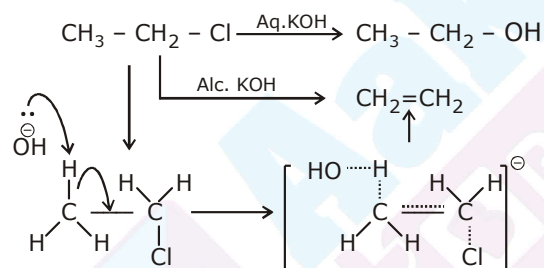


2. Haloform reaction



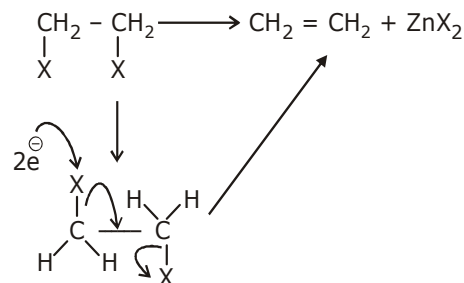
Step 1 : Attack of the nucleophile Step 2 : Elimination of the leaving group Step 3 : Proton transfer

Dehydrohalogenation (-HX) E₂



Anti elimination

Dehalogenation : - (-X₂) E₂

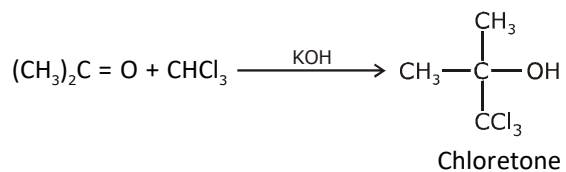


Anti elimination

ALKYL HALIDE

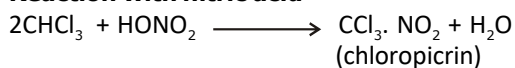


4. Reaction with acetone :



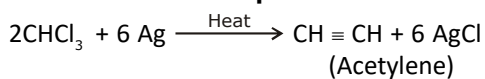
Use : Chloretone is used as hypnotic (a sleep inducing) drug.

5. Reaction with nitric acid

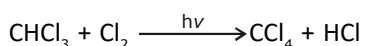


Use : Chloropicrin is used as an insecticide and war gas.

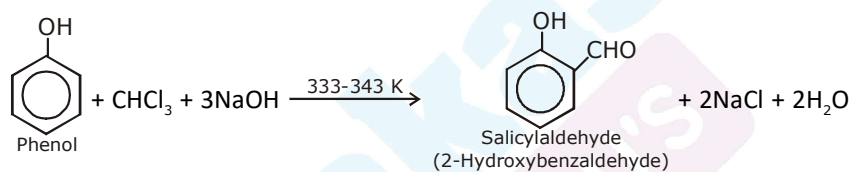
6. Reaction with silver powder :



7. Chlorination :



8. Reimer-Tiemann reaction:



Uses of chloroform

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



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Aliphatic Halogen Derivatives :

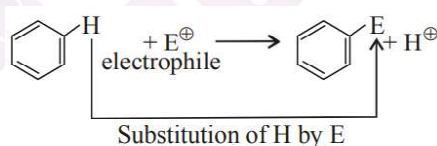
Compounds obtained by the replacement of one or more hydrogen atom(s) from hydrocarbons are known as halogen derivatives. The halogen derivatives of alkanes, alkenes, alkynes and arenes are known as alkyl halide (haloalkane), alkenyl halide (haloalkenes), alkynyl halides (haloalkynes) and aryl halides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

Electrophilic aromatic substitution (EAS) :

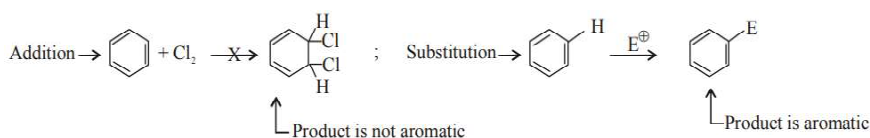
Based on its structure and properties, what kind of reaction should benzene undergo? Are any of its bonds particularly weak? Does it have an electron-rich or electron-deficient atom?

- * Benzene has six π -electrons delocalized in six p -orbitals that overlap above and below the plane of the ring. These loosely held π -electrons make the benzene ring electron-rich, and so it reacts with an electrophile.
- * Because benzene's six π -electrons satisfy Huckel's rule, benzene is especially stable. Reactions that keep the aromatic ring intact are therefore favored.
- * The electron cloud above and below the plane of benzene shields the ring carbons from the attack of a nucleophile.

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



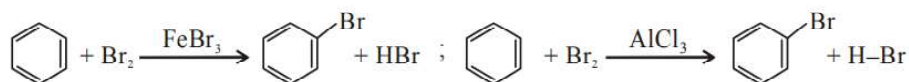
Benzene does not undergo addition reactions like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic. Substitution of a hydrogen on the other hand, keeps the aromatic ring intact.





Preparation of haloarene

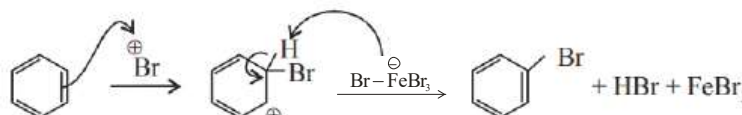
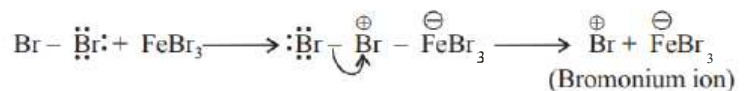
- The introduction of halo (-X) group on benzene known as halogenation of benzene



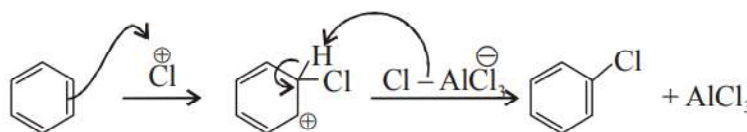
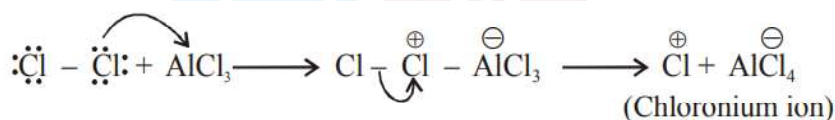
The bromination or chlorination of benzene requires a Lewis acid catalyst such as FeBr_3 , AlBr_3 , FeCl_3 or AlCl_3 .

Sometime Fe or Al is used but real catalyst is not Fe or Al itself but FeX_3 or AlX_3 is formed from the reaction between halogen and Fe or Al.

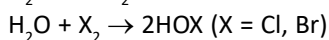
Mechanisms for Bromination



Mechanisms for Chlorination

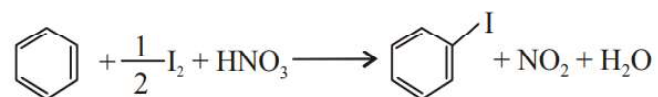


Bromination and chlorination also occur by $\text{HOBr}^{\ominus+}$ and $\text{HOCl}^{\ominus+}$, obtained by reaction between H_2O and X_2 .

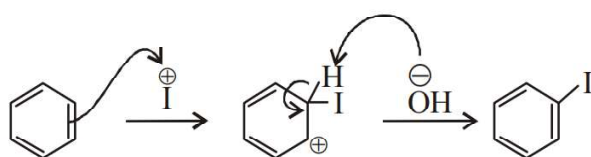
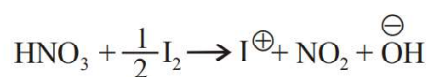


Iodination of benzene requires an acidic oxidizing agent such as nitric acid. Nitric acid is consumed in the reaction, so it is a reagent rather a catalyst.

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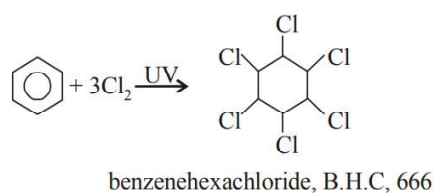


Mechanisms for Iodination



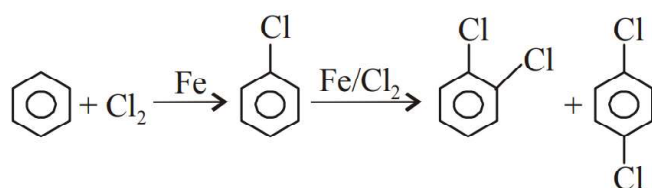
The electrophile required for halogenation reaction is halonium ion (X⁺)

2. Addition of Halogen



Benzenehexachloride (BHC, C₆H₆Cl₆) is also called Lindane or Gammexene (γ-isomer) and is used insecticide.

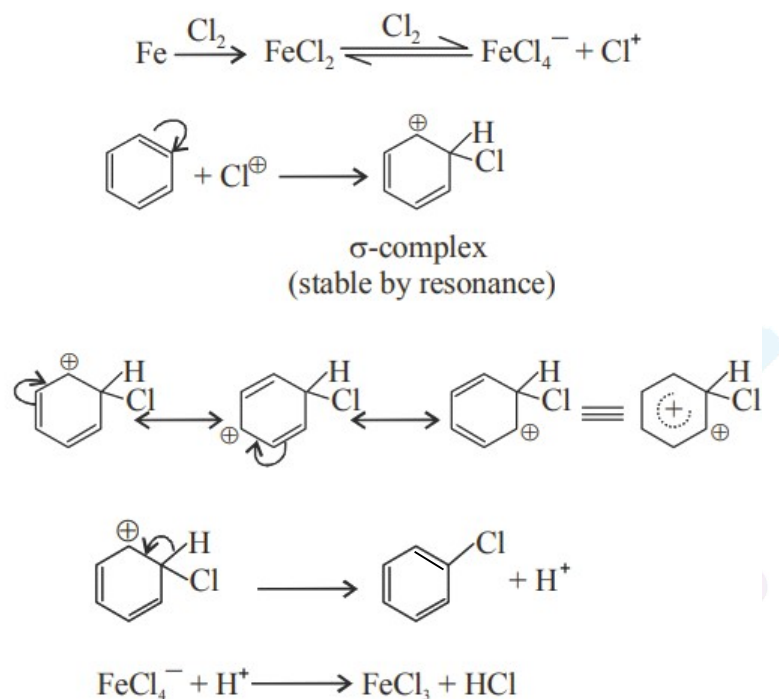
3. Direct halogenation :



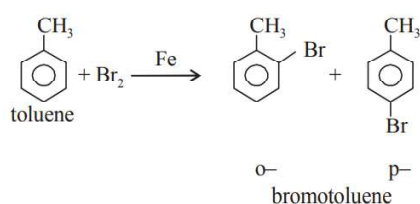
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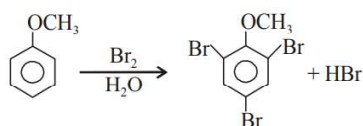
Low temperature and the presence of a halogen carrier favour nuclear substitution. The chlorides or bromides of Al, Fe, Sb may be used :



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



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

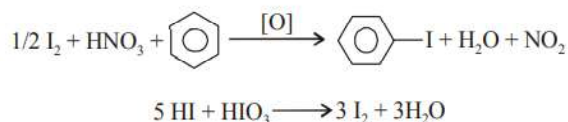


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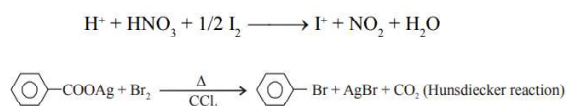


Direction iodination is not possible since, iodine is least reactive and HI formed makes reaction reversible.

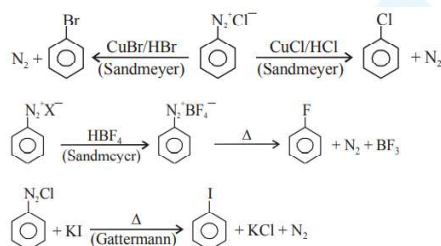
In presence of oxidising agents like HNO_3 or HIO_3 , iodination of benzene is possible and HI formed is converted to I_2 :



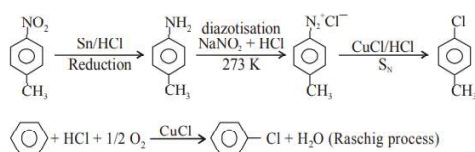
Iodination probably involves an electrophilic aromatic substitution with iodonium (I^+) acting as the electrophile. I^+ is formed from iodine byoxidation with HNO_3 .



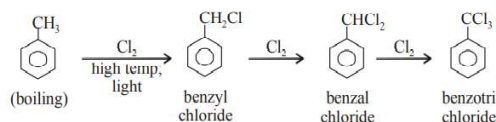
Diazonium salts are converted to halogen compounds :



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



Side-Chain Derivatives



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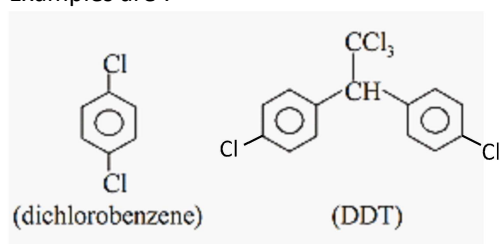


Side-chain halogenation involves free radical mechanisms due to lower bond energy of the benzyl C–H bond.

Physical Properties

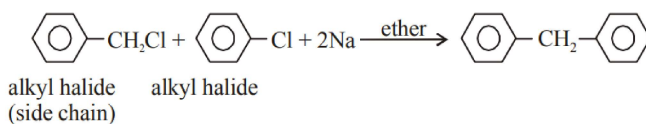
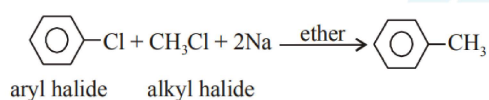
- Less polar, insoluble in water but soluble in organic solvents like ethanol and ether.
- They show physiological activity and are used as insecticides.

Examples are :



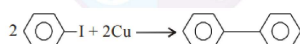
Chemical Properties

(a) Wurtz-Fitting Reaction



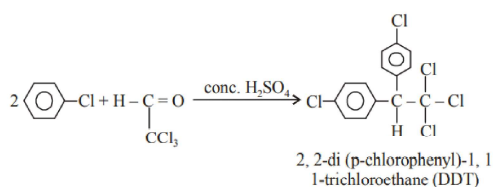
Only aryl halide is involved, diphenyl is formed (Fitting reaction)

(b) Ullman synthesis



(c) Reaction with Chloral

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

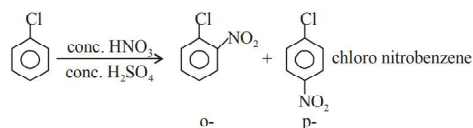


DDT is causing ecological problems, its use as insecticides is being banned.

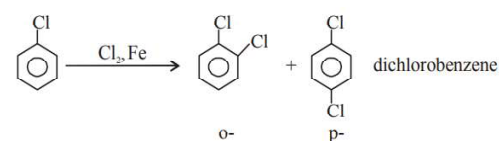
ARYL HALIDE



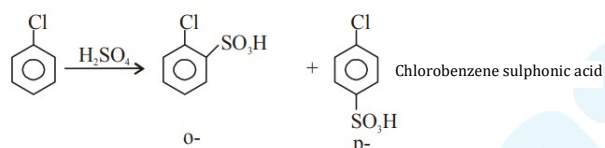
Nitration



Chlorination

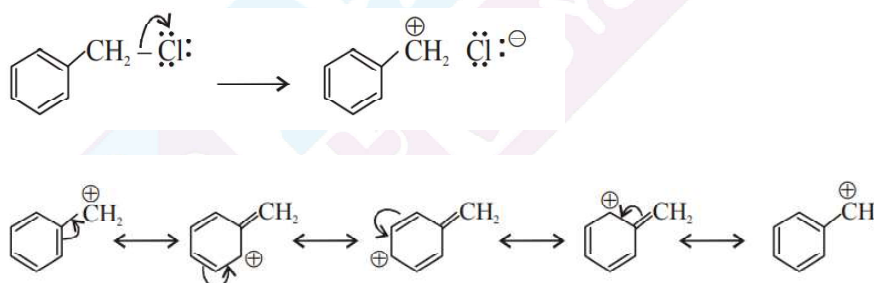


Sulphonation

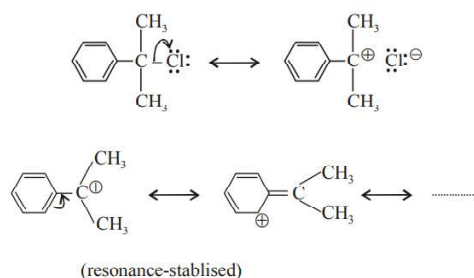


- Chlorine is not a good donor of electrons by resonance due to its high electronegativity. Thus, the inductive effect of the Cl atom overcomes the resonance effect, and thus, it deactivates the benzene ring.

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



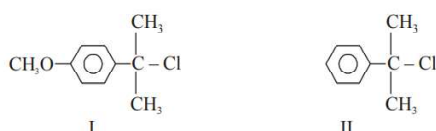
Tertiarycumyl chloride ionises to a carbocation with four important resonance structure :



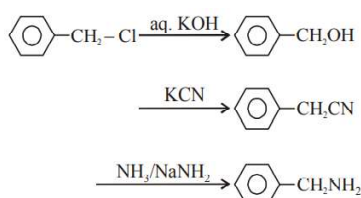
ARYL HALIDE



Because of the possibility of resonance, ortho and para substituent group on the benzene ring that activate electrophilic aromatic substitution further accelerate S_N1 reaction at the benzylic position. Thus p-methoxytert-cumyl chloride (I) undergoes hydrolysis about 3400 times faster than tert-cumyl chloride II.



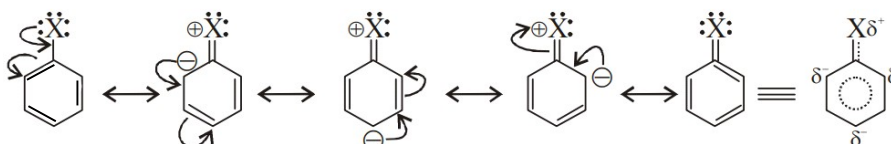
Benzylic halides undergo S_N reactions like aliphatic halides.



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

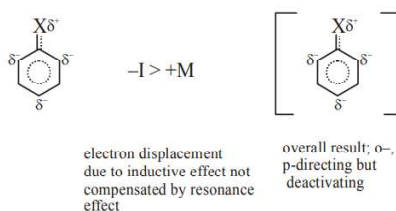
Anomalous behaviour of halogen substituent :

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



Rate \propto single step reaction

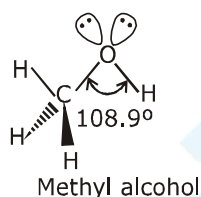
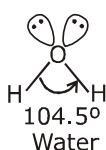
This deactivating nature is attributed to high electronegativity of the halogen atom due to which they withdraw electrons; resonance effect explains its electron-donating behaviour.





ALCOHOL

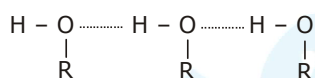
Introduction



Physical Properties

(1) Boiling point :

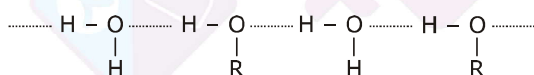
- Alcohols show increase in boiling point with increase in molecular weight amongst homologous series.
- Alcohols have higher boiling point than hydrocarbons of the same molecular weight. The reason for higher boiling point is the intermolecular H-bonding present in alcohols.



Intermolecular H bonds in alcohol

(2) Solubility in water :

As molecular weight increases solubility in water decreases. The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.

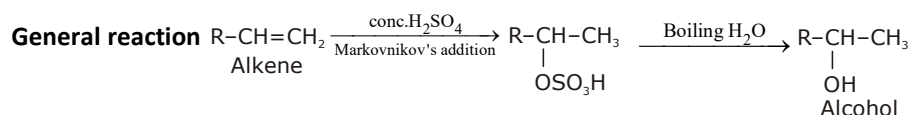


Intermolecular H bond between water & alcohol molecules

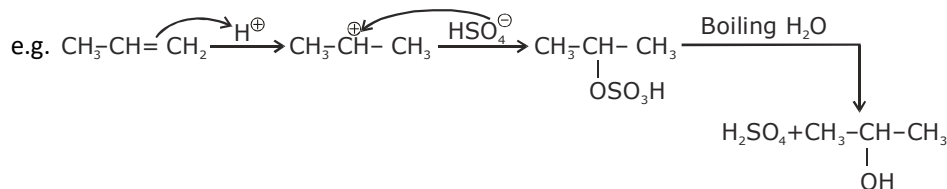
Preparation of alcohols

(1) From alkenes

- By acid catalyzed hydration of alkenes :** Formation of carbocation intermediate (Markovnikov addition, rearrangement possible).



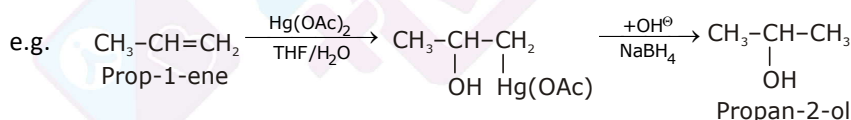
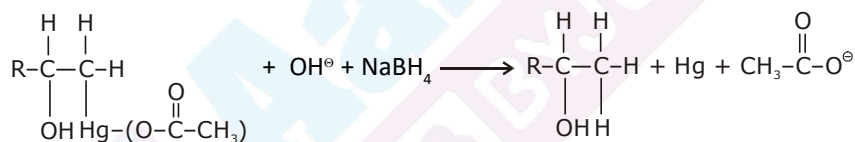
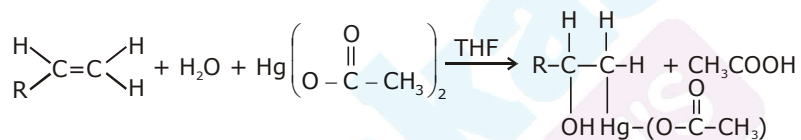
ALCOHOL



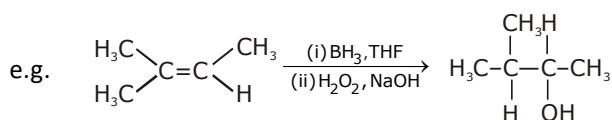
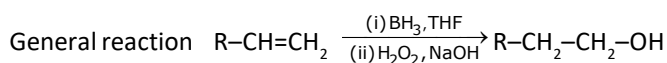
(b) By Oxymercuration - demercuration process :

- (1) Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a mercurinium ion, an organometallic cation containing a three-membered ring.
- (2) In the second step, water from the solvent attacks the mercurinium ion to give (after deprotonation) an organomercurial alcohol.
- (3) The third step is demercuration to remove the sodium borohydride (NaBH_4 , a reducing agent) replaces the mercuric acetate fragment with hydrogen.

General reaction



(c) By Hydroboration - oxidation process : (Forms anti-markovnikov alcohol, no rearrangement)

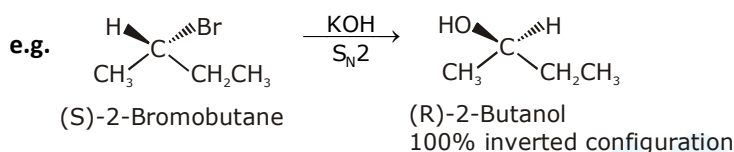
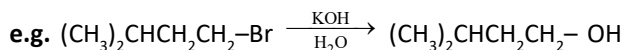
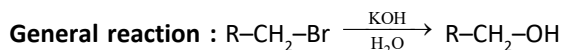


ALCOHOL

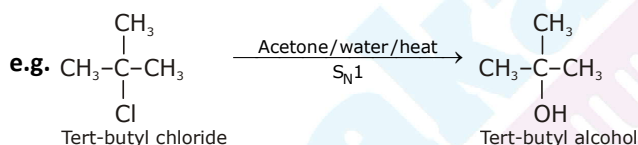
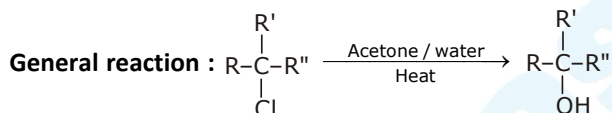


(2) From alkyl halides : By nucleophilic substitution reactions

(a) By S_N2 mechanism (second-order substitution) : It is given by primary (and some secondary) halides



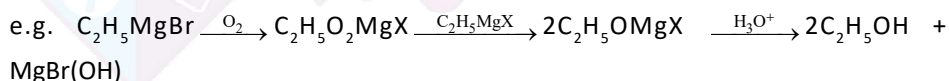
(b) By S_N1 mechanism : It is given by tertiary and some secondary halides



(3) From Grignard reagents

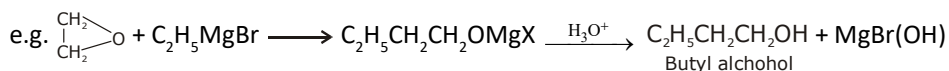
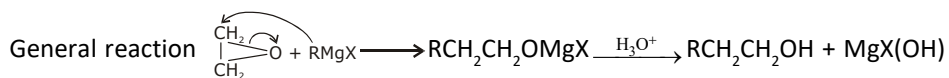
(a) From air

A Grignard reagent may be used to synthesize an alcohol by treating it with dry oxygen and decomposing the product with acid :

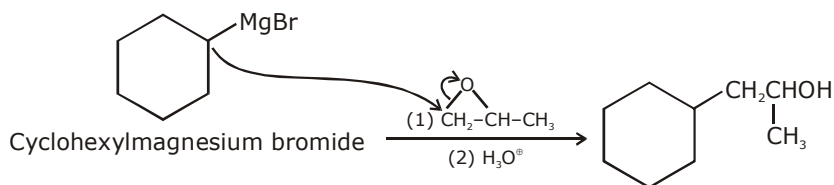


(b) From ethylene oxide

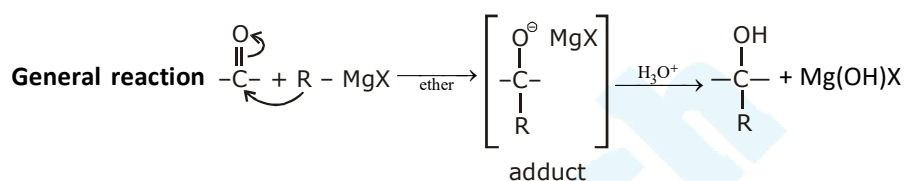
Addition of Grignard reagent to ethylene oxide gives a primary alcohol (with two carbon atoms added)



ALCOHOL



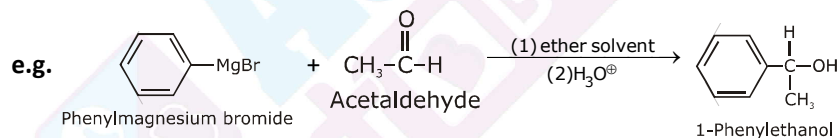
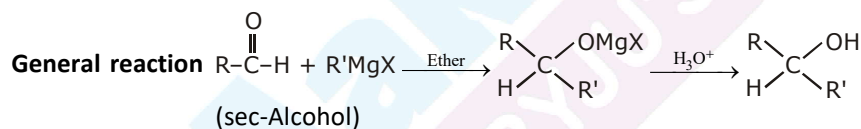
(c) From carbonyl compounds : Nucleophilic addition to the carbonyl groups by Grignard reagent



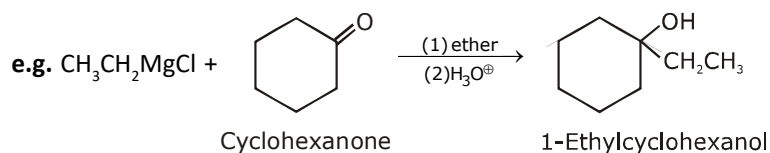
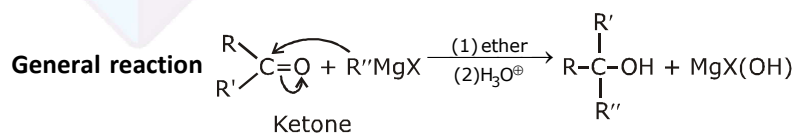
(i) Addition of formaldehyde gives a primary alcohol



(ii) Addition to an aldehyde (other than formaldehyde) gives a secondary alcohol



(iii) Addition to a ketone gives a tertiary alcohol



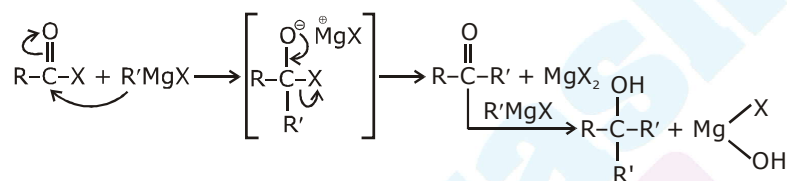
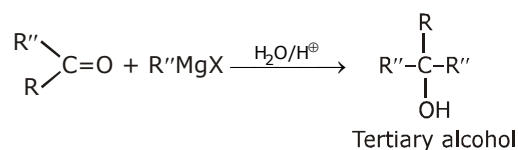
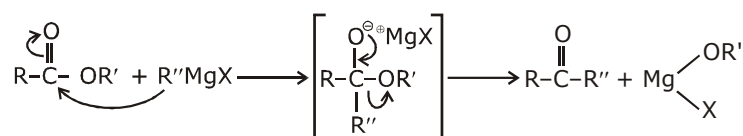
ALCOHOL



(iv) Addition to an acid halide or an ester gives a tertiary alcohol

Esters on treatment with Grignard reagent first form ketones which then react with second molecule of Grignard reagent and form tertiary alcohol.

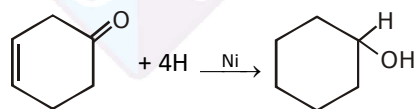
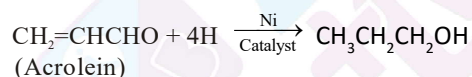
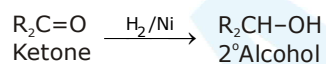
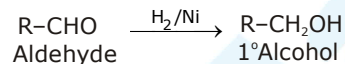
General reaction



(4) By reduction of carbonyl compounds

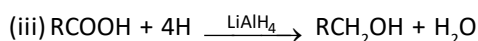
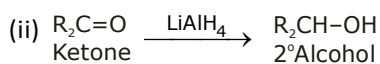
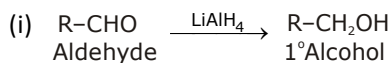
(a) Catalytic hydrogenation of aldehydes and ketones

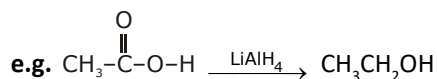
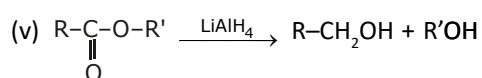
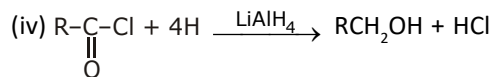
General reaction



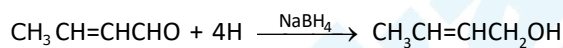
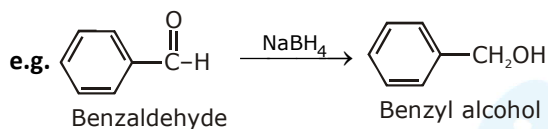
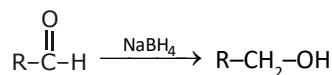
(b) Lithium aluminium hydride reduction of aldehydes and ketones

General reaction

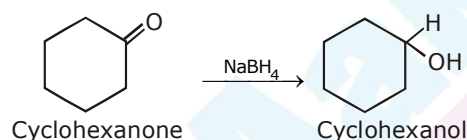




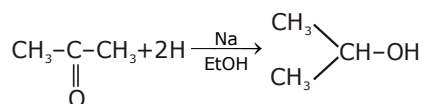
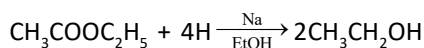
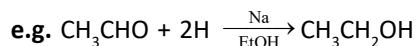
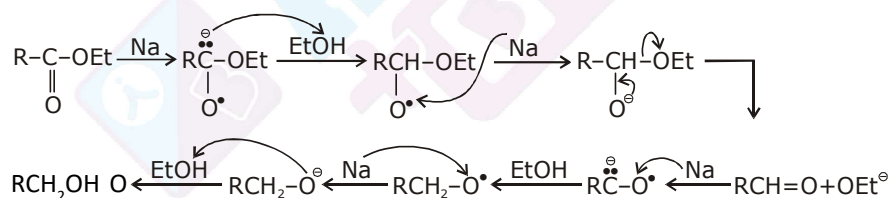
(c) **By NaBH₄ (sodium borohydride)** : It is insoluble in ether and is used in aqueous ethanolic solution to reduce carbonyl compounds. It does not reduce esters and acids.



(ii) Reduction of a ketone gives a secondary alcohol

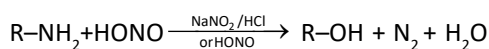


Mechanism



(5) **By reaction of nitrous acid on aliphatic primary amines**

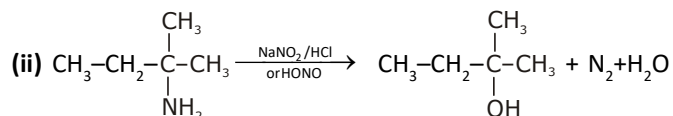
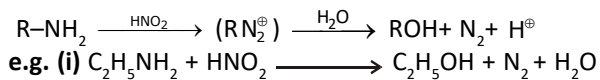
General reaction



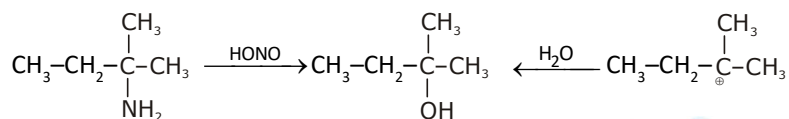
ALCOHOL



Mechanism



Mechanism

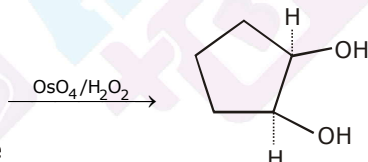
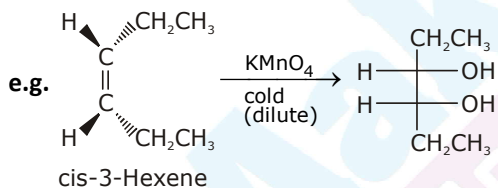
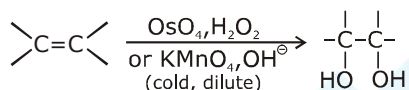


(6) Hydroxylation : Forms vicinal diols (glycols)

Converting an alkene to a glycol requires adding a hydroxy group to each end of the double bond. This addition is called hydroxylation of the double bond.

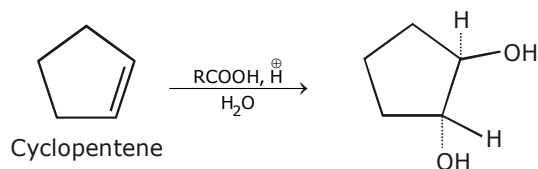
(a) Syn hydroxylation, using $KMnO_4$ / $NaOH$ or using OsO_4/H_2O_2

General reaction :



cis-Cyclopentane-1, 2-diol

(b) Anti hydroxylation, using per acids



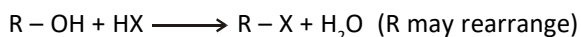
trans-Cyclopentane-1, 2-diol



Chemical reactions of alcohols

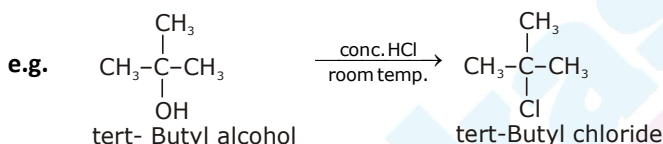
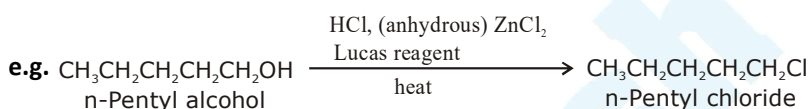
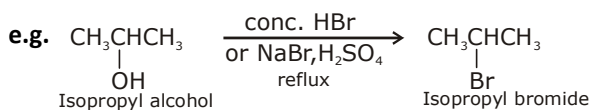
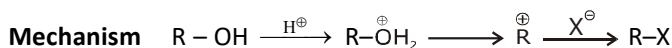
1. Reaction with hydrogen halides

General reaction :



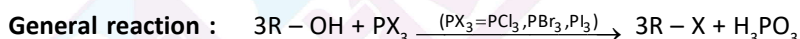
Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : Allyl, benzyl > 3° > 2° > 1°



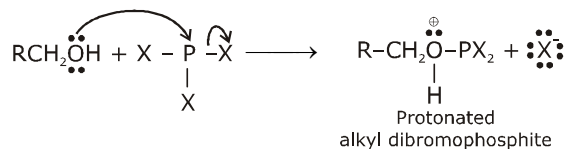
2. Reaction with Phosphorus trihalides

- Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr₃, PCl₃, & PCl₅ work well and are commercially available.
- Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with tertiary alcohols. The two phosphorus halides used most often are PBr₃ and the P₄/I₂ combination.



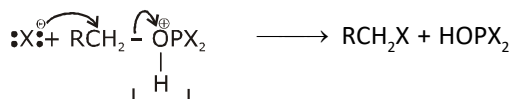
Mechanism

The mechanism for the reaction involves attach of the alcohol group on the phosphorus atom, displacing a bromide ion and forming a protonated alkyl dibromophosphite (see following reaction).

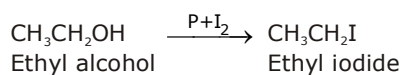
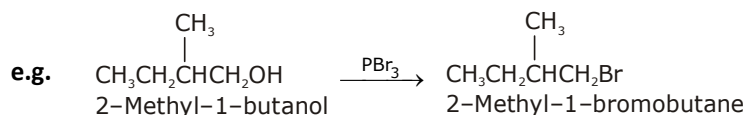


In second step a bromide ion acts as nucleophile to displace HOPBr₂, which is a good leaving group due to the electronegative atoms bonded to the phosphorus.

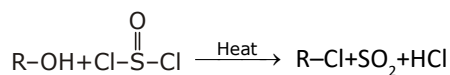
ALCOHOL



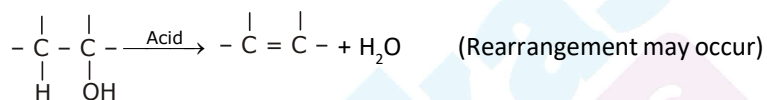
A good leaving group



3. Reaction with thionyl chloride

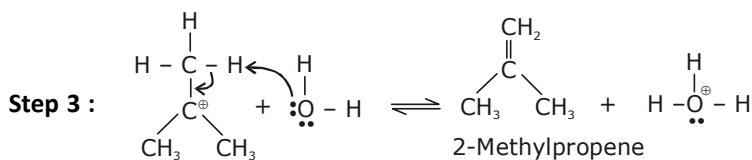
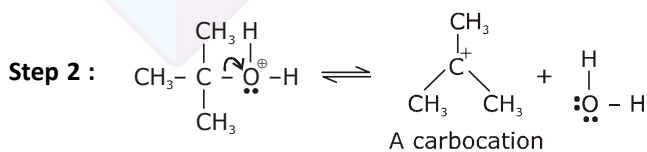
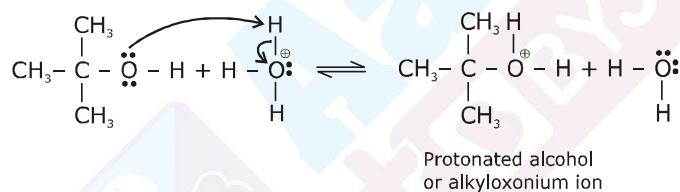


4. Dehydration of alcohols



Mechanism

Step 1 :

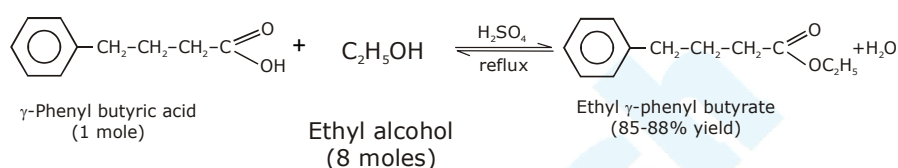
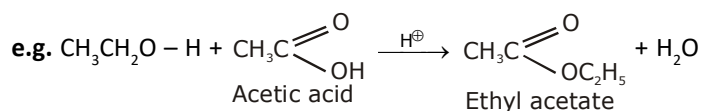
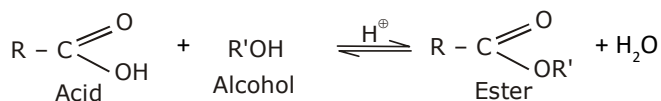


Reactivity of ROH : $3^\circ > 2^\circ > 1^\circ$



5. Ester formation

General reaction



6. Oxidation reactions

(a) oxidation of primary alcohols

Oxidation of a primary alcohol initially forms an aldehyde. Obtaining the aldehyde is often difficult, since most oxidizing agents are strong enough to oxidize the aldehydes formed. CrO_3 acid generally oxidizes a primary alcohol all the way upto the carboxylic acid

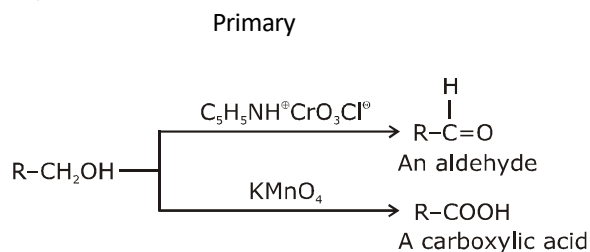
(b) oxidation of secondary alcohols

Secondary alcohols are easily oxidized to give excellent yields of ketones. The chromic acid reagent is often best for laboratory oxidations of secondary alcohols. The active species in the mixture is probably chromic acid,

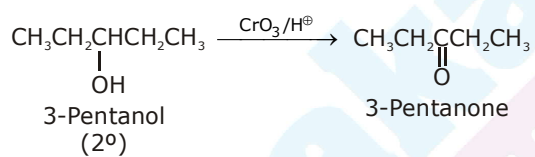
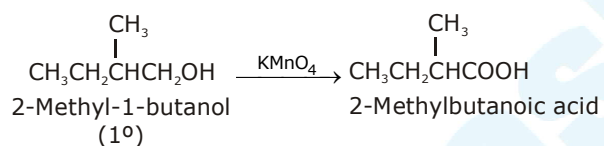
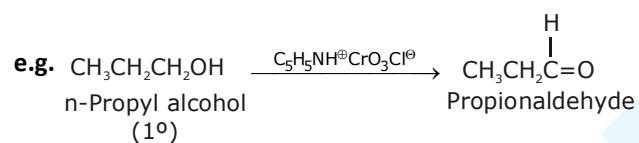
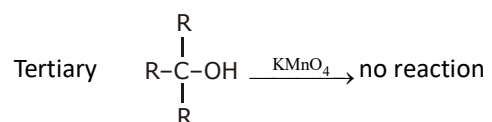
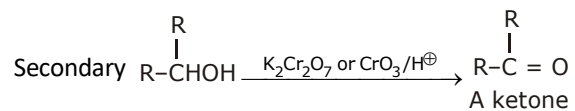
H_2CrO_4 , or the acid chromate ion, HCrO_4^{\ominus}

(c) Resistance of tertiary alcohols to oxidation

Oxidation of tert-alcohol is not an important reaction in organic chemistry. tert-alcohols not have hydrogen atoms on the carbinol carbon atom, so oxidation must take place by breaking C-C bonds. These oxidations require severe conditions and result in mixtures of products.



ALCOHOL





CARBONYL COMPOUND

Introduction

These have general formula $C_nH_{2n}O$ and contains $>C=O$ group which is present in aldehyde

$\begin{matrix} R \\ \diagdown \\ C \\ \diagup \\ H \end{matrix} = O$ and $\begin{matrix} R \\ \diagdown \\ C \\ \diagup \\ R \end{matrix} = O$ ketone. Thus aldehydes and ketones are collectively called as carbonyl compounds.

IUPAC Nomenclature of Aldehydes and Ketones

	Ketones	IUPAC name
1.	$\begin{array}{c} O \\ \\ CH_3 - C - CH_3 \end{array}$	Propanone
2.	$\begin{array}{c} O \\ \\ CH_3 - C - CH_2 - CH_3 \end{array}$	Butanone
3.	$\begin{array}{c} O \\ \\ CH_3 - C - CH_2 - CH_2 - CH_3 \end{array}$	Pentan-2-one
4.	$\begin{array}{c} O \quad O \\ \quad \\ CH_3 - C - C - CH_3 \end{array}$	Butanedione
5.	$\begin{array}{c} CH_3 \quad O \quad CH_3 \\ \quad \quad \\ CH_3 - CH - C - CH - CH_3 \end{array}$	2, 4-Dimethyl pentan-3-one
6.		1-Phenylpropan-1-one
7.		3-Methylcyclopentanone
8.		Cyclohex-2-en-1-one or 2-Cyclohexenone
9.	$\begin{array}{c} O \quad OH \\ \quad \\ CH_3 - C - CH_2 - C - CH_3 \\ \\ CH_3 \end{array}$	4-Hydroxy-4-methyl pentan-2-one

CARBONYL COMPOUND



	Aldehyde	IUPAC name
1.	$\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$	Ethanal
2.	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$	Propanal
3.	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$	Butanal
4.	$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$	3-Hydroxybutanal
5.	$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CHO}$	Pent-2-en-1-al or Pent-2-enal
6.	$\text{CH}_3\text{CH}_2\text{CH}_2 - \underset{\text{Br}}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$	4-Bromo-3-methyl heptanal
7.		Cyclohexanecarbaldehyde
8.		2-Hydroxycyclopentane-1-carbaldehyde
9.	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CHO}$	3-Oxopentanal
10.	$\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{COOH}$	3-Oxobutanoic acid
11.		2-Formylbenzoic acid
12.		2-(3-Oxobutyl)-cyclohexanone
13.		2-Ethylhex-2-en-1-al
14.		2,5-Dimethylheptan-3-one
15.	$\text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH} = \text{O}$	3-Chloro-2-methylbutanal
16.		3-Ethylcyclobutanone

CARBONYL COMPOUND

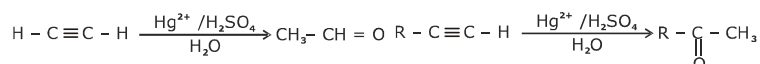


Section A

3. General methods of preparation of Aldehyde and Ketones

(I) Hydration of Alkyne :

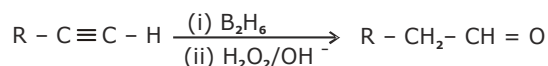
It is addition of water in the presence of heavy metal ion. Acetylene on hydration gives aldehyde while any higher alkyne gives ketone.



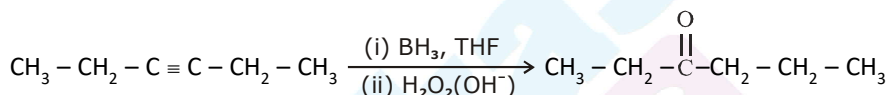
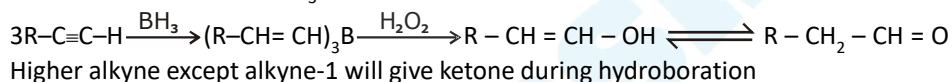
The preparation of carbonyl compounds from alkyne depends upon R part of alkyne and also presence of inductive effect group attached to R.

(II) Hydroboration of alkyne :

It is used to get aldehyde from alkyne-1. Here reagents are (i) diborane (B_2H_6) (ii) $\text{H}_2\text{O}_2(\text{OH}^-)$

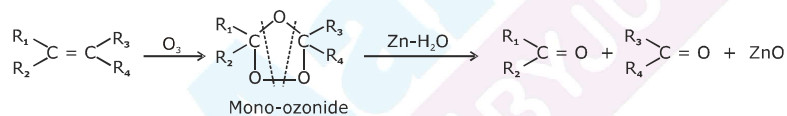


In this reaction Borane (BH_3) is electrophile.

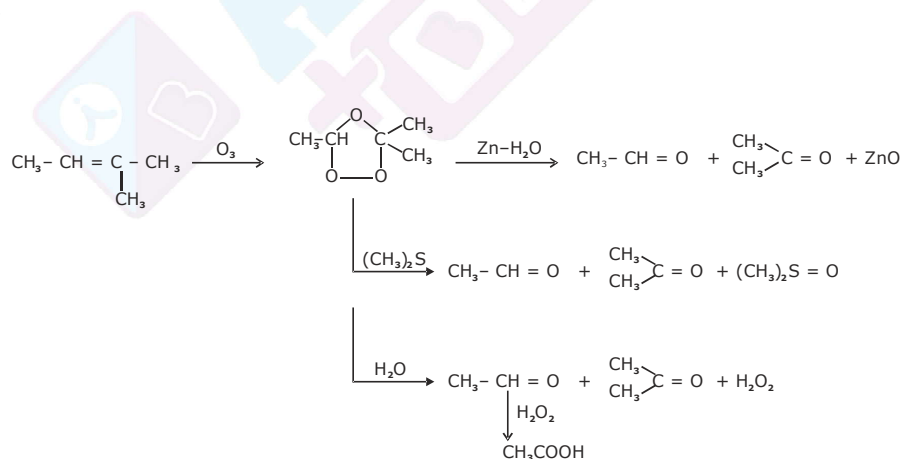


(III) Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is



Ex.



CARBONYL COMPOUND

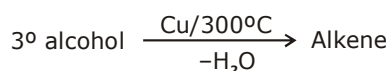
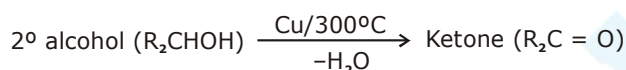
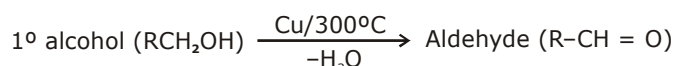


Note :

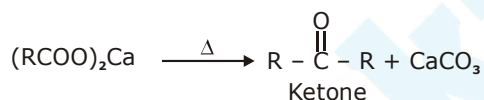
- (I) During the cleavage of ozonide Zn is used to prevent further oxidation of aldehyde into acid.
- (II) By this method we can locate double bond in olefin or exact structure of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen of two carbonyl compounds.

(IV) Dehydrogenation of Alcohol :

Dehydrogenation means removal of hydrogen and the reagent used is heated copper.

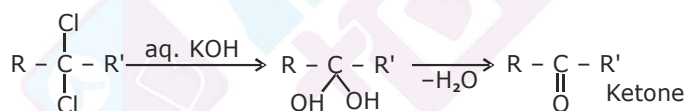
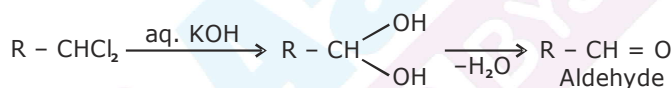


(V) Dry distillation of Calcium salt of acid :



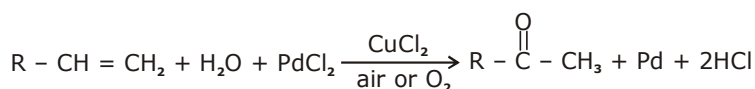
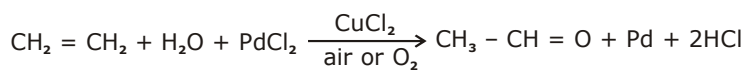
(VI) On aqueous alkali hydrolysis of gem-dihalides :

Terminal gemdihalides will give aldehyde while non-terminal will give ketones as follows,



(VII) Wacker Process :

Alkenes can directly be oxidised to corresponding aldehydes or ketone by treating them with a solution of PdCl_2 containing a catalytic amount of CuCl_2 in presence of air or O_2 . Except ethene any higher alkene will give ketone.



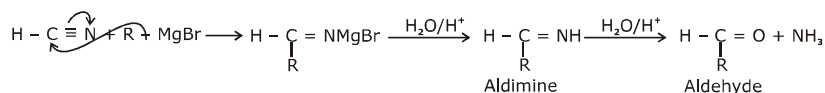
Note : During the reaction PdCl_2 is reduced to Pd and CuCl_2 is reduced to Cu(I)

CARBONYL COMPOUND

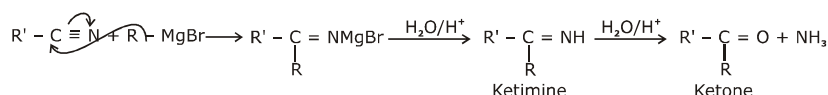


(VIII) Preparation of Carbonyl compounds using Grignard's Reagent :

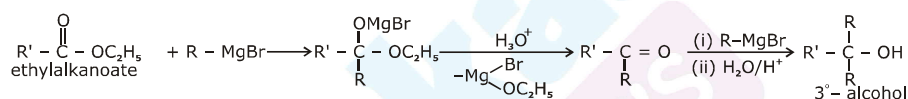
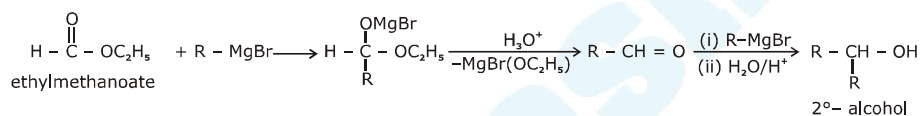
(a) Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives aldehyde via imine.



Alkylcyanide by using above process gives ketone via ketimine



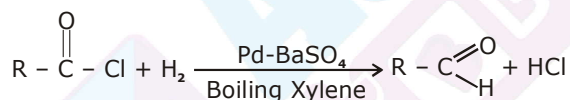
(b) Alkyl formate with Grignard reagent gives 2° alcohol via aldehyde, while alkyl alkanoate under similar condition gives 3° alcohol via ketone



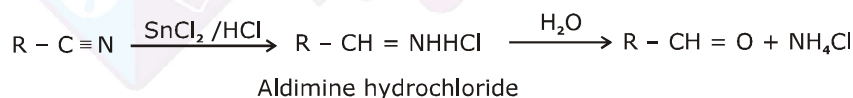
(A) Methods used for the preparation of Aldehydes only.

(i) Rosenmund's reaction :

Here acid chlorides are reduced to aldehyde with H₂ in boiling xylene using palladium as a catalyst supported on barium sulphate.

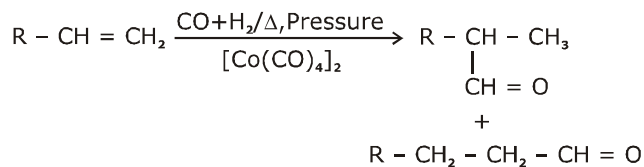


(ii) Stephen's reduction :



(iii) Oxo-process :

It is also called as formylation, here alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.



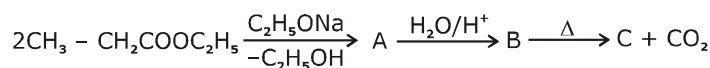
CARBONYL COMPOUND



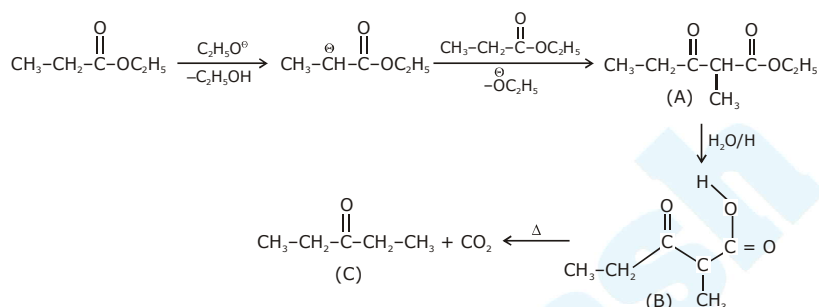
Note :

(ii) If two ester units are same then it is intermolecular Claisen ester condensation

Q. Predict the unknown (s) for the following :

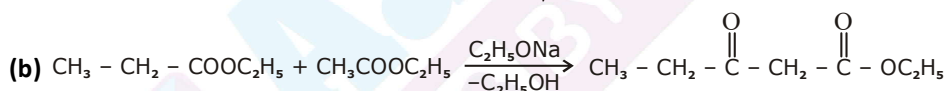
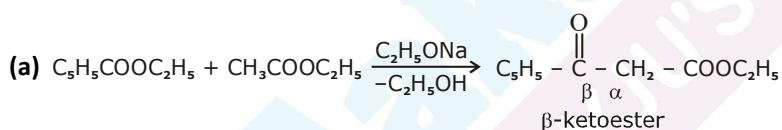


Sol.



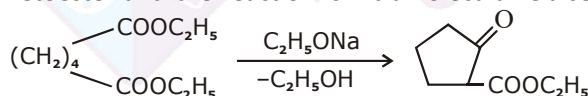
Note :

(iii) If two ester units are different then it is crossed Claisen ester condensation



Note :

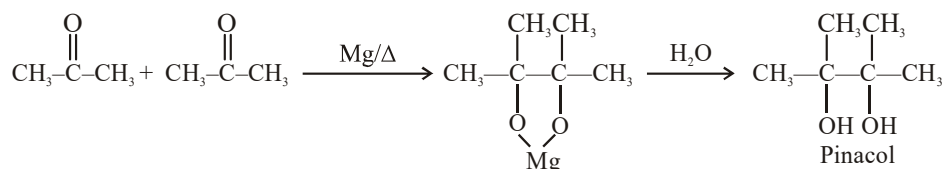
(iv) If two ester units are present with in the same molecule then we get cyclic β-ketoester and the reaction is intramolecular Claisen ester condensation.



Note : Active methylene group hydrogen is too acidic that it can be replaced by alkyl or aryl halide in the presence of base like sodium ethoxide.

(C) Pinacol-Pinacolone rearrangement :

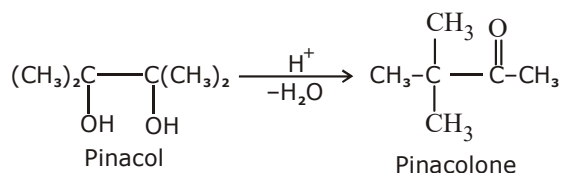
Pinacol is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water.



CARBONYL COMPOUND



Pinacol undergoes rearrangement in acidic media to give pinacolone

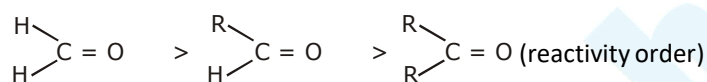


Section B

4. Chemical Reactions of Carbonyl Compounds :

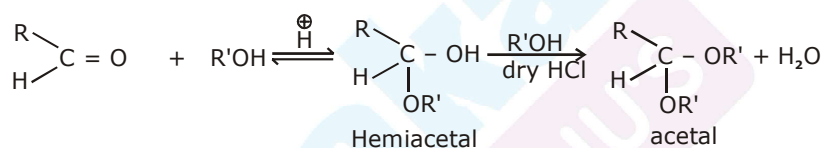
Carbonyl compounds undergo nucleophilic addition reaction and reactivity order will be :

(I) Nucleophilic Addition Reaction :



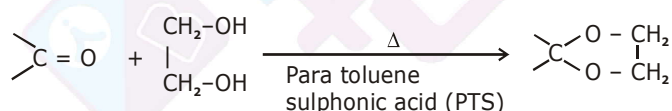
(i) Reaction with alcohol :

Carbonyl compounds react with alcohols in the presence of dry HCl gas to give acetal (if aldehyde) and ketal (if ketone) via formation of unstable hemiacetal and hemiketal respectively.

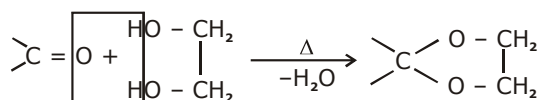


Note :

- (i) Acetal is formed to protect aldehyde for a long time.
- (ii) Acetal has ether as the functional group.
- (iii) Acetal formed can be decomposed to original aldehyde by dilute acids.
- (iv) On treating with ethylene glycol we get cyclic acetal or ketal (1, 3-dioxolane)



Mechanism :



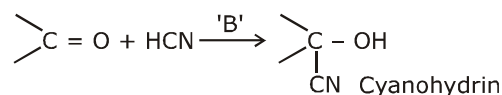
- (v) Acetal formation is found to be more favourable than ketal formation if both the carbonyl groups are present within the molecule.

CARBONYL COMPOUND

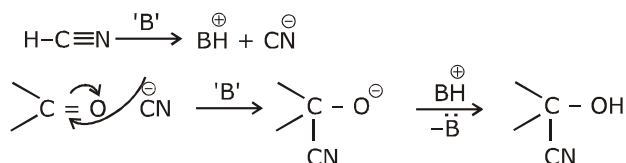


(ii) Addition of HCN :

Base catalysed addition

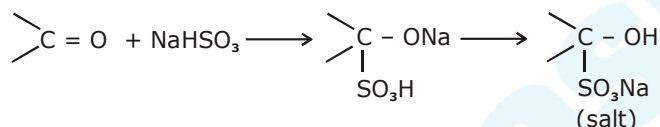


Mechanism:

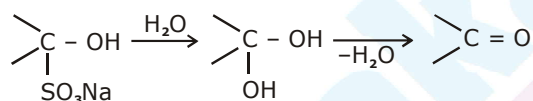


(iii) Addition of sodium bisulphite (NaHSO₃):

This addition is used to isolate carbonyl compounds from the mixture as we get salt.

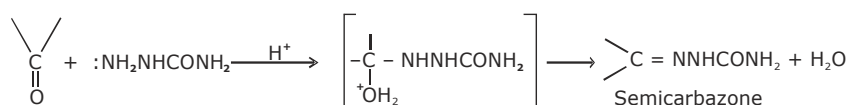
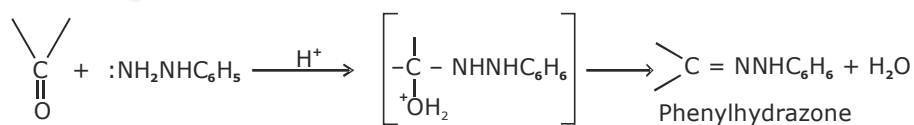
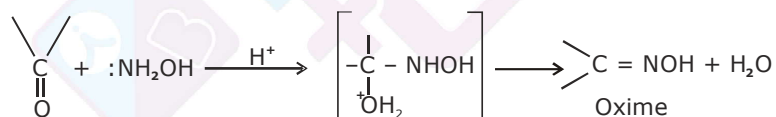


Salt on acidification gives carbonyl compounds again.



(II) Addition elimination reactions :

Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and ketones, the product contain a carbon nitrogen double bond resulting from elimination of a molecule of water from the initial addition products.

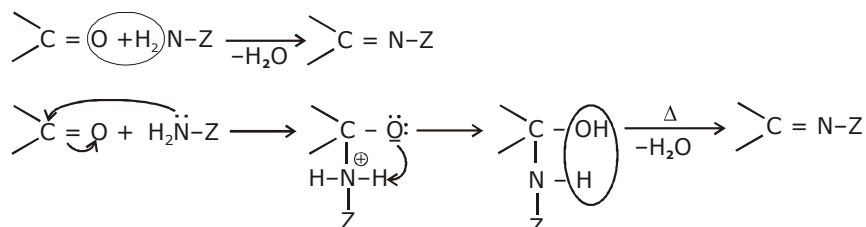


CARBONYL COMPOUND

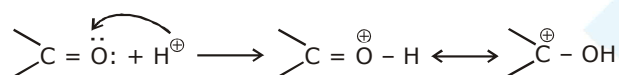


(i) Reaction with ammonia derivatives ($\text{H}_2\ddot{\text{N}}-\text{Z}$) :

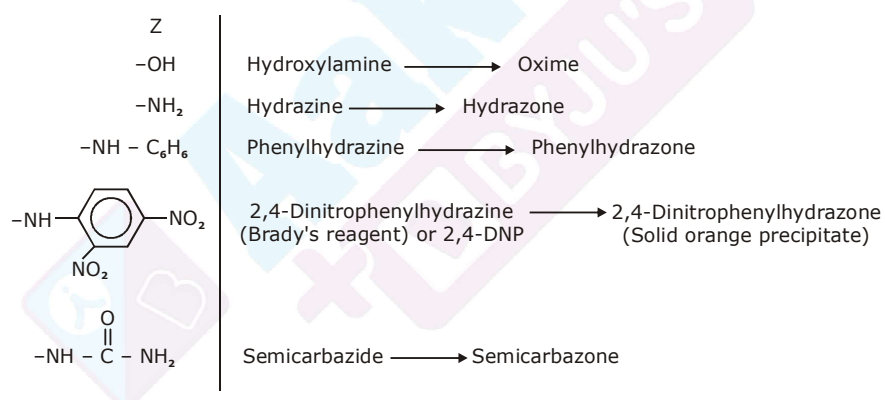
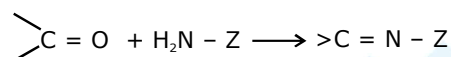
This reaction is nucleophilic followed by water elimination :



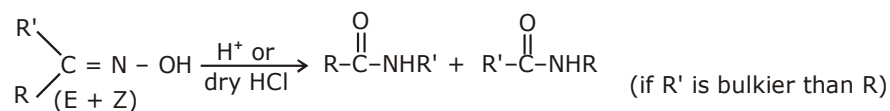
This reaction is carried out in slightly acidic media which will generate a nucleophilic centre for weak base ammonia derivatives.



On using strong acidic media lone pair of electrons present at N-atom of ammonia derivatives will accept proton forming protonated ammonia derivatives which cannot act as nucleophile for carbonyl carbon.



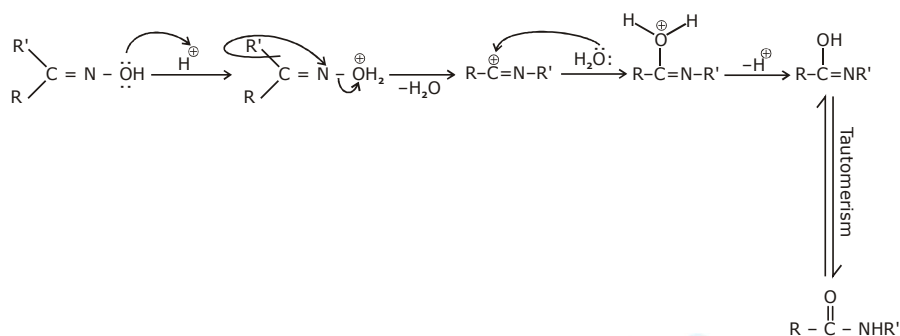
(III) Beckmann Rearrangement in Oxime :



CARBONYL COMPOUND

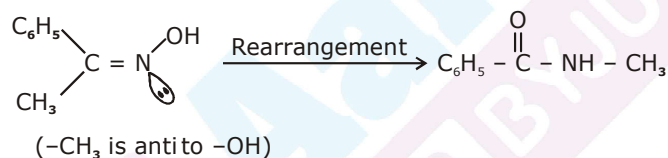
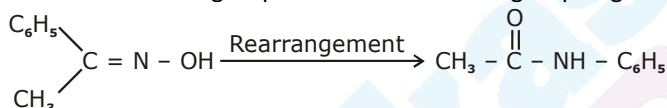


Mechanism :



Note :

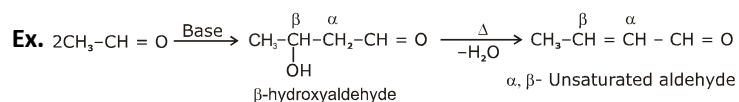
- Brady's reagent is used to distinguish carbonyl compounds from the mixture.
- Oxime undergoes Beckmann rearrangement to give its isomer amide.
- In this reaction the group which is anti to $-\text{OH}$ group migrates.



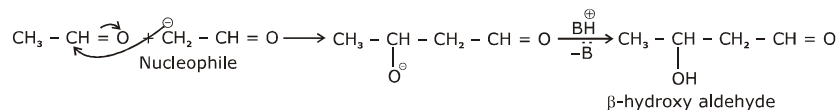
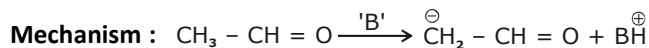
Section C

(IV) Aldol Condensation :

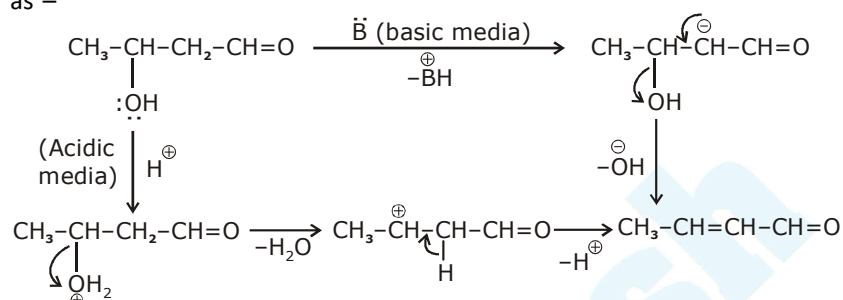
It is condensation between two moles of carbonyl compounds among which at least one must have two α -hydrogen atoms in dilute basic media to get α,β -unsaturated aldehyde / ketone via the formation of β -hydroxy aldehyde / ketone.



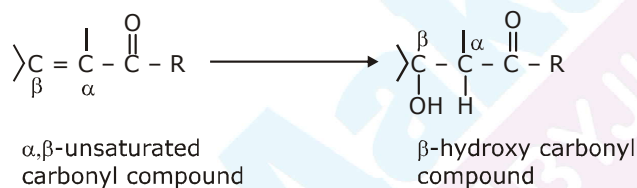
CARBONYL COMPOUND



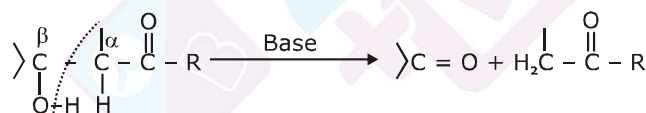
From β -hydroxy aldehyde / ketone, water is eliminated on using either acidic or basic media as –



Now try to get carbonyl compounds from α, β -unsaturated carbonyl compounds as –
 Keep 'H' at α -position and $-\text{OH}$ at β -position of α, β unsaturated carbonyl compounds to get β -hydroxy carbonyl compounds.



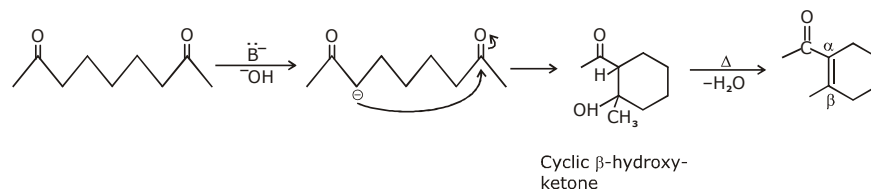
Now break α and β carbon as shown below to get carbonyl compound.



These two carbonyl compounds can be obtained on ozonolysis of hydrocarbon $\text{>C} = \underset{\text{R}}{\text{C}} - \text{CH}_2$

if it is asked.

Intramolecular aldol condensation :

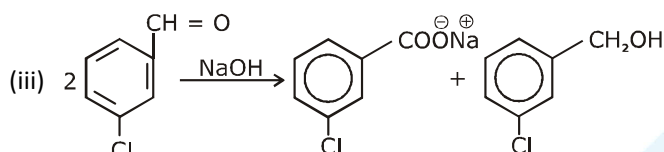
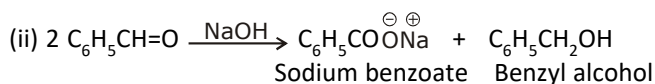
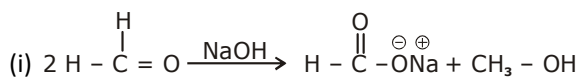


CARBONYL COMPOUND



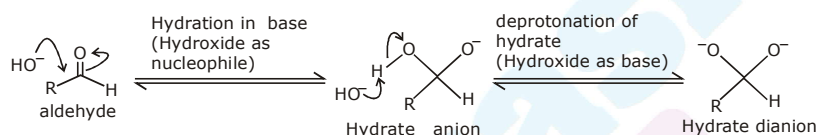
(V) Cannizzaro reaction :

Carbonyl compounds having no α -hydrogen atom undergo disproportionation or redox reaction in strong basic media.



These reaction are intermolecular cannizzaro reaction :

Mechanism :



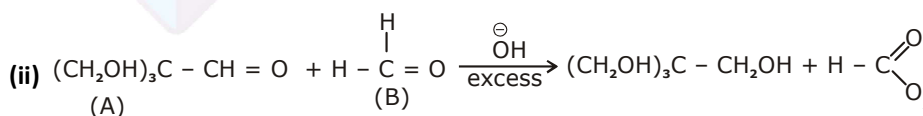
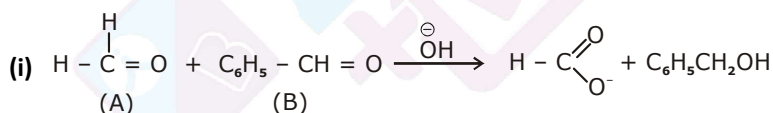
By this mechanism it is clear that acid is corresponding to that carbonyl compound over which OH is going easily as nucleophile.

Note : It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

Crossed Cannizzaro reaction :

On using two types of carbonyl compounds having no α -hydrogen atom, acid will be corresponding to that aldehyde over which OH will approach without any hindrance.

Example

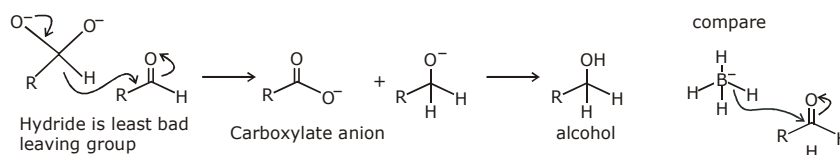
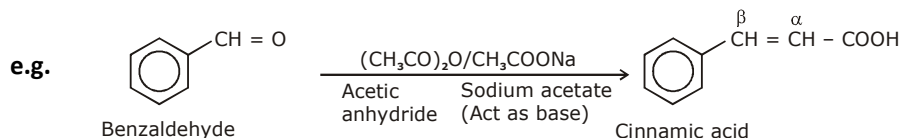


In case (i) OH will easily go to (A) and in case (ii) it will go to (B) hence acid will be formate ion in both the cases.

(VI) Perkin reaction :

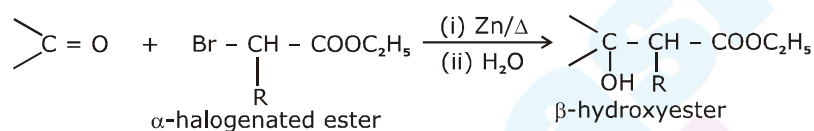
When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived, we get α,β -unsaturated acid.

CARBONYL COMPOUND

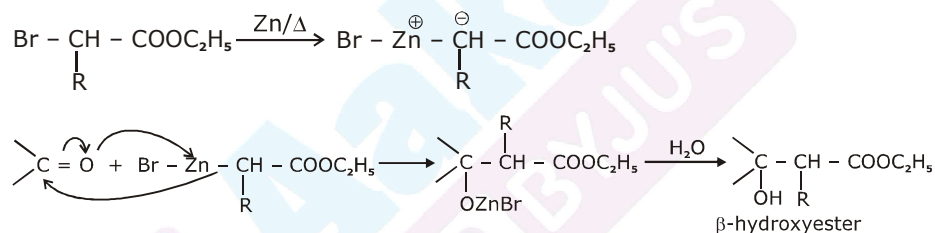


(VII) Reformatsky reaction :

When carbonyl compound and α -halogenated ester are heated with zinc followed by treating with water we get β -hydroxyester.

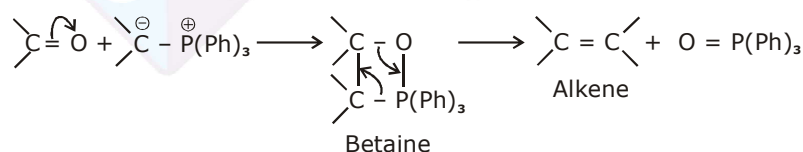


This reaction can be represented as –

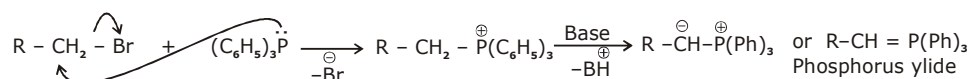


(VIII) Wittig reaction :

It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.



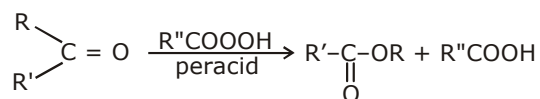
Note : Phosphorus ylides are prepared from alkyl halide and triphenylphosphine in the presence of base like sodium ethoxide as –



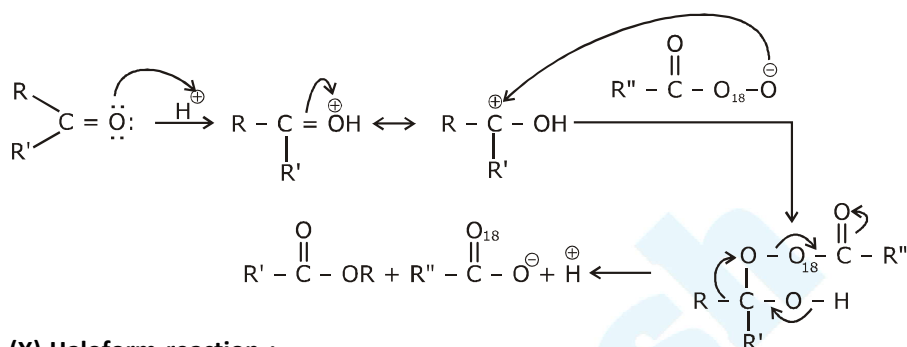
CARBONYL COMPOUND



(IX) Baeyer-Villiger oxidation : It is the preparation of ester from ketone using peracid.

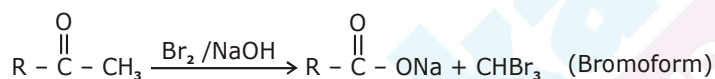


Mechanism :



(X) Haloform reaction :

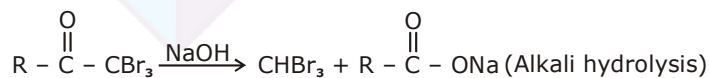
Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2 , Br_2 or I_2) in the presence of alkali to give haloform and acid salt.



In this reaction $-\text{CH}_3$ of $\text{CH}_3-\text{C}(=\text{O})-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having one less carbon atom corresponding to alkyl ketone.

(a) Halogenation

(b) Alkaline hydrolysis



Note : This reaction is used to distinguish the presence of $\text{CH}_3-\text{C}(=\text{O})-$ group.

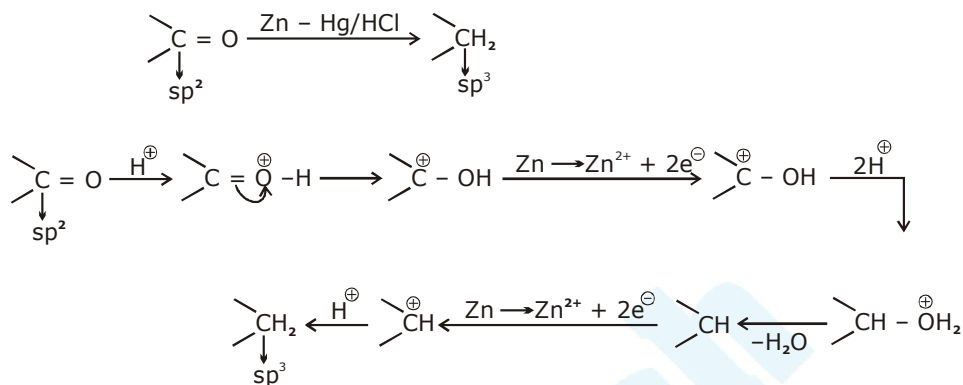
CARBONYL COMPOUND



Section D

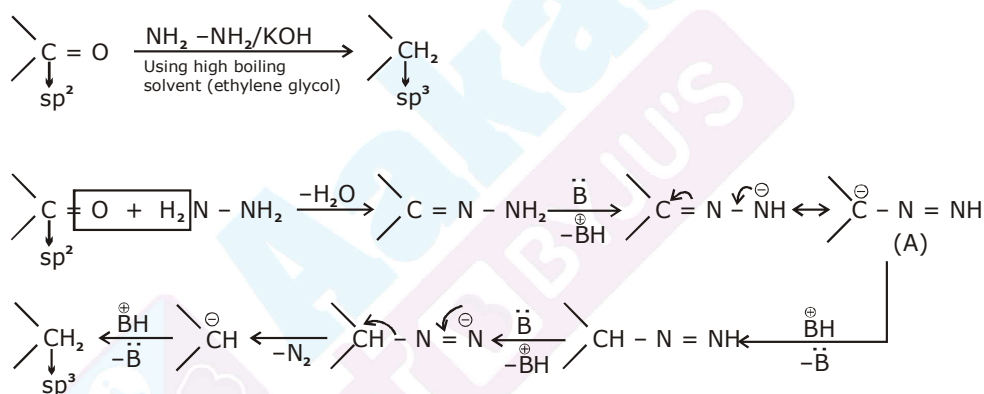
(XI) Clemmensen reduction :

Used to get alkane from carbonyl compounds.



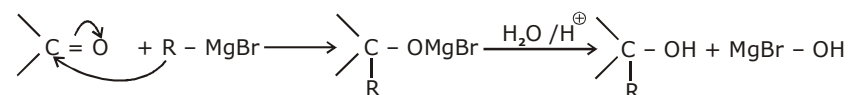
(XII) Wolff-Kishner reduction :

(Used to get alkane from carbonyl compounds)



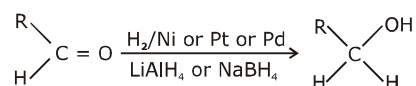
(XIII) Addition of Grignard reagent over Carbonyl compound :

It gives alcohol

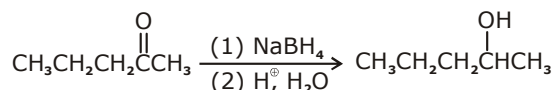
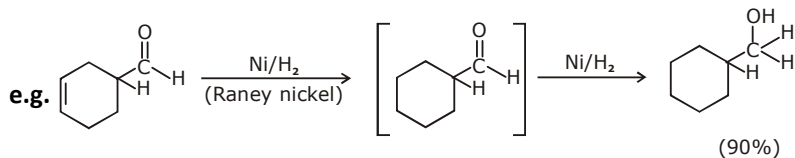


(XIV) Reduction of Carbonyl Compounds :

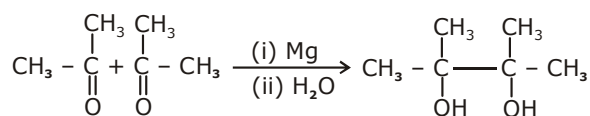
(i) Reduction to alcohols



CARBONYL COMPOUND

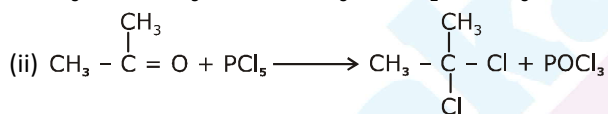
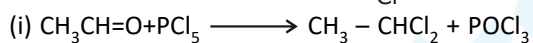
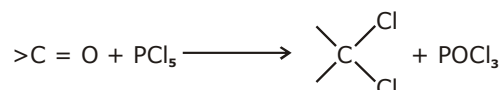


(ii) Reduction to pinacols

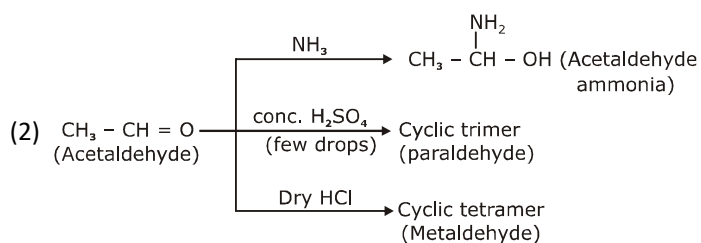
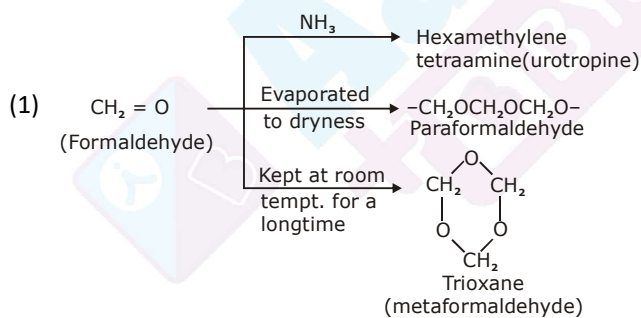


(XV) Reaction with PCl_5 :

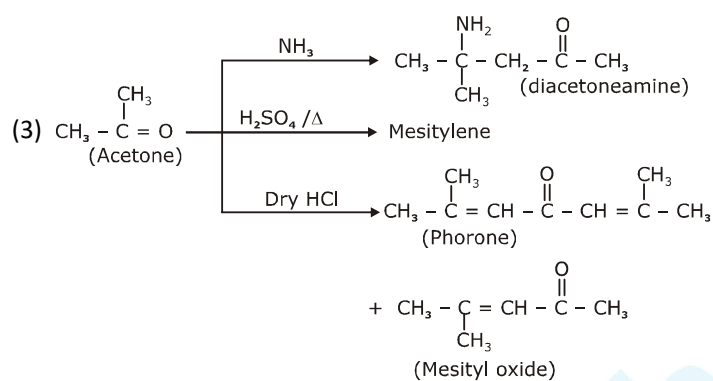
Carbonyl compounds give geminal dihalides



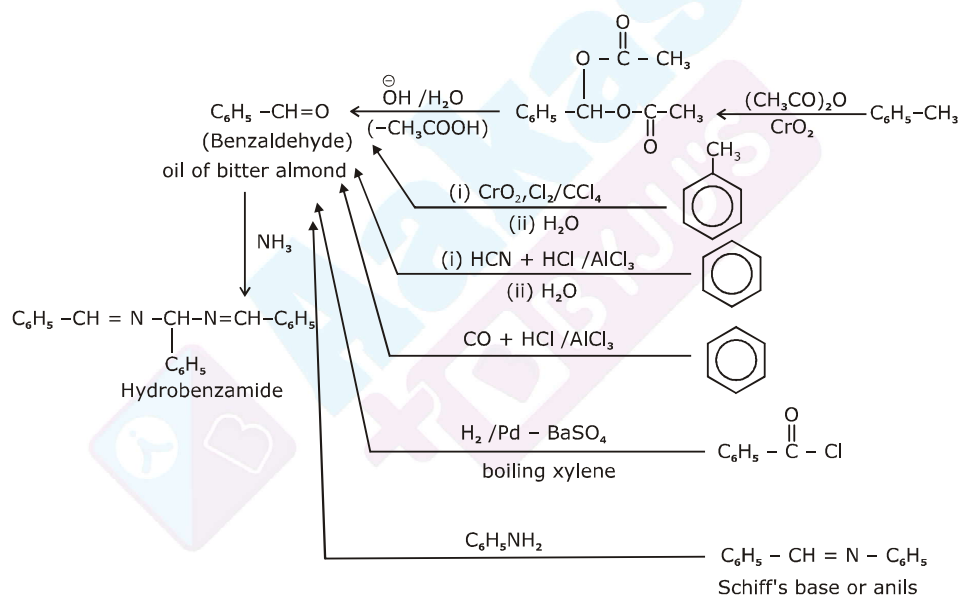
Other reaction :



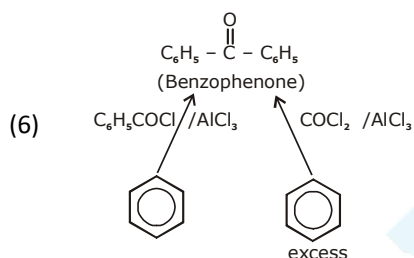
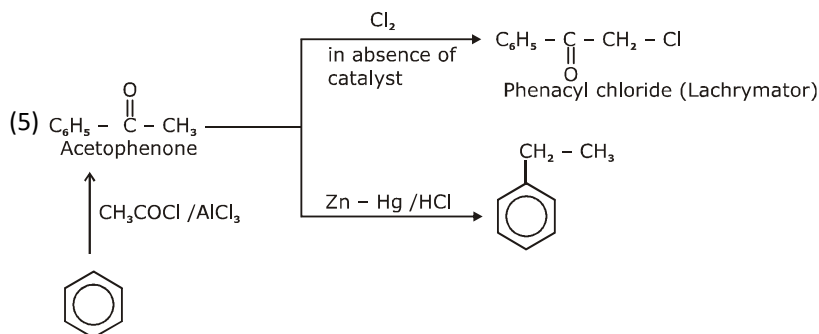
CARBONYL COMPOUND



(4)



CARBONYL COMPOUND

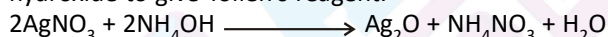


Section E

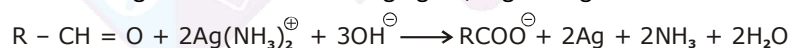
Some important reagents used for identification of aldehyde.

(i) Tollen's reagent :

It is an ammoniacal silver nitrate solution, prepared by adding ammonium hydroxide to AgNO_3 solution. During reaction, first Ag_2O is formed which is dissolved in ammonium hydroxide to give Tollen's reagent.

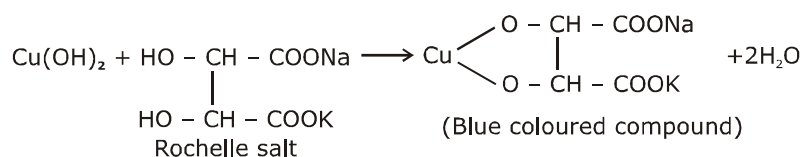
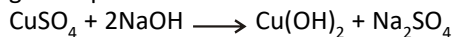


Tollen's reagent is a weak oxidising agent, it gives Ag mirror test with aldehyde.



(ii) Fehling's solution :

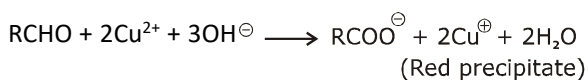
It is an alkaline solution of cupric ion complexed with sodium potassium tartrate. Two solutions are kept by naming Fehling solution (I) (CuSO_4 solution) and Fehling solution (II) (Alkaline solution of sodium potassium tartrate). When these two solutions are mixed we get deep blue coloured solution.



CARBONYL COMPOUND

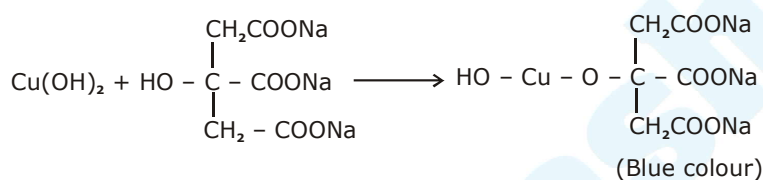
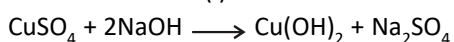


Equal volume of both the solution are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.



(iii) Benedict solution :

It is a solution of CuSO_4 , sodium citrate and sodium carbonate. It also consists of two solution. Solution (I) is alkaline solution of sodium citrate and solution (II) is CuSO_4 solution.



Aldehyde gives positive test with Benedict solution.

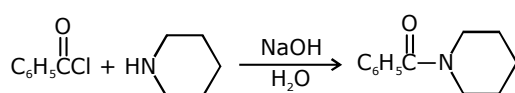
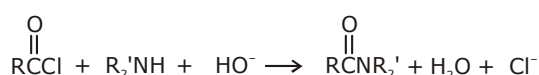
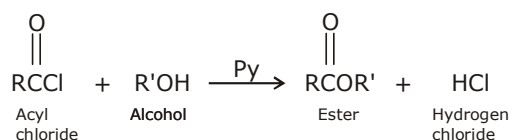
(iv) Schiff's reagent :

It is a dilute solution of rosaniline hydrochloride whose red colour has been discharged by passing SO_2 . Aldehyde restores red colour when treated with schiff's reagent (Magenta solution in H_2SO_4).

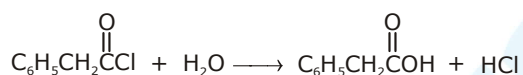


Reaction with alcohols :

Acyl chlorides react with alcohols to form esters. The reaction is typically carried out in the presence of pyridine.

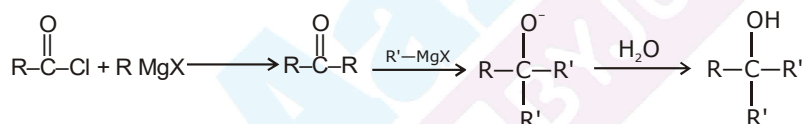


Hydrolysis :



Reaction of acid halide with organometallic reagent :

(a) With Grignard reagent

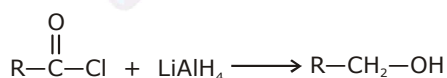


(b) Reaction with Gilman reagent

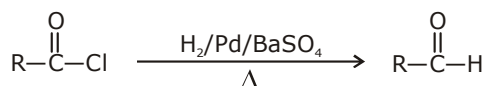


Reduction of acid halide

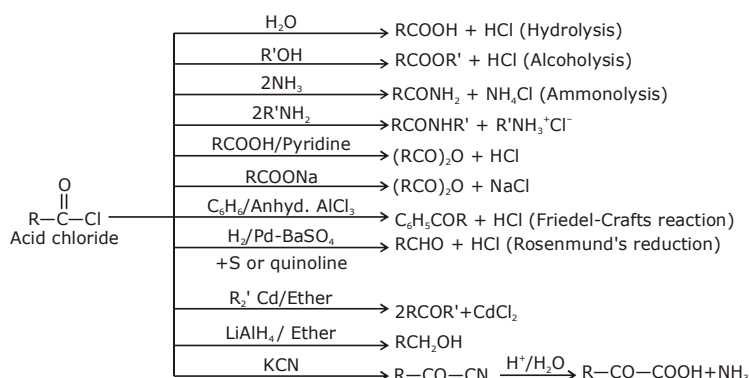
(a) Reduction with LiAlH_4



(b) Reduction with $\text{H}_2/\text{Pd}/\text{BaSO}_4$ (Rosenmund reduction)



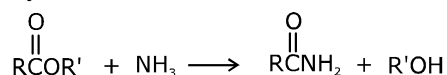
CARBOXYLIC ACID & IT'S DERIVATIVES



Acid Amides

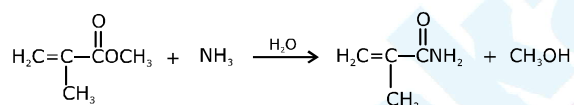
Methods of preparation of acid amides

1. By reaction of esters with ammonia and amines :

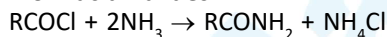


Ammonia is more nucleophilic than water, making it possible to carry out this reaction using aqueous ammonia.

Ex.



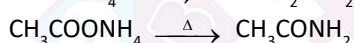
2. From acid halides :



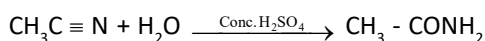
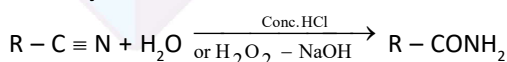
3. From anhydride :



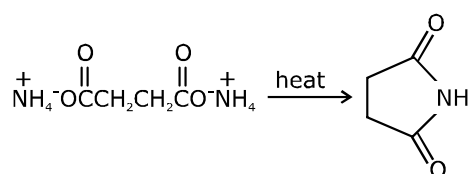
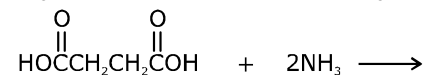
4. From ammonium salt of carboxylic acid :



5. From cyanides :



6.

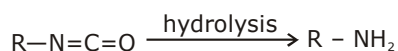
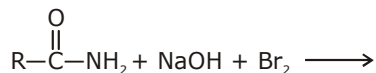




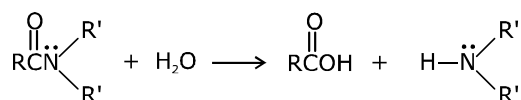
Chemical reactions

Hoffmann rearrangement

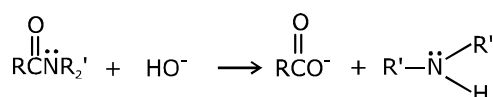
General reaction :



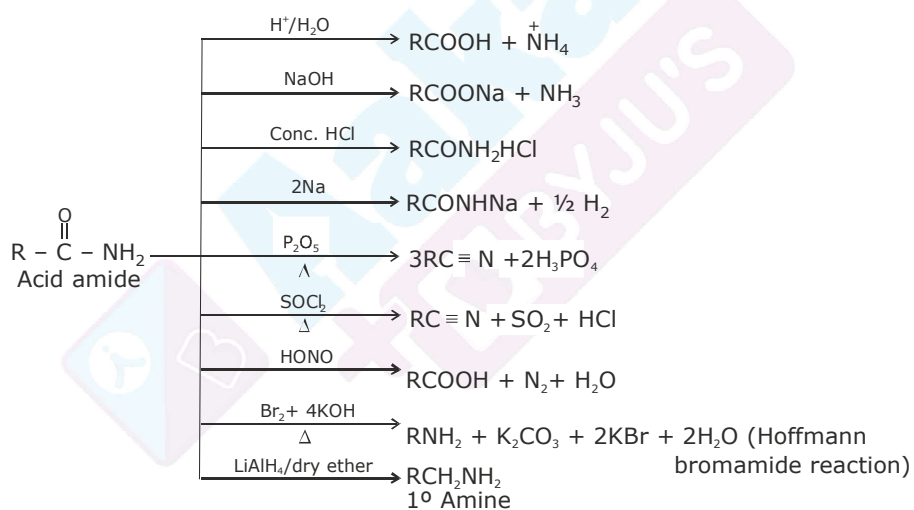
Hydrolysis of amides :



In acid, however, the amine is protonated, giving an ammonium ion, $\text{R}_2\overset{+}{\text{N}}\text{H}_2$

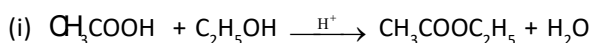


Summary of reaction of amide:

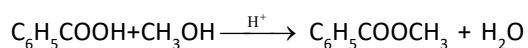


Esters

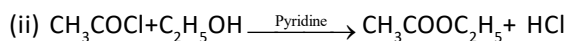
Methods of Preparation



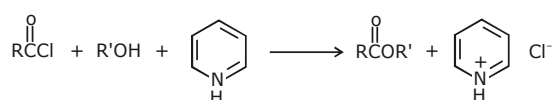
Acetic acid



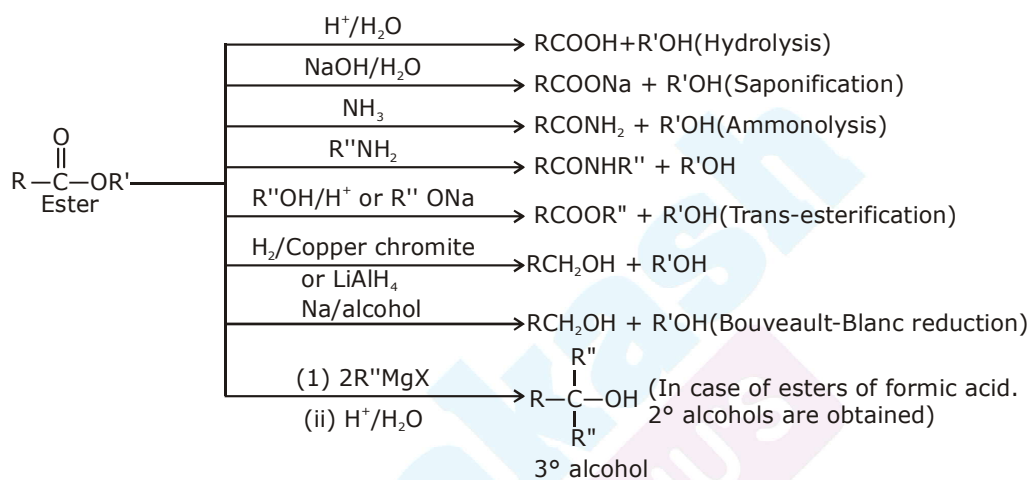
CARBOXYLIC ACID & IT'S DERIVATIVES



Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.



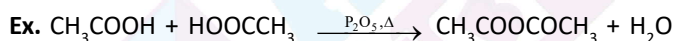
SUMMARY OF REACTION OF ESTERS



Acid anhydrides

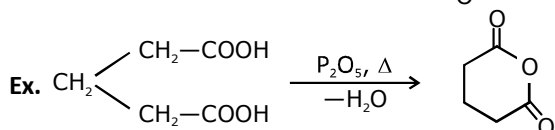
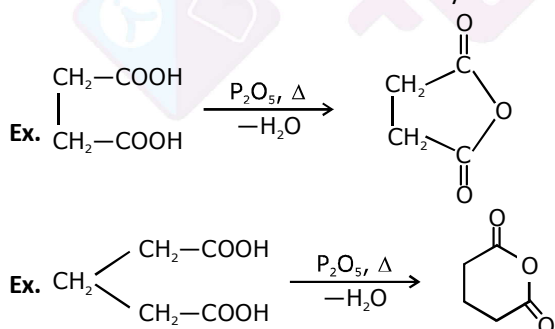
Methods of preparation of acid anhydrides

1. From carboxylic acids :



Acetic acid

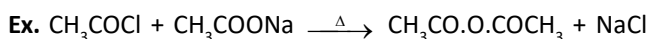
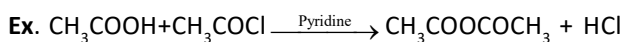
Acetic anhydride



CARBOXYLIC ACID & IT'S DERIVATIVES

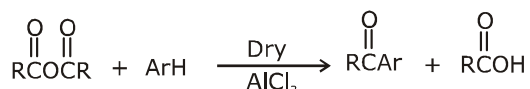


2. From acid and acid halide :

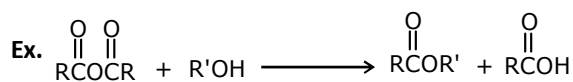


Chemical reactions

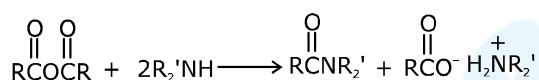
1. Reaction with aromatic compounds (Friedel crafts acylation)



2. Reaction with alcohols :

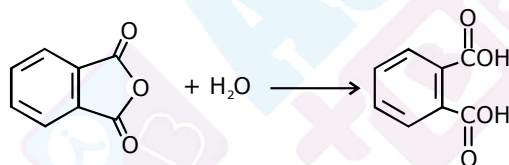


3. Reaction with ammonia and amines :



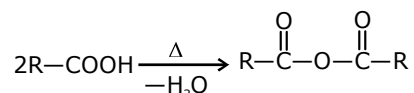
4. Hydrolysis :

Acid anhydrides react with water to yield two carboxylic acids. Cyclic anhydrides yield dicarboxylic acids.

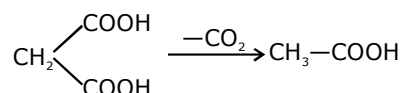


5. Heating Effects :

(a) Heating effect on monocarboxylic acid

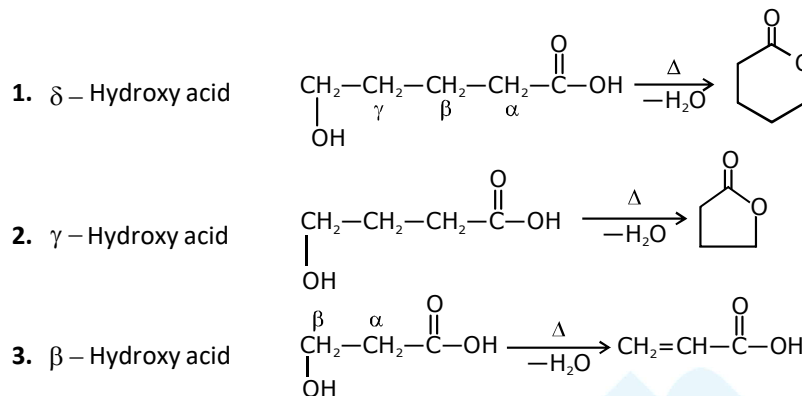


(b) Heating effect on dicarboxylic acid

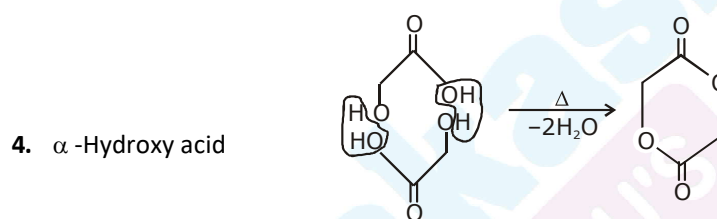




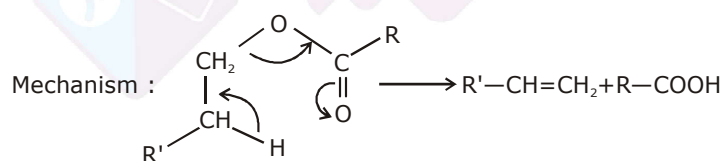
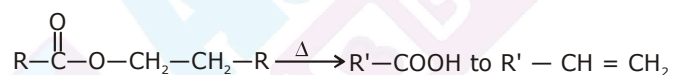
(c) Heating effect on Hydroxy acids



Since 4 or 8 membered rings are less stable therefore β -Hydroxy acids on heating produce α, β -unsaturated carboxylic acid.



• Heating effect on esters



This reaction follows syn elimination & Hoffmann product is formed.