ALKYL HALIDES

Replacement of one or more Hydrogen atoms by halogen atom (s)in hydrocart gives Halo hydrocarbons (or)Alkyl halides.

The general formula of Alkyl halides is C,H_2n+iX.

Nomenclature:

Formula	Common name	IUPAC Name
CH_3-Cl	Methyi Chloride	Chloro methane
CH_3-CH_2-Cl	Ethyl chloride	Chloro Ethane
CH_3-CH_2-CH_2-Cl	n-propyi chloride	1-chloro propane
CH—CH——CH	Iso propyl chloride	2-chloro propane

Classification of alkyl halides

Compounds containing Sp^3C-X bond:

1)Alkyl halides:The compounds in which halogen atom is attached to Sp^3hybridised atom are called Alkyl halides

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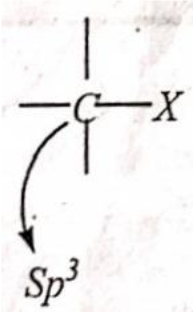
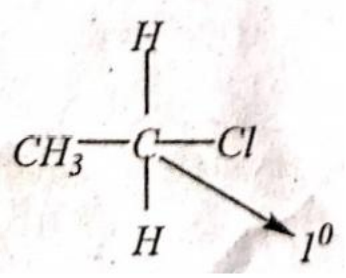
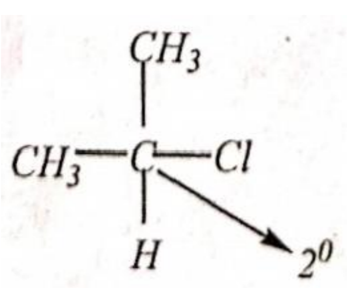


(X=F/Cl/Br/I)

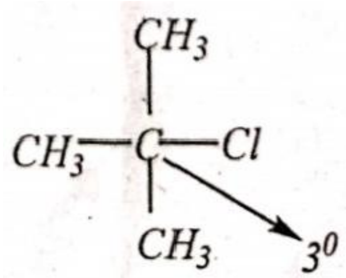
Further alkyl halides may be primary 19,secondary 20 and Tertiary 30 depend upon whether the halogen atom is attached to a 10,20 and 30 carbon atom.



1^0-alkyl halide

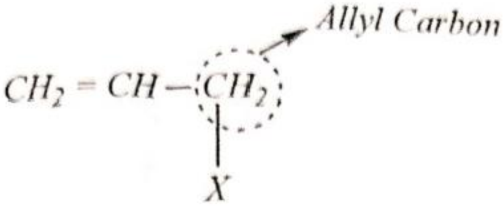


20 -alkyl halide

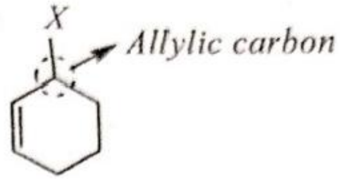


30 -alkyl halide

2) Allylic halides :In these compounds the halogen atom is bonded to an Sp^3hybridised carbor atom next to carbon-carbon double bond (C=C)

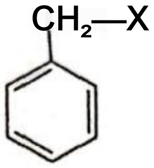


Allylic halide

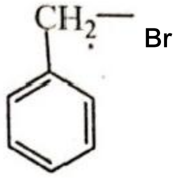


a)Benzylic halides and Aralkyl halides:The compounds in which the halogen atom is bonded tc an Sp^3-hybridized carbon atom next to an aromatic ring

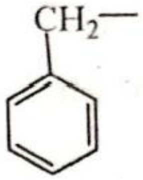
Ex:-



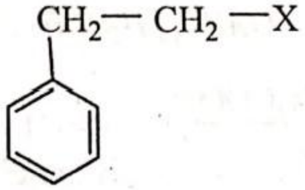
Benzyl halide



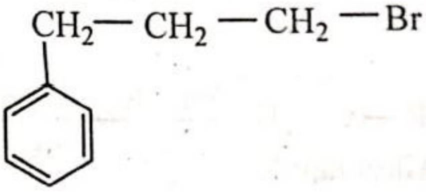
Benzyl bromide



Benzyl group



Aralkyl halide



1-bromo-3 -phenyl propane

)compounds containing Sp^2C-X bond:

1.Vinyl halides:The compounds in which the halogen atom is directly attached to Sp^2-hybridised carbon atom(or)a unsaturated system.

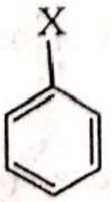
Ex: $CH_2{=}{=}CH—X$

(Sp2)

$CH_2=CH—Cl$

Vinyl chloride

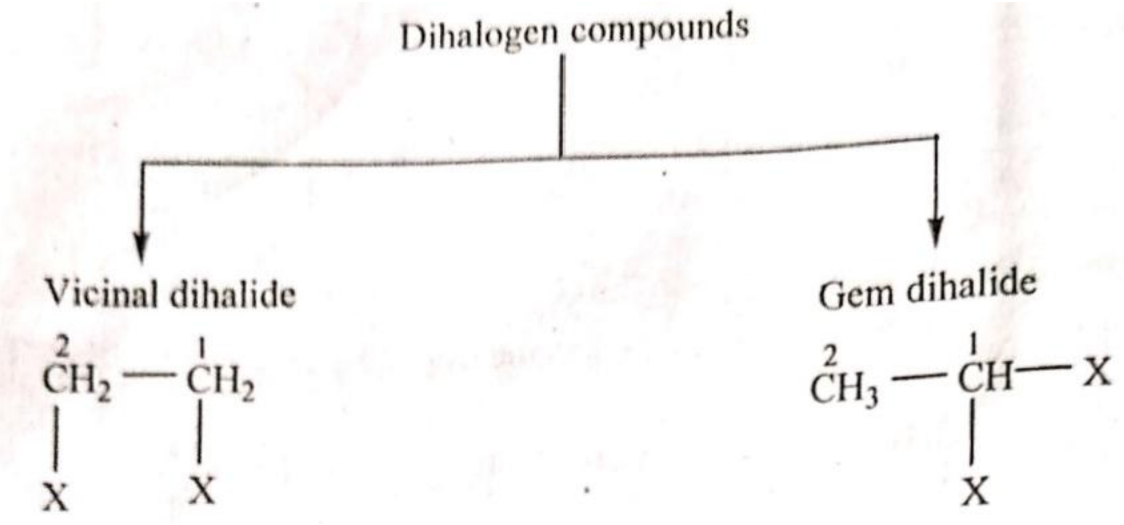
2.Aryl halides:The compounds in which halogen atom is directly attached to Sp^2hybridised the carbon atom of Aromatic ring.



Halo benzene (or)Aryl halide

Chloro benzene.

Bromo benzene



1.2-dihalogen comp 1,1-dihalogen comp

:hemical reactivity(or)Chemical reactions:

Reduction:reduction of alkyl halldes in presence of reducing agents like

$Zn+HCl, Zn+CH_3COOH, LiAlH_4, H_2/Ni/Pt/Pd$ *gives alkanes*

$$\underset{\text{Alkyl halide}}{R-X} + [H] \xrightarrow[\text{LiAlH}_4]{Zn+HCl\,/\,Zn+CH_3COOH} \underset{\text{Alkane}}{R-H}$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}I + 2[H]\text{-}LiAlH_4 \rightarrow CH_3\text{-}CH_2\text{-}CH_3 + HI$$

n-Propyl Iodide Propane

,<u>Formation of Grignard reagent(RMgx):Alkyl</u> halides reacts with 'Mg'.Metal in presence o y ether give alkyl magnesium halides.Known as grignard reagents.

$$R-x + Mg \xrightarrow[\text{Ether}]{\text{Dry}} R-Mg-x$$

$$Ex:- \quad CH_3-Br+Mg \xrightarrow[ether]{Dry} CH_3MgBr$$

Methyl Mag.bromide

$$CH_3-CH_2-Br+Mg \xrightarrow[ether]{Dry} CH_3-CH_2-Mg-Br$$

Ethyl Mag.bromide

Nucleophilic substitution reactions(NPSR): The substitution reactions in which one nucleophile(Halogen (or)-ve natt is relacod another nucleophile is called nucleophilic substitution reactions.

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

$$\left(Where\ Nu^{\ominus} = OH^{\ominus}, \overset{\ominus}{N}H_2, O\overset{\ominus}{C}_2H_5, \overset{\ominus}{S}H, CH_3COO^{\ominus}\ etc......\right)$$

Depending upon the mechanism NPS reactions are of two types.

1)SN¹reactions 2)SN²reactions

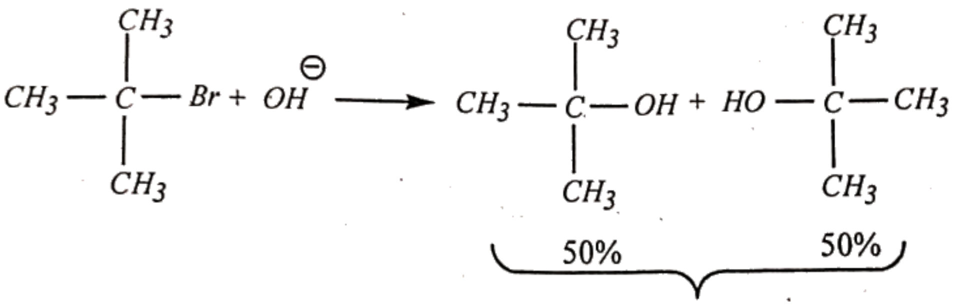
UNI MOLECULAR NUCLEOPHILIC REACTION

The rate of reaction depends only on the concentration of one reactant hence it is called unimolecular reaction.In sn'reaction 3°-Alkyl halides are involved.

Rate a[R-X]......unimolecula

Ex:The reaction between Tert.butyl bromide and hydroxide ion gives tert.butyl

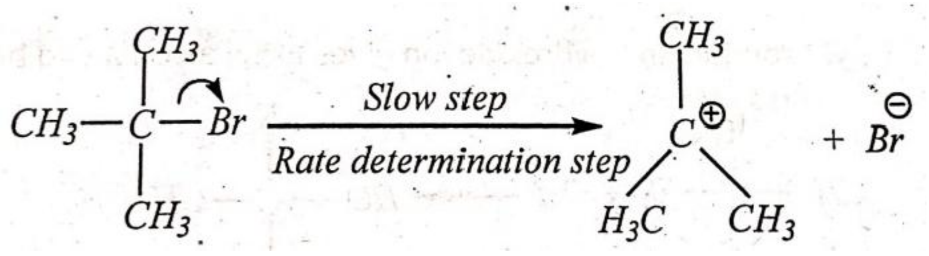
Ex:-



Racemic mixture

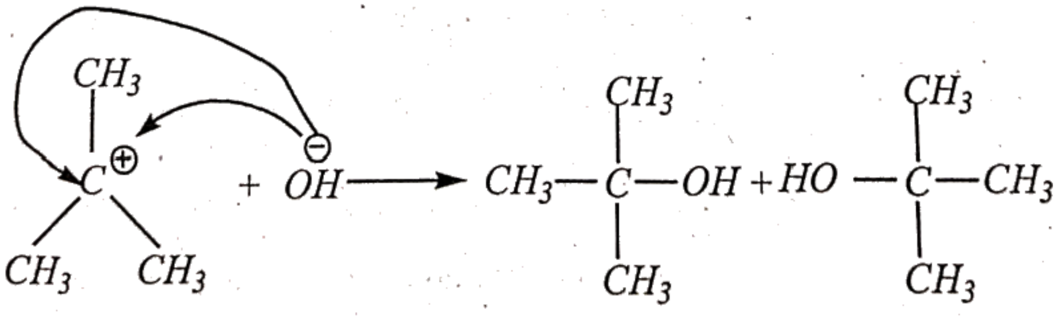
Mechanism:SNl reaction takes place in two steps.

Step-I:This is also called "rate determining step"(rds),the alkylhalide ionises to give carbonium ion.



Carbocation (Symmetrical)

Step-II:This is fast step,the incoming nucleophile attacks on carbocation either from front side (or)backside to give 1:1 ratio of products known as Racemic mixture.



50% 50%

Tert.buyl alcohols

Recemic mixture

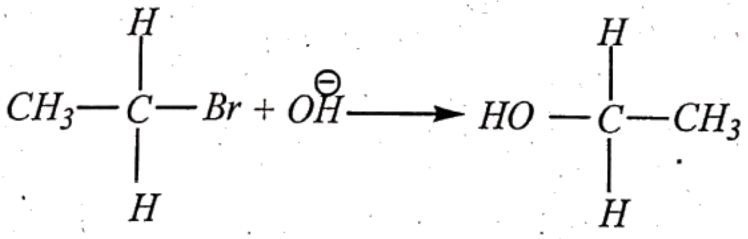
2)Bimolecular nucleophilic substitution reactions (or)Sw2-reactions:

The rate of reaction depends on the concentration of alkylhallde as well as the base (nucleophile),hence it is called bimolecular reaction.

Rade a[R-x][on°]......Blomolecular:

10_Alkyl halides are involved in SN^2reactions,these are facilitated by non-polar solvents.

Ex:Reaction between Ethyl bromide and hydroxide ion gives Ethyl alcohol and bromide ion.

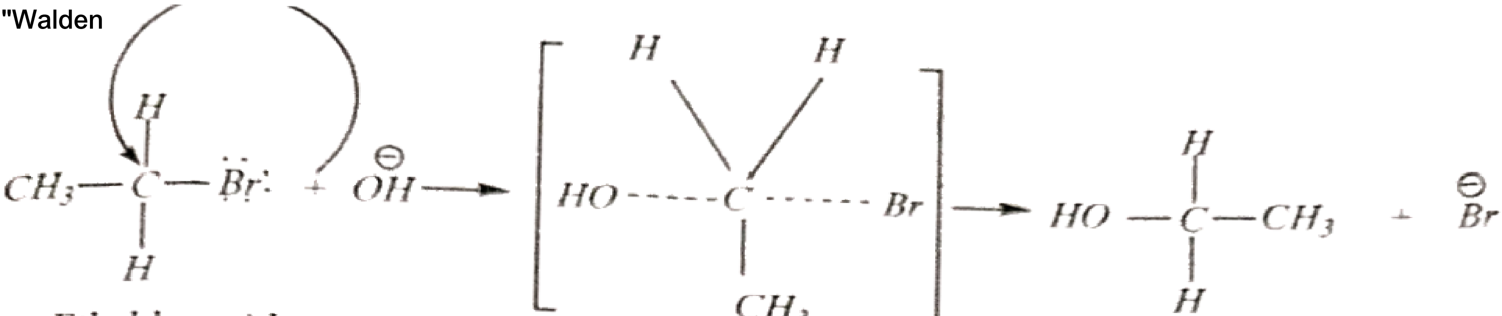


Ethyl bromide *Ethyl alcohol*

(Walden Inversion)

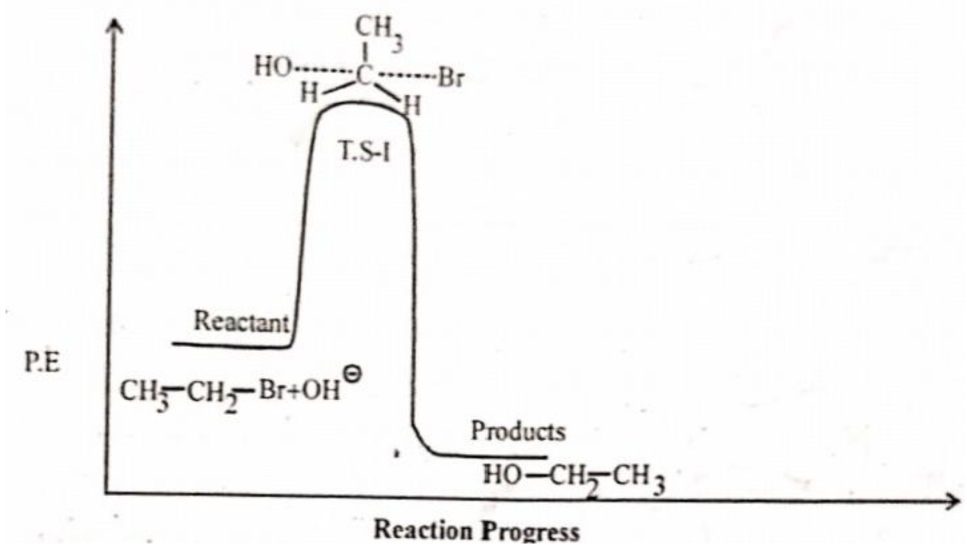
<u>Mechanism:</u>Sw^2reactions takes place in single step.In Sw2 reactions Nucleophile attacks on alkyl halide carbon from opposite side to that of Halogen atom(B?)gives an unstable Transttion state,simultaneously the Bion is ctleaved from carbon atom to give the product alcohol.

Thus the alcohol formed has opposite configuration to that of the bromide (has been inverted just as an umbrella turn inside out in a strong wind),the change in configuration is called "Walden



Ethyl bromide

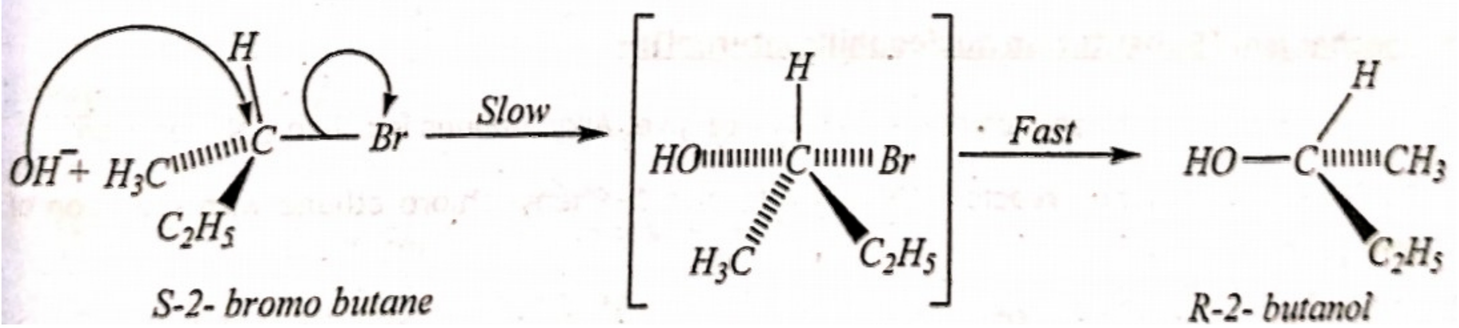
neray profle diaqram of SN^{2}reactions



Stereo chemistry of SNI **&** Sv^2 **reactions:**

SN^2-reaction:(Walden Inversion) Ex:2-bromo butane

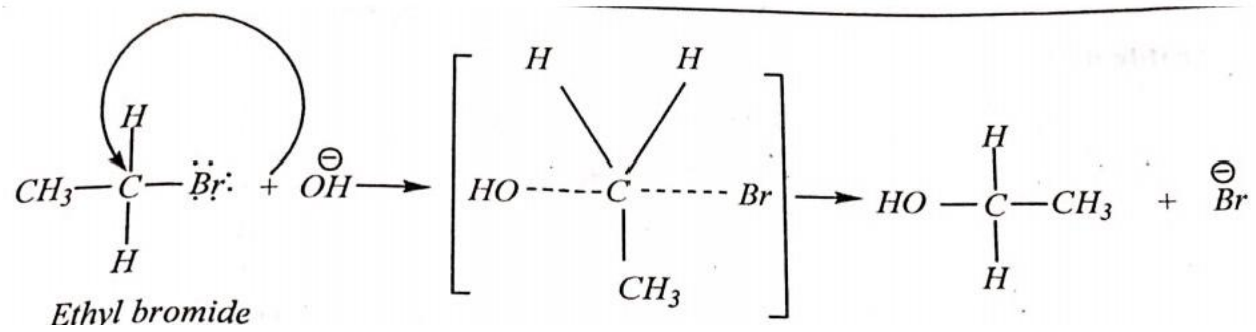
When S-2-bromo butane (optically active)is allowed to react with hydroxide ion gives R-2-butanol which is inversion of configuration (Walden Inversion)



Transition state *(Walden*
Imersion)

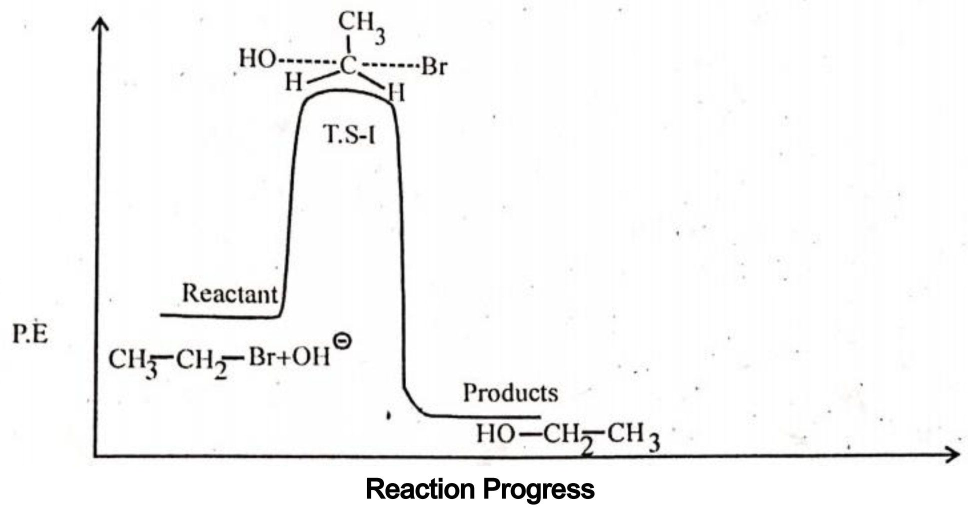
SNI **-reaction(Racemisation):**

Ex:1-bromo-1-phenyl propane has chiral centre so it exhibit optical activity.The compound is involved in svl reaction gives 1:1 ratio of enantiomer mixture (Racemic mixture)of 1-Hydroxy-1- phenyl propane.



Transition state

Energy profile diagram of SN² **reactions**



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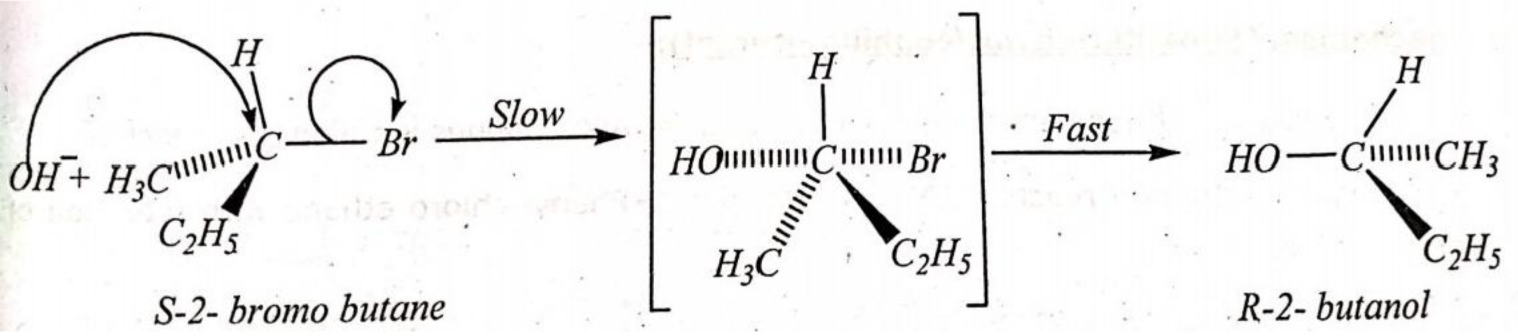
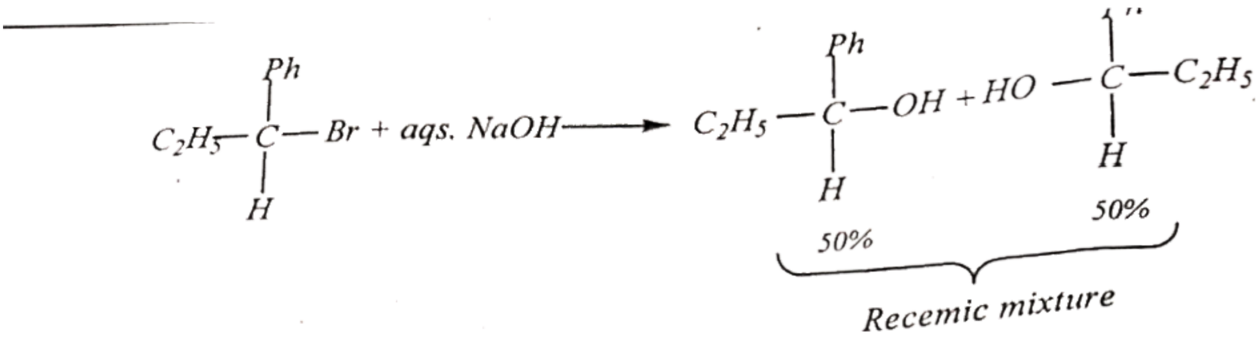
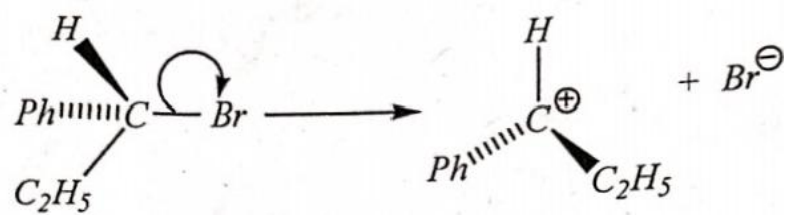




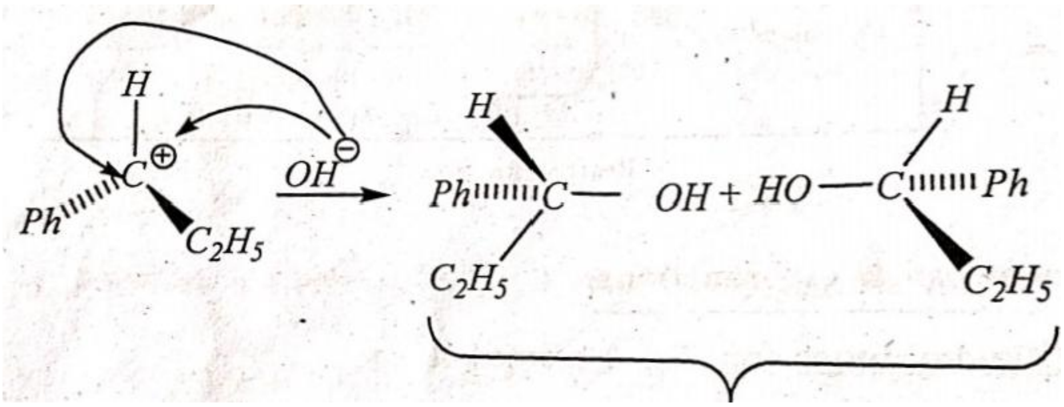
Mech;

Step-I:



Carbo cat ion

Step-II:

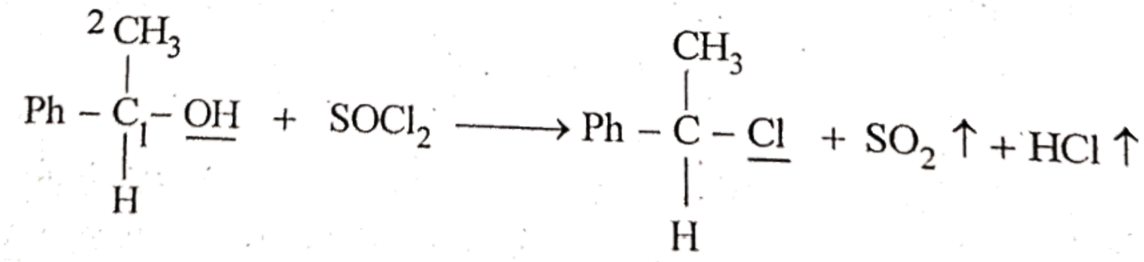


Recemic mixture

SNi mechanism (Substitution nucleophilic internal):-

Aleohols react with thiony chlorde ($SOCl_2$)to gve.Alsyl halides is caled SNi reacion.

Ex:1-Phenyl ethonol,reacts with $SOCl_2$to give 1-Phenyl chloro ethane with retentic configuration.

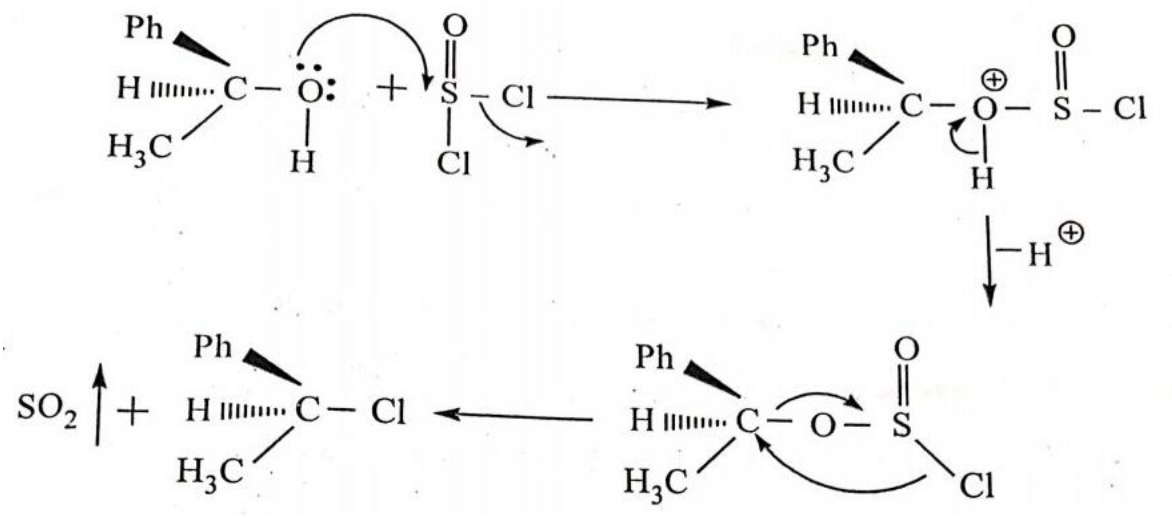


$$Ph-\overset{\overset{2\,CH_3}{|}}{\underset{\underset{H}{|}}{C_1}}-\underline{OH}+SOCl_2\longrightarrow Ph-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\underline{Cl}+SO_2\uparrow+HCl\uparrow$$

1 - Phenyl ethanol

1 - Phenyl chloro ethane

(Retention of configuration



(Alkyl chloro sulphite)

internal nucleophilic substitution(SNi)reaction

Factors affecting reaction SNI&SN?:-

(1)Nature of substrate:

SN'_Reaction:

Carbocation intermediate involved in the reaction.So the order of reactivity of Alkyl halides in SN|reaction is 30-Alkylhalide >2º-Alkyl halide >1°-Alkyl halide >.methylhalide.

SN^2_Reaction:

Nucleophi attacks from backside of Alkyl halide and due to steric effect the order ~~reactivity of Alkylha~~lides in SN^2reaction is methyl halide >10-Alkyl halide >2º-Alkyl halide >30-Alkyl halide.

2) Nature of nucleophile

Strong nucleophiles favours SN^2reaction.While weak nucleophiles favours SN'reaction (SN'reaction is independent on nature of nucleophile)

Williamson's synthesis :-

Alkylhalides reacts with sodium alkoxide to form ethers is known as williamson's synthesis.

$$R\text{-}\underline{X+NaoR!} \longrightarrow R\text{-}O\text{-}R^1+NaX$$

ether

Ex: $CH_3\text{-}Br+NaOCH_3$ $\text{-}CH_3\text{-}O\text{-}CH_3+NaBr$

Methyl bromids Dimethyl ether

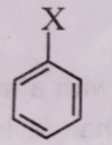
Sod.ethoxide

$$C,H_5\text{-}Cl+NaOC_2Hs \rightarrow C_2H_3\text{-}O\text{-}C,Hs+NaCl$$

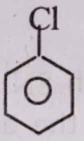
Ethyl chloride Sod.ethoxide Diethyl ether

Best results are obtained when Alkylhalide is taken as primary and alkoxide is taken as

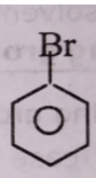
ARYL HALIDES



Halobenzene / Aryl halide



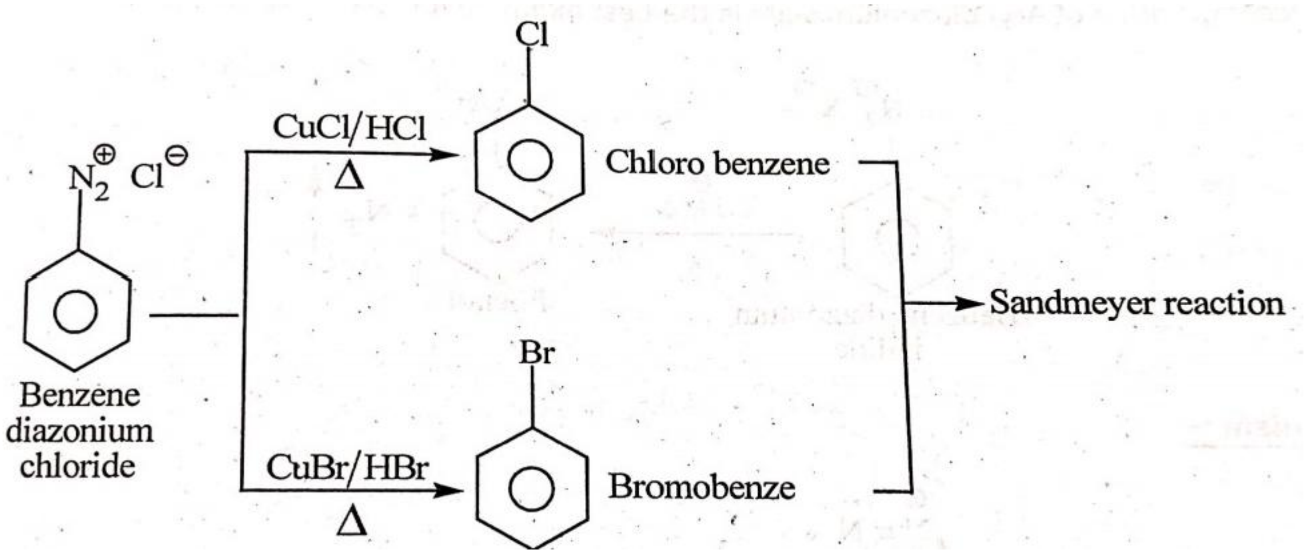
Chloro benzene

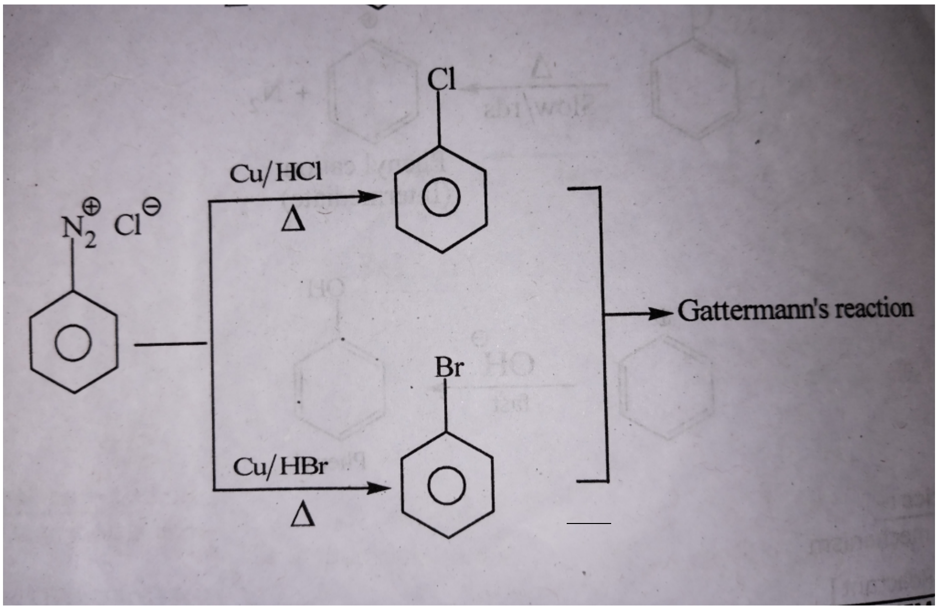


Bromo benzene

2.By decomposition of diazonium salts:

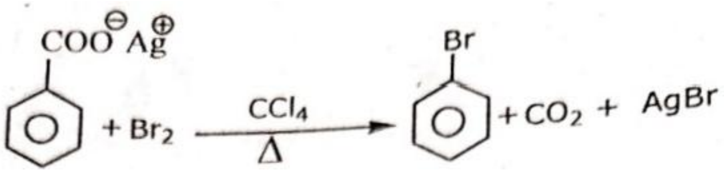
Aryl halides can be prepared by the decomposition of aryl diazonium salts in the





3.From silver salt of carboxylic acids ;-

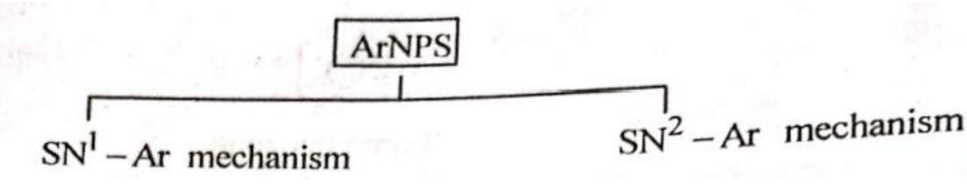
The silver salt of carboxyllc acids when heated with bromine and CCl



Silver benzoate

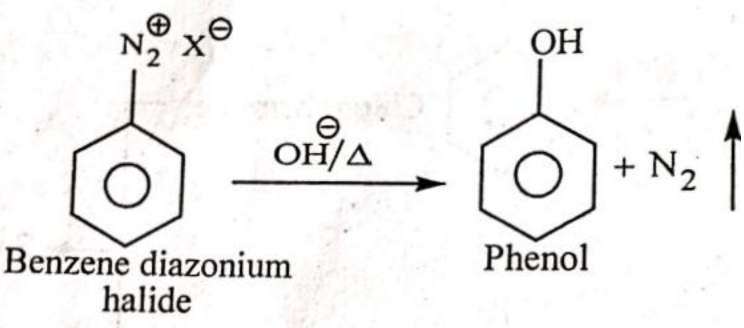
Bromobenzene

Nucleophilic aromatic substitution (ArNPs):-

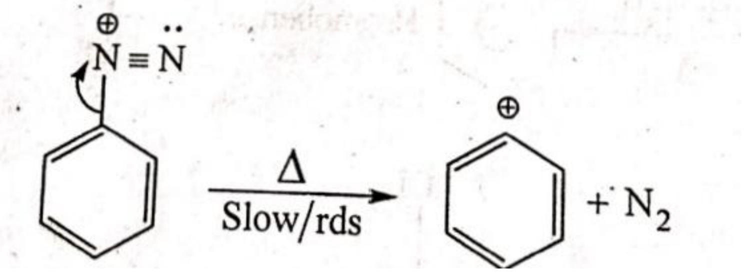


SN¹-Ar mechanism:-

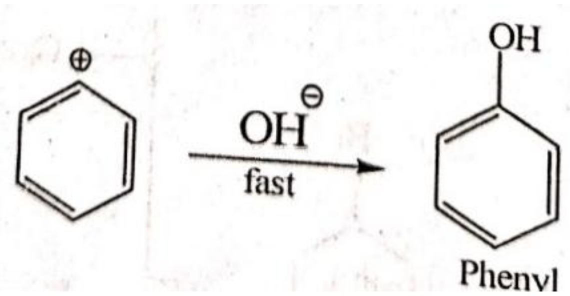
Decompostion of Aryl diazonlum salts is the best example for SN'-Ar reaction.



Mechanism :-



Phenyl cation (Intermediate



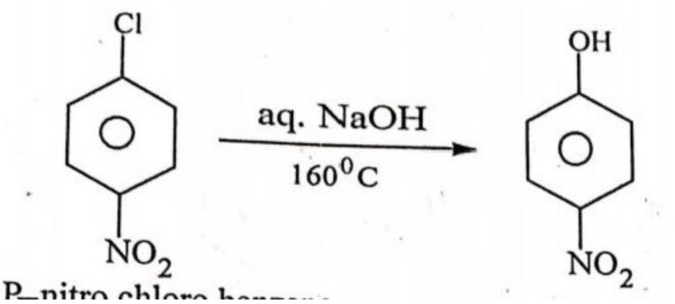
C haracterstics ;-

Two step mechanism

Rate x [Reactant]

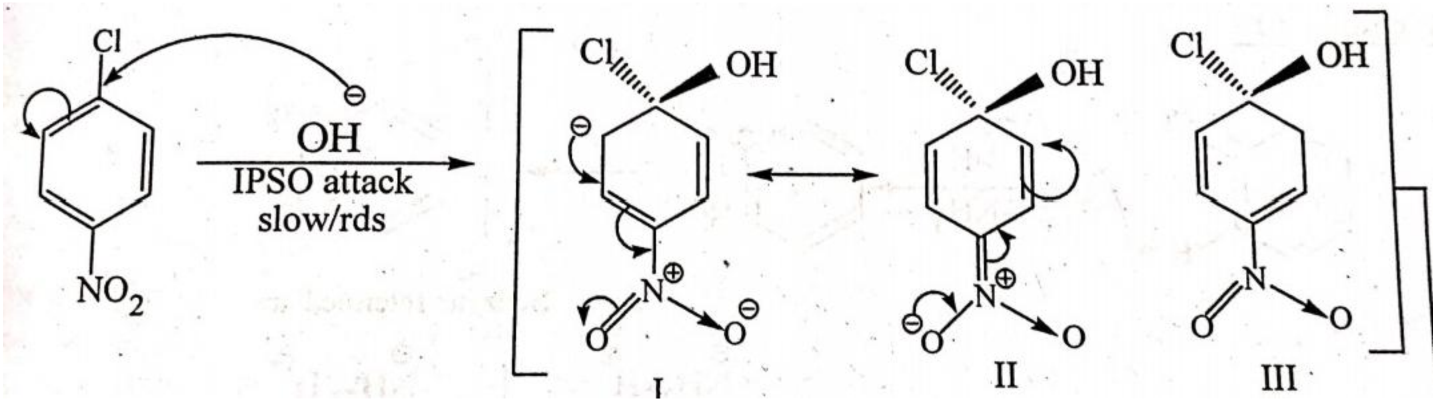
SN2 -Ar mechanism (biomolecular aromaticNPS)

Activated aryl halides(aryl halides with electron withdrawing groups at ortho /para Postions Will undergoes nucleophille substutlon reactlons via SN2-Ar mechanism.

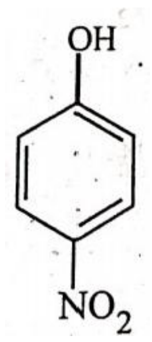


P-nitro phenol

Mechanism ;-

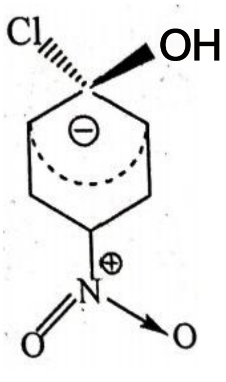


Resonance structures



-Cl $^{\odot}$

fast



Resonance hybride (o- anionic complex

Characterstics :-

Single step mechanism

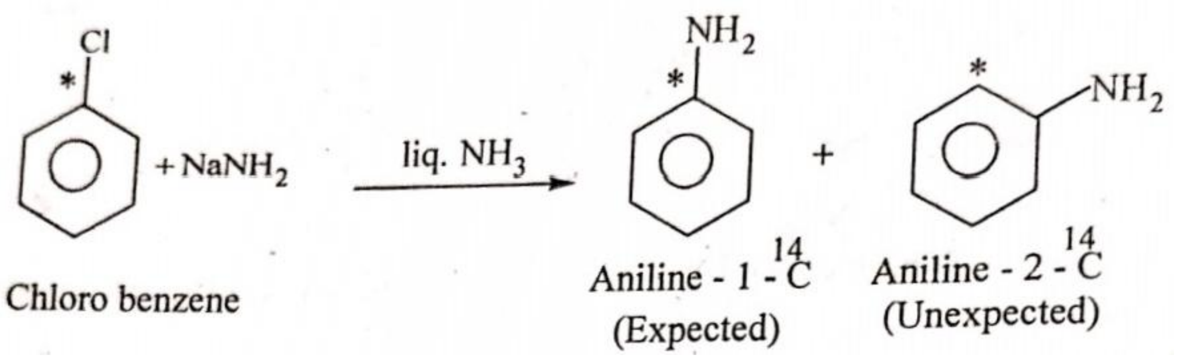
Rate a [Reactant][OH]]

Bio molecular & second order

Benzene mechanism:

(1)$NaNH_2$/liq.NH

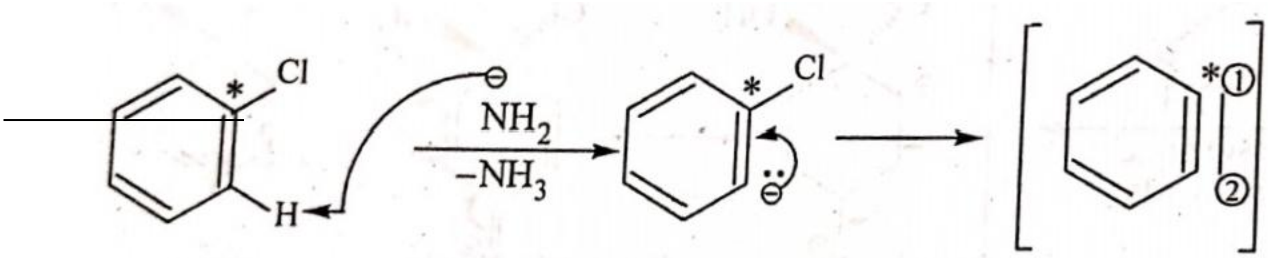
(2)KNH_2/liq.NH_3



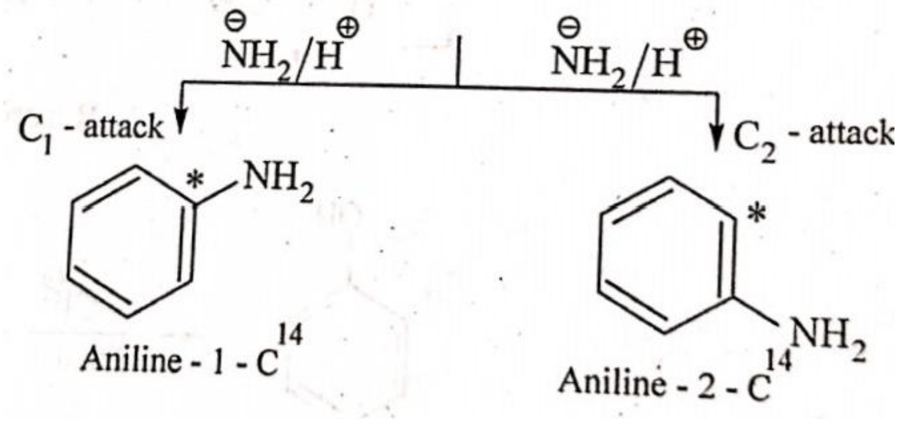
* ____-c''isotope

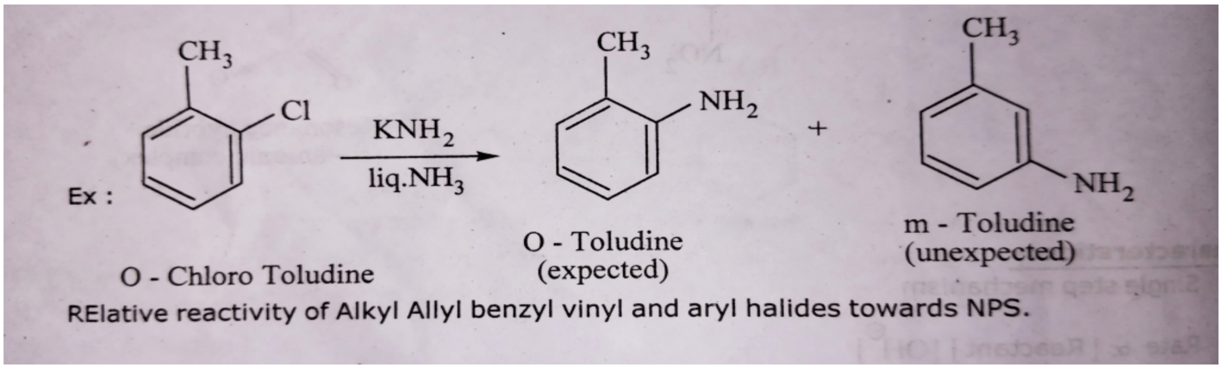
In benzyne mechanism along with expected product an unexpected product always formed.

Mechanism ;-



Benzyne Intermediate





Ex :

O - Chloro Toludine

O - Toludine
(expected)

m - Toludine
(unexpected)

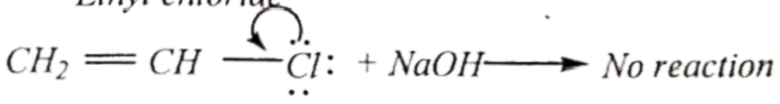
RElative reactivity of Alkyl Allyl benzyl vinyl and aryl halides towards NPS.

Reactivity of halogen in vinyl ,aryl halides

VINYL HALIDES

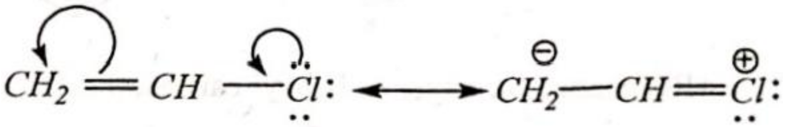
$CH_3—CH_2—Cl+NaOH \rightarrow CH_3—CH_2—OH+NaCl$

Ethyl chloride



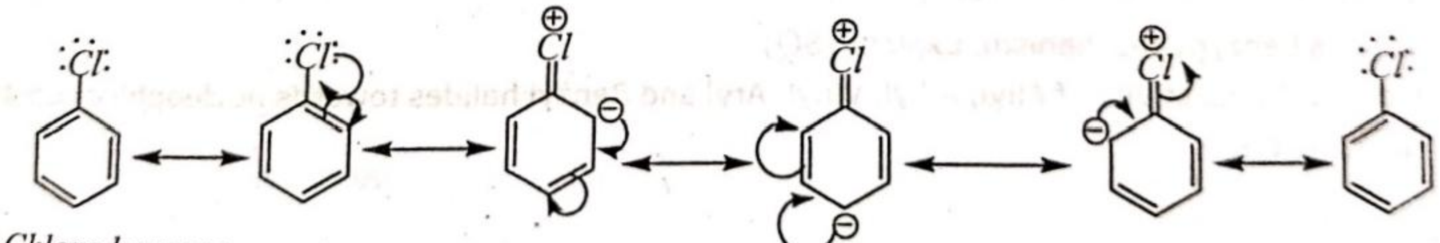
Vinyl chloride

In vinyl chloride due to +m effect of chlorine atom the carbon-chlorine bond acquire partial double bond character,due to this shortening of bond length,the chlorine atom is more strongly attached to carbon atom cannot be replaced easily.



The delocalisation of electrons in vinyl chloride results in its increased stablility.There fore it is defficult to remove halogen.

Aryl halides:Unlike alkyl halides;but like vinyl halides do not undergo nucleophilic sub"under normal conditions and in aryl halides the electron pair on halogen atom involved in resonance with benzene ring,due to resonance carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be easily replaced by other nucleophiles.



Chloro benzene

(Resonance Structures)

Reactivity of Halogen in Allyl,Benzyl halides:

Reactivity of halogen atom in allyl and benzyl halides is greater than alkyl halides.In these compounds Halogen atom is attached to Sp^3hybridised carbon atom.

.The High reactivity of halogen atom in Allyl halides is due to its ionization to formallyl carbocation.Once the allyl carbocation is formed it is stablIsed by resonance.

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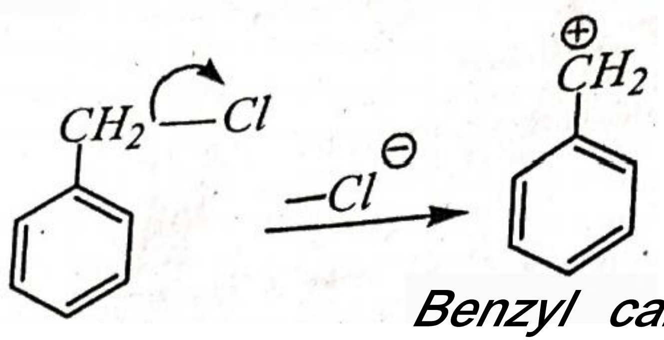
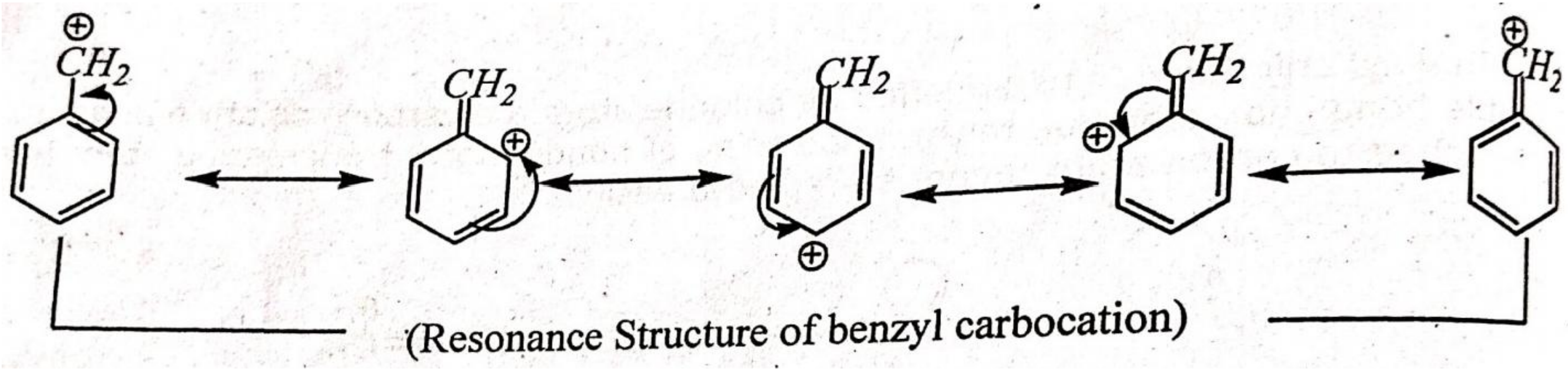
Benzyl halides;

The High reactlvlty of halenen atom in benzyl hallde is also due to stabils benzyl carbocation by resonance.



Benzyl carbocation

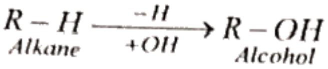
Benzyl chloride



(Resonance Structure of benzyl carbocation)

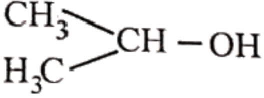
ALCOHOLS

Compunds which are formed by replacing one Gr more hvdtogen atoms of alkanes by hydroxy (-OH)group are called alcohols.They are indicated



$$\underset{Alkane}{R-H} \xrightarrow[+OH]{-H} \underset{Alcohol}{R-OH}$$

Nomenclature

S.No	Formula	Common name	IUPAC name
1	CH_3-OH	Methyl alcoho	methano
2	CH_3-CH_2OH	Ethyl alcoho	ethano
3	CH_3-CH_7CH_2-OH	n-propyl alcoho	1-propano
4		Iso propyl alcohol	2-propano
5	CH_3-CH_2CH_2-CH_2-OH	n-Butyl alcohol	1-Butanol

Classification;

Alcohols are classified into 4-classes according to the number of hydroxy groups.

a)Monohydric alcohols b)Dihydric alcohols

c)Trihydric alcohols d)Polyhydric alcohols

a)Monohydric alcohols:

These alcohols contain only one -OH group

Ex:-CH_3OH-Methyl alcohol

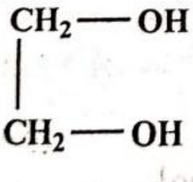
CH_3-CH_2-OH-Ethyl alcohol

CH_2=CH-OH-Vinyl alcohol

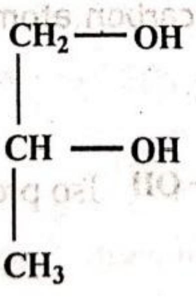
CH_2=CH-CH_2-OH-Allyl alcohol

b)Dihydric alcohols:

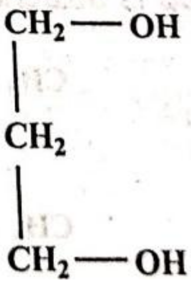
These alcohols contain two -OH groups



Ethylene Glycol



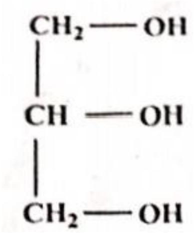
Propylene-1,2-Glycol



Propylene-1,3-Glycol

)Trihydric alcohols:

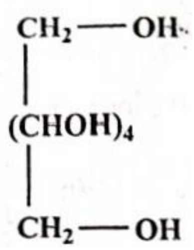
Alcohols contain three -OH groups



Glyeero1 (Pгорапе-1,2,3- Tгio1)

a) Polvhvdric alcohOlst

Асопоіб мпгсП сопtатп тоге ЕНап tпгее -ОН дгоир



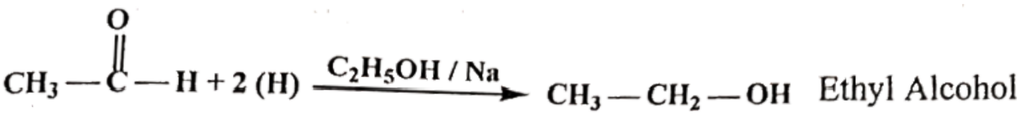
Mannitol

Monohydric alcohols again classifled Into 3 types. They are

Preparation methods

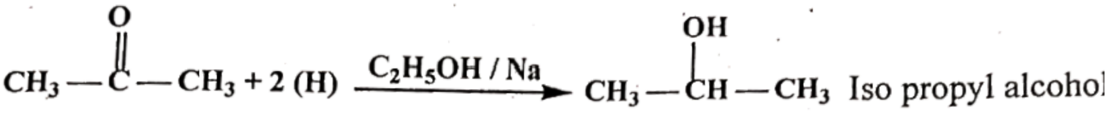
1.Reduction of carbonyl compounds

Reduction of carbonyl compounds with Na/C_2HH_3OH glves Alcohols.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + 2\,(H) \xrightarrow{C_2H_5OH\,/\,Na} CH_3-CH_2-OH \quad \text{Ethyl Alcohol}$$

Acetaldehyde

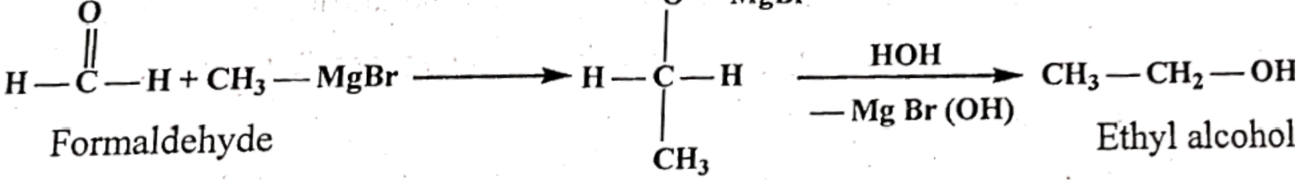


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 2\,(H) \xrightarrow{C_2H_5OH\,/\,Na} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \quad \text{Iso propyl alcohol}$$

2.From Grignard reagents:

)Primary alcohols are obtained by reaction of Grignard reagent with formaldehyde.

$$\boxed{\text{Formaldelyde} \xrightarrow{Rmgx} \text{Ethyl alcohol } \left(1^0\right)}$$



$$H-\overset{\overset{O}{\|}}{C}-H + CH_3-MgBr \longrightarrow H-\overset{\overset{O-MgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-H \xrightarrow[-\,Mg\,Br\,(OH)]{HOH} CH_3-CH_2-OH$$

Formaldehyde

Ethyl alcohol

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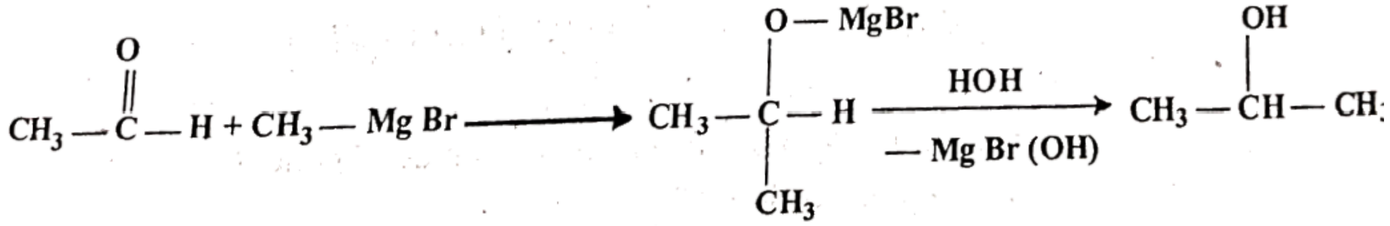
ii)Aldehydes(otherthan formaldelyde)reacts with Grignard reagent gives sec.alcohols.

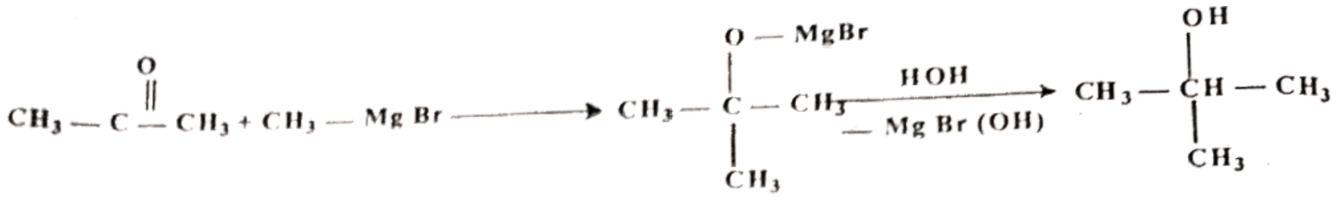
$$\boxed{\text{Acetaldelyde} \xrightarrow{RMgx} \text{Iso propyl alcohol}}$$



$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3-MgBr \longrightarrow CH_3-\underset{CH_3}{\overset{O-MgBr}{C}}-H \xrightarrow[-MgBr(OH)]{HOH} CH_3-\overset{OH}{CH}-CH$$

n)Ketones reacts with Grignard reagent gives 3°-Alcohols

Acetone- RMgx30 Butyl alcohol



$$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3+CH_3-MgBr\longrightarrow CH_3-\overset{\overset{O-MgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3\xrightarrow[-MgBr(OH)]{HOH}CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{CH}}-CH_3$$

3.From Ester hydrolysis:

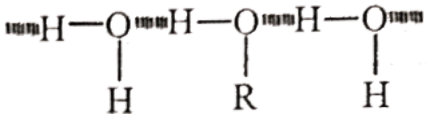
Acidic hydrolysis of esters gives alcohols and carboxylic acids

$$\underset{ester}{RCOOR^1}+H_2O\xrightarrow{H^{\oplus}}\underset{Acid}{RCOOH}+\underset{Alcohol}{R^1OH}$$

$$Ex: \underset{Ethyl\ acetate}{CH_3COOC_2H_5}+H_2O\xrightarrow{H^{\oplus}}\underset{Acetic\ acid}{CH_3COOH}+\underset{Ethyl\ alcohol}{C_2H_5OH}$$

Physical properties:

1.The lower alcohols are soluble in water due to formation of hydrogen bond with water.



2.Alcohols shows higher boiling points than those isomericethers due to formation of intermoleculer H-bonding.It is absent in ethers.

3.Due to high polarisation of O-H bond in alcohols,They loose Hion and act as a weak acids.So they form salts with strong bases.

Ex:Ethyl alcohol reacts with NaOH to form sod.ethoxide.

$$C_2H_5OH+NaOH\longrightarrow C_2H_5ONa+H_2O$$

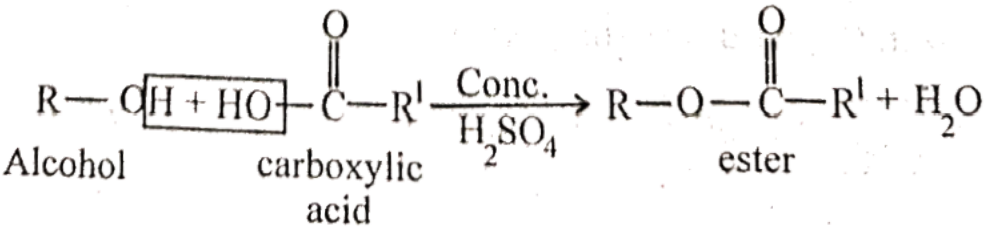
Chemical properties:

1.Reaction with sodium metal:Alcohols react with'Na'metal to liberate H,gas

$$Ex:-\quad CH_3OH+Na\longrightarrow CH_3ONa+\frac{1}{2}H_2\uparrow$$

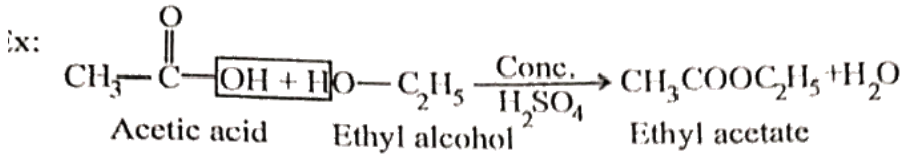
$$C_2H_5OH+Na\longrightarrow C_2H_5ONa+\frac{1}{2}H_2\uparrow$$

2.Esterification:Alcohols react with Carboxylic acids in presence of conc.$H_2SO_4$to form esters.This process is called esterification.



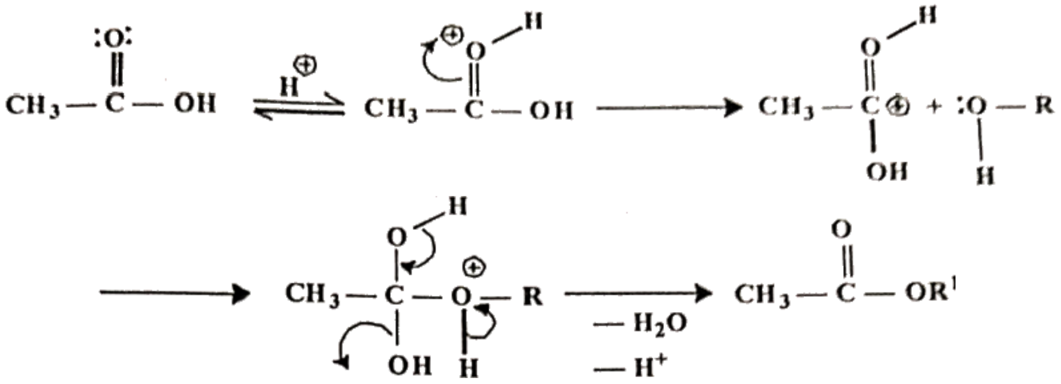
$$\underset{Alcohol}{R-O}\boxed{H+HO}-\underset{carboxylic\ acid}{\overset{\overset{O}{\parallel}}{C}}-R^1\xrightarrow[H_2SO_4]{Conc.}R-O-\underset{ester}{\overset{\overset{O}{\parallel}}{C}}-R^1+H_2O$$

Ethyl alcohol reacts with acetic acid to form ethyl acetate



$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}O-C_2H_5 \xrightarrow[H_2SO_4]{Conc.} CH_3COOC_2H_5 + H_2O$$

Mechanism;



.oxidation with PCC(Pyridinium chloro chromate)

oxidation of 1^0-alcohols by PCC gives Aldehydes.

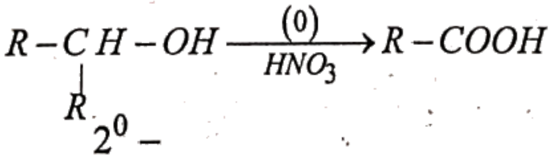
$$R-CH_2-OH \xrightarrow[(0)]{PCC} R-CHO$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[(0)]{PCC} \underset{\text{Acetaldehyde}}{CH_3-CHO}$$

4.Oxidation with Conc.HNO_3:

oxidation of 1^0-,2^0-Alcohols by Conc.HNO_3gives Carboxylic acids.

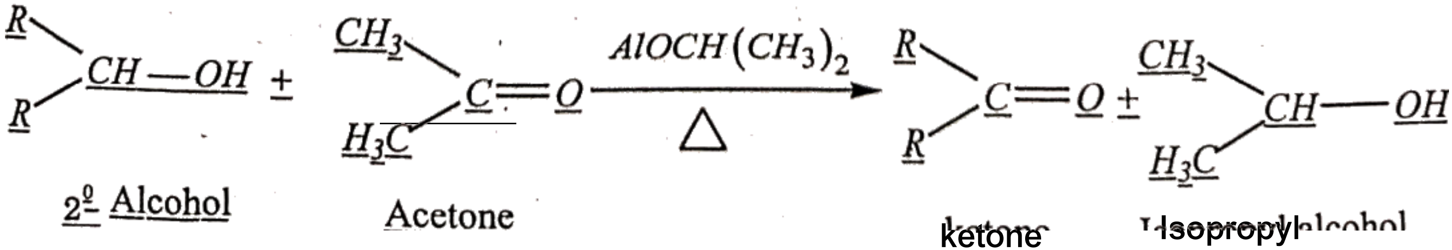
$$\underset{1^0-}{R-CH_2-OH} \xrightarrow[HNO_3]{(0)} \underset{\text{Acid}}{R-COOH}$$



$$\underset{2^0-}{R-\underset{R}{\underset{|}{C}}H-OH} \xrightarrow[HNO_3]{(0)} R-COOH$$

5.Oppenouer oxidation:

2^0-alcohols reacts with Alluminium Isopropoxide In presence of acetone gives ketones.



ketone alcohol

Isopropyl

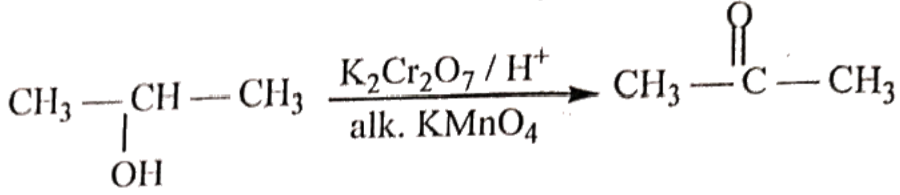
6.Oxidation with KMnO,and acidic dichromates

Oxidation of 1°,2º,&3'-alcohols with $KMno_4$(basic)and

$K_2Cr_2O_7/H_2SO_4$gives Aldelydes,ketones and alkenes respectively

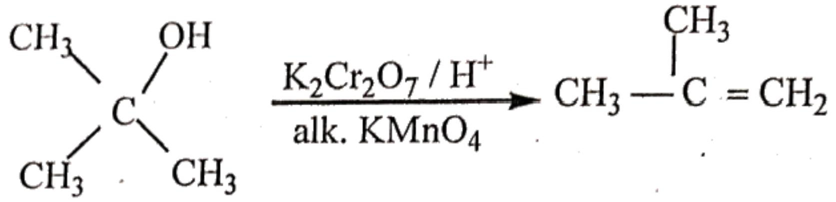
$$CH_3-CH_2-OH \xrightarrow[\text{alk. } KMnO_4]{K_2Cr_2O_7 / H^+} CH_3-CHO$$

Acetaldehyde



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{alk. } KMnO_4]{K_2Cr_2O_7 / H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

2-Propanone



$$(CH_3)_3C-OH \xrightarrow[\text{alk. } KMnO_4]{K_2Cr_2O_7 / H^+} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

Isobutene

Diols:

Compounds which contains two hydroxyl groups are known as dihydric alcohols (or)diols(c

Glycols.

Ex:

CH_2—OH
CH_2—OH

1,2-Ethane diol
(Ethylene glycol)

CH_2—OH
CH_2
CH_2—OH

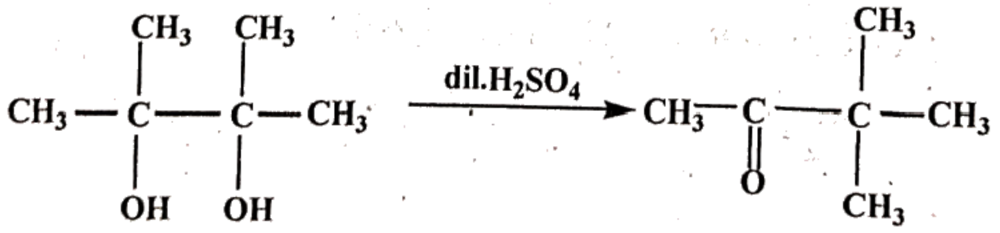
1,3-Propane diol

CH_2—OH
CH—OH
CH_3

1,2-Propane diol (Propylene glycol)

Pinacol-Pinacolone rearrangement:

The conversion of pinacols(1,2-glycols)into ketones in presence of acids is known; pinacol-pinacolone rearrangement.

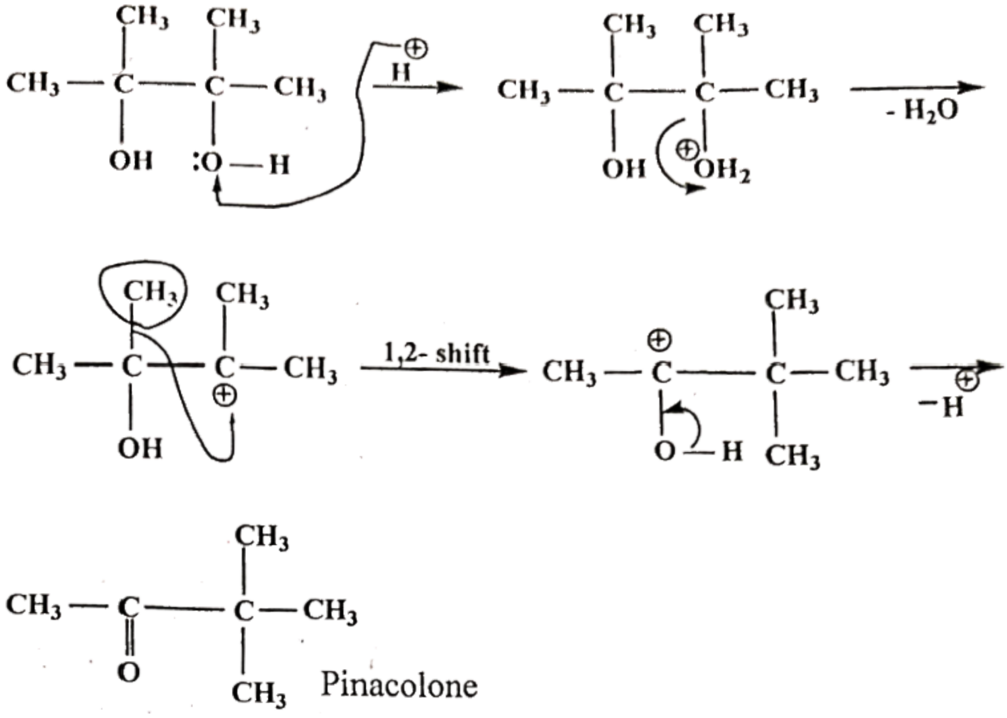


$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{\text{dil.}H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2,3-dimethyl-2,3-butane diol
(pinacol)

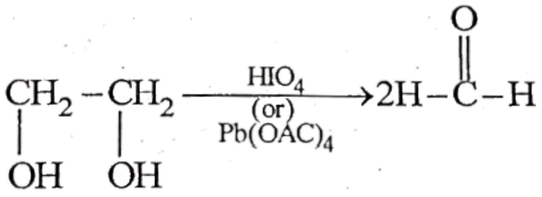
3,3-dimethyl 2-butanone
(pinacolone)

Mechanism



Oxidation of diols

Ethylene glycol)with periodic acid and lead tetra acetate gives formaldehyde.



$$\underset{OH}{CH_2}-\underset{OH}{CH_2}\xrightarrow[Pb(OAC)_4]{HIO_4\ (or)}2H-\overset{O}{\overset{\|}{C}}-H$$

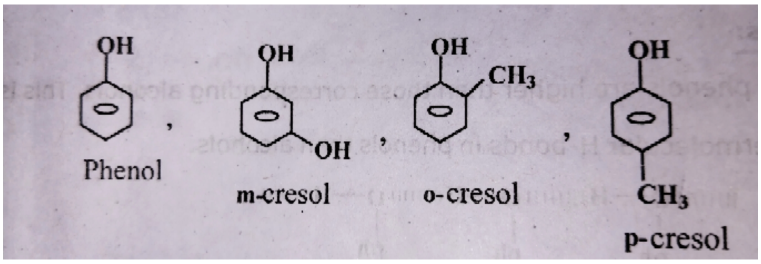
Ethylene glycol Formaldehyde

PHENOLS

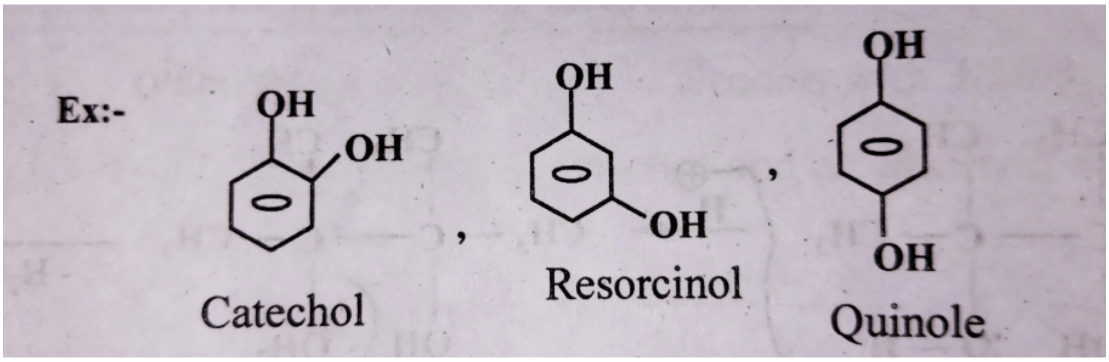
The aromatic hydroxy.compounds in which hydroxyl group is directly attached to an aromatic(benzene)ring are called phenols.

Phenols are classified into(1)mono hydric (2)Dihydric (3)Tri hydric phenols depending on number of hydroxy groups attached to an aromatic ring.

1.Monohydric phenols:Only one -OH group is attached to aromatic ring.



2.Dihydric phenols:In these two -OH groups are attached to aromatic ring


Ex:-

Catechol, Resorcinol, Quinole

3.Trihydric phenols:In these three -OH groups are attached at aromatic ring.

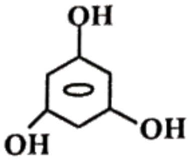
Ex:-

QH

OH

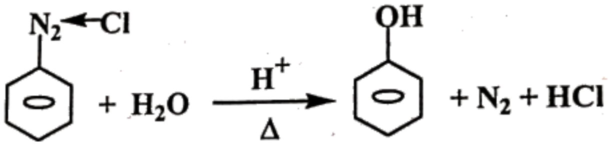
OH

Pyrogallol

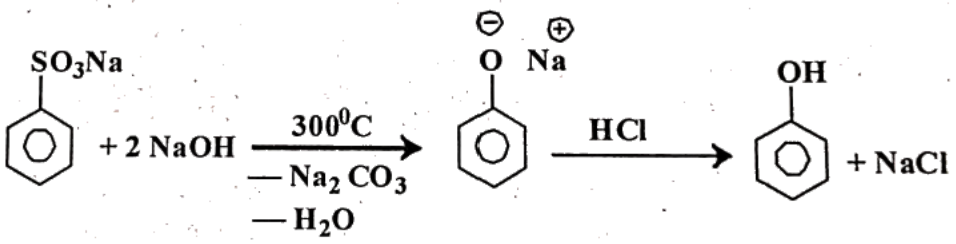

Fluoro Glucinol

Preparation methods of phenol:

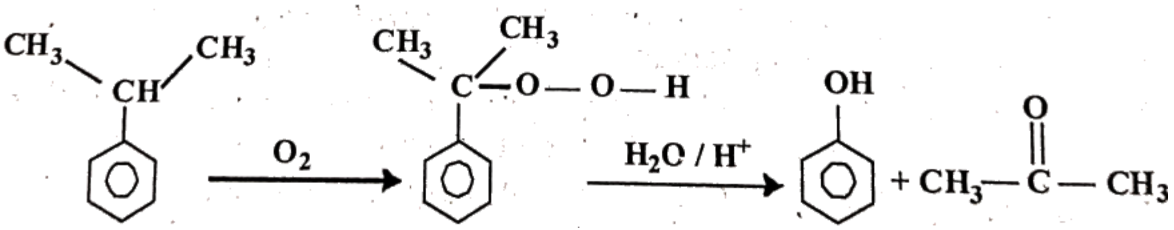
1.Heating of benzene diazonium salts with dil.H_2SO_4gives phenol.



2.Reaction of sodium benzene sulphonate with NaOH at 300°C gives phenol.

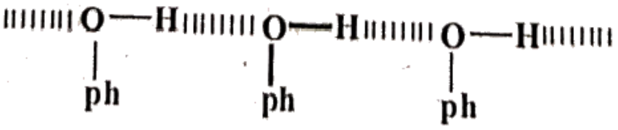


3.From cumene:Isopropyl benzene(cumene)is oxidised by atmospheric oxygen qives cumer hydroperoxide,which decompose into phenol and acetone in presence of an acid.

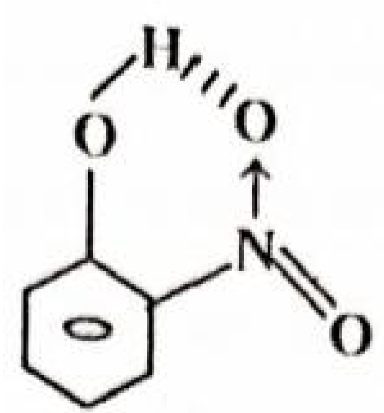


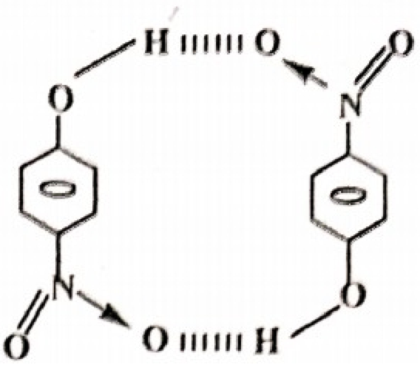
Physical properties:

1.Boiling points of phenols are higher than those corresponding alcohols.This is due to relatively strong intermolecular H-bonds in phenols than alcohols.



2.Ortho nitro phenol has Low boiling point than those isomeric P-nitro phenol,due to



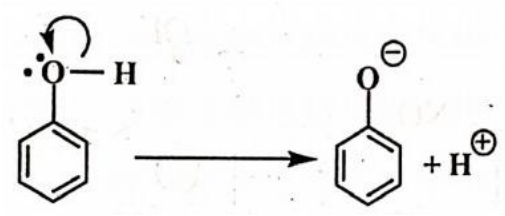


intramc lecular H bonding.

3.Pure phenols are colourless solids/liquids.The light colour usually associated with phenols either due to its oxidation by air or light.

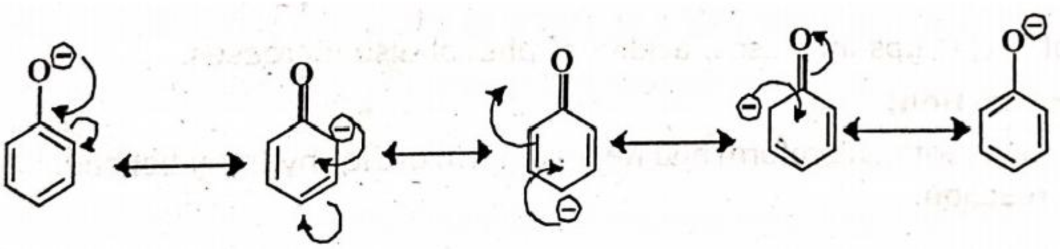
Acidic nature of phenol:

In phenol due to resonance,The oxygen atom of the-OH group acquires a +Ve charge and hence attracts the electron pair of O-H bond leading to the release of hydrogen atom as proton,and form phenoxide ion.



Phenoxide ion

Once the phenoxide ion is formed,it stabilises it self by resonance

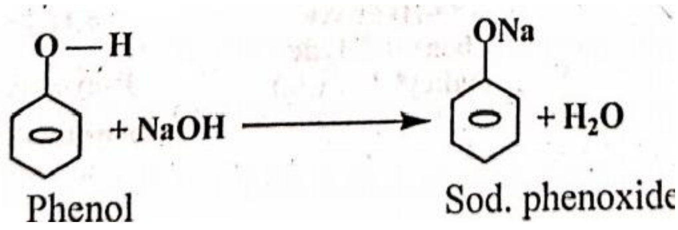


The stabllity of phenoxide ion is greater than parent phenol.Therefore phenol easily

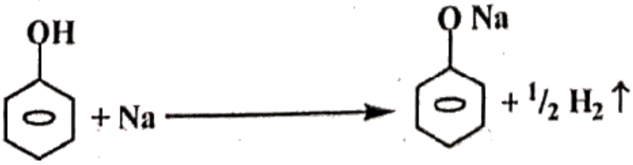
oose H*and act as a weak acid.

Eyidence:

1)



2)



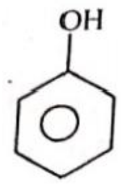
In above reactions phenol reacts with strong bases to form a salt.So phenol is con

ormed as acid.

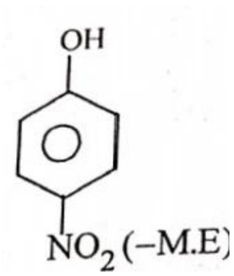
Acidity of phenol-creases the acidity of pheno

+ME groups decreases the acidity of phenol

Ex:1

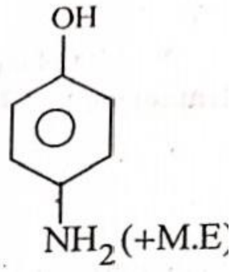


Phenol



P-Nitro phenol

I

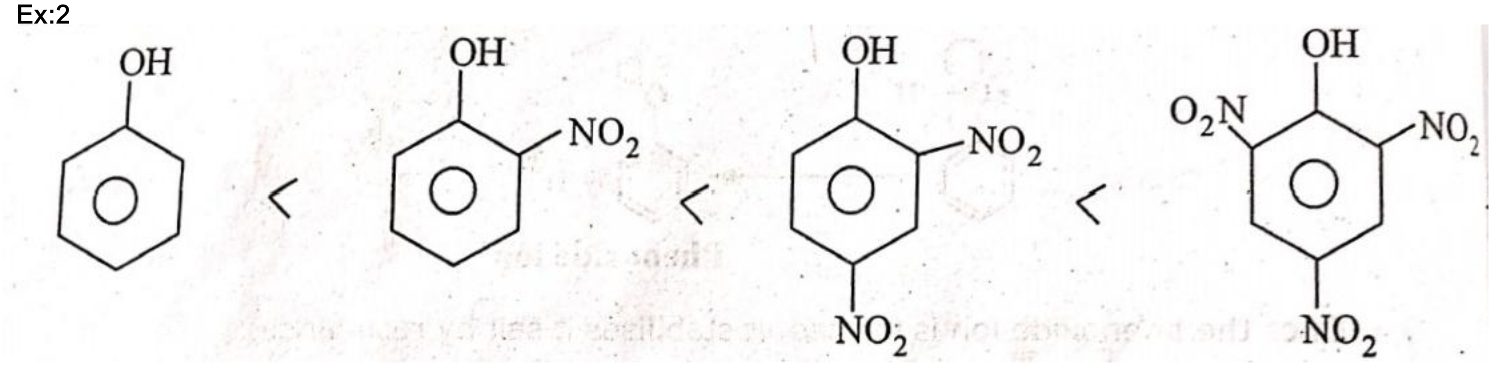


P-Amino phenol

III

Acidity:I>I>III

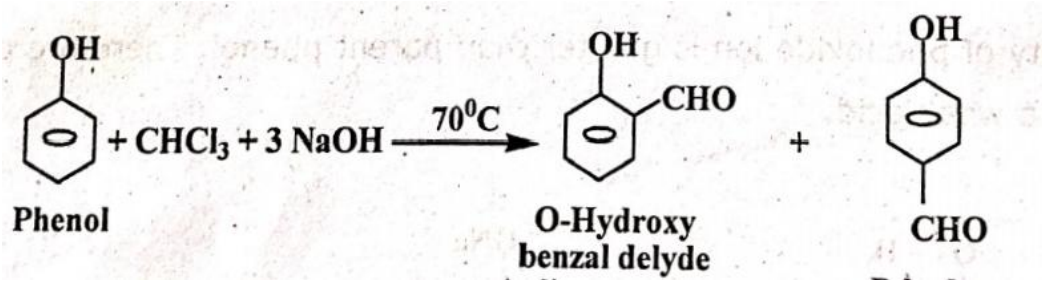
Ex:2



As the no.of -M.E gps increases,acidity of phenol also increases.

Riemer-Tiemann reaction:

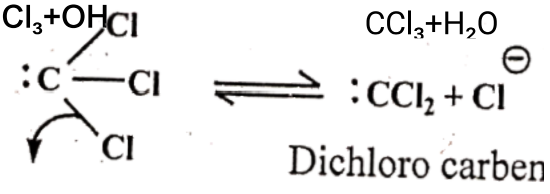
Phenol reacts with chloroform and NaOH to form ortho-hydroxy benzaldehyde is knoi as Riemer-tiemam reaction.



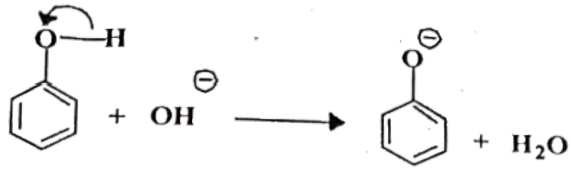
(salicylaldelyde) P-hydroxy benzaldelyde

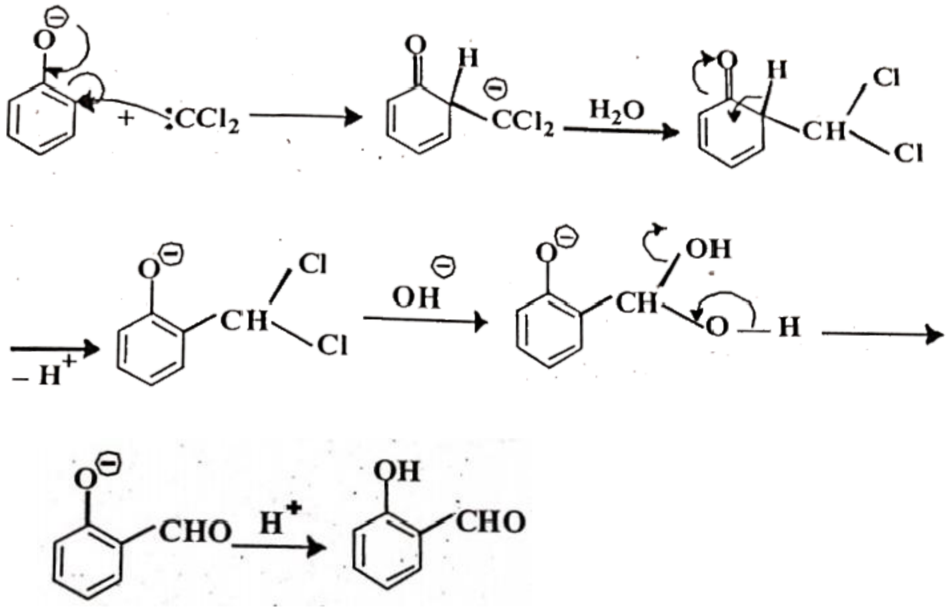
Mech:

$H\text{-}CCl_3 + \overset{\odot}{OH}$ $\overset{\odot}{CCl_3} + H_2O$



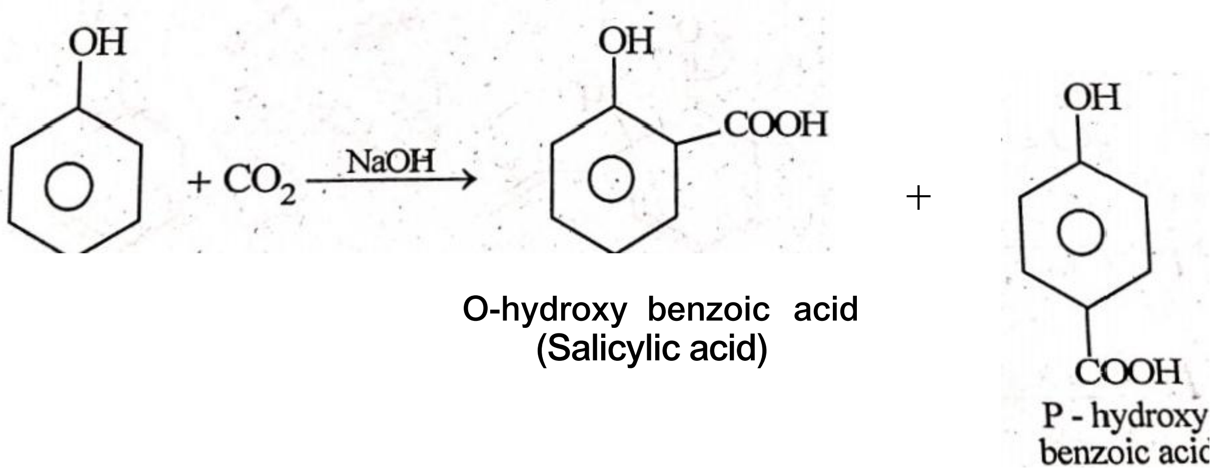
e(neutral electrophile)





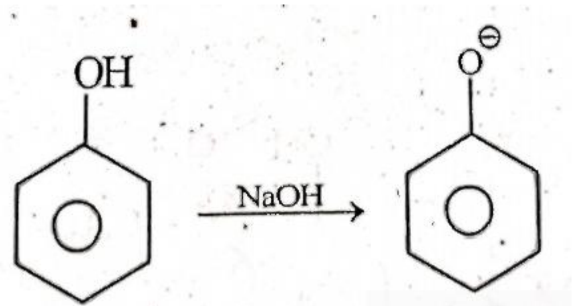
~~Kolbe's-Schmidt reaction :-~~

Phenol reacts with CO_2 in presence of base to give salicylic acid and P-hydroxy benzoic acid.

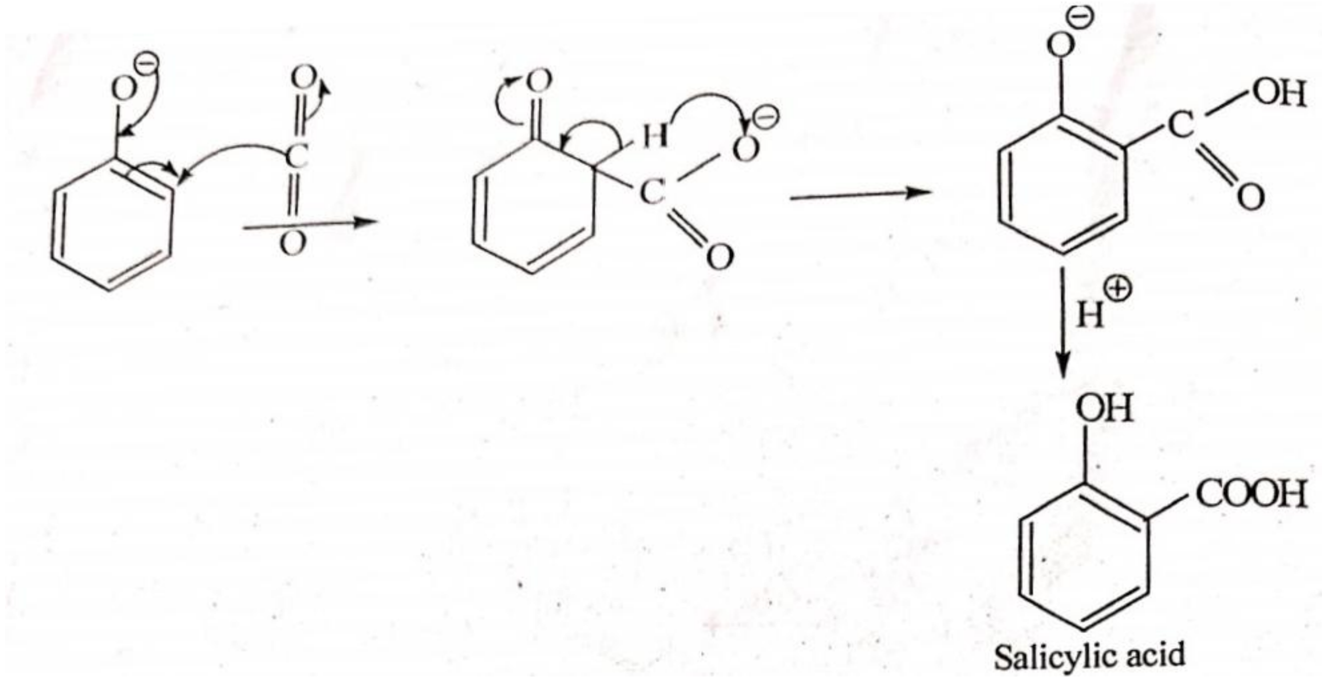


O-hydroxy benzoic acid
(Salicylic acid)

Mechanism :-

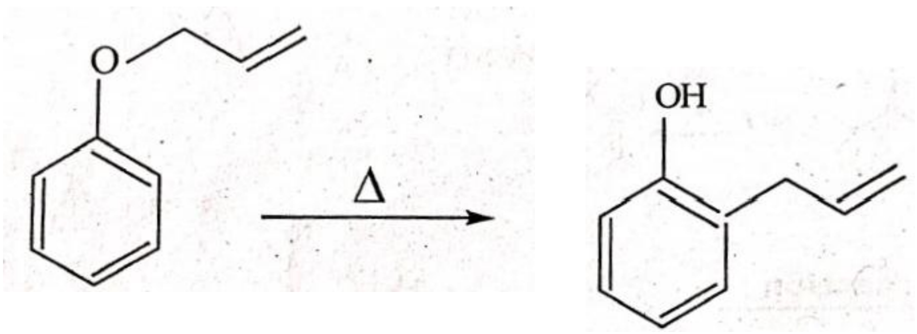


Phenoxide ion



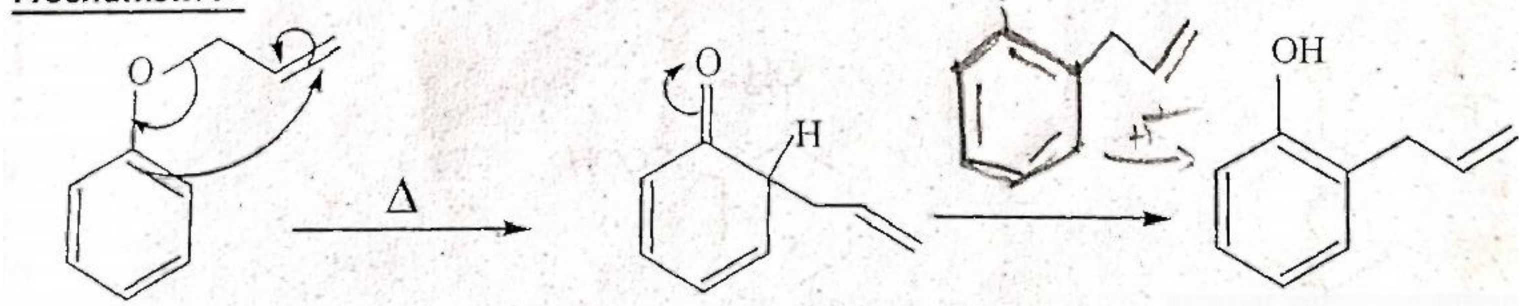
Claisen Rearrangement :-

Thermal rearrangement of allyl phenyl ether into ortho -allyl phenol is called clais rearrangement.



Allyl phenyl ether O-Allyl phenol

Mechanism :-

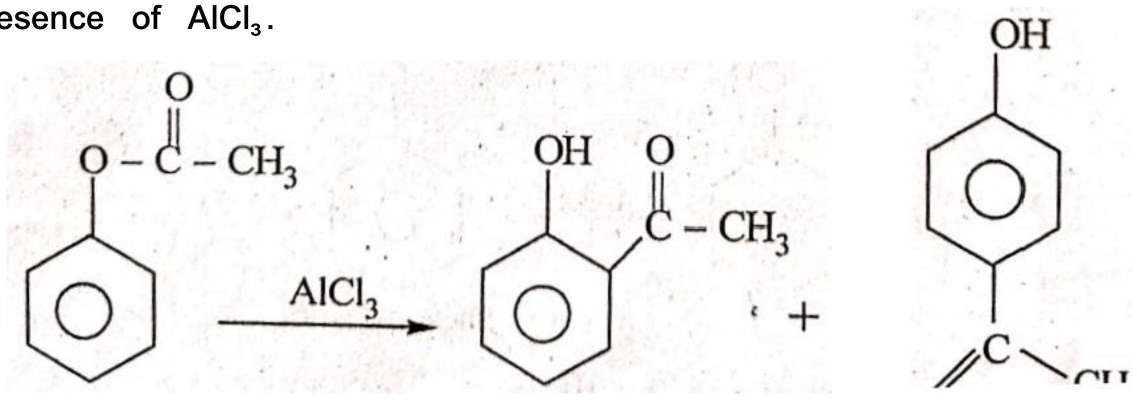


0-Allyl phenol ether:

Fries rearrangement;

Conversion of phenolic ester into O-and P-acyl phenol in presence of $AlCl_3$is called fri rearrangement.

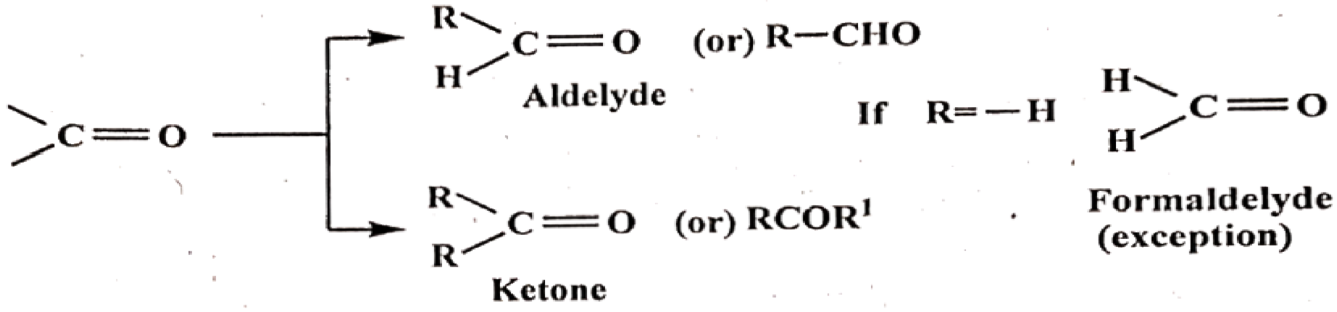
Ex:Phenyl acetate rearrange to O-hydroxy aceto phenone and P-hydroxy acetophenoi in the presence of $AlCl_3$.



UNIT-II

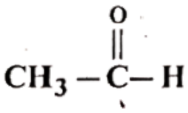
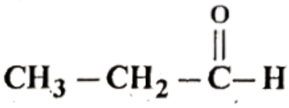
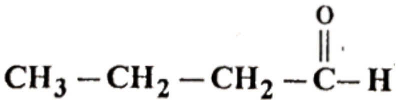
compounds which contains carbonyl group are called carbonyl compounds

General formula of these compounds is CnH2nO



Nomenclature:

1.Aldehydes(R=CHo):

Compound	IUPAC Name	Common name
m-1 (Uhi	Methanal	Formaldehyde
 $CH_3-\overset{\overset{O}{\parallel}}{C}-H$	Ethanal	Acetaldehyde
 $CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-H$	Propanal	Propeonaldelyde
 $CH_3-CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-H$	Butanal	Butyraldelyde

Aromatic aldehydes:

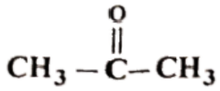
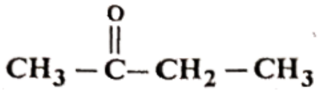
CHO

Benzaldehyde
(or)
Benzene carbaldelyde

CH_2-CHO

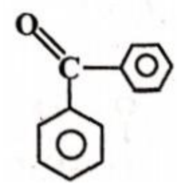
2-phenyl ethanal (IUPAC)
(or)
Phenyl acetaldelyde(commo
\

2.Ketones:

Compound	IUPAC Name	Common name
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	2-propanone	Acetone(or) Dimethyl ketone
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$	2-Butanone	Ethyl.methyl ketone

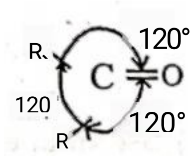
CH_3

Aceto phenone



Benzo phenone

In these compounds carbonyl carbon undergo sp²hybridisation and having planar shape.The Bond angle is 120° .



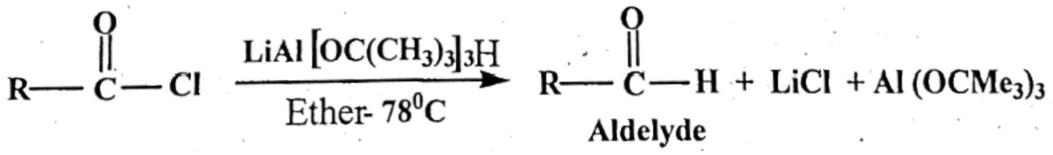
Planar

Preparation methods:

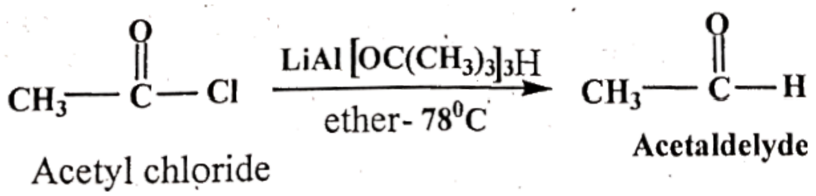
I.Preparation of Aldehydes &ketones:

1.From acid chlorides:

Reaction of acid chlorides with Lithium tri tert.butoxy alluminium hydride(LBAH)in presence of ether at -78°c gives aldehydes.



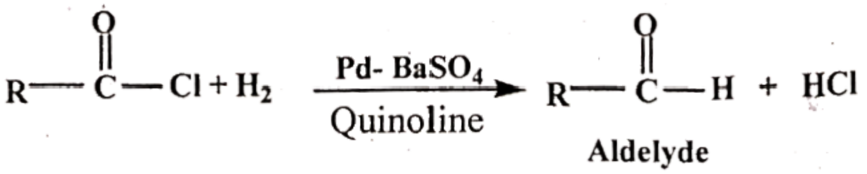
$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\text{Ether- }78^0C]{LiAl[OC(CH_3)_3]_3H} \underset{\textbf{Aldelyde}}{R-\overset{\overset{O}{\|}}{C}-H} + LiCl + Al(OCMe_3)_3$$



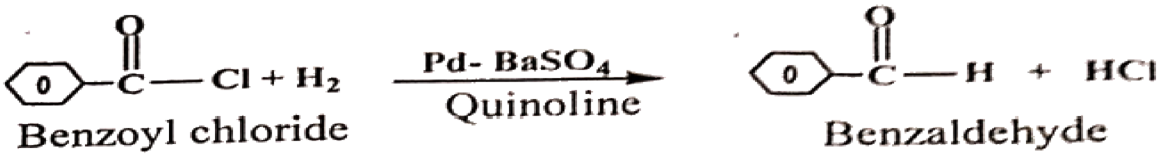
$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow[\text{ether- }78^0C]{LiAl[OC(CH_3)_3]_3H} \underset{\textbf{Acetaldelyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$

Roseunmund's reduction (only for aldehydes):

Reduction of acid chlorides with Pd/BaSO4 in presence of quinoline gives aldehydes.

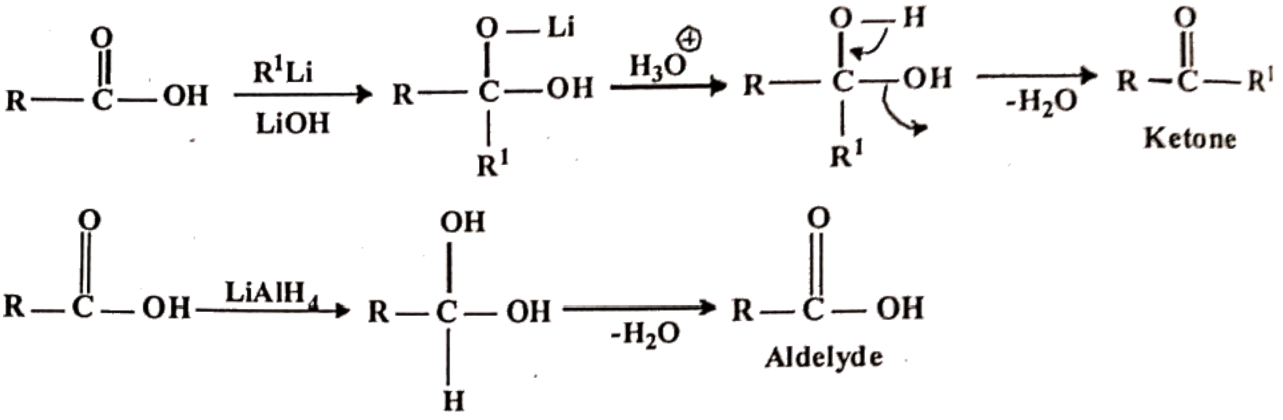


$$R-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Quinoline}]{Pd-BaSO_4} \underset{\textbf{Aldelyde}}{R-\overset{\overset{O}{\|}}{C}-H} + HCl$$



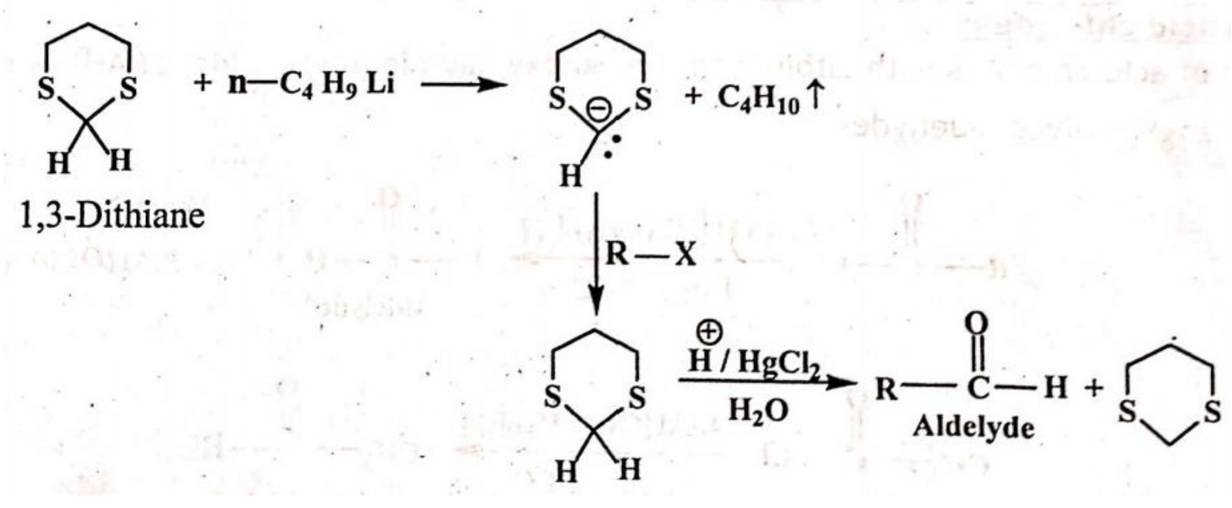
3.from carboxylic acids:

Carboxyllc acids reacts with $LiAlH_4$ (or)alhyl lithium(R-LI)to form carbonyl con pounds,



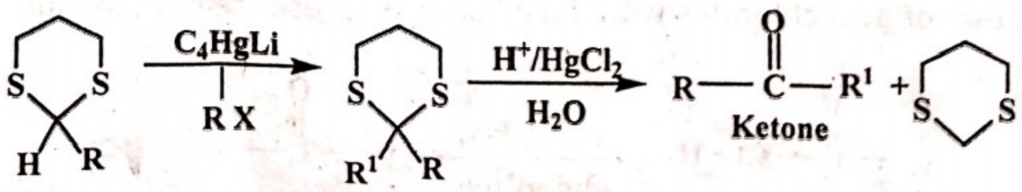
4.from 1,3-dithianes:

1,3-dithianes reacts with n-butyl lithium first give 1,3-dithianeanion,which reacts with R-X to for thio-acetal which on reaction with HgClz in acid followed by hydrolysis gives carbonyl con pound,



Thio Acetol

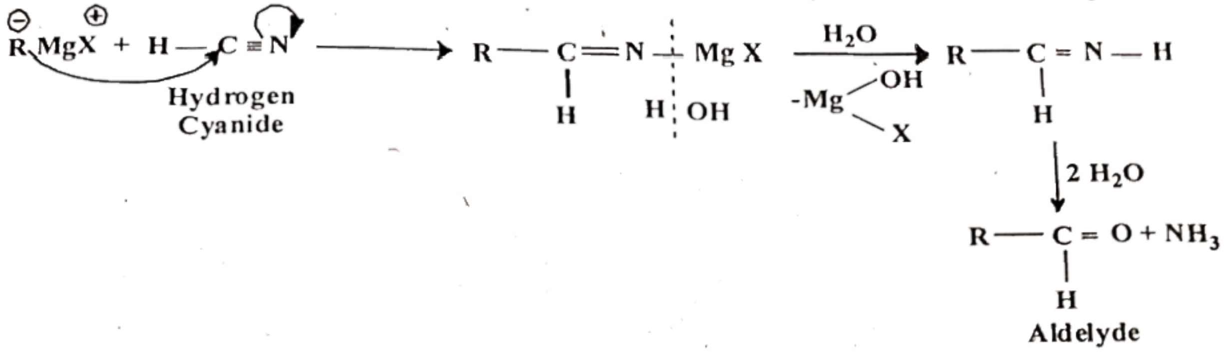
Alkylation and hydrolysis of thioacetal gives ketone

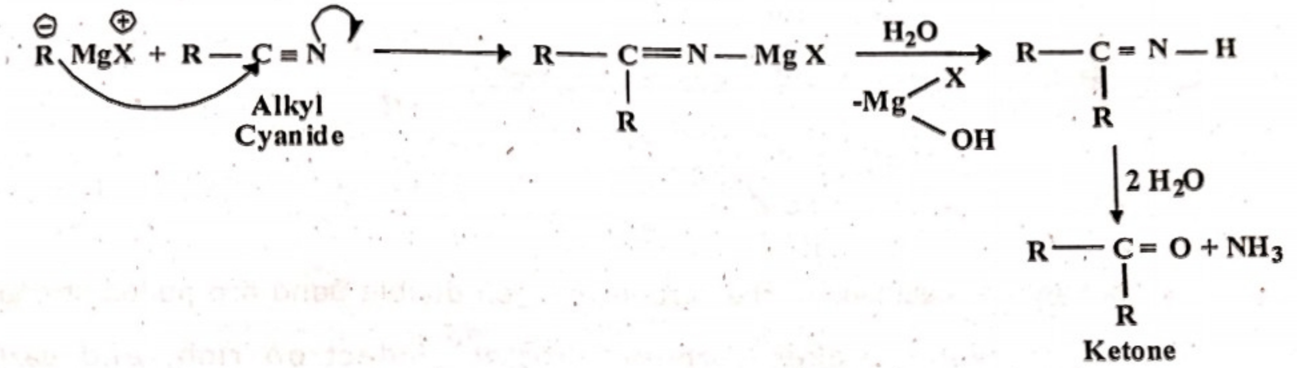


Thio Acetal

5.From nitriles/Grignard reagents:

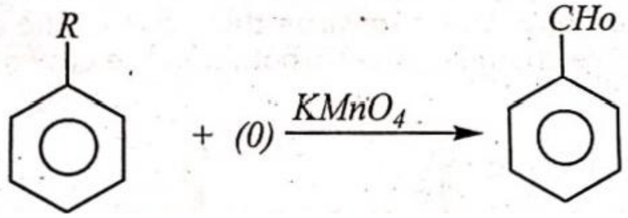
Grignard reagent (RMgX) reacts with HCN gives aldelydes and with RCN gives ketone





Special methods:

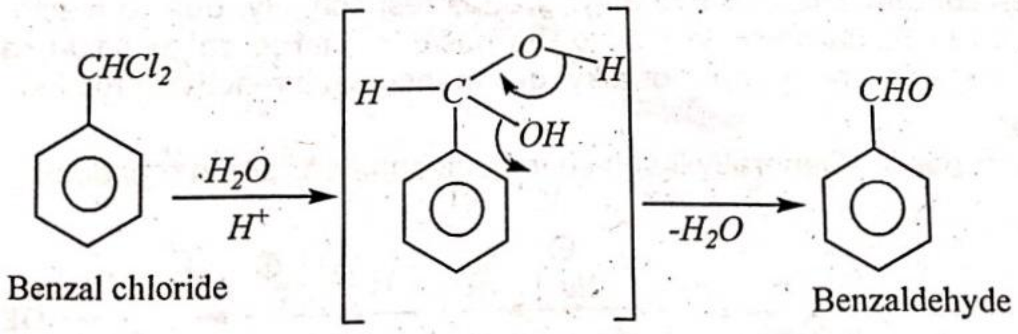
1.Oxidation of arenes:Oxidation of alkyl benzene (or)arenes with KMnO4 gives benzaldehyde

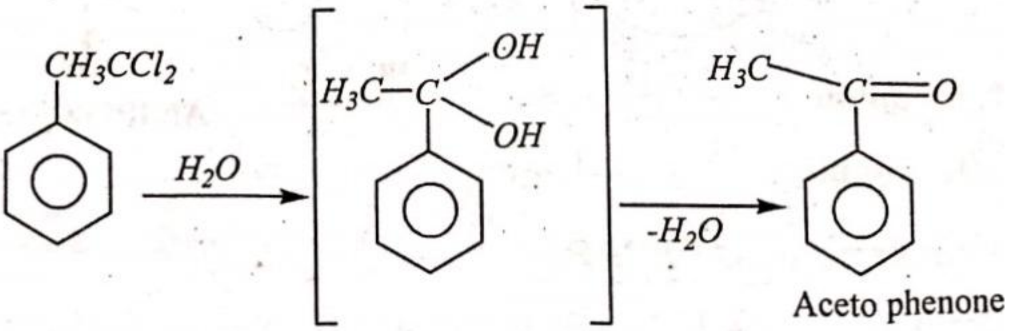


Benzaldehyde

$(R=-CH_3,-CH_2-CH_3,-CH_2-CH_2-CH_3.....)$

2.Hydrolysis of benzal halides:Hydrolysis of benzal halides gives benzaldelyde(or)aceto phenone.

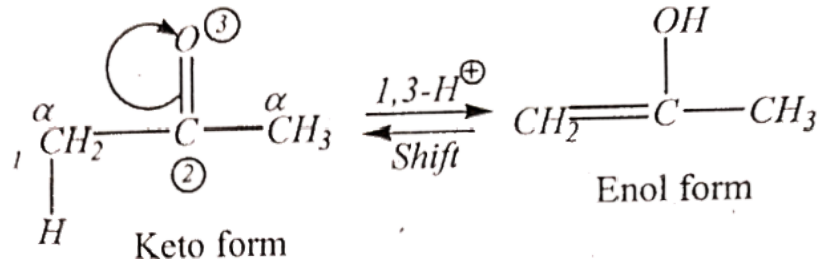




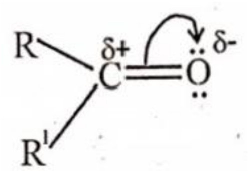
PHYSICAL PROPERTIES

1.keto-enol tautomerism Ketones(Aldelydes)with x-H atoms tautomerises to form e, compound is known as keto-enol tautomerism

1,3-H shift is called tautomerism



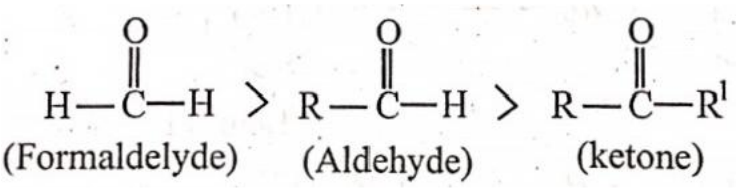
2.<u>Reactivity of carbonyl group in aldehyds &ketones:</u>



The mobile π-electrons of the carbon-oxygen double bond are pulled strongly t wards oxygen atom,which makes carbonyl osygen^{8}-)electron rich,and carbon carbon(δ+)electron deficient.The positive charge on the carbonyl carbon facilitate the attac ing of nucleophile.So carbonyl compounds undergoes nucleophilic addition reactions.

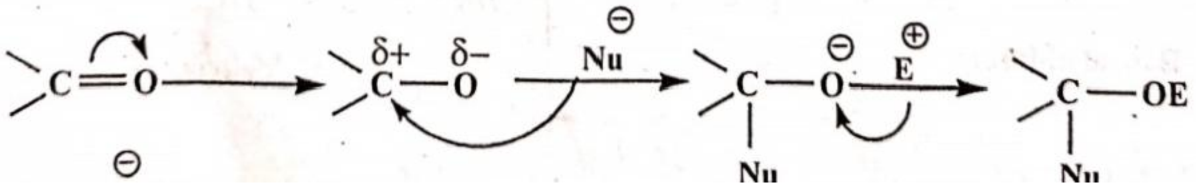
The reactivity of the carbonyl group towards the nucleophilic addition reactions di pends upon the magnitude of positive charge on the carbon,and the crowding around the carbc atom.

Ex:



(Reactivity order

To observe the above reactivity order. We concluded that reactivity of Aldelydes is more than ketone. This is explained as followes. Formaldelyde has no alkyl groups, wheras other aldehyde and ketones contain one and two alkyl groups respectively. due to electron releasing nature of alkyl groups (+I.E) partially neutralize the positive charge on carbonyl carbon hence reactivity also decreases. and The number of alkyl group increases reactivity further decreases



$Nu^{\ominus}$ -Nucleophile

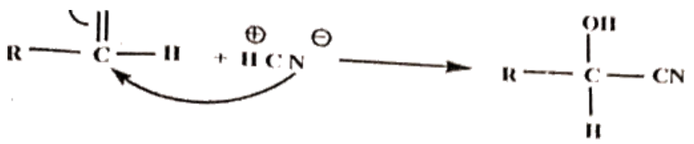
Addition product

$E^{\oplus}$ -Electrophile

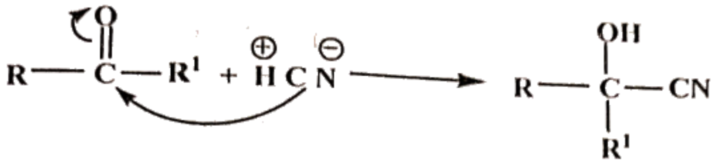
<u>Nucleophilic addition reactions (NPAR)</u>

with H N:

1.Addition Addition ofCc arbonyl compound with HCN gives cyanohydrines.

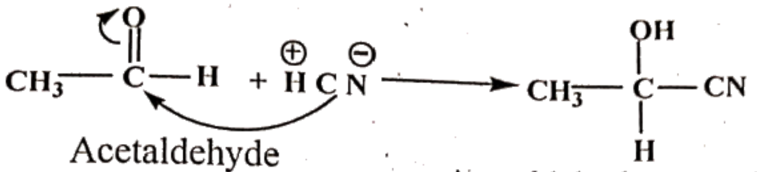


Cyanohydrine(Aldehyde)



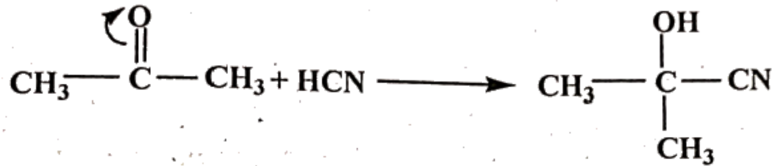
Cyanohydrine

Ex:-



Acetaldehyde

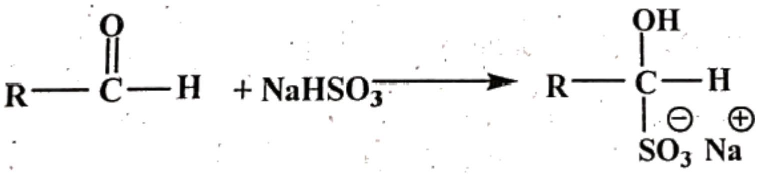
Acetaldehyde cyano hydrine



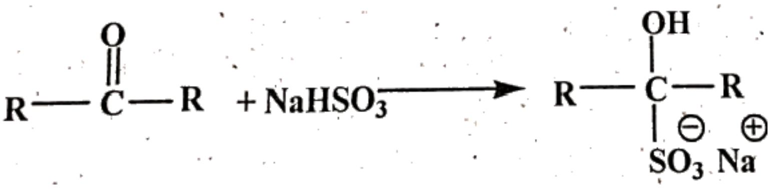
Acetone cyano hydrine

2.Addition with NaHSO$_3$(Sod.bisulphite):

Carbonyl compounds adds with NaHSO$_3$to form bisulphite addition products.

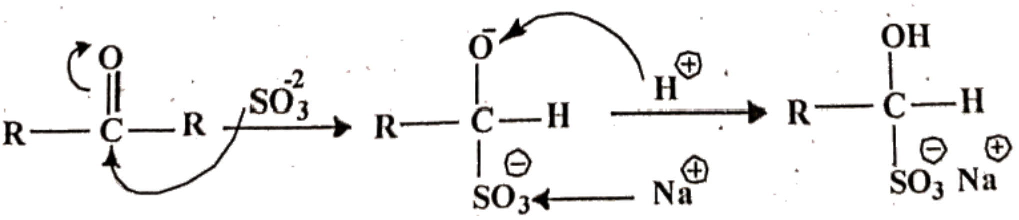


Sod.bi sulphite Additon product.



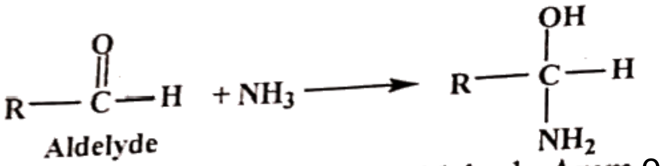
Mech:- NaHSO$_3$— Na++HSO$_1$

HSO$_3$——— H+so?

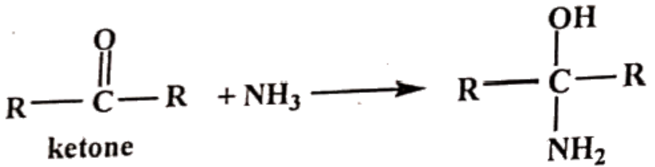


3.Addition with Ammonia (NH$_3$):

Addition of carbonyl compound with NH$_3$to give addition products

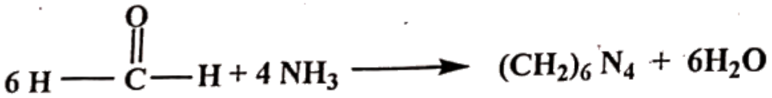


Aldehyde Ammonia



produci Ketone Ammonia
produci

Formaldelyde reacts with $NH_3$to form Hexe metlylene tetramine (or)Eurotropine (W an addition product).



$$6\,H-\overset{O}{\overset{\|}{C}}-H+4\,NH_3 \longrightarrow (CH_2)_6N_4+6H_2O$$

Formaldelyde

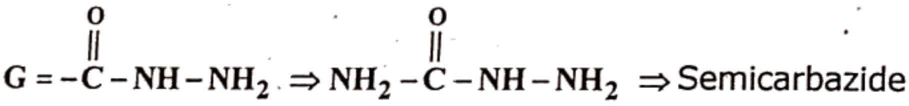
Hexa methylene tetramine

4.Addition with Ammonia derivatives (H_2 N-G):

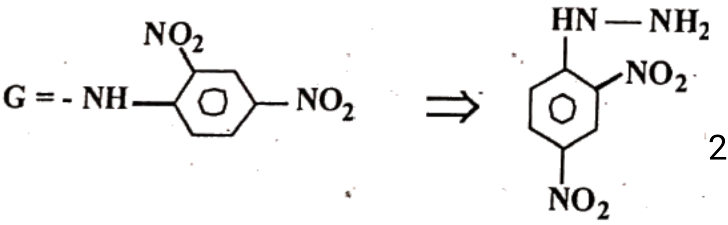
Carbonyl compounds adds with H_2N-G(derivatives of ammonia to form correspond ing addition products.

If G=-NH_2 → NH_2-NH_2-Hydrazine

G=-NH-Ph → Ph-NH-NH_2-Phenyl hydrazine



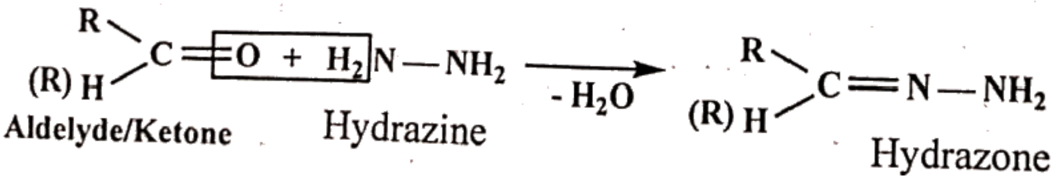
$$G=-\overset{O}{\overset{\|}{C}}-NH-NH_2 \Rightarrow NH_2-\overset{O}{\overset{\|}{C}}-NH-NH_2 \Rightarrow \text{Semicarbazide}$$

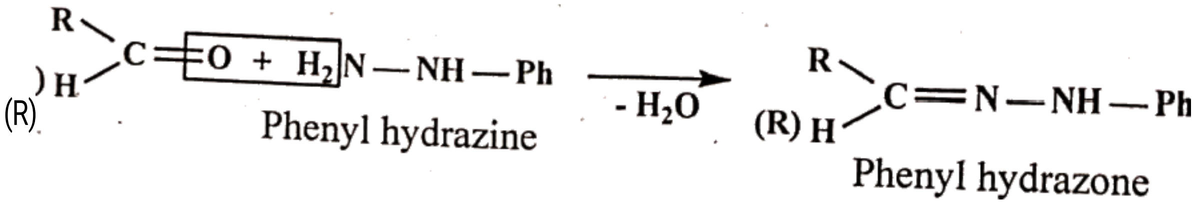


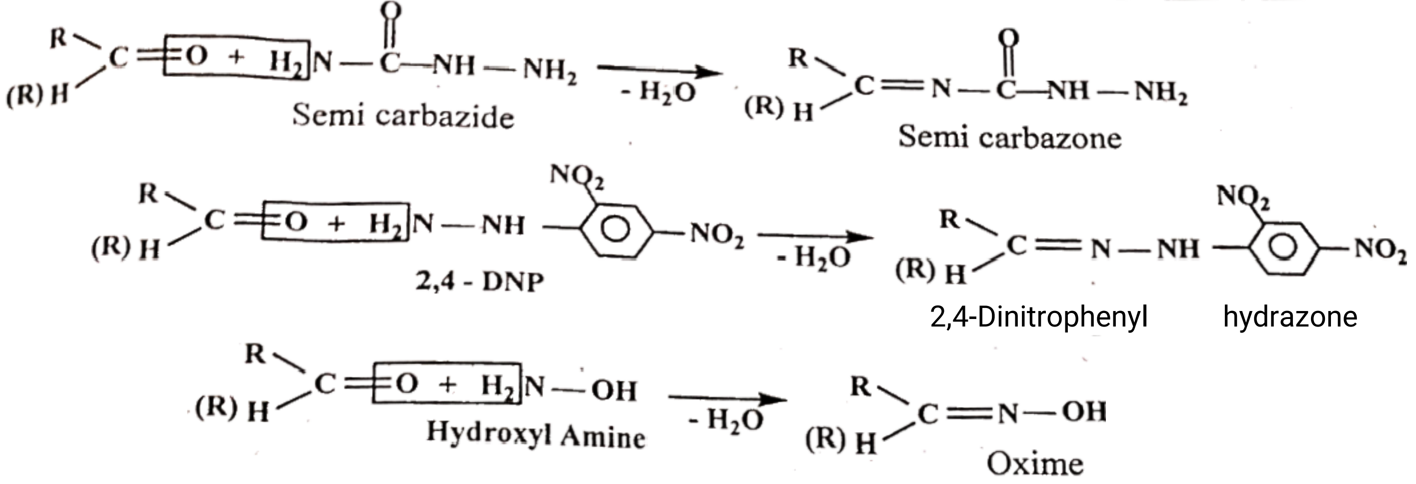
2,4-Di nitrophenyl hydrazine(2,4 DNP)

G=-OH → NH_2-OH-Hydroxyl amine

Ex:-







5.Reaction with hydroxyl amine NH_2OH:

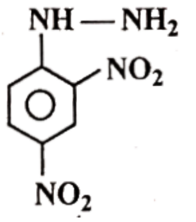
Aldelydes ketones reacts with NH_2-OH to formaldoximes ketoximes respectively

R R
+ H_2 —OH
.H -H_2O H >C=N—OH If R=-CH_3 → Acetaldoxime
Aldelyde Aldoxime

R R
O + H_2 —OH
R -H_2O R c=N—OH If
Ketoxime R=R=CH_3 → Acetonoxime

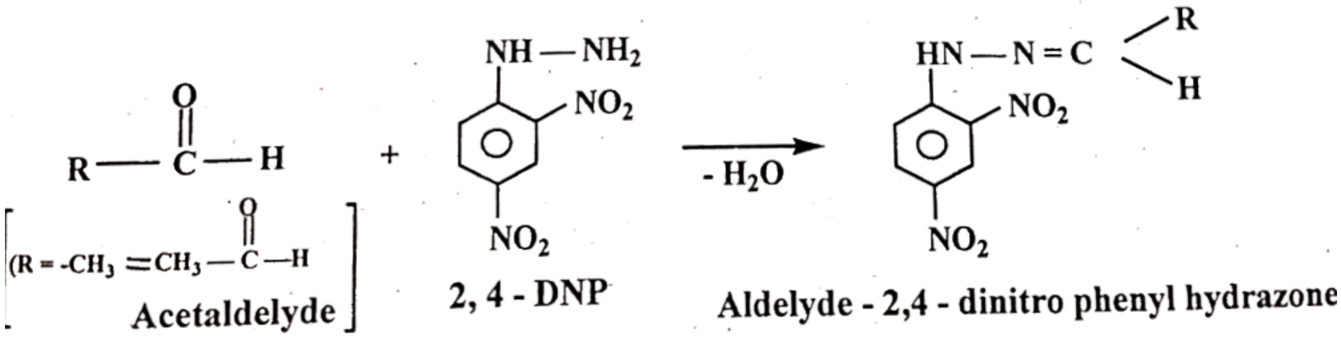
6,Reaction with 2,4-DNP

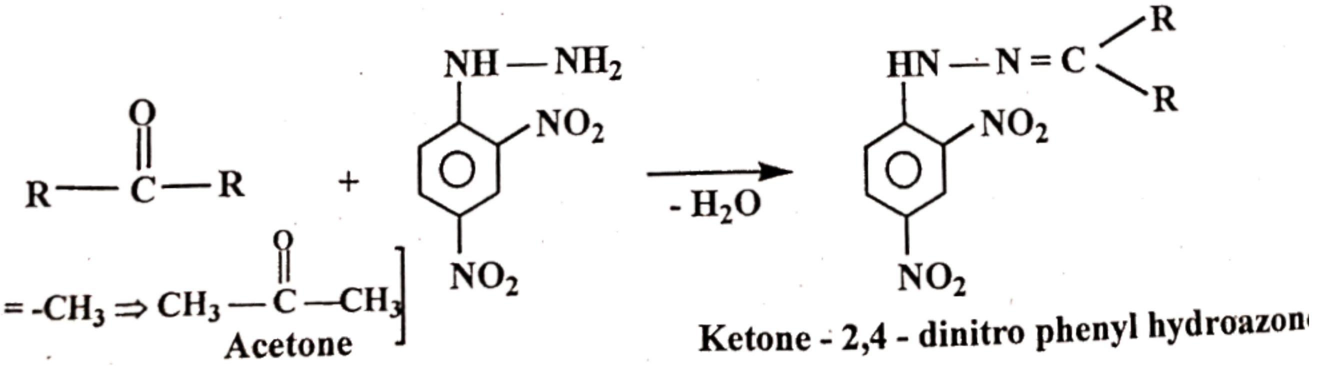
Aldelydes and ketones reacts with 2.4-DNT to form 2,4-dinitrophenyl hydrazones.



2,4-DNP(2.4-dinitrophenyl hydrazine)

Ex:-





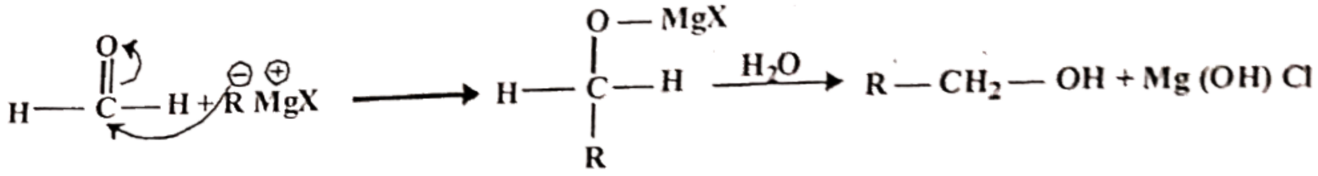
7.Reaction withRMgX:

Carbonyl compounds reacts with grignard reagent (Rmgx)to form 10.2°3-alcoh

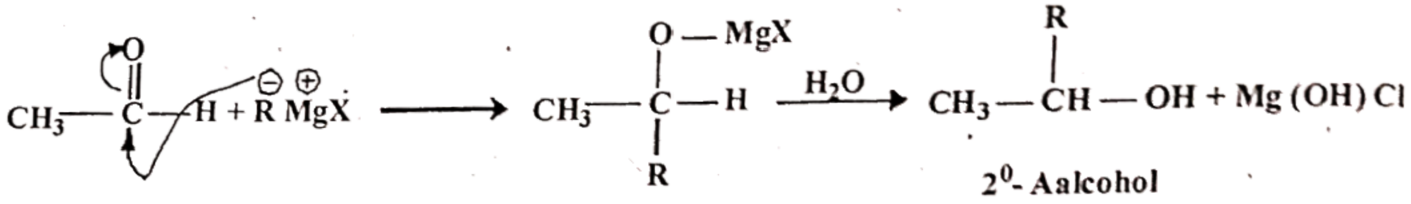
Formaldehyde+RMgX ⟶ I°-alcohol

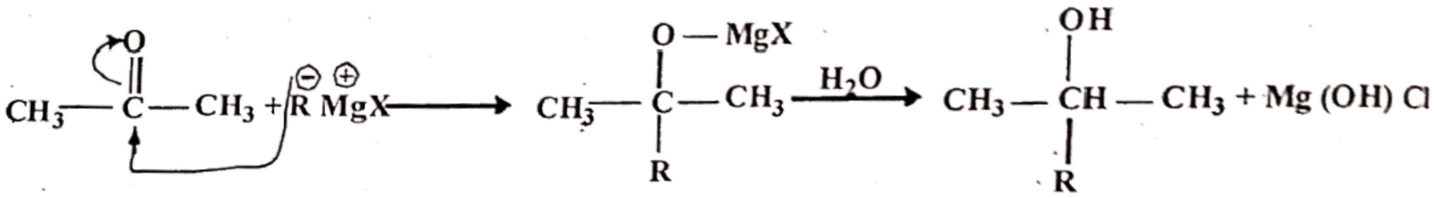
Other aldehyde+RMgX ⟶ 2°-alcohol

Ketone+RMgX —— 3°-alcohol

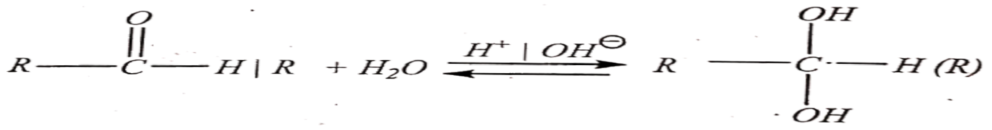
1)


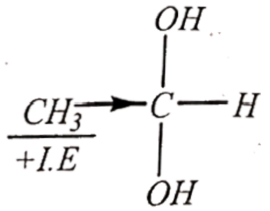
(R=CH_3,X=Cl)

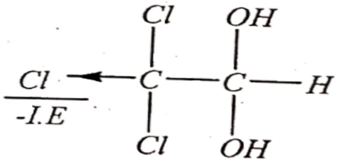
2)


3)


8.Addition with H_2O(or)Hydrate formation: Aldehydes,ketones reacts with water inpresence of acid /base to form hydrates.

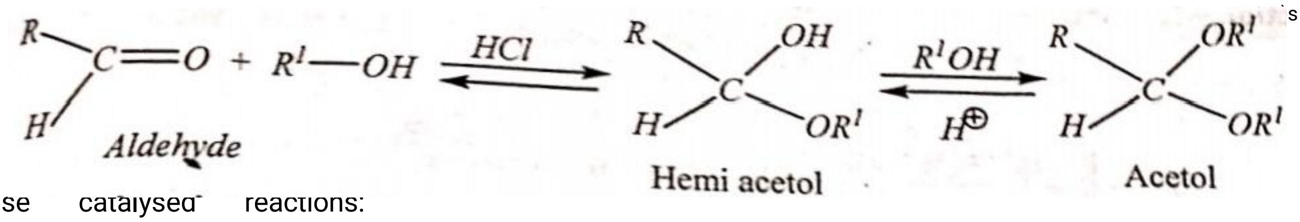






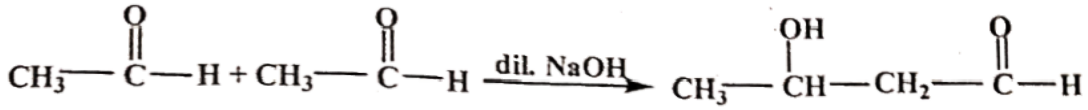
9.Addition with alcohol;

Alcohols react with aldelydes in the presence of HCl to form unstable addition produ lemiacetal,which on further react with alcohol to form stable compound known as acetal



Base catalysed reactions:

.Adol condensation reaction;:Aldelydes containing g-hydrogens underoo sel.addton ln the presence of dil.base (NaoH)to form β-hydroxy aldehyde (Aldol)is known as aldolcondensatlon·

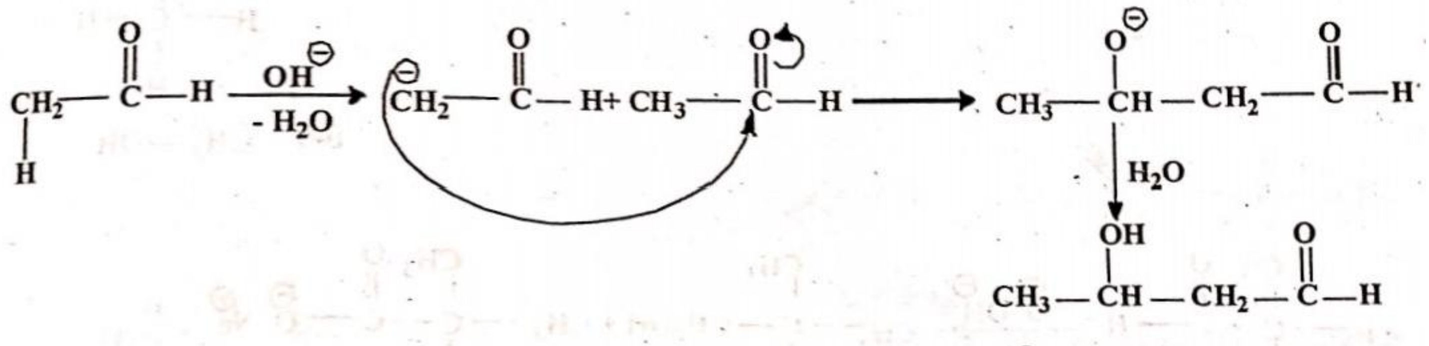
1) 

$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

β-hydroxy butyraldehyde

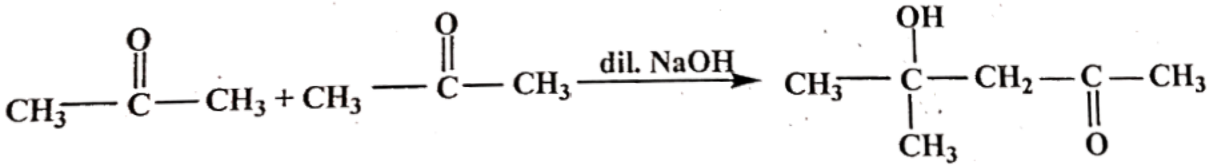
Mechanism:

$NaOH \leq Na + OH^{\odot}$



β -Hydroxy butaraldelyde

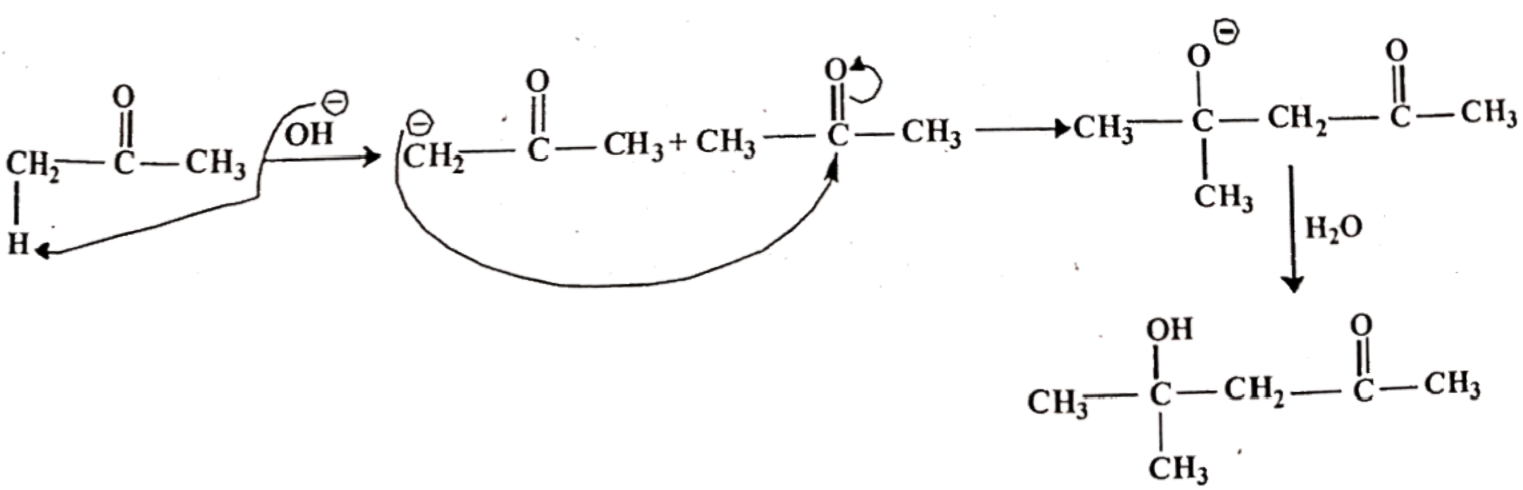
2)Self addition of ketones containing -hydrogens in presence of dil.base to form β-hydroxy ketone (ketol).

2) 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{dil. NaOH}} CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

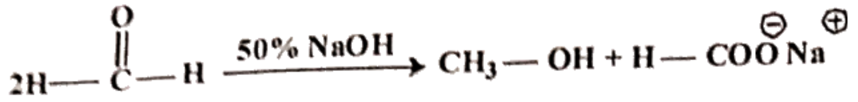
4-Hydroxy 4-Methyl 2-Pentanone

Mechanism



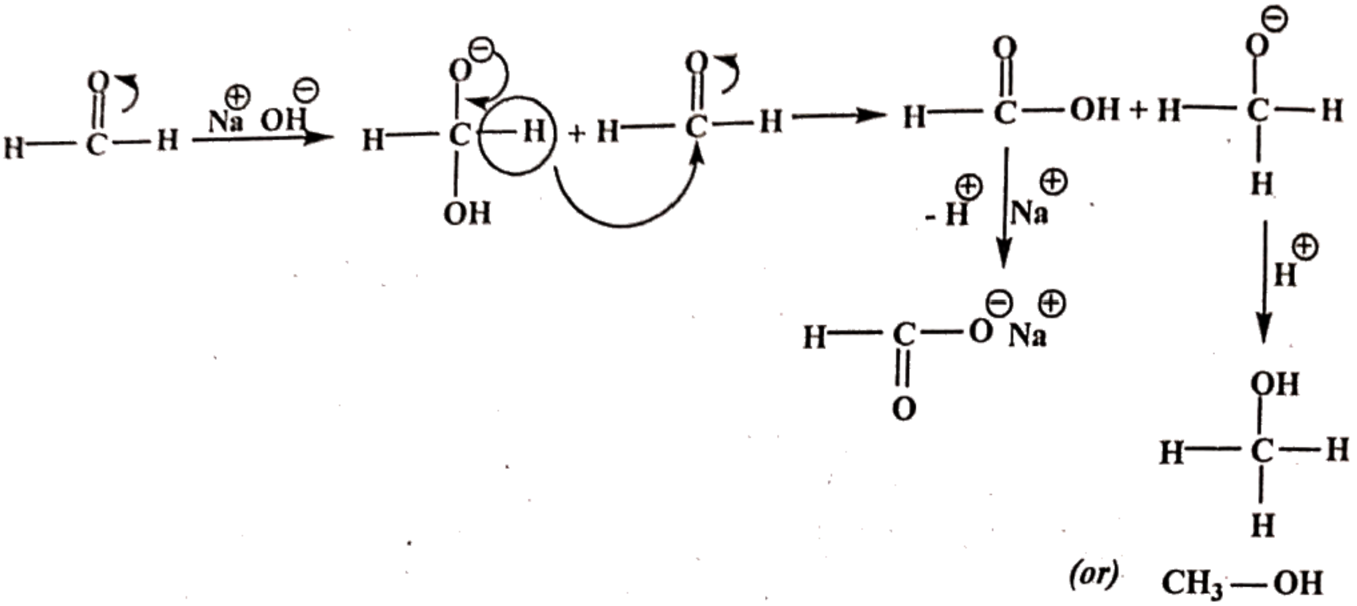
4-hydroxy 4methyl
2pentanonc

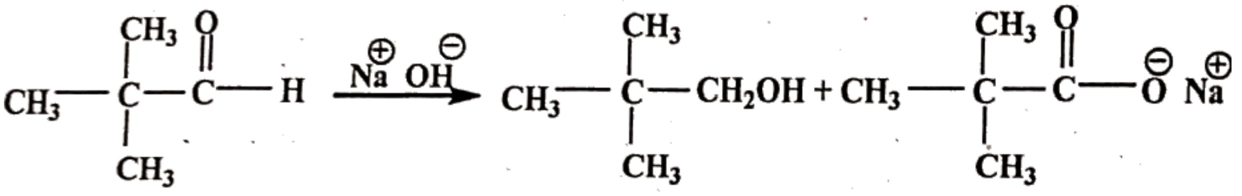
2.Cannizzaro's reaction



$$2H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{50\%\ NaOH} CH_3-OH + H-CO\overset{\ominus}{O}\overset{\oplus}{Na}$$

Mechanism:



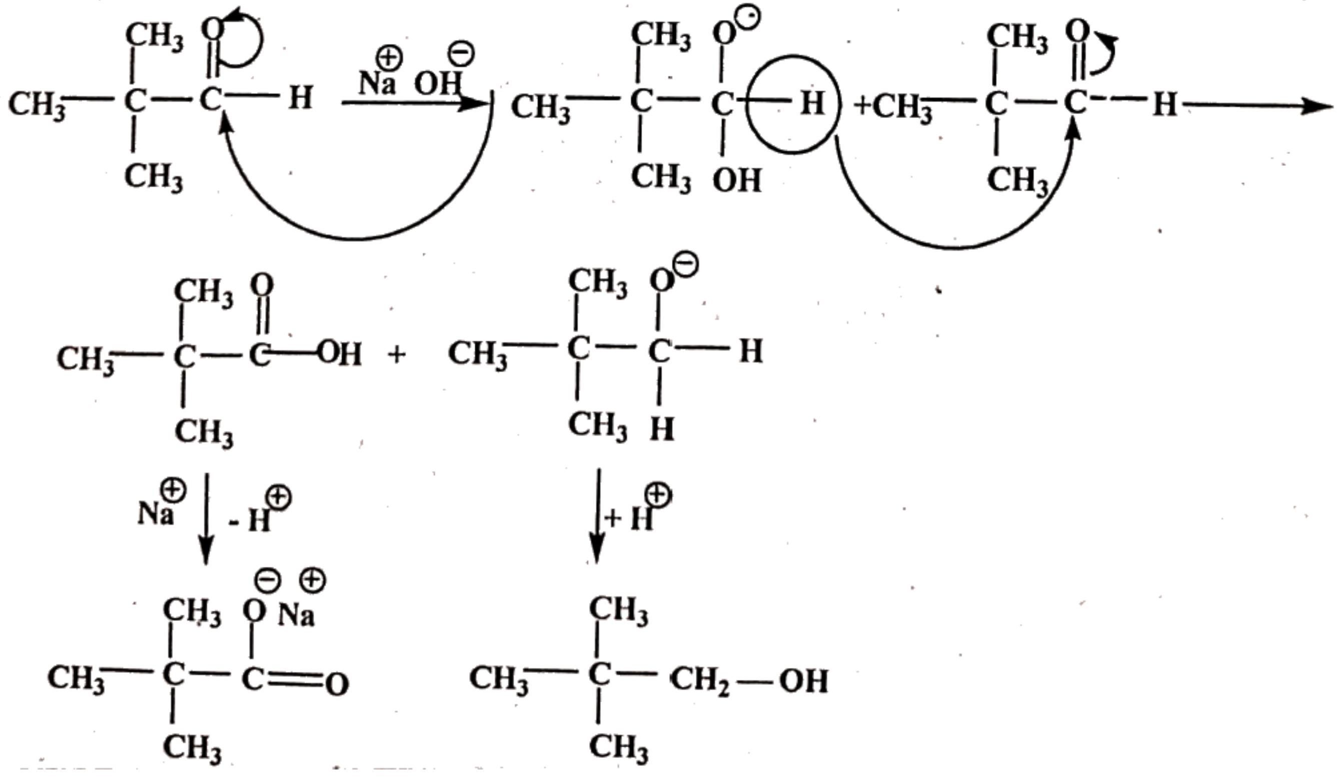
2) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\overset{\oplus}{Na}\ \overset{\ominus}{OH}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\ \overset{\oplus}{Na}$$

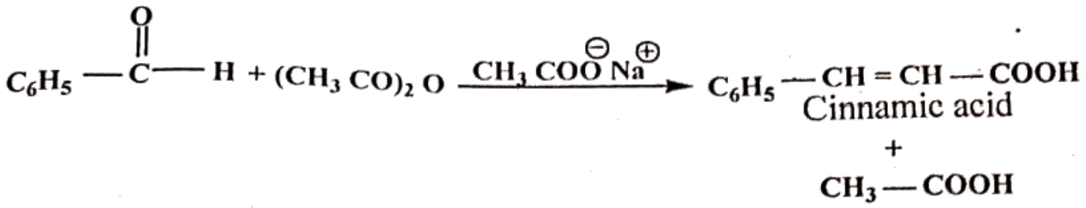
2,2-Dimethyl 1-Propanol

2,2-Di methyl Sod.Propanoate

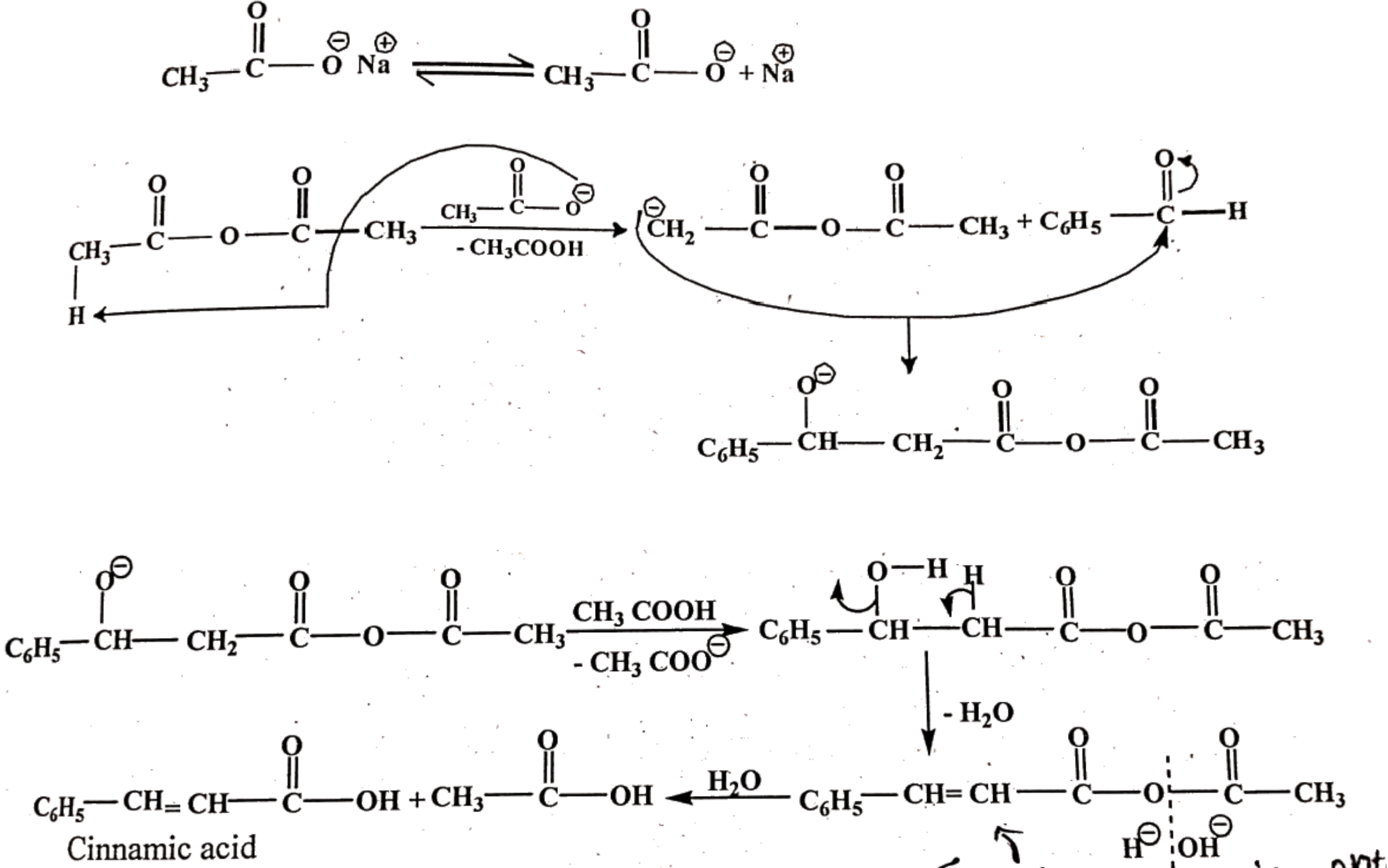
Mechanism:



3.perkin reaction :benzaldehyde reacts with acetic anhydride in presence of sodium acetate to form cinnamic acid is called perkin reaction



Mechanism;



[See in the Running Not

4. Benzoin condensation: Two moles of benzaldehyde reacts with alcoholic KCN to form
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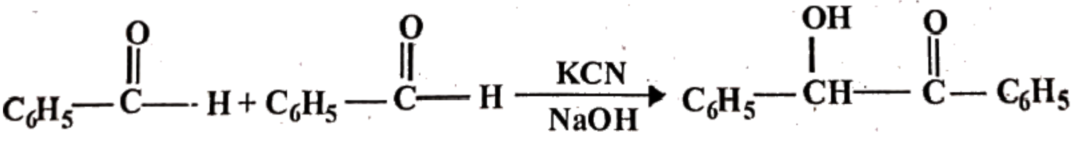
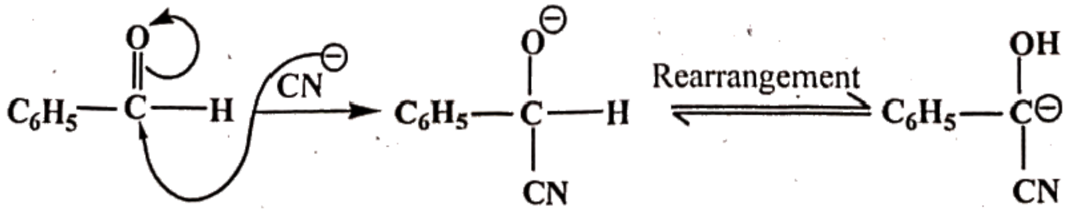
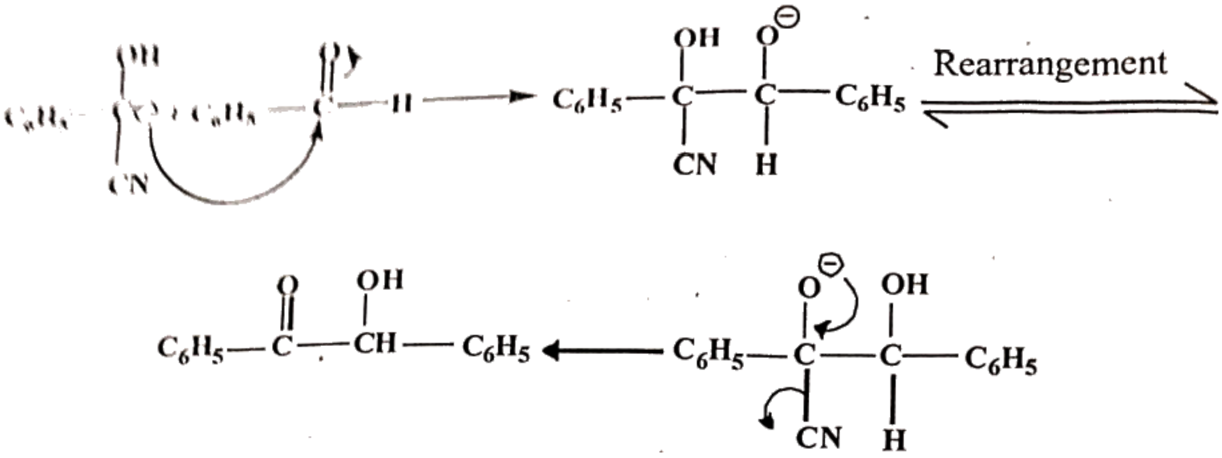


шзшиецээи

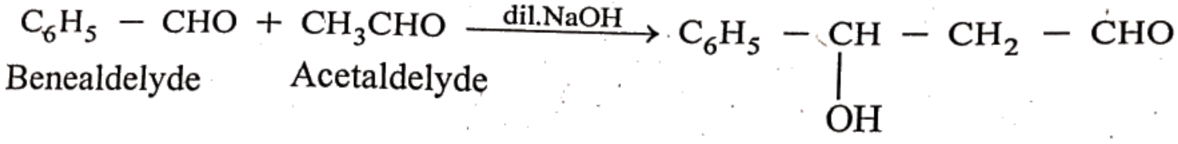
АЭЯ Я + CN ⊙





Claisen -schmidt reaction

The base catalysed cross -aldolcondensation between an aromatic aldehyde and aliphatic aldehyde or a ketone is called claisen -schmidt reaction.



$$\underset{\text{Benealdelyde}}{C_6H_5-CHO}+\underset{\text{Acetaldelyde}}{CH_3CHO}\xrightarrow{\text{dil.NaOH}}C_6H_5-\underset{\substack{|\\OH}}{CH}-CH_2-CHO$$

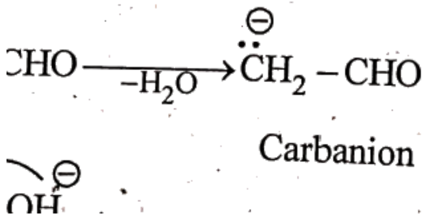
β-hydroxy aldehyde

$-H_2O$

C_6H_5-CH=CH-CHO
Cinnamaldehyde

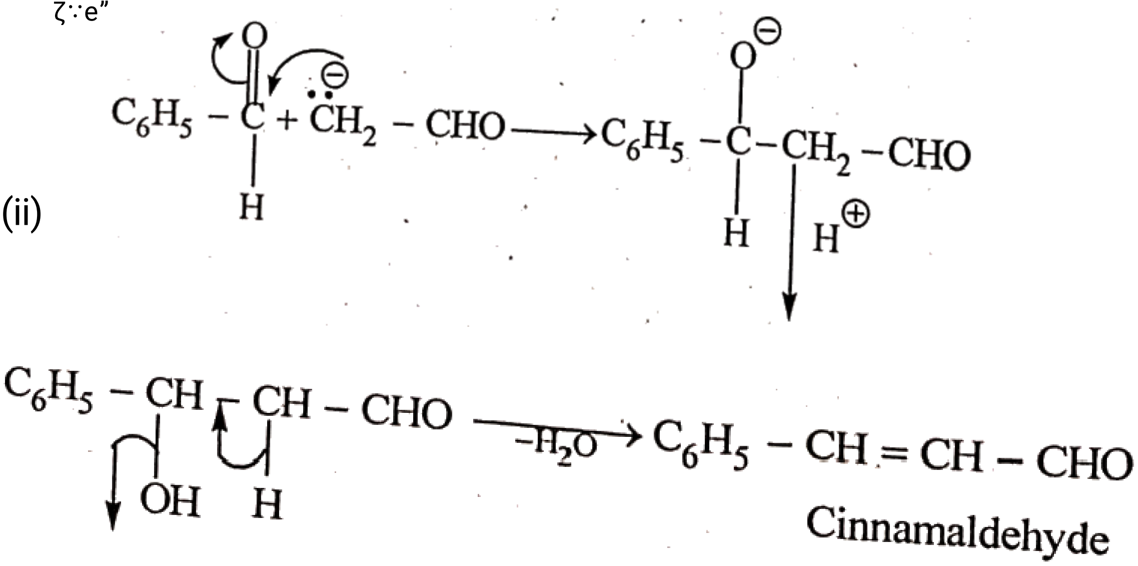
Mechanism :-

(i)


Carbanion

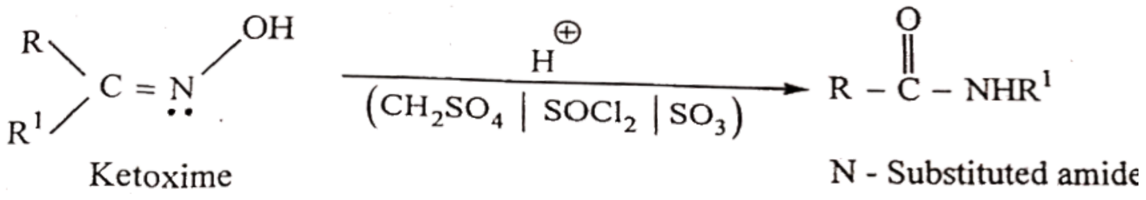
ζ∵e”

(ii)

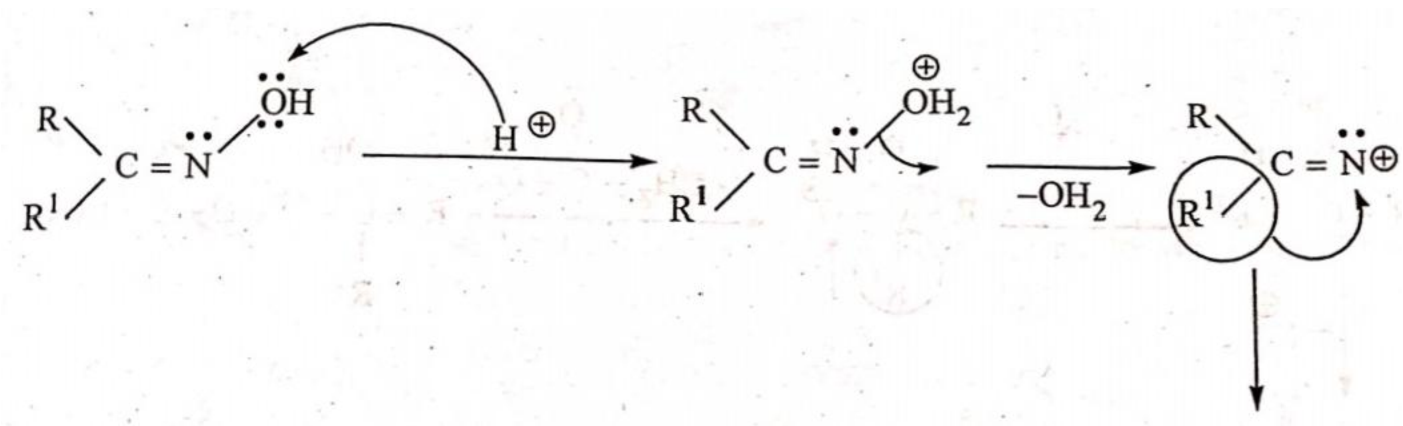

Cinnamaldehyde

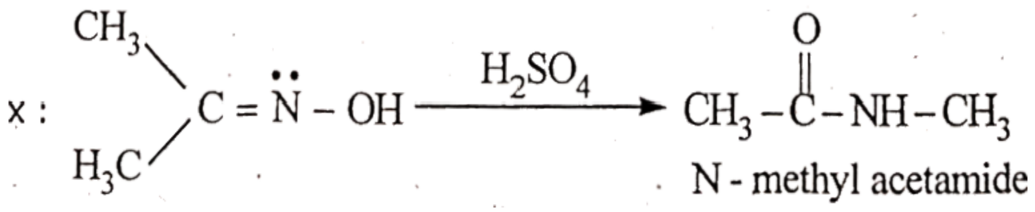
C

The acid catalyzed conversion of ketoximesinto N-substituedamides is known as beckmann rearrangement.



Mechanism ;-





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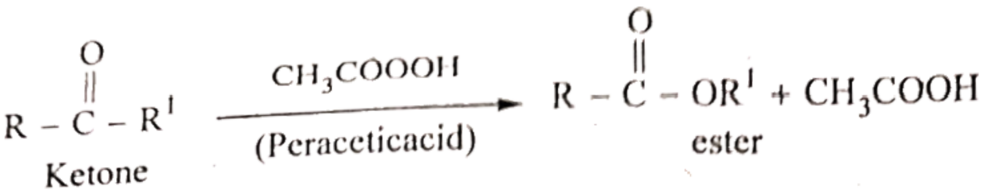
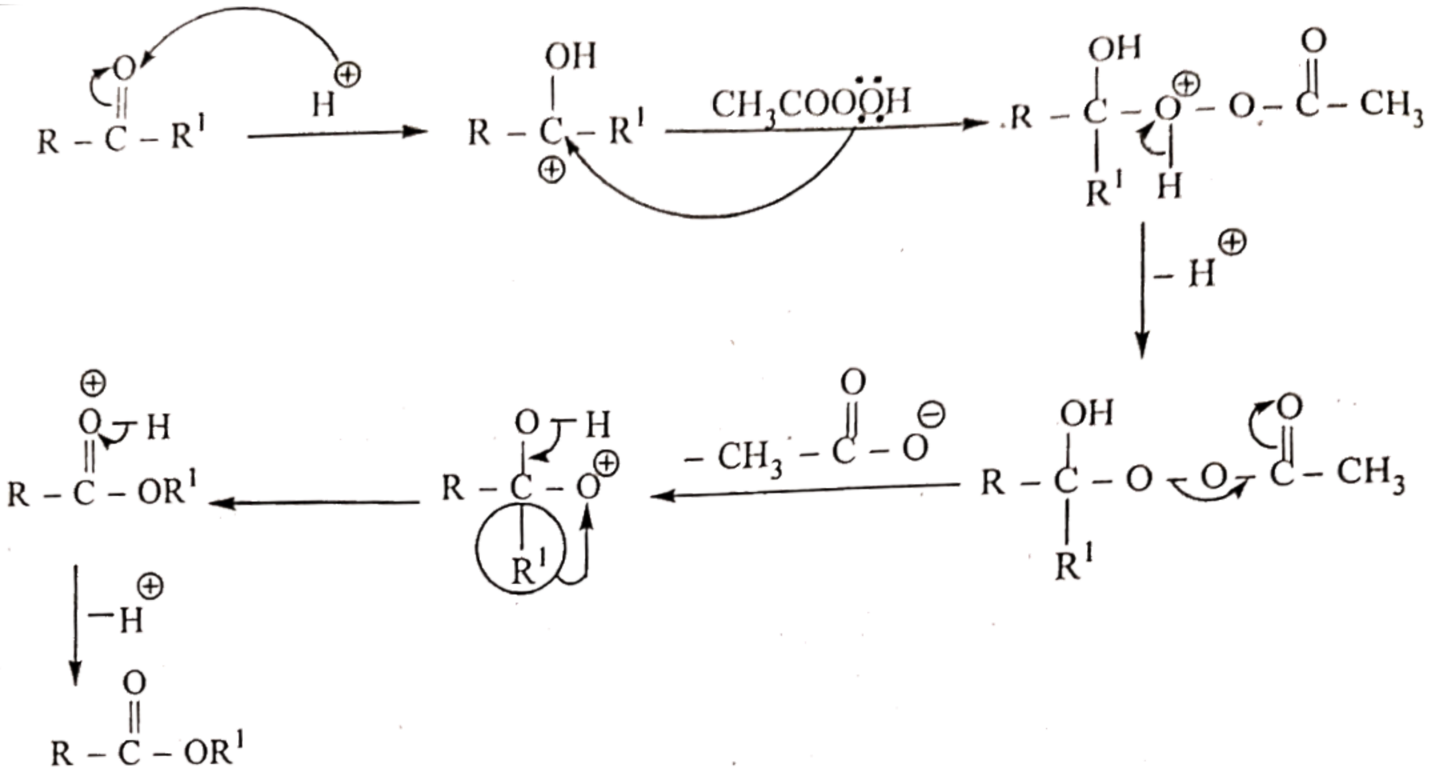
Bayers-villegers oxidation

Oxidation of ketones to esters by the reaction with peracids like peracetic acid perbenzoic acid ………is called baeyer villiger oxidation.

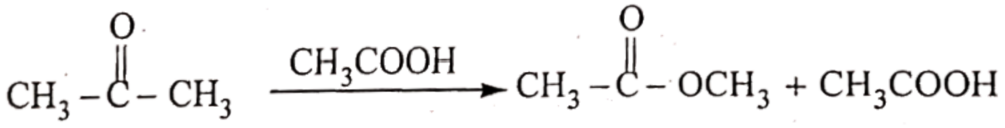


$$R-\overset{\overset{O}{\|}}{C}-R^1 \xrightarrow[\text{(Peracceticacid)}]{CH_3COOOH} R-\overset{\overset{O}{\|}}{C}-OR^1 + CH_3COOH$$

MECHANISM:



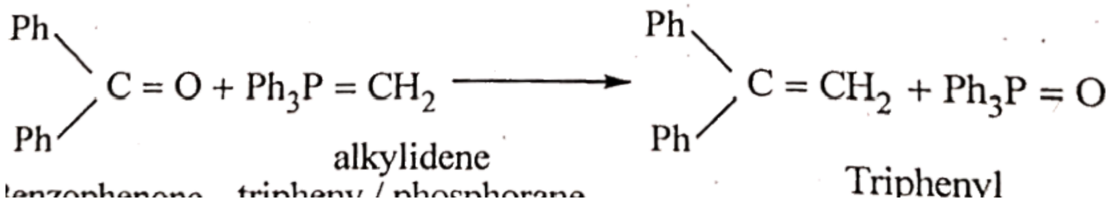
ester

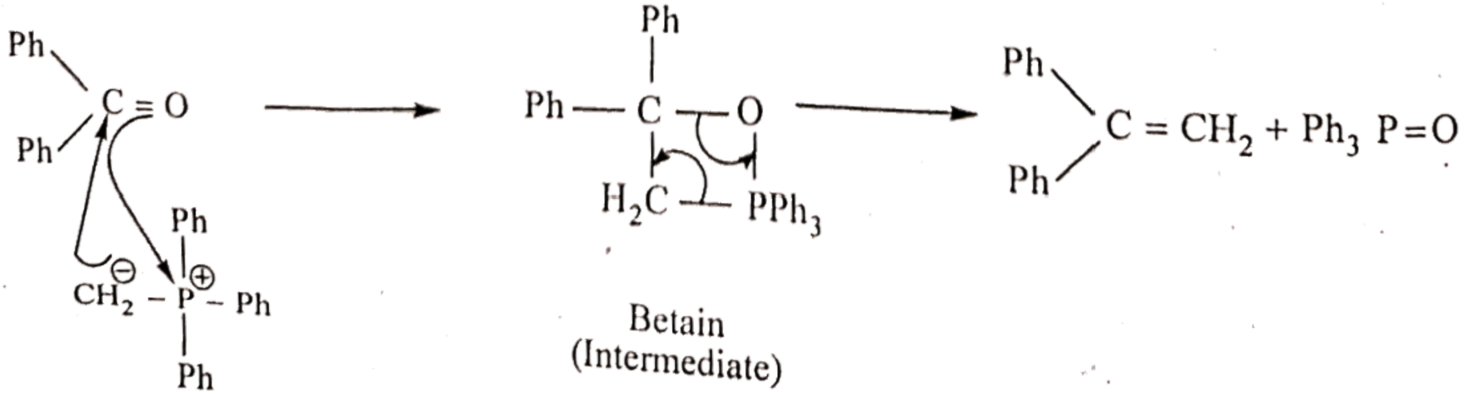
Ex: 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CH_3COOH} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + CH_3COOH$$

Acetone

Aldehydes and ketones reacts with alkylidene triphonyl -phosphorane(ylide)to give alkenescalled witting reaction





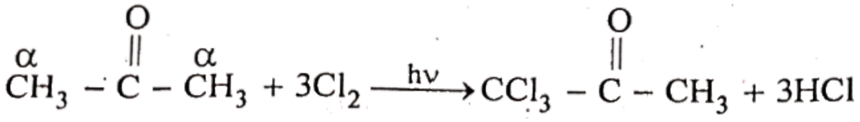
Betain
(Intermediate)

x -substitution reaction

Aldehydes and ketones with a-hydrogen atom(S)are replaced by chlorine atoms in pres-ence of light.

$\&H_3\text{-CHo}+3Cl_2{}^1 \rightarrow ccl_3\text{-CHO}+3Hcl$

Ex: Acetaldehyde Trichloro acetaldehyde (Chloral)



$$\overset{\alpha}{CH_3} - \overset{\overset{O}{||}}{C} - \overset{\alpha}{CH_3} + 3Cl_2 \xrightarrow{h\nu} CCl_3 - \overset{\overset{O}{||}}{C} - CH_3 + 3HCl$$

Ex:

Acetone Trichloro acetone

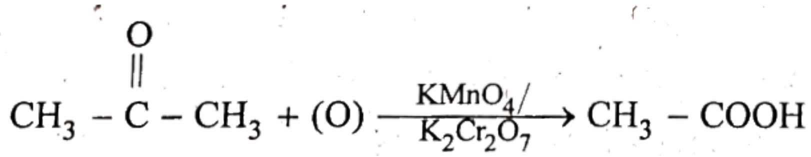
oxidation and reductions :-

<u>(i)Oidation :=</u>

With strong oxidising agents like $KMnO_4$,$K_2Cr_2O_7$/HNO_3.Aldehydes gives carboxylic acids with same number of carbon atom and ketones gives carboxylic acids with less number of carbon atoms.

Ex : $CH_3 - CHO + (O) \xrightarrow[K_2Cr_2O_7]{KMnO_4/} CH_5 - COOH$

Acetaldehyde (C_2) Acetic acid (C_2)



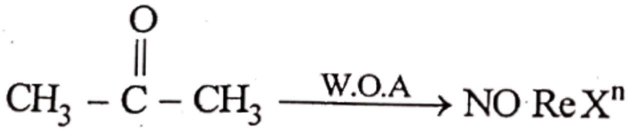
$$CH_3 - \overset{\overset{O}{||}}{C} - CH_3 + (O) \xrightarrow[K_2Cr_2O_7]{KMnO_4/} CH_3 - COOH$$

Acetone (C_3) Acetic acid (C_2)

Br_z/H_2O………Aldehydes gives carboxylic acids but ketones donot oxidised by weak oxidising agents.

$CH_3 - CHO \xrightarrow{W.O.A} CH_3 - COOH$

Aldehyde



$$CH_3 - \overset{\overset{O}{||}}{C} - CH_3 \xrightarrow{W.O.A} NO\ ReX^n$$

Ketone

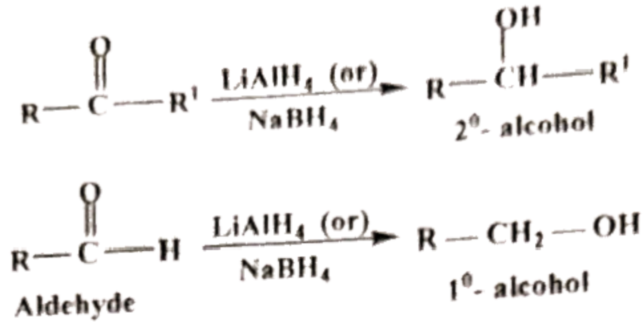
REDUCTION

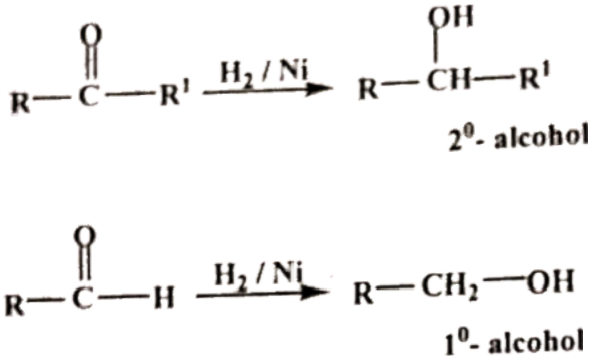
9,stro

1.catalytic hydrogenation (or)Reduction with.H,/Ni:

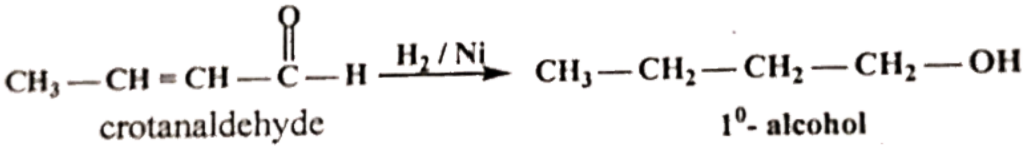
Reductien of carhenyl comeute with L/Ni(or)LialH,(or)NaBH

alcohols

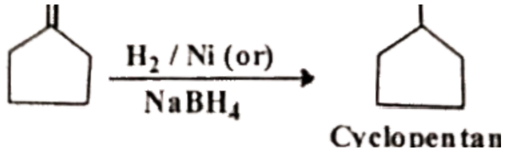




Ex:-



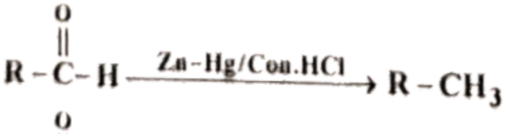
$$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2/Ni} CH_3-CH_2-CH_2-CH_2-OH$$



2.Clemenson reduction

Aldelydes and ketones reduced to hydrocarbons (Alkanes)in presence of Zinc-an gam and conc.HCl is called clemenson reduction.

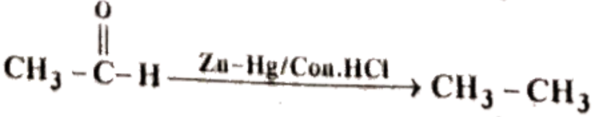
Zn-Hg+Conc.HCl is called clemenson reducing agent



$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{Zn-Hg/Con.HCl} R-CH_3$$

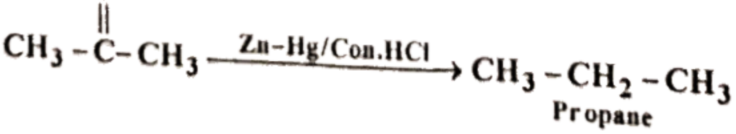
$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{Zn-Hg/Con.HCl} R-CH_2-R$$

Ex :-



$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{Zn-Hg/Con.HCl} CH_3-CH_3$$

ethane



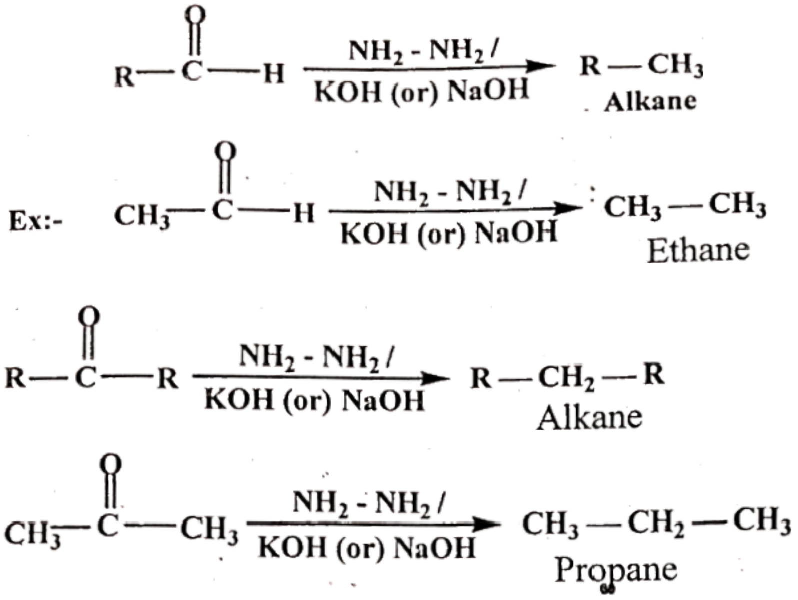
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{Zn-Hg/Con.HCl} CH_3-CH_2-CH_3$$

Propane

3.wolf kishner reaction:

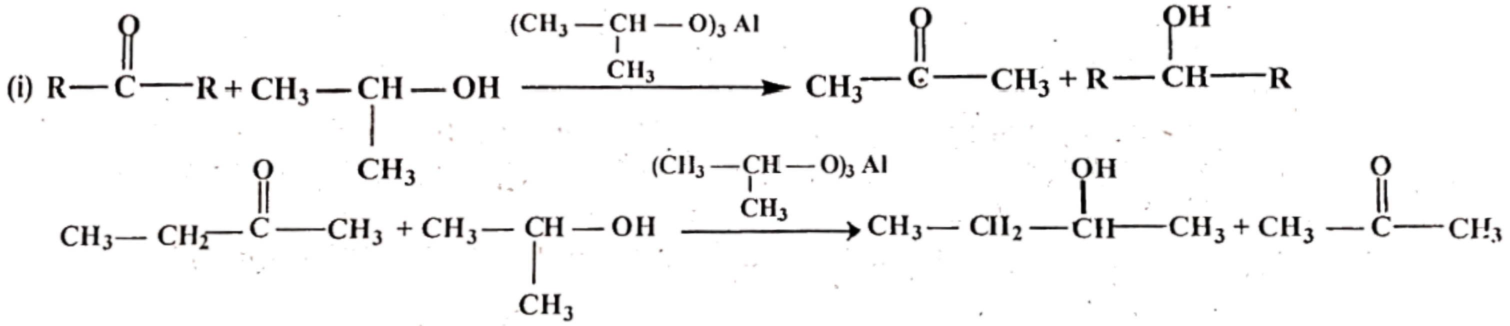
Ketones reduced to hydro carbons in the presence of hydr~~azine and~~ strong base like NaOH /KOH is called wolf -kishner reduction

NH_2-NH_2+NaOH(or)KOH is called wolf-kishner reducing agent.



4.Meerwin-pondorf-verley Reduction (MPV reduction):

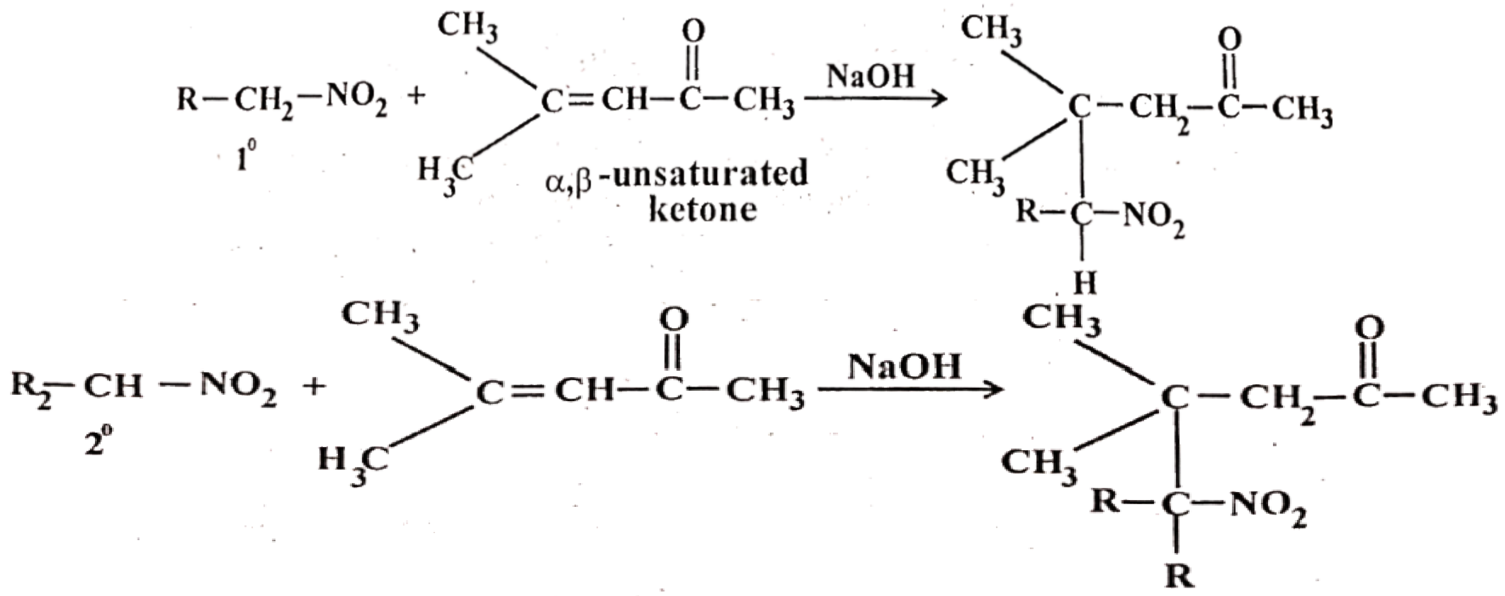
Ketones are reduced to 2⁰-alcohol in presence of Alluminium isopropoxide and isopropyl alcohol is known as MPV reduction.



Mechanical addition:

Addition between compounds with electron withdrawing groups and Olefinic double bonds is known as michael addition.

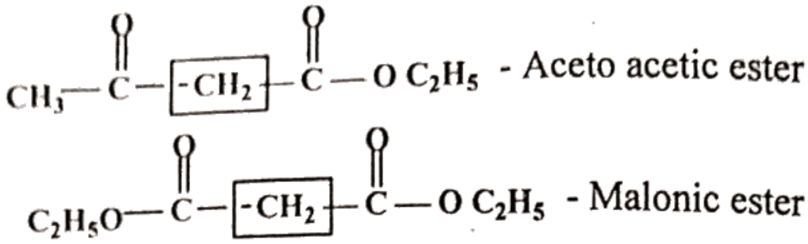
with electron withdrawing groups and Olefinic double



ACTIVE METHYLENE COMPOUNDS

groups (>C=0.-CN.NO_2...)s known as "kctve methv/ene qoup?,and he compounts contain such methylene group are known as "active methylene compounds".

E x:

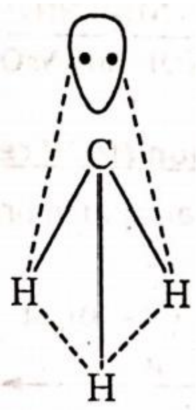


$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{-CH_2}-\overset{O}{\overset{\|}{C}}-OC_2H_5$ - Aceto acetic ester

$C_2H_5O-\overset{O}{\overset{\|}{C}}-\boxed{-CH_2}-\overset{O}{\overset{\|}{C}}-OC_2H_5$ - Malonic ester

Structure of carbanion

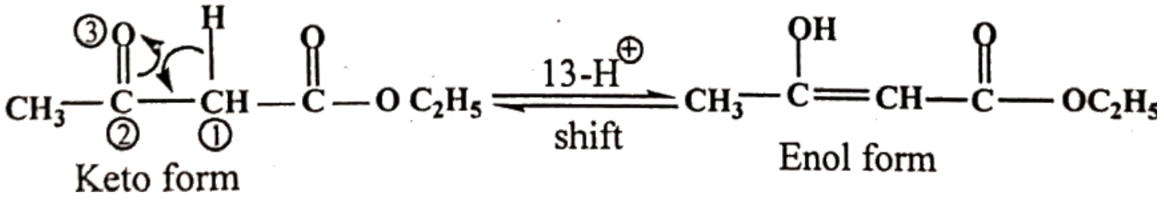
Ex:CH3 methyl carbonion:



Hybridisation:Sp³

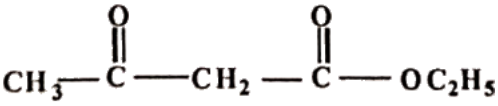
Shape:Pyramidal

Keto -Enol tautomerism: Acetoacetic ester shows keto enol tautomerism.This is ence of œ-Hydrogen atoms(Active methylene group).In this keto form converted by tautomerism(1,3-H+shift).Hence it is called keto enol tautomerism.



$CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \underset{shift}{\overset{13\text{-}H^{\oplus}}{\rightleftharpoons}} CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$

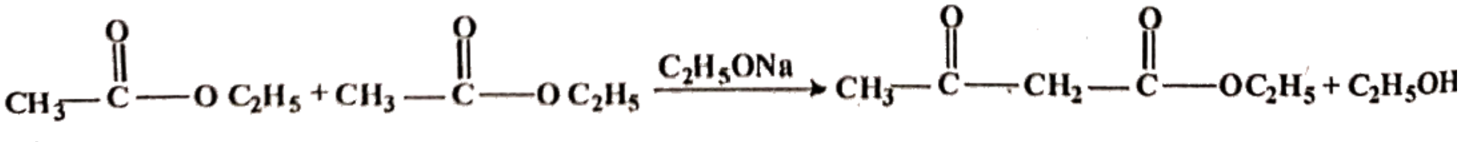
Aceto acetic Ester(or)Ethyl Acet Acetate(EAA):



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

Preparation:

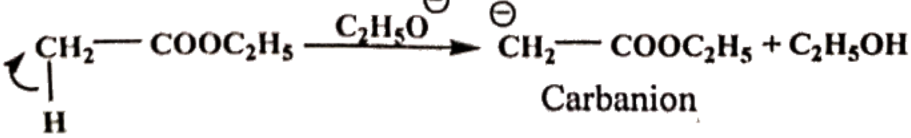
1.Claisen condensation: Condensation of two moles of ethyl acetate in the presence of so Ethoxide to form Aceto acetic ester is called clalsen condensation.



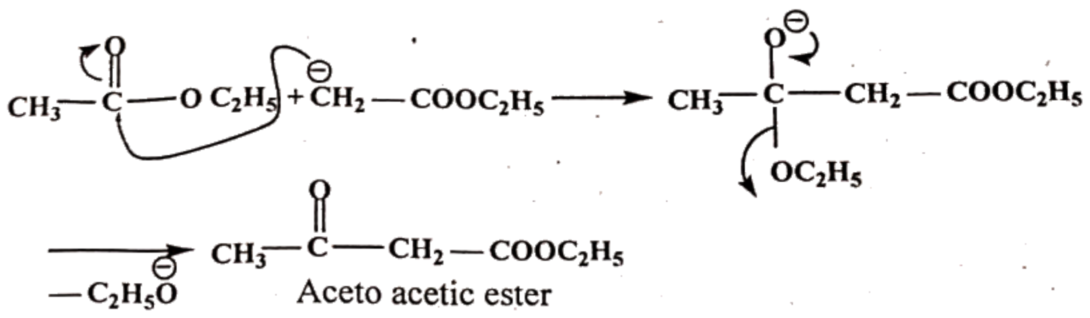
$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5+C_2H_5OH$

Mechanism:

C_2H_3ONa Na^4+C_3H,δ

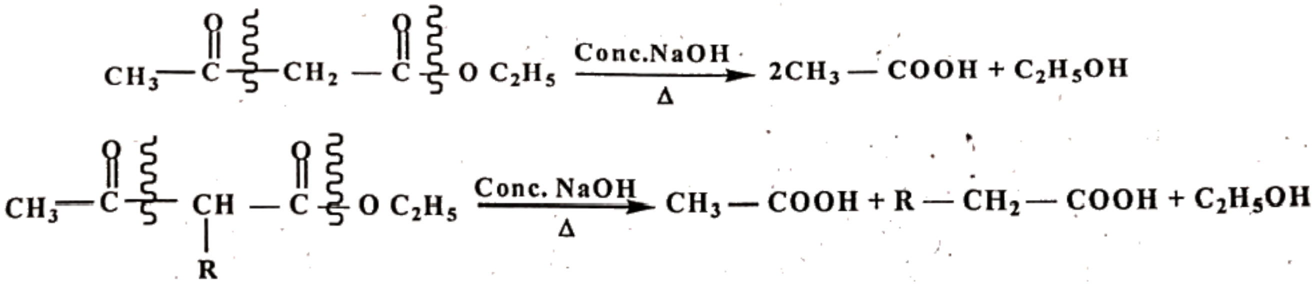


$\underset{H}{\underset{|}{CH_2}}-COOC_2H_5 \xrightarrow{C_2H_5\overset{\ominus}{O}} \overset{\ominus}{C}H_2-COOC_2H_5+C_2H_5OH$

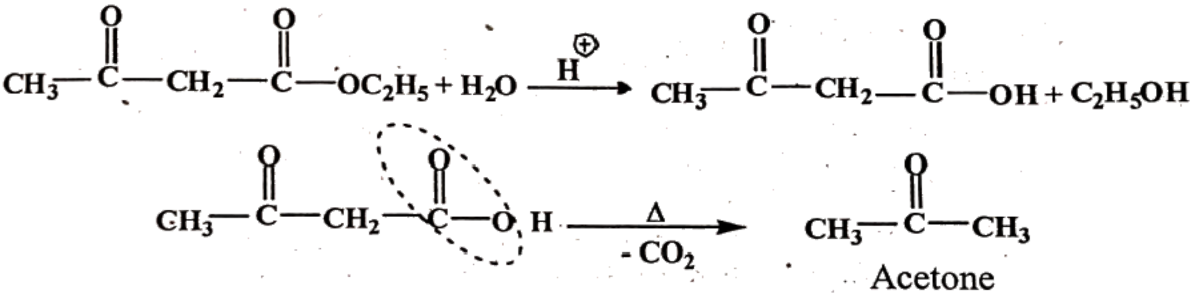


synthetic applications of auto acetic ester

.Acidic hydrolysis:Hydrolysis of EAA with Conc.alcoholic KOH or NaOH gives carboxylic acids. Since here carboxylic acids are the main products,then hydrolysis is called acidic



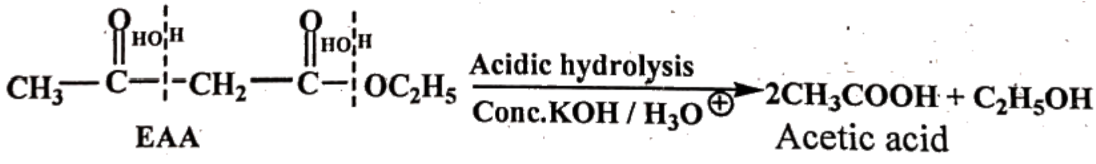
2.Ketonic hydrolysis: Hydrolysis of EAA with dilute acid (or)bases gives ketones.



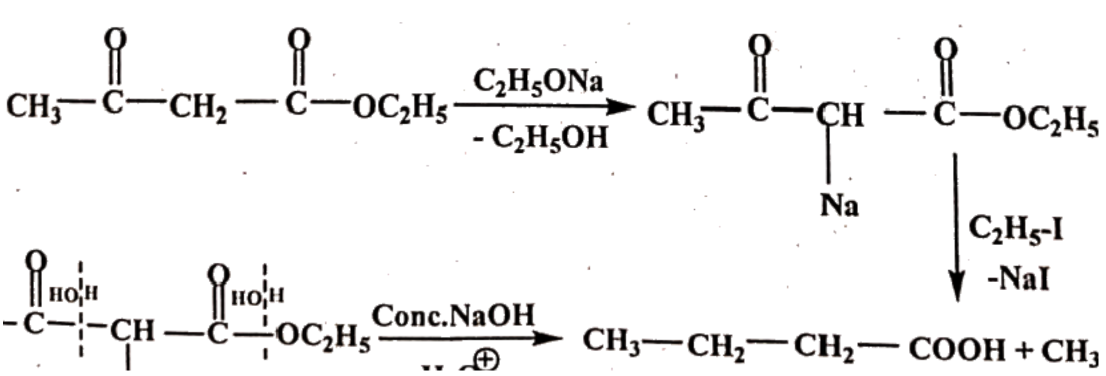
Application of EAA:

1.Preparation of Mono carboxylic acids :Hydrolysis of EAA and their derivatives gives mong carboxy ic acid s.

a) Ace ticaci d :(CH_3-COOH



b)Butanoic acid:



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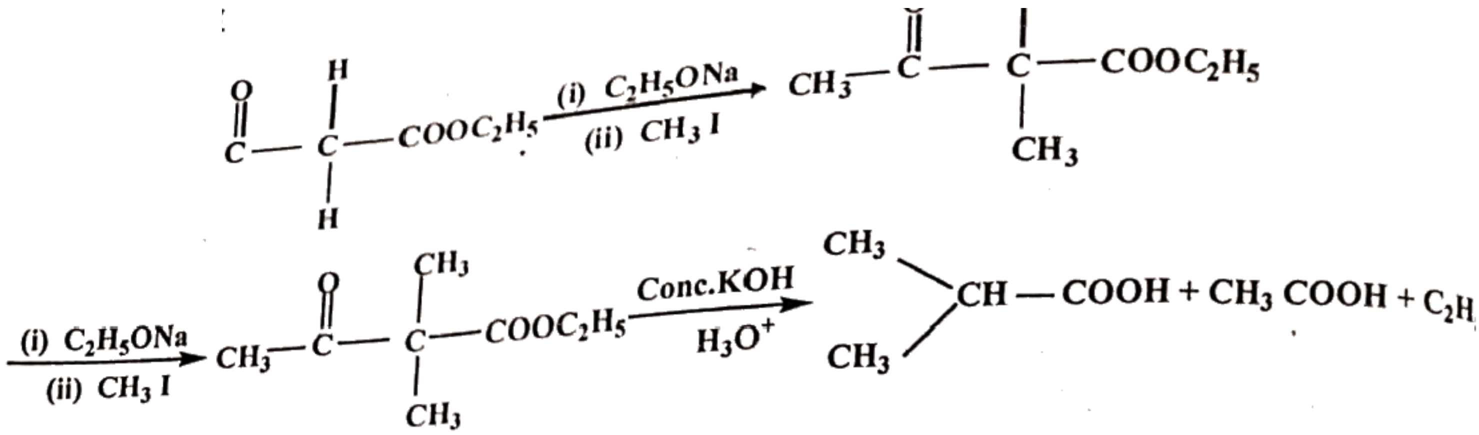
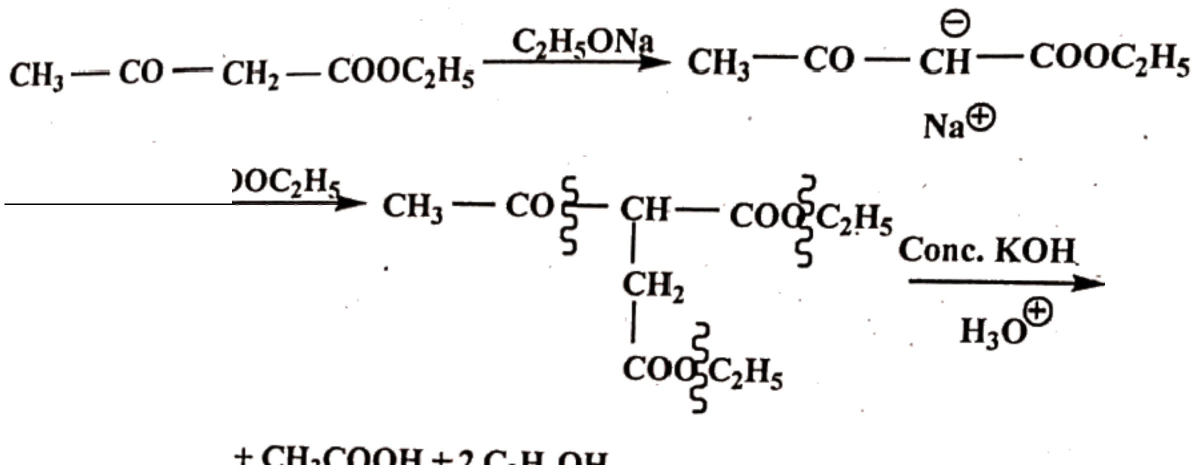
ISO BUTIRIC ACID



2.Preparation of dicarboxylic acid

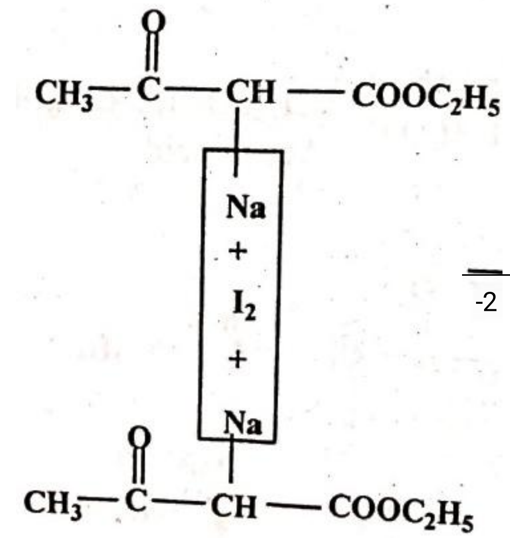
EAA reacts with chloro ethyl acetate followed by acidic hydrolysis with strong gives dicarboxylic acids.

Ex:(a)Succinic acid:



$CH_2—COOH$

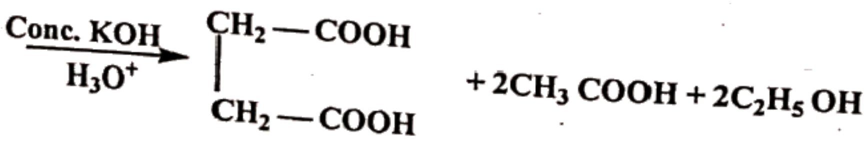
An alternate method used for preparation of succinic acid from EAA is as follows.

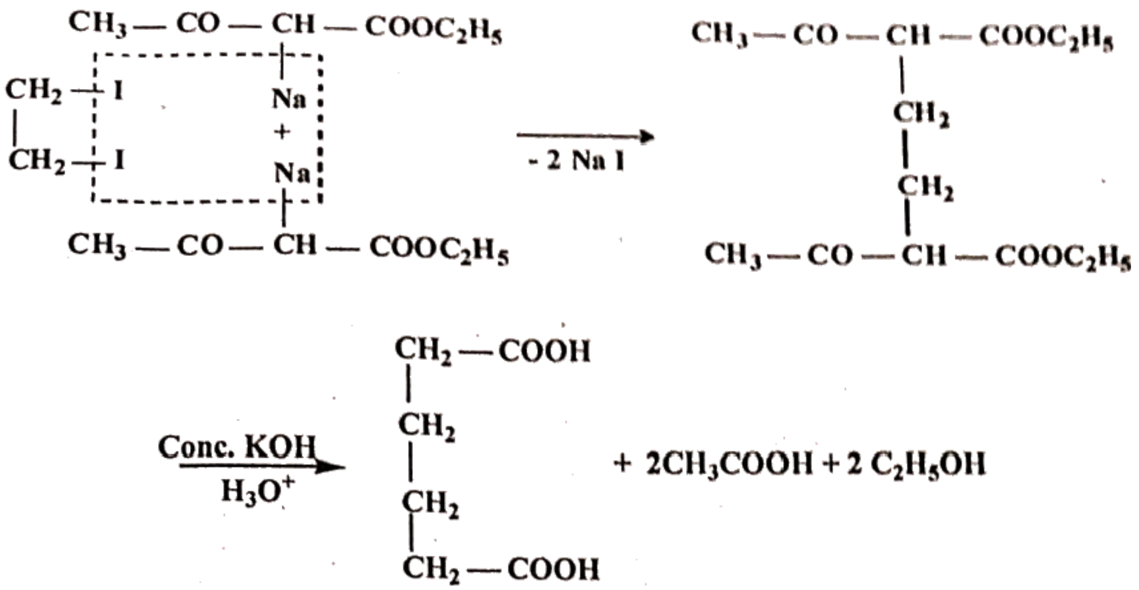


$COOC_2H$

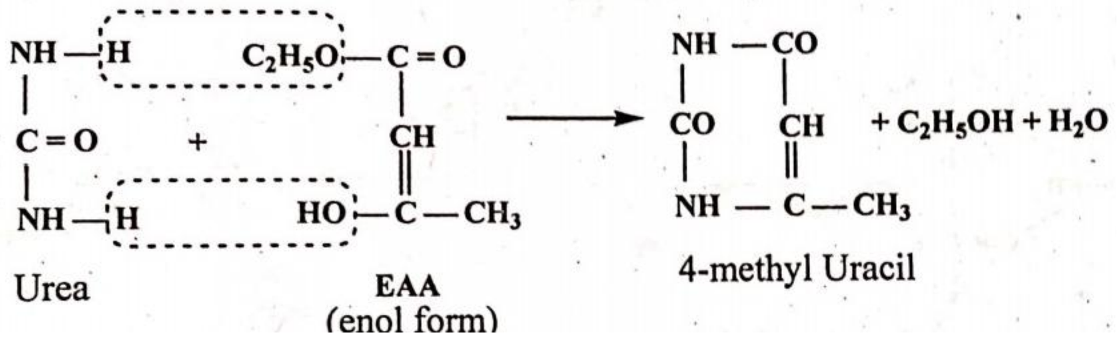
-2 Na]

$—CH—COOC_2Hs$





(C) Preparation of 4-methyl uracil: EAA reacts wlh игеа to Гогт 4-тetyl игacl



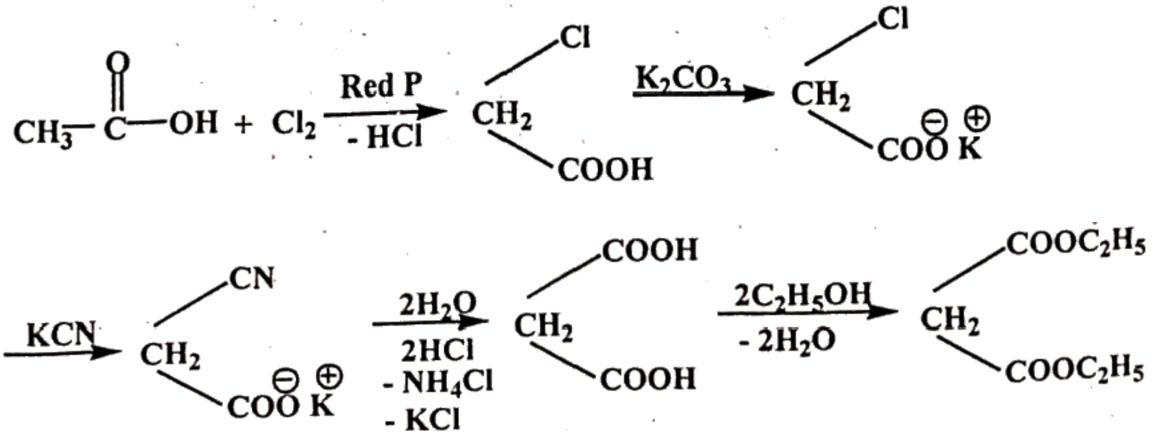
II. MALONIC ESTER

CH2;

Preparation:

1.From acetic acid

Acetic acid reacts with Cl2 | Red.P gives chloroacetic acid, which on reaction with K2CO3, KCN followed by hydrolysis with HCl and reaction with 2 moles of Ethyl alcohol gives malonic ester.



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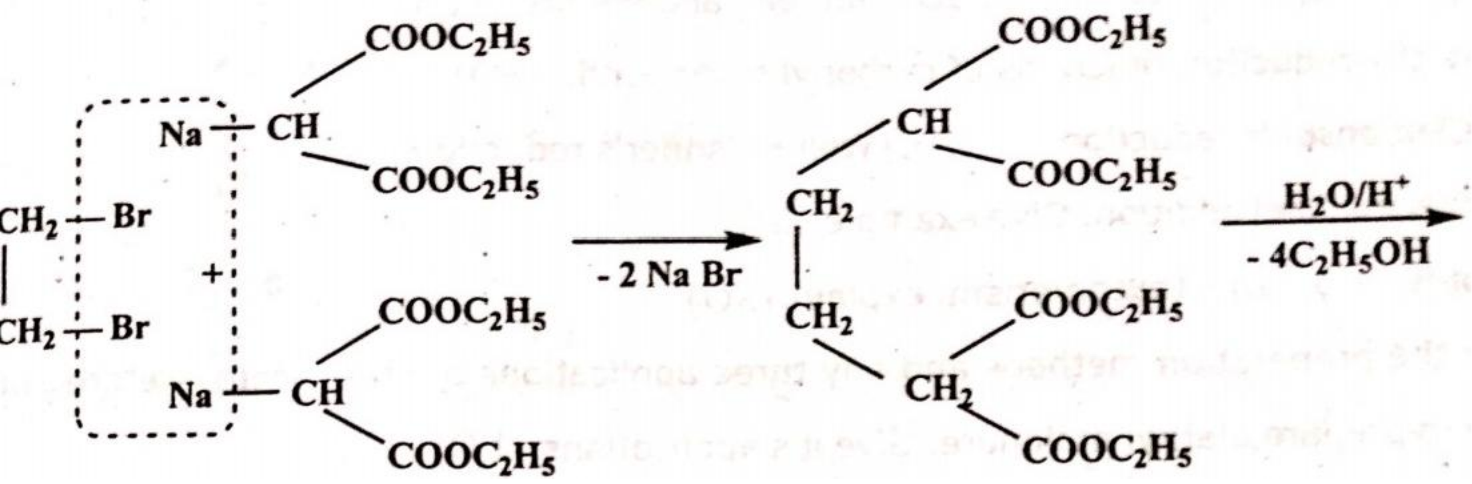
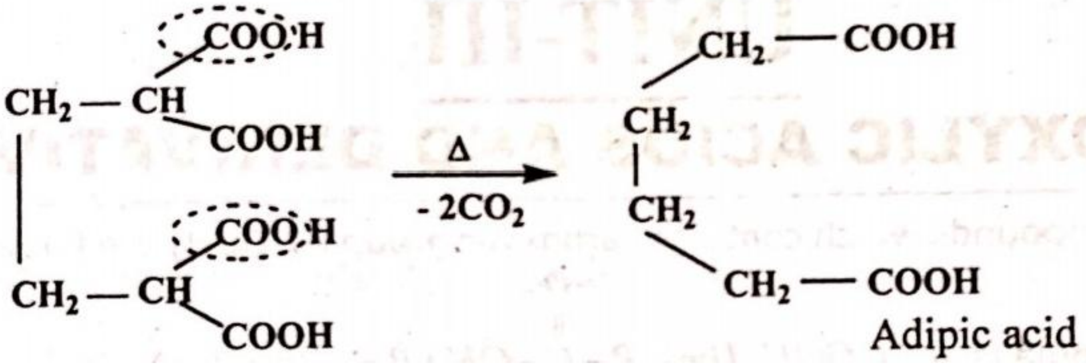
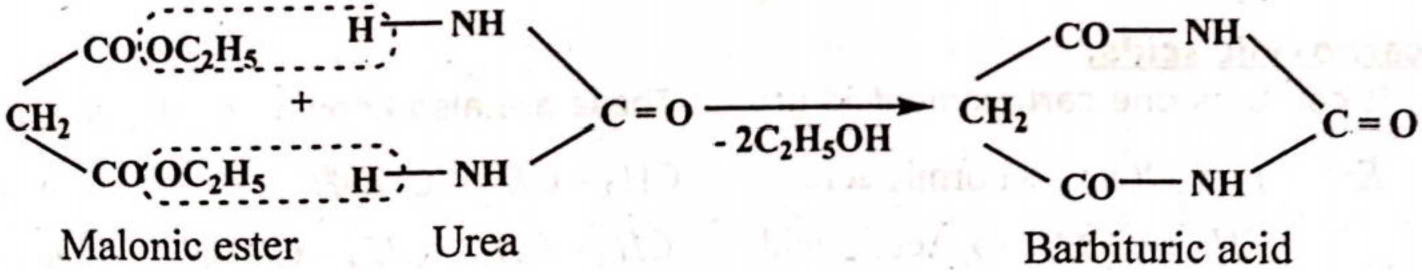
Preparation of adipic acid:

Two moles of mono sodium malonic ester reacts with 1,2-dibromo ethane followed b is gives"Adipic acid".

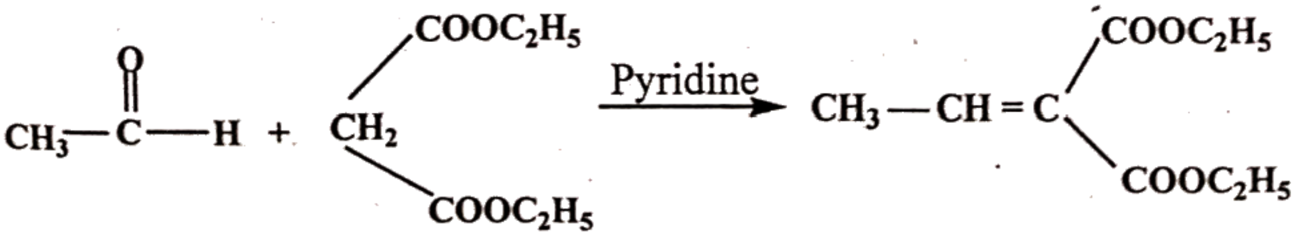


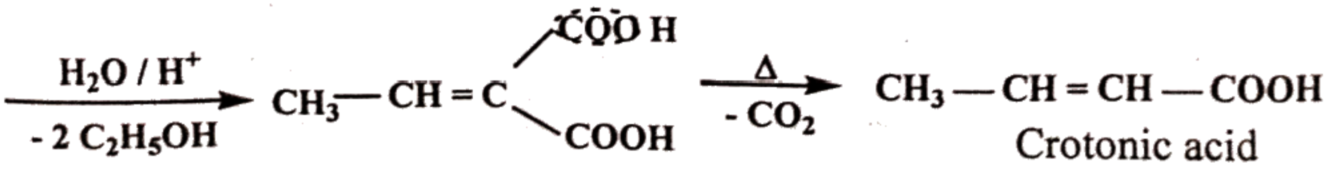


Preparation with urea: malonicester reacts with Urea gives Barbituric acid



<u>**Knovenagel reaction:**</u>Malonic ester reacts with Aldelydes to form a,β-unsaturated ci ylic acids.This reaction is called knoevenagel reactions.



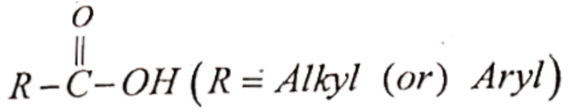


$$\xrightarrow[-\,2\,C_2H_5OH]{H_2O\,/\,H^+} CH_3-CH=C\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} \xrightarrow[-\,CO_2]{\Delta} CH_3-CH=CH-COOH$$

Crotonic acid

UNIT-III

Огganc сотроиnds whch contans саґЬохуПс дгоир (-COOH) аге Кпомп саґЬoxylic acid the general formula is



$$R-\overset{\overset{O}{\|}}{C}-OH\left(R=Alkyl\ (or)\ Aryl\right)$$

2

<u>Classlfcaton:</u> Based on numberof-COOH groups present,The carboxylic acids are classlfedi

; 3 types,

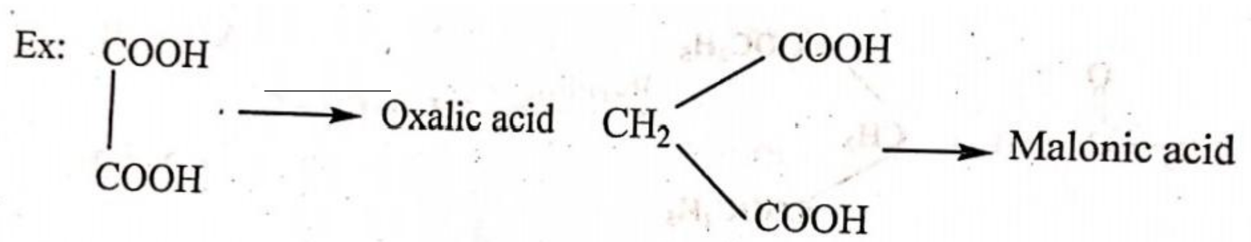
MONO CARBOXYLIC ACIDS

It contains one carboxylc acid groиp. These are.also known as fatty acids.

Ex:: H -COOH — Formic acid CHз -CHг-COOH — Propanoic acid

CHз -COOH — Acetic acia CHз -CHэ-CHэ—COOH —> Butanoic acid

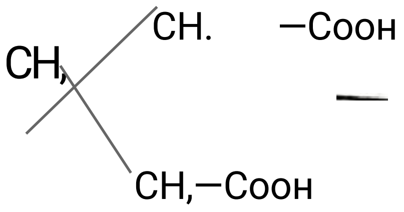
<u>2)Dlcarboxylc acids:Th</u>ese contains lwo carboxyllc acid groups.



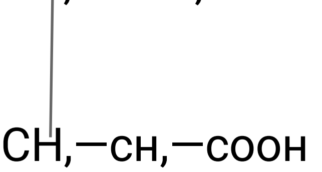
CH,——cooн

Succinic acid

CH,—cooн



— Glutaric acid



~~—3—~~ Adipic acid

3)Tri carboxylic acids:these acids contains three-cooH groups

Ex: CHз—COOH

C(OH)—CooH — Сйиптс асйд

CH —COOH

Мопо Carboxylic acid

These are aqain classified Into two types

1.saturated carboxylic acids: acid which contains saturated carbon chain.

Ex: CH. —COOH. —»- Ethanoic acid

CH;——сн, —соон — Propanoic acid

сн, — Сн,—сн, —соон —— Buanoic acid

2. Unsaturated carboxyllc acids: whlchcontalns unsaturated carbon chain.

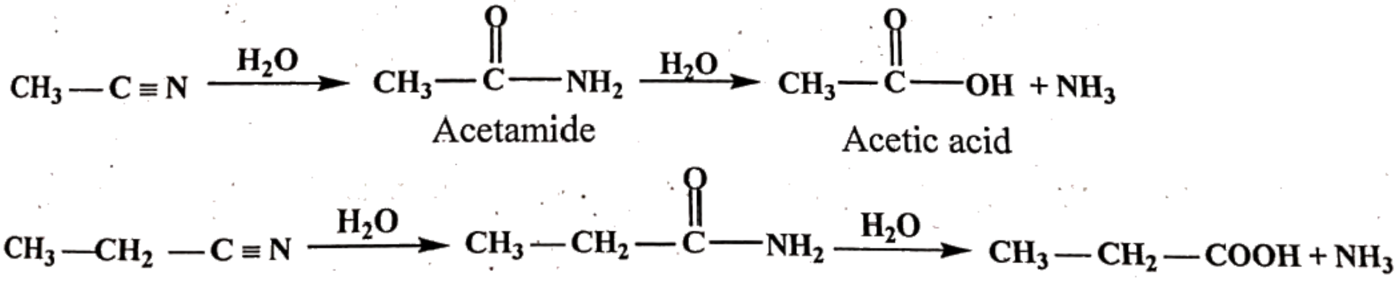
Ex: CH,— сн —CoOH —»- АсгоНс acід

CH, — сн —сн —соон —> Crotonic acid

С,н,— CH —CH —COOH — Cinnamic acid

PREPARATION OF CARBOXYLIC ACIDS

A)**from nitriles**: drolysis of nitriles with acid or base to form carboxvlic acids.

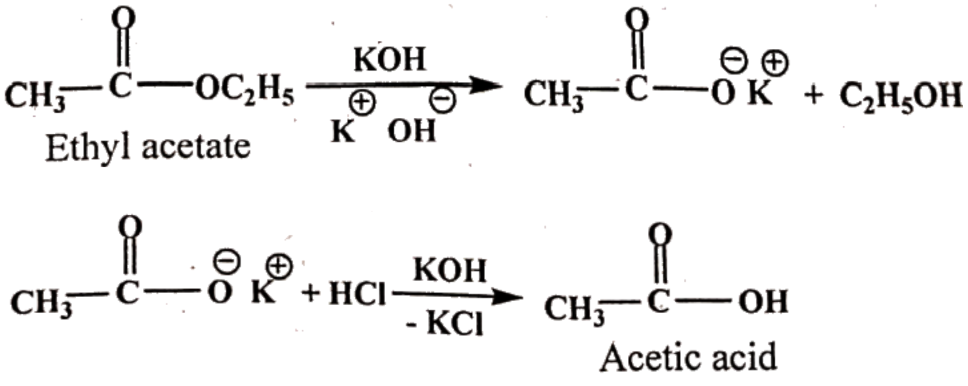


$$CH_3-C\equiv N \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3$$

$$CH_3-CH_2-C\equiv N \xrightarrow{H_2O} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} CH_3-CH_2-COOH + NH_3$$

Propanoic acid

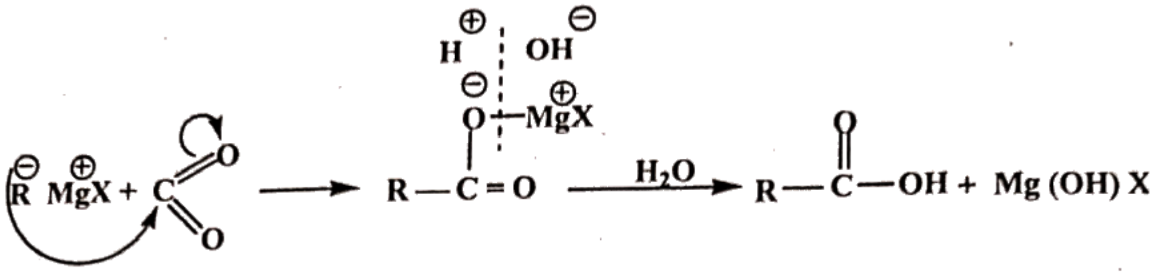
b)**By Hydrolysis of ester** :on bolling with alkali give the correspondinq salt of the асід Whch on treatment with acid gives carЬoxylc acia.



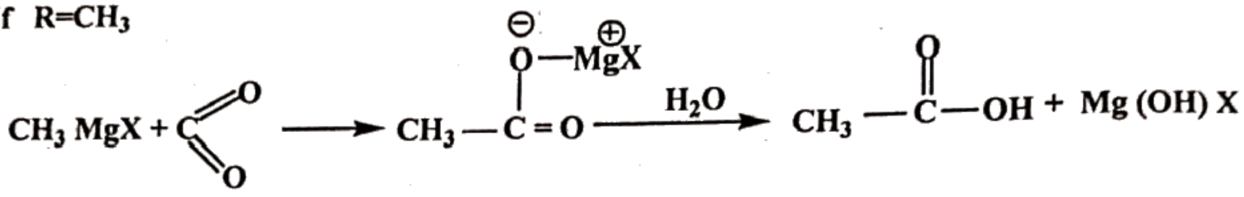
$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\overset{\oplus}{K}\ \overset{\ominus}{OH}]{KOH} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{K} + C_2H_5OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{K} + HCl \xrightarrow[-KCl]{KOH} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

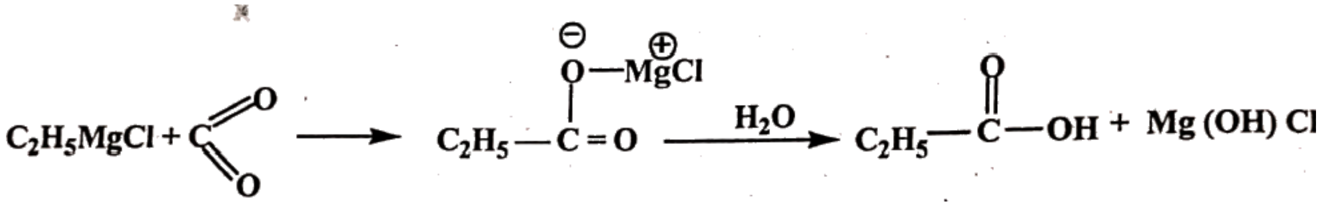
From Grignard reagents/Carbonation of arignard reagents: Grignard reagents react CO_2followed by hydrolysis gives carboxylic acids.



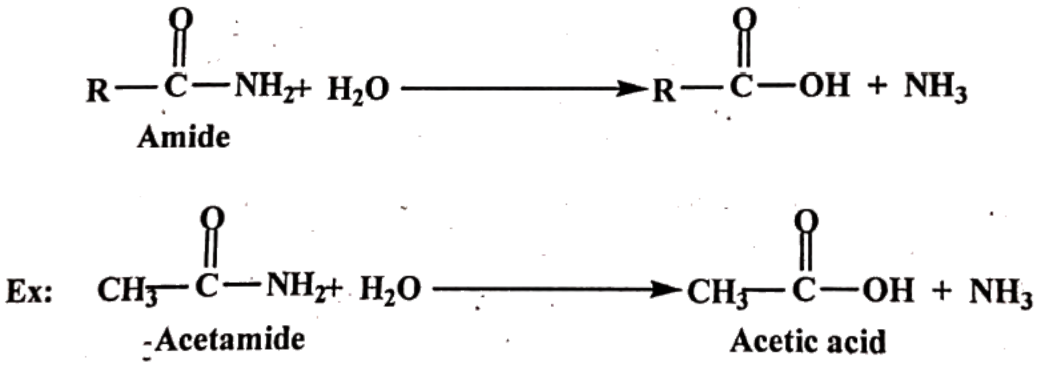
If R=CH₃



If R=C_2Hs,X=Cl

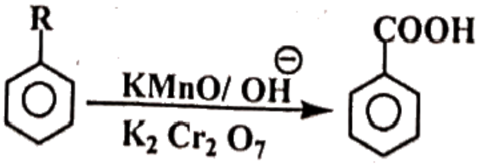


d)**By the hydrolysis of Amides**:Hydrolysis of Amides gives carboxylic acids.

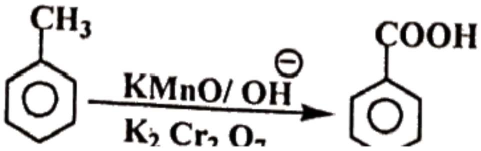


Aromatic acids:

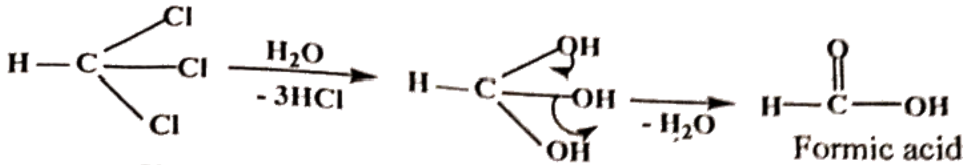
.By oxidation of Alkyl benzenes: Oxidation of an alkyl group attached to benzene nucleus hich will be oxidised to-COOH group in the presence of alkaline KMnO4(or)acidified $K_2Cr_2O_7$ respective of the size of the alkyl group.

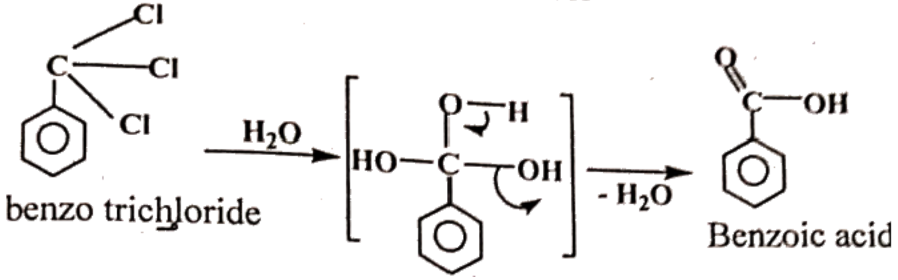


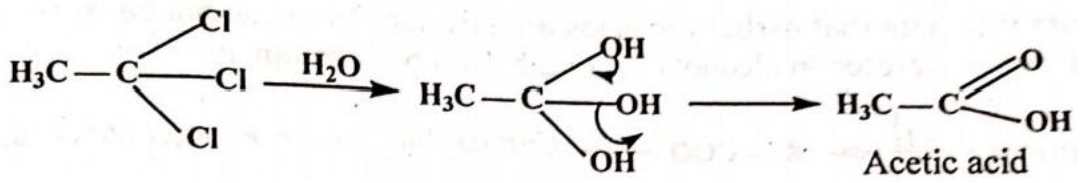
Ex:-



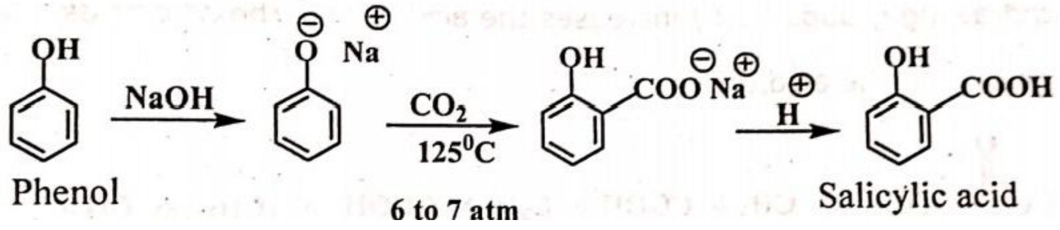
2.By the hydrolysis of tri halogen derivative: Hydrolysis of tri halogen derivative of alkanes gives carboxylic acids







3.Kolbe's reaction: Phenol reacts with $CO_2$and NaOH at 125°C and 6-7 atm pressure gives salicylic acid,is called kolbe's reaction.



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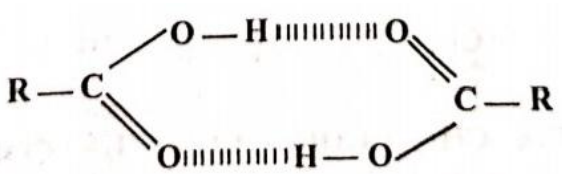
Physical properties:

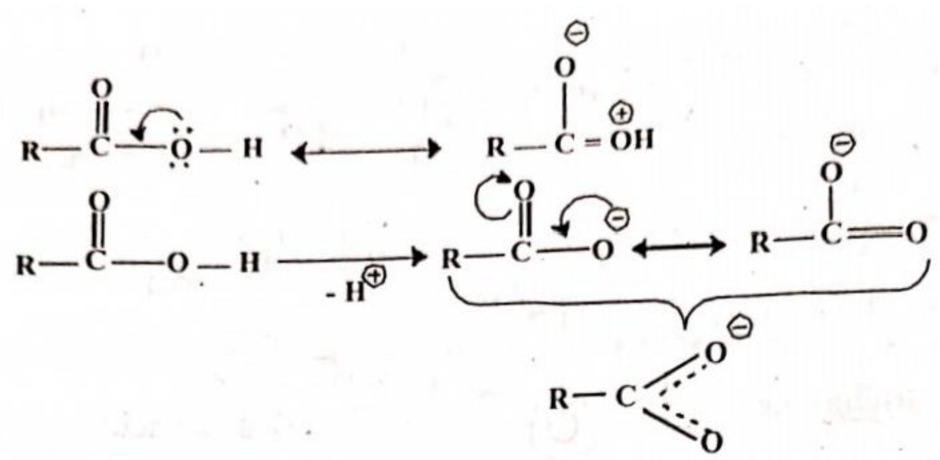
1.Carboxylic acids upto 3.Carbons are colourless,pungent smelling liquids.

2.Acids upto 4 carbons are freely soluble in water.due to Hydrogen bonding with water mol

3.Lower members shows higher B.P S,than Higher members,due to the fact that hydrogen bonding and they exist as dimers



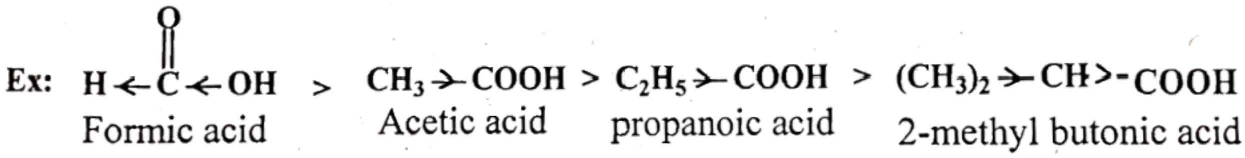
4.Acidity of carboxyllc acids:acids as compared to inorganic acids.The acidic carboxvlicaridc ic due to resonance in the acidic group which imparts electron character of



з.Itis important to note that carboxylc acids are stronger than alcohol because alkoxide t. formed bythe removal proton in alcoholls not stabiised by resonance.

Strength ofthe acids- affecting factors:

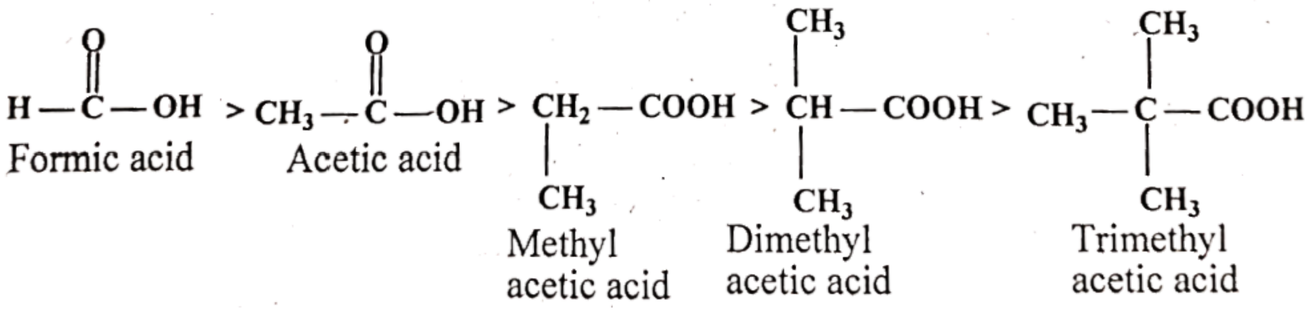
1. Electron wlthdrawing groups (-1.E) increases the acidlty of carboxyllc acids, electron relez. ing groups decreases the acidity.



Ex: $H\leftarrow\overset{O}{\overset{\|}{C}}\leftarrow OH > CH_3\rightarrow COOH > C_2H_5\rightarrow COOH > (CH_3)_2\rightarrow CH\rightarrow COOH$

Formic acid, Acetic acid, propanoic acid, 2-methyl butonic acid

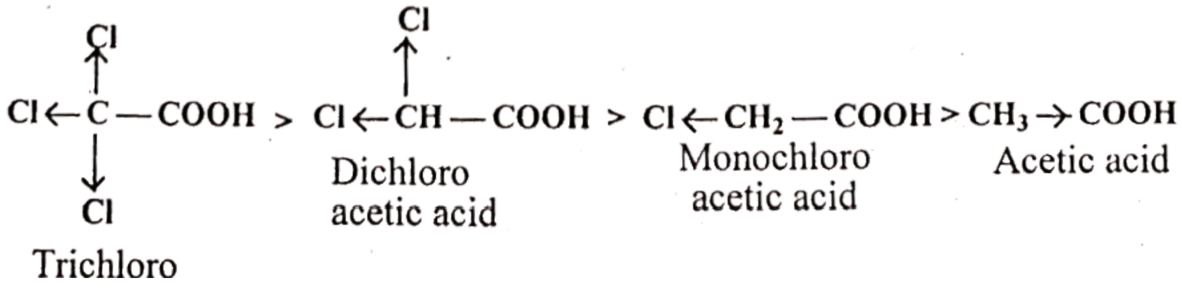
2. As the +I.E groups increases on carboxylic acid group decreases aciditv. This is due to electron density on oxygen increases.



$H-\overset{O}{\overset{\|}{C}}-OH > CH_3-\overset{O}{\overset{\|}{C}}-OH > \underset{CH_3}{\underset{|}{CH_2}}-COOH > \overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{CH}}}}-COOH > CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COOH$

Formic acid, Acetic acid, Methyl acetic acid, Dimethyl acetic acid, Trimethyl acetic acid

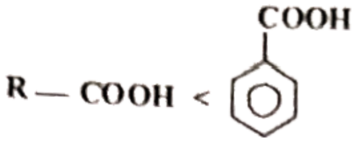
3. As the -1.E groups lncreases acldlty lncreasess. due to decrease the electron



$Cl\leftarrow\overset{Cl}{\overset{\uparrow}{\underset{Cl}{\underset{\downarrow}{C}}}}-COOH > Cl\leftarrow\overset{Cl}{\overset{\uparrow}{CH}}-COOH > Cl\leftarrow CH_2-COOH > CH_3\rightarrow COOH$

Trichloro acefie aeid, Dichloro acetic acid, Monochloro acetic acid, Acetic acid

Due to resonance (-M.E)Aromatic carboxylic acids are stronger than aliphatic carboxylic acids,

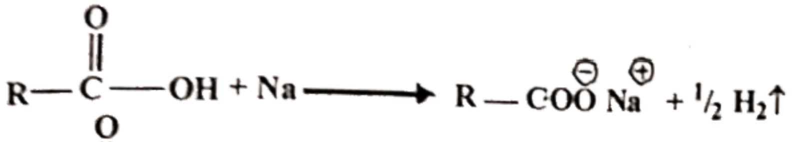


uike Aliphatic,Aromatic acids acidity also increased by electron with drawing groups

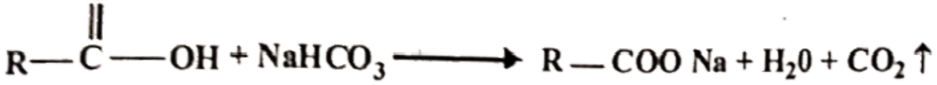
$(-NO_2, -Cl, -SO_3H \ldots;$

Reactions involving H-atom of-COOH group: Carboxylic acids reacts with metals and bases form metal carboxylates

1)



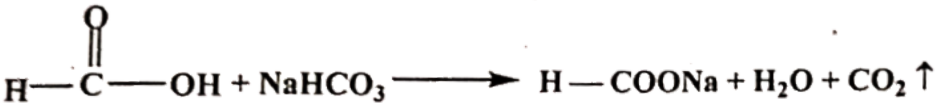
$$R-\overset{O}{\overset{\|}{C}}-OH + Na \longrightarrow R-COO^{\ominus}Na^{\oplus} + \tfrac{1}{2}H_2\uparrow$$



$$R-\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow R-COONa + H_20 + CO_2\uparrow$$

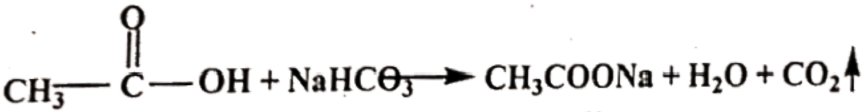
2)

Sodium salt of acid



$$H-\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow H-COONa + H_2O + CO_2\uparrow$$

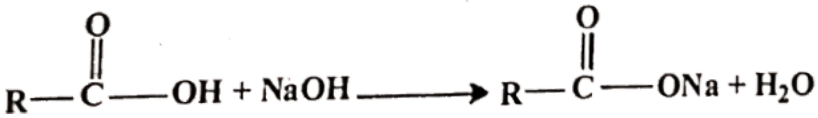
Sodium formate



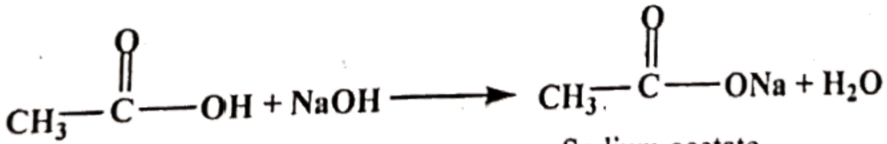
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2\uparrow$$

Sodium acetate

3)

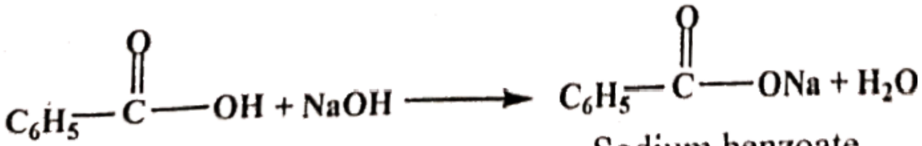


$$R-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + H_2O$$



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + H_2O$$

Sodium acetate



$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-ONa + H_2O$$

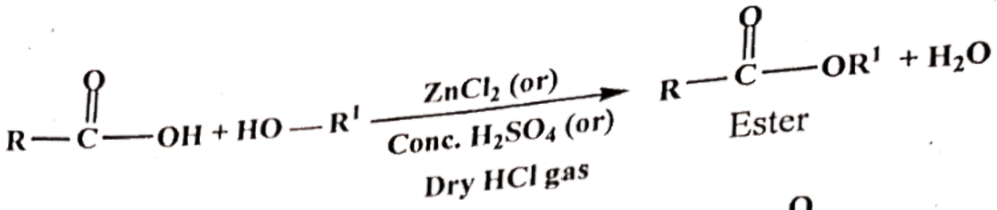
Benzoic acid

Sodium benzoate

B Reactions involving -OH part of the -COOH

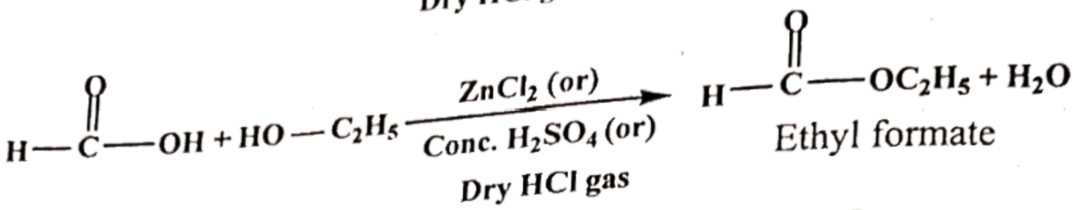
Esterification:Carboxylic acids react with Alcohols In the presence of Anhydrous

onc.H_2SO_4(or)dry HCl gas to form esters.This reactlon Is known as



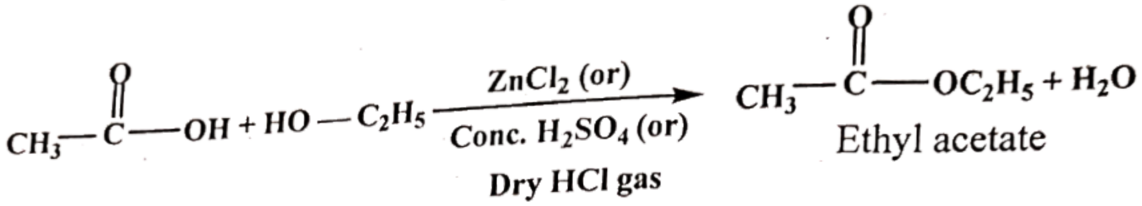
$$R-\overset{O}{\overset{\|}{C}}-OH + HO-R^1 \xrightarrow[\text{Conc. } H_2SO_4 \text{ (or) Dry HCl gas}]{ZnCl_2 \text{ (or)}} R-\overset{O}{\overset{\|}{C}}-OR^1 + H_2O$$

Ester



$$H-\overset{O}{\overset{\|}{C}}-OH + HO-C_2H_5 \xrightarrow[\text{Conc. } H_2SO_4 \text{ (or) Dry HCl gas}]{ZnCl_2 \text{ (or)}} H-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O$$

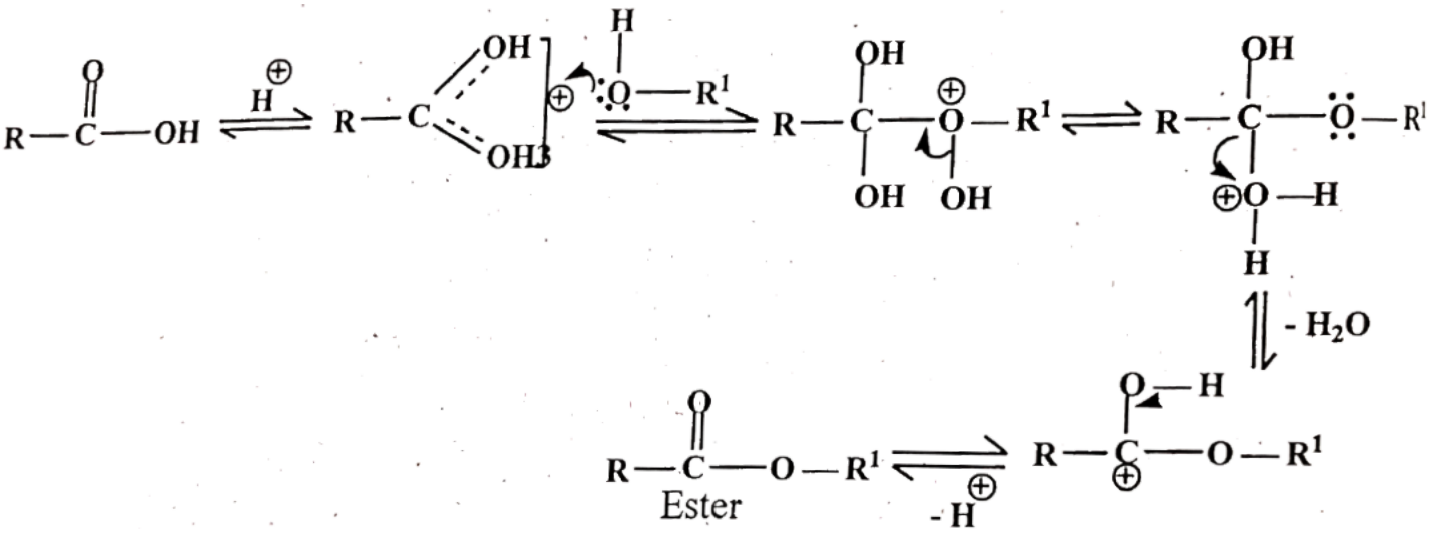
Ethyl formate



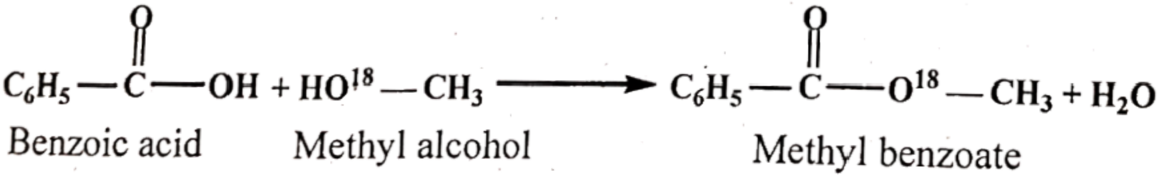
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-C_2H_5 \xrightarrow[\text{Conc. } H_2SO_4 \text{ (or) Dry HCl gas}]{ZnCl_2 \text{ (or)}} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O$$

Ethyl acetate

Mechanism:



Ex:-

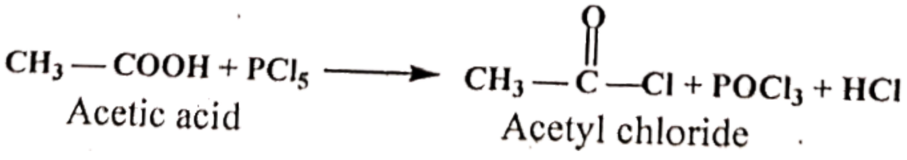


$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + HO^{18}-CH_3 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-O^{18}-CH_3 + H_2O$$

Benzoic acid Methyl alcohol Methyl benzoate

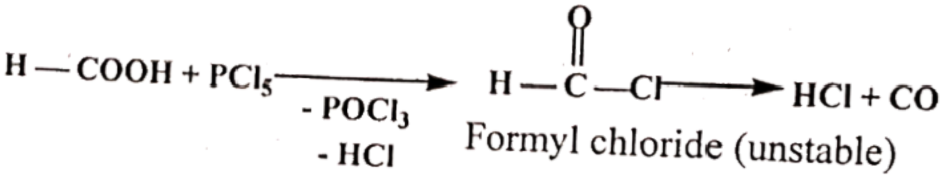
2.Reaction with PCls,$SOCl_2$:Carboxylic acids react with PCls,$SOCl_2$to form acid chlorides

1)



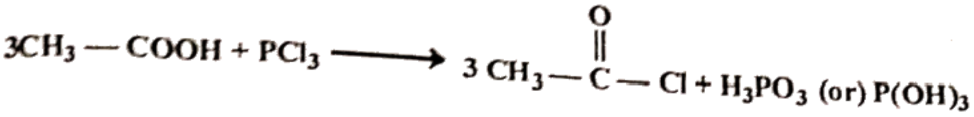
$$CH_3-COOH + PCl_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

Acetic acid Acetyl chloride

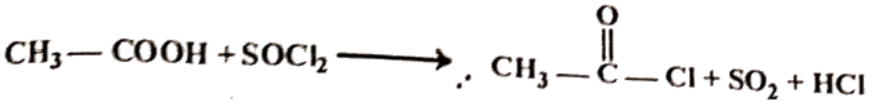


$$H-COOH + PCl_5 \xrightarrow[- HCl]{- POCl_3} H-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow HCl + CO$$

Formyl chloride (unstable)

2) 

$$3CH_3-COOH + PCl_3 \longrightarrow 3\,CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3 \text{ (or) } P(OH)_3$$

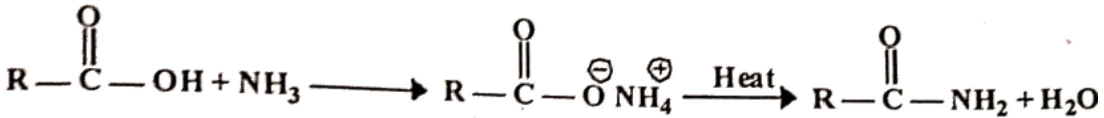
3) 

$$CH_3-COOH + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

Benzoyl chloride

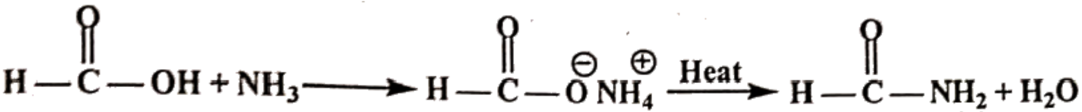
3,Reaction with Ammonia:Carboxylic acids react with Ammonia to form Amides.



$$R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{NH_4} \xrightarrow{Heat} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Ammonium Carboxilate

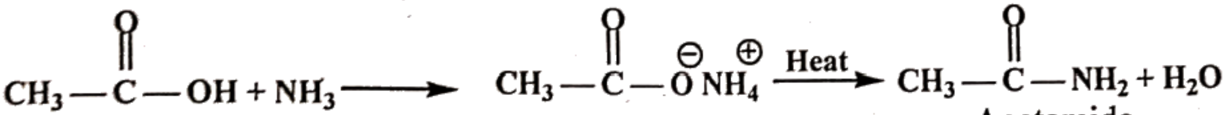
Acid amide



$$H-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow H-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{NH_4} \xrightarrow{Heat} H-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Ammonium formate

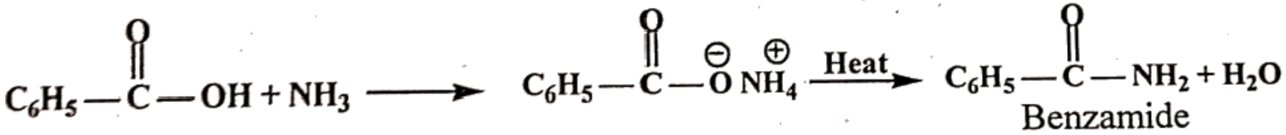
Formamide



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{NH_4} \xrightarrow{Heat} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Ammonium Acetate

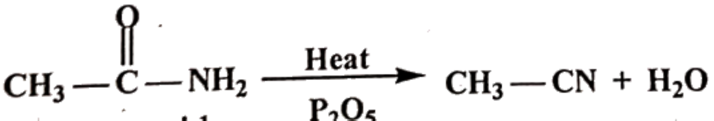
Acetamide



$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{NH_4} \xrightarrow{Heat} C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Benzamide

Note:Acetamide which on heating with F2Os to give methyl cyanide



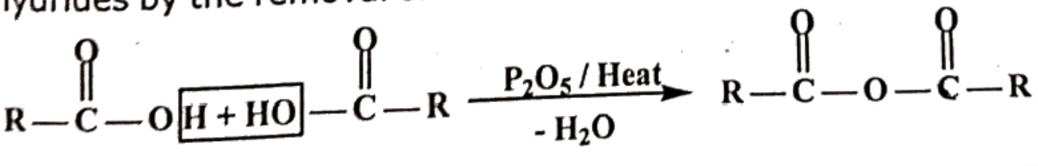
$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[P_2O_5]{Heat} CH_3-CN + H_2O$$

Acetamide

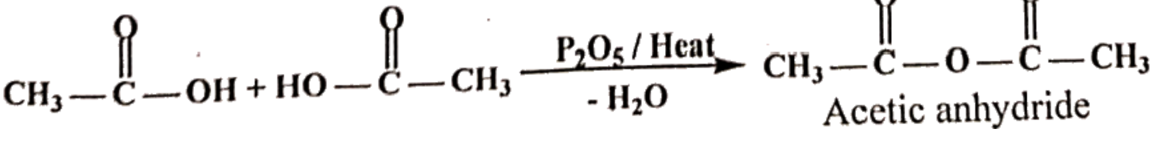
Methyl cyanide

4,Formation of Anhydrides;Heating of two moles of carboxylic acids in the presence of BO

gives Anhydrides by the removal of water molecule.

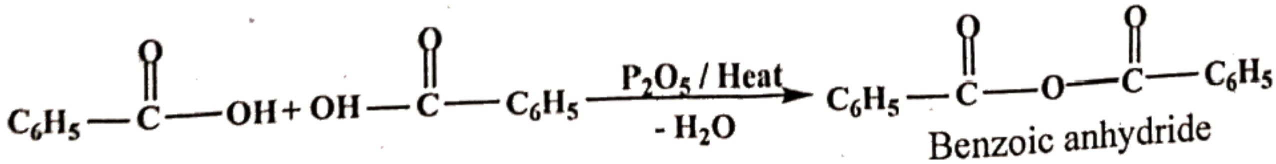


$$R-\overset{O}{\overset{\|}{C}}-O\boxed{H + HO}-\overset{O}{\overset{\|}{C}}-R \xrightarrow[-\,H_2O]{P_2O_5 / Heat} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[-\,H_2O]{P_2O_5 / Heat} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

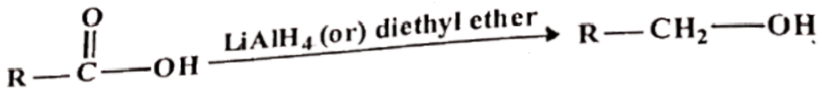
Acetic anhydride



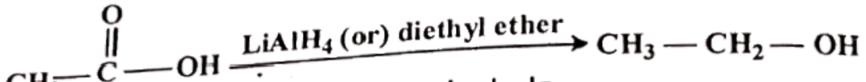
$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + OH-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[-\,H_2O]{P_2O_5 / Heat} C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$$

Benzoic anhydride

Reduction reactions(-CO-Group involving reactions

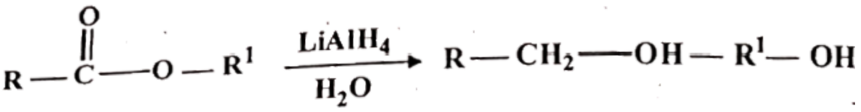


$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{LiAlH_4\ (or)\ diethyl\ ether} R-CH_2-OH$$

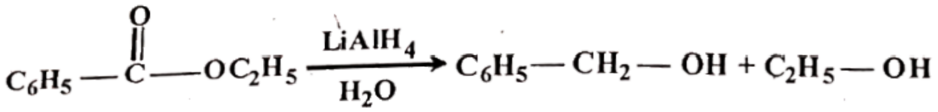


$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{LiAlH_4\ (or)\ diethyl\ ether} CH_3-CH_2-OH$$

Similarly reduction of ester also gives alcohols.

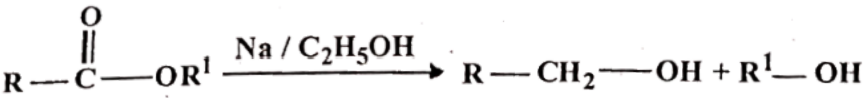


$$R-\overset{O}{\overset{\|}{C}}-O-R^1 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-OH-R^1-OH$$

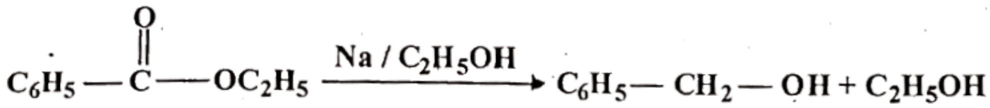


$$C_6H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[H_2O]{LiAlH_4} C_6H_5-CH_2-OH+C_2H_5-OH$$

<u>Bouveault -Blanc reduction:</u>Reduction of esters with Na in alcohol gives Alcohols.



$$R-\overset{O}{\overset{\|}{C}}-OR^1 \xrightarrow{Na\ /\ C_2H_5OH} R-CH_2-OH+R^1-OH$$



$$C_6H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{Na\ /\ C_2H_5OH} C_6H_5-CH_2-OH+C_2H_5OH$$

<u>Hunsdiecker reaction:</u>A heavy metal (Ag.Hg.Pb)salt of a carboxylic acids heated with bron or iodine gives an alkyl halide with one carbon less than the starting carboxylic acid.The read is called Huns diecker's reaction.

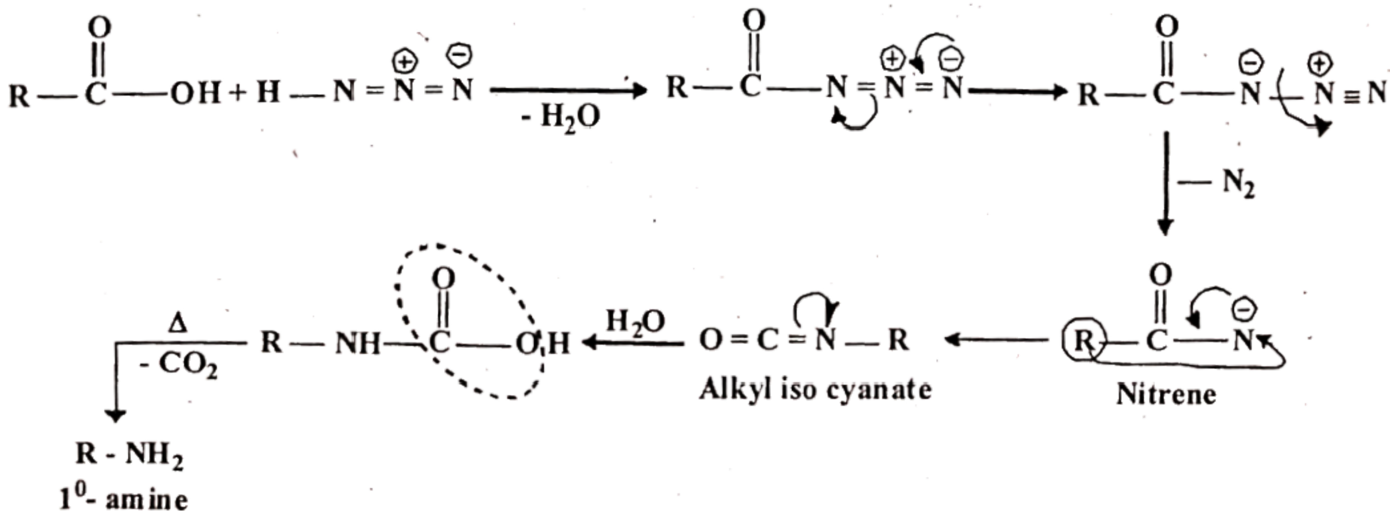
$$R-CH_2-COOAg \xrightarrow[Heat]{Br_2} R-CH_2-Br+CO_2+AgBr$$

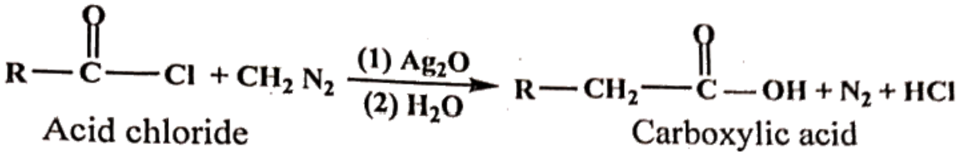
Ex:- $$CH_3-CH_2-COOAg \xrightarrow[Heat]{Br_2} CH_3-CH_2-Br+CO_2+AgBr$$

<u>Schmidt reaction:</u>Carboxylic acids reacts with hydrazoic acid in the presence of Conc.H,SO give 1⁰-Amines.is known as schmidt reaction.

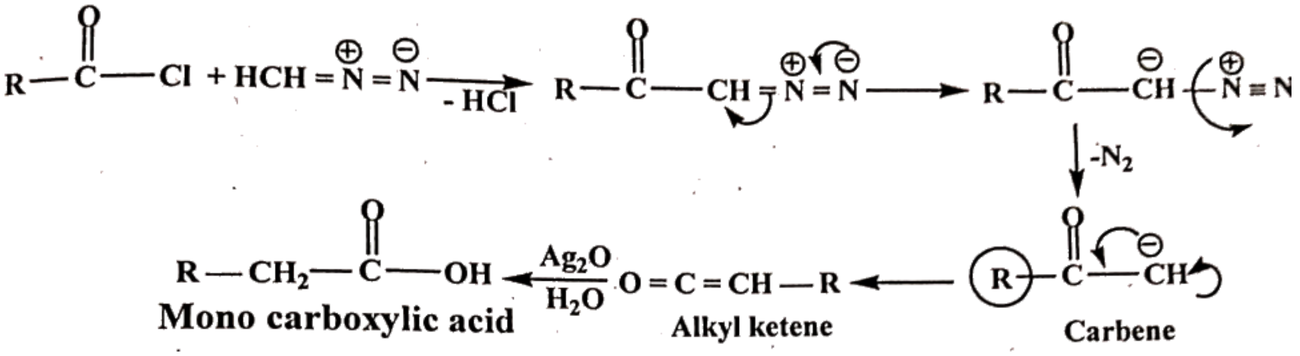
$$R-COOH+\underset{\substack{Hydrazoic\\acid}}{N_3H} \xrightarrow{Conc.\ H_2SO_4} R-NH_2+CO_2+N_2$$

<u>Mechanism:</u>





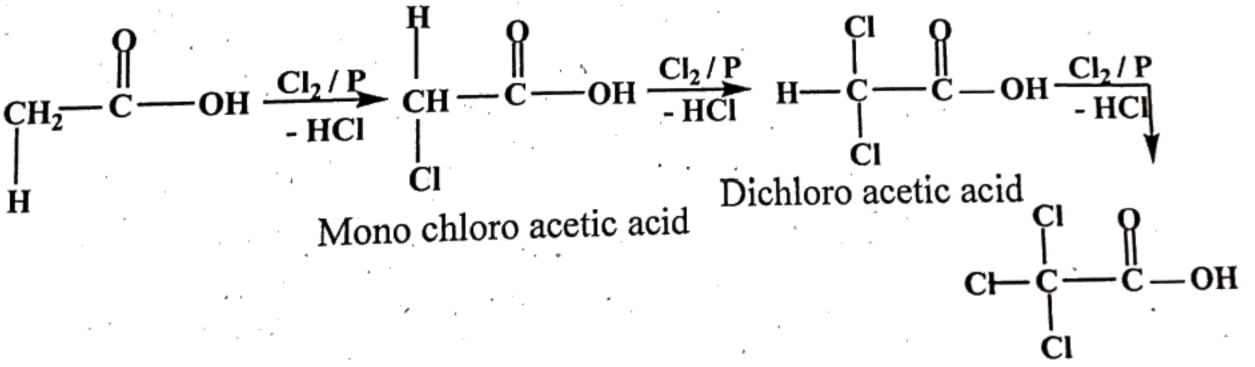
Mechanism!



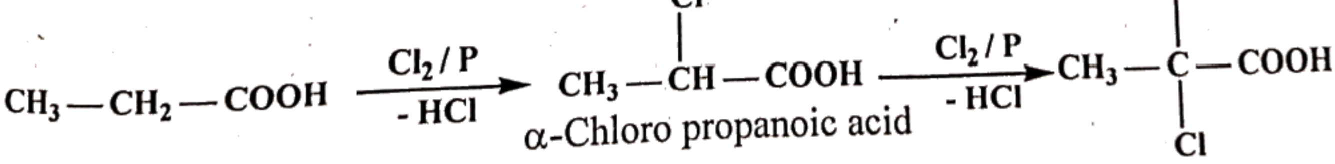
Halogenation:

Hell-volhard- Zelensky reaction (HYZ)

Mono carboxylic acids reacts with cl2(or) br2 in the presence of Red - phosphorous to form halo substituted product .the reaction is known as HVZ reaction



Trichloro acetic acid

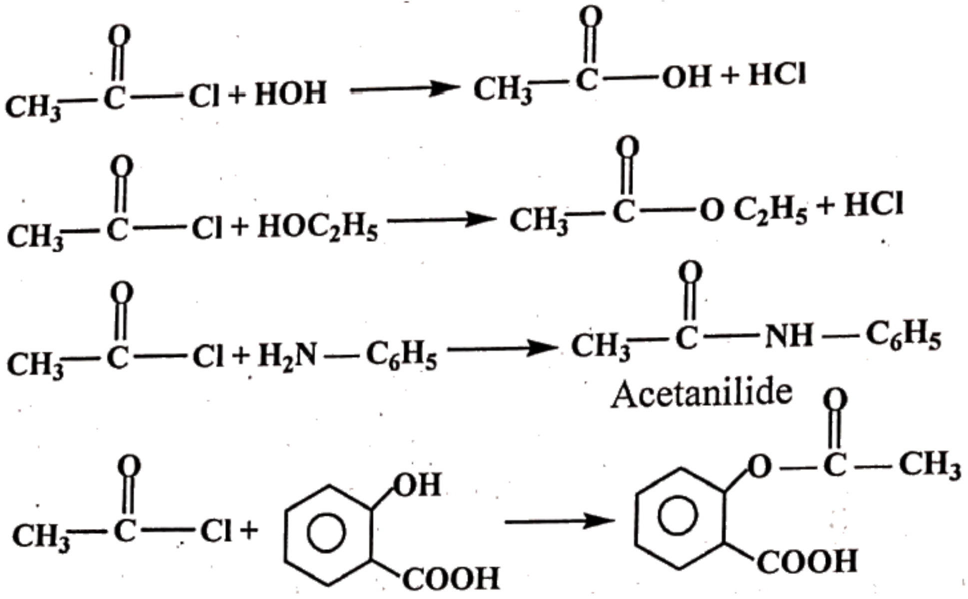


1.Acylation

;Acid chlorides are important acylating agents for compounds naving -UH,、

-NH_2&-NHR groups.During acylation hydrogen atom of these groups is replaced by

group.



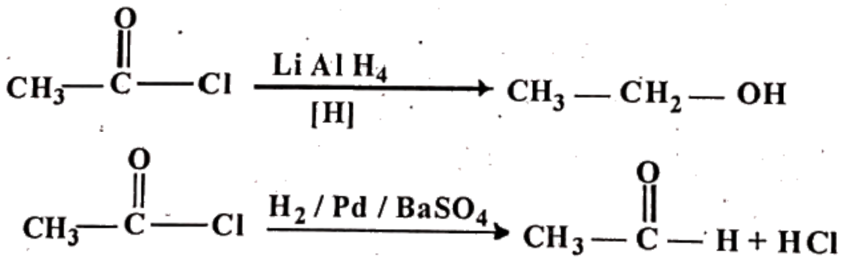
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + HOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + HOC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O\,C_2H_5 + HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2N-C_6H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-C_6H_5$$

Acetyl salicylic acid (Aspirin)

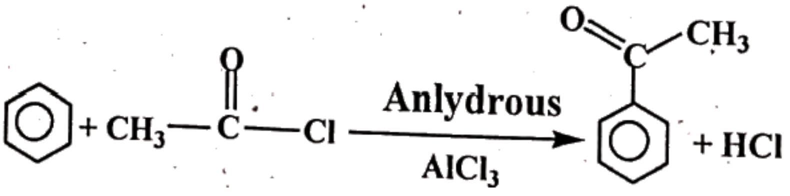
<u>2.Reduction:</u>Acetyl chloride reduced to Acetaldehyde in the presence of Pd /BaSO4 and alcohol in the presence of LiAlH4.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{[H]}]{LiAlH_4} CH_3-CH_2-OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2/Pd/BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl$$

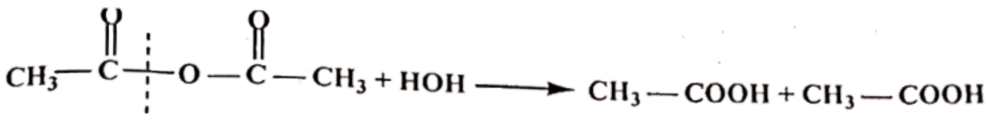
3.Fredal crafts reaction: Benzene reacts with Acetyl chloride in the presence of Anhyd



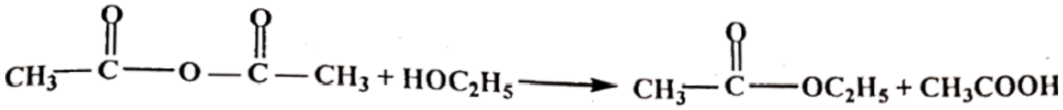
Acetophenone

Reactions of Acetic anhydride

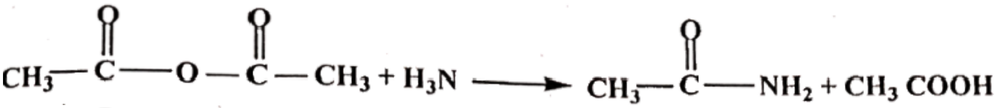
1.Acylation:



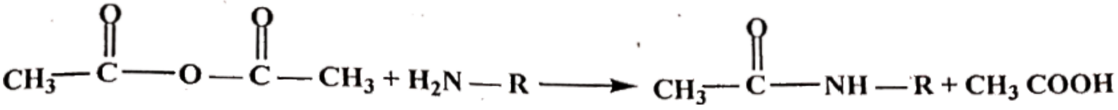
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+HOH\longrightarrow CH_3-COOH+CH_3-COOH$$



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+HOC_2H_5\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+CH_3COOH$$

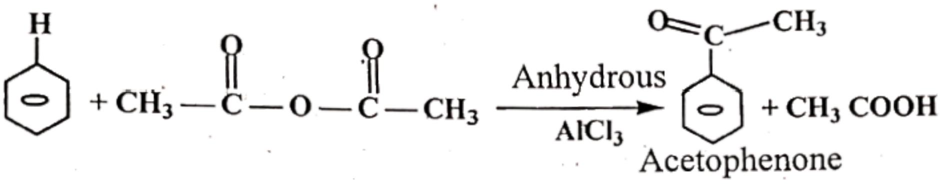


$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+H_3N\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2+CH_3\,COOH$$



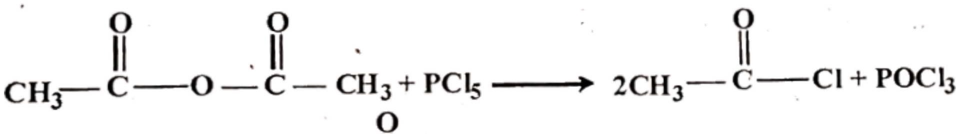
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+H_2N-R\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-R+CH_3\,COOH$$

2.Benzene reacts with Acetic anhydride in.the presence of $AlCl_3$gives Acetophenone.



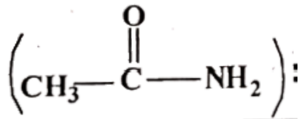
3.Reaction with PCls:

Acetic anhydride reacts with PCls to form Acetyl chloride.



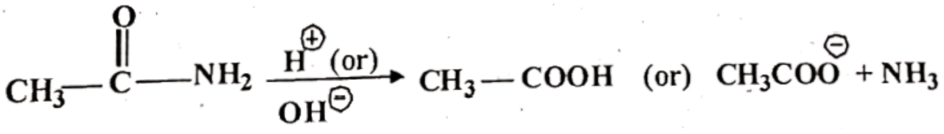
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+PCl_5\longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-Cl+POCl_3$$

Reaction of acetamide



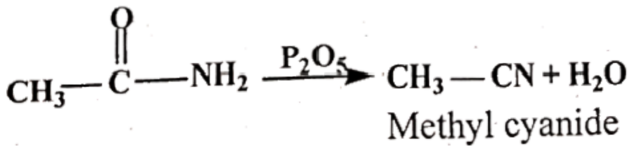
$$\left(CH_3-\overset{O}{\overset{\|}{C}}-NH_2\right):$$

1.Hvdrolysis:Hydrolysis of Acetamide in the presence of Acid /Base to form Acetic acid and Ammonia,



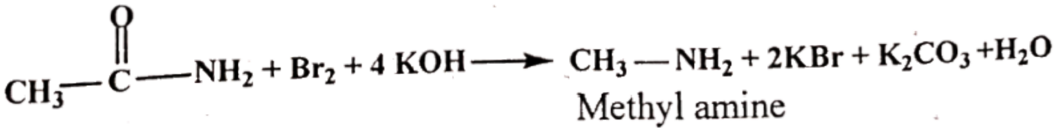
$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2\xrightarrow[OH^{\ominus}]{H^{\oplus}\text{ (or)}}CH_3-COOH\text{ (or) }CH_3COO^{\ominus}+NH_3$$

2.Dehydration:Dehydration of Acetamide with.R2Os gives methyl cyanide



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2\xrightarrow{P_2O_5}CH_3-CN+H_2O$$

Methyl cyanide

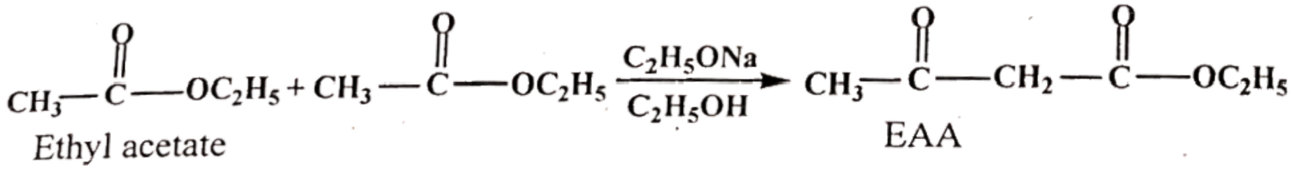


$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2+Br_2+4\,KOH\longrightarrow CH_3-NH_2+2KBr+K_2CO_3+H_2O$$

Methyl amine

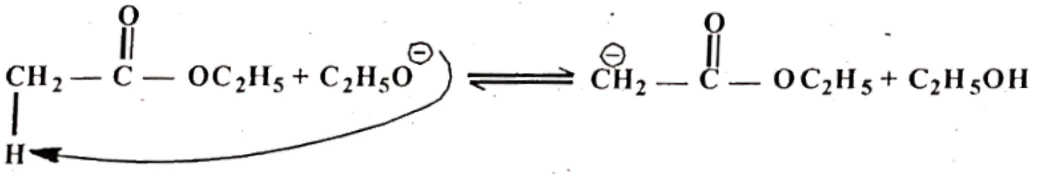
Reactions of ester(Ethyl acetate -CH_3-$COOC_2H_5$)

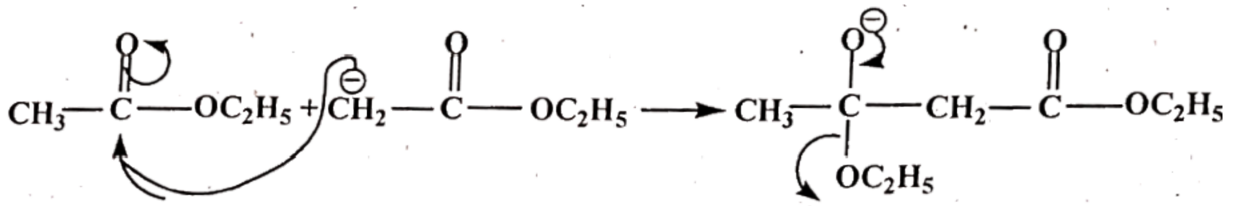
1.Claisen condensation reaction:Two moles of ethyi acetate react with sodium ethoxi
Acetoacetic ester is called claisen condensation rm


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5\xrightarrow[C_2H_5OH]{C_2H_5ONa}CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

ec hanism.

C_2H_5OH+Na _____ C,H$_2$ ONa ____$C_2H_5\delta N^3$

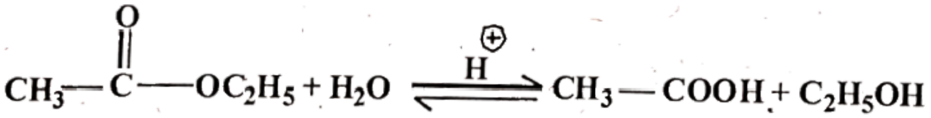




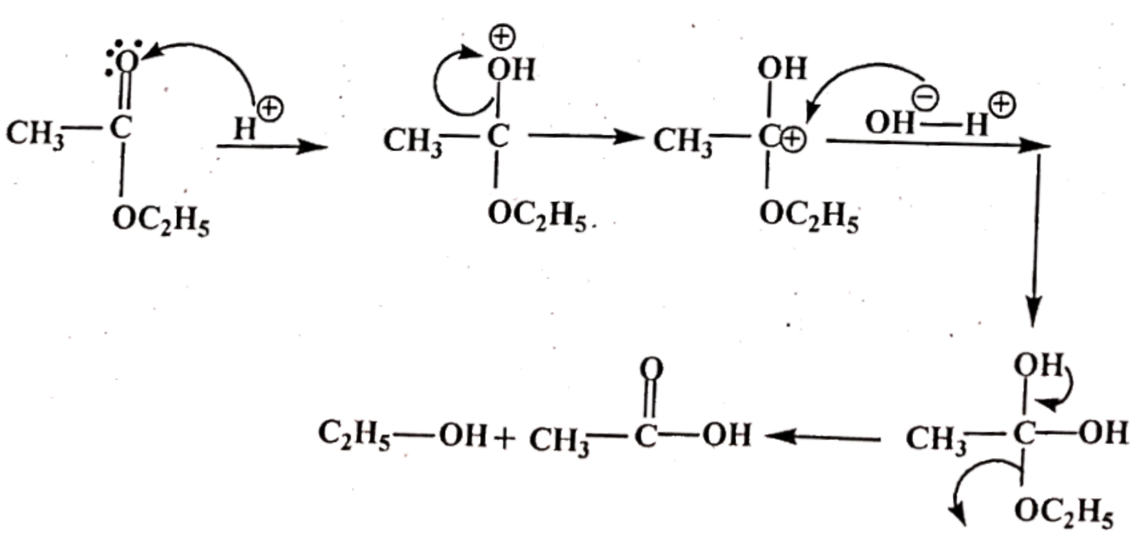
Aceto acetic est

Hydrolysis of ester:

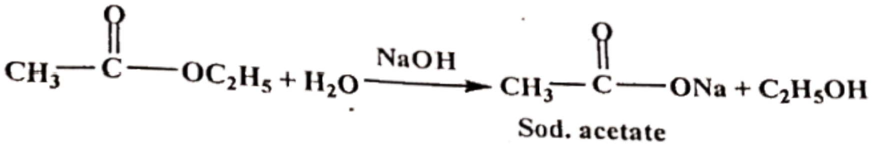
<u>1.**Ester hydrolvsis by an acid /Acidic hydrolysis**: H</u>ydrolysis of ethyl acetate in the presem of an acid gives acetic acid and ethyl alcohol.


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+H_2O\overset{\overset{\oplus}{H}}{\rightleftharpoons}CH_3-COOH+C_2H_5OH$$

Mechanism:

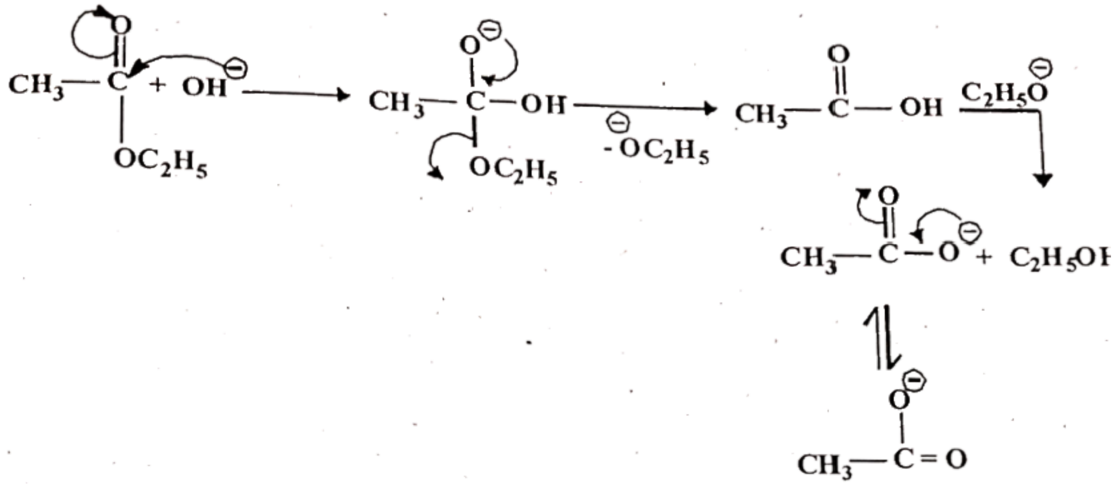


2.BASICHYDROLYSIS OF ESTER acetate reacts with NaOH to form sodium acetate and Ethyl

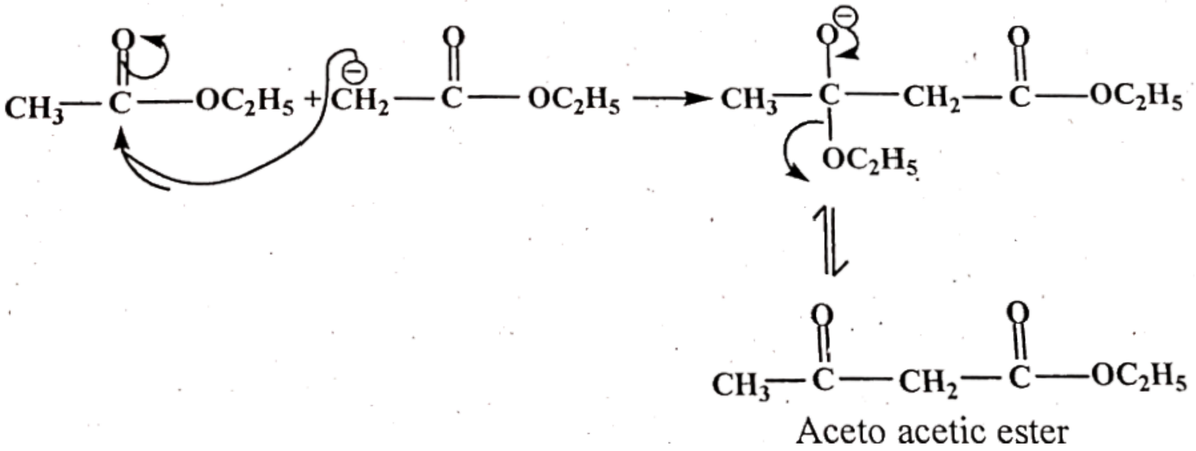


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O \xrightarrow{NaOH} CH_3-\overset{O}{\overset{\|}{C}}-ONa + C_2H_5OH$$

Mechanism:

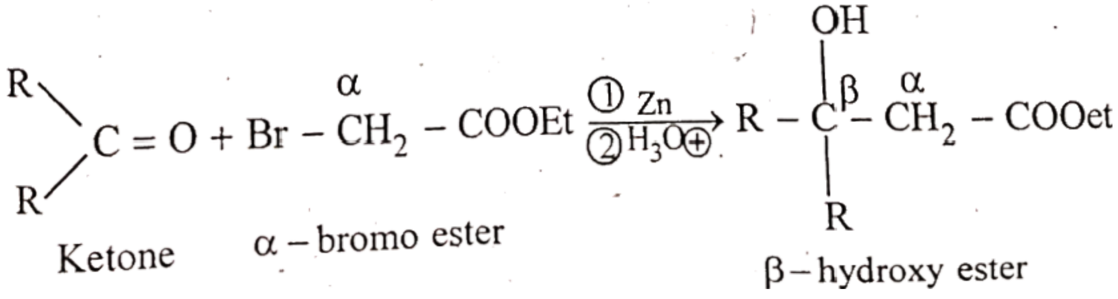


3.Reaction with Grignard reagent:Ethyl acetate react with grignard reagent to form ketone when excess reagent is used followed by hydrolysis give 30 -Alcohol



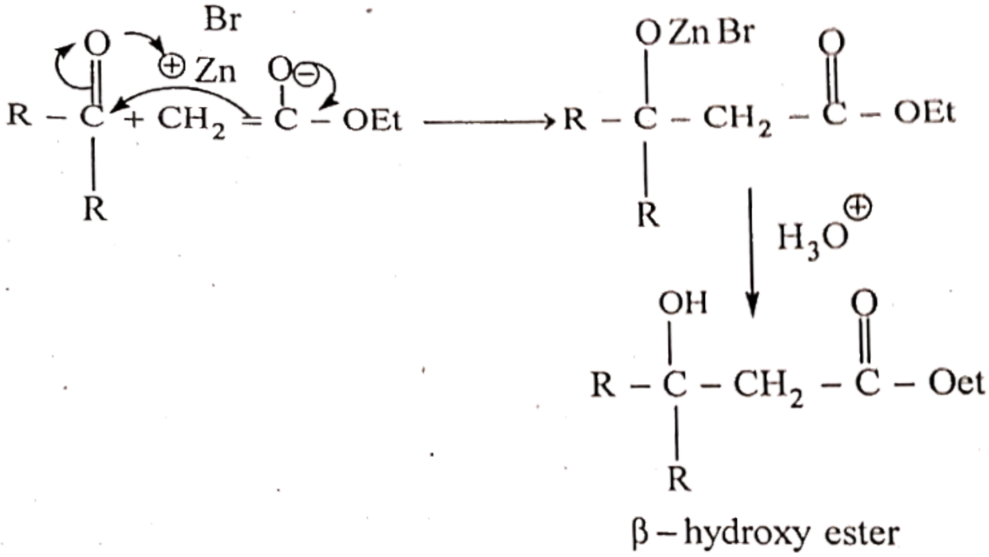
Reformatsky reaction :=

Carbonyl compounds reacts with a-haloesters in the presence of zinc metal to form β - hydroxy esters.



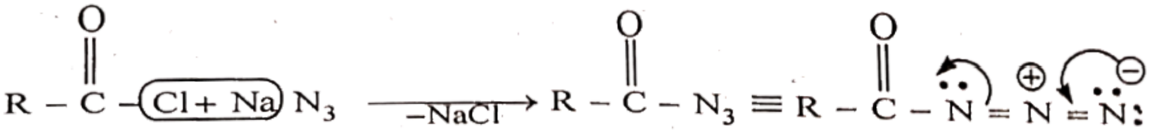
$$\begin{matrix}R\\R\end{matrix}\!\!>C=O + Br-\overset{\alpha}{CH_2}-COOEt \xrightarrow[②H_3O^{\oplus}]{①Zn} R-\overset{OH}{\underset{R}{\overset{|}{\underset{|}{C}}}}\,{}^{\beta}-\overset{\alpha}{CH_2}-COOet$$

Organo zinc intermediate

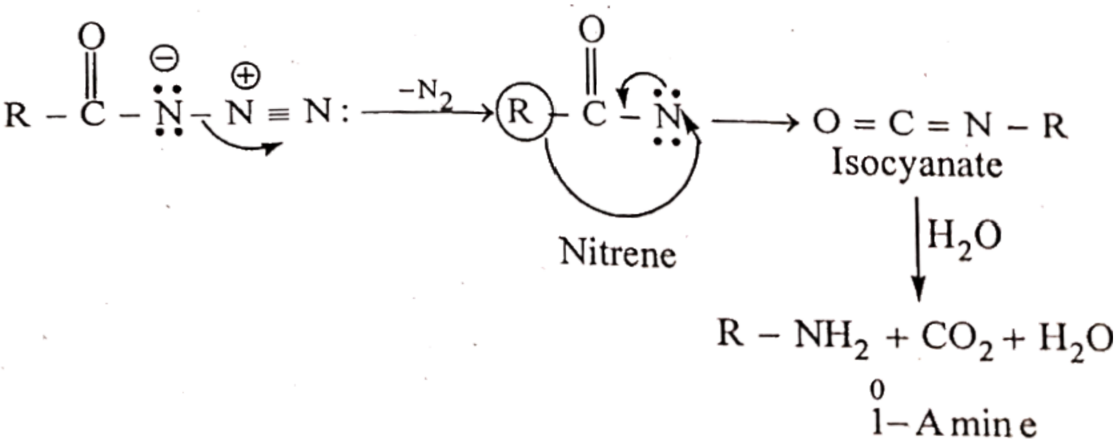


Curtius rearrangement :-

Acid chloride reacts with sod-azide to form acyl azide which on rearrangement to isocyanates,on furture reaction gives amines.



Acid chloride sod.azide



UNIT-IV

MOLECULAR SPECTROSCOPY

In earlier days the structure and properties of organic compounds was determined by chemical methods.But in modern days it is done by using physical methods known as spectroscopic methods.These are most suitable methods than the other physical and classical chemical methods,by using these methods structure determination is possible in less time and accurately.

Advantages of spectroscopic methods:-

1.The sample required for spectroscopic analysis is very less(1mg /2mg)

2.Highly sensitive methods.

3.Time requird for structure determination is very less (<1min)

4.Accurate results are obtained.

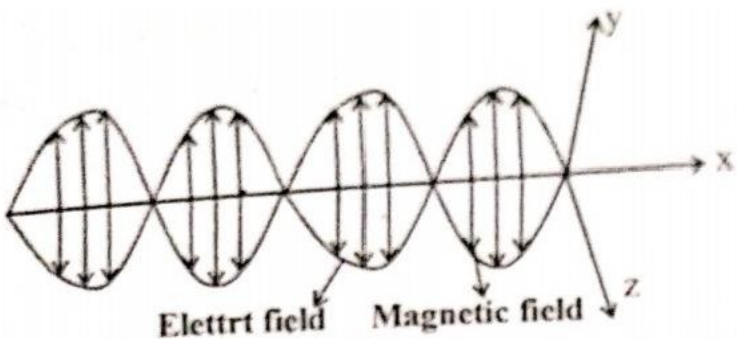
5.Sample recovery is possible and which is used for another time.

Some common spectroscopic methods are:
1)UV-Vissible spectroscopy -To know unsaturation &conjugation.
2)Infrared(IR)Spectroscopy -To know nature of the functional group.
3)Raman spectroscopy -To known bond lengths &bond energies.
4)Microwave spectroscopy -To know various rotation of molecules.
5)Proton magnetic Resonance spectroscopy(pmr)-To know different types of protons 6)Mass spectros copy -To known molecular weight &molecular formula of compounds. 7)Electron spin Resonance spectroscopy(ESR)-To know free radicals.

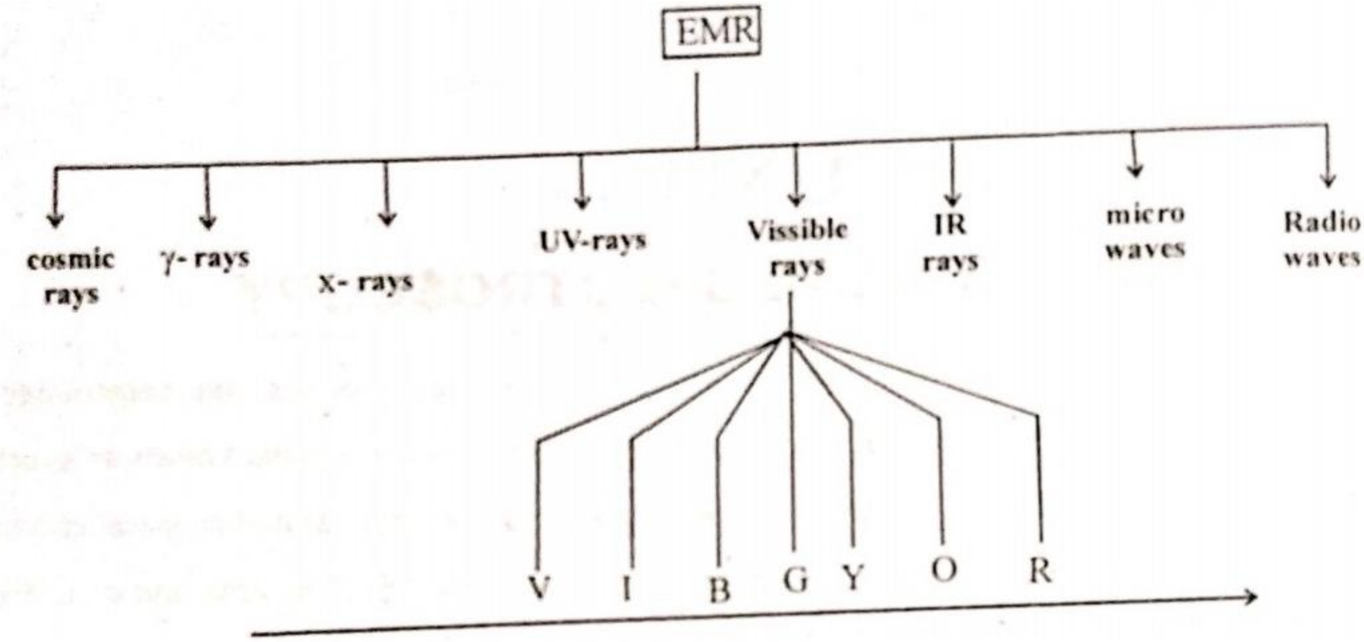
Electro Magnetic radiation -EMR:-

The radiation which pocess both electric and magnetic fields in right angles which are perpendicular to each other is called electromagnetic radiation.

In spectroscopic methods these EMR are used



Types of EMR's;



Wave length (z.) increases (x1)
(or)
Frequency (o)deereases (vL)
(or)
Energy (E)decreases (E↓)
(Electro magnetic spectrum)

Interaction of electromagnetic radiation with molecules:-

When EMR is passed through a molecule/compound,it absorbs light energy and undergs some internal changes.due to absorption of energy electrons of molecules gets excited.but thisl unstable state.In this state changes occurs in energy levels of molecule.The difference in enel; of excited state and normal state is equal to the energy absorbed,by the molecule /compound

h=planck's constant
γ=frequency

Depending upon the nature of EMR passed,The following changes occur in the molecules.

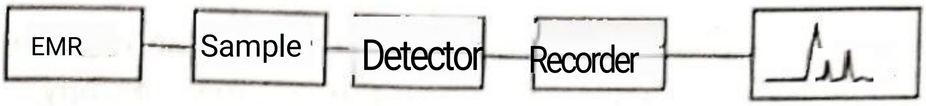
1.Translation motions 2.Rotations 3.Vibrations
4.Electronic Transitions 5.Magnetic energy changes

Spectrum:-

The arrangement of group of wavelenths |Frequencies of light is called spectrum.

O spectrum is recorded by using spectrophotometer instrument.

Principle;-



Spectrum

(Devices in spectrophotometer)

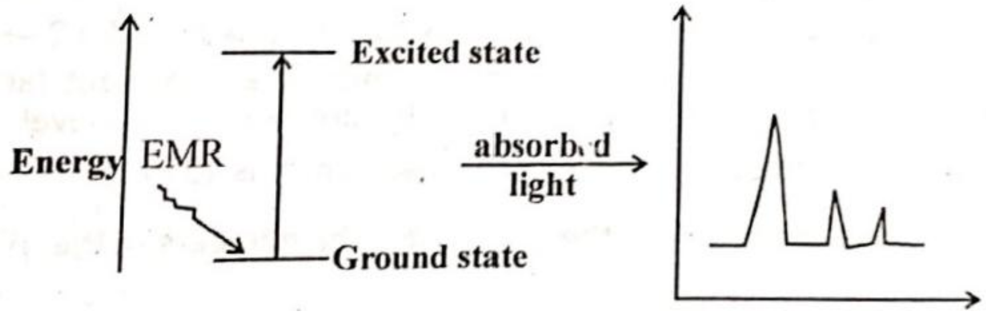
Types of molecular spectras:-

There are mainly two types of spectras.

(1) Absorption spectras: The spectrum which consist the lines corresponds to the waverength of absorbed light is called absorption spectrum.

O Absorption spectrum consist dark lines on bright background.

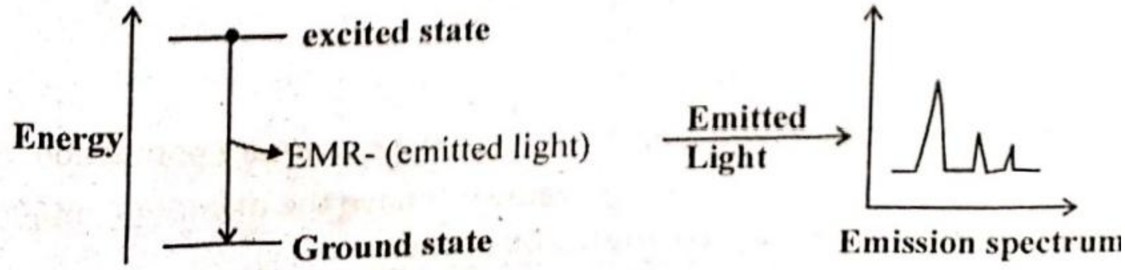
Ex:NMR, UV,I.R....



Absorption spectra

(2) **Emission spectra:** spectrum which consist,the lines corresponds to the wavelengths of emitted light is called emission spectrum. O Emission Spectrum Consist bright lines on dark background.

Ex:Fluorescence,Phosphorescence



ROTATIONAL SPECTROSCOPY (MICROWAVE SPECTROSCOPY)

Principle:-

Sample Iradiated with microwave range (λ=0.1-30cm)of radiation brings about change, in rotational energy levels of molecules is called rotational spectroscopy,

Sample must be in gaseous (or)vapour state.

Molecules should be with permenant ($\mu \neq 0$)dipolemoment so Homo atomic molecules canng show M.W spectra.

Ex:-H_2,O_2,Cl_2,N_2......

Rotational axis:

The axis passes through the centre of the body /molecule around which the molecule can take infinite number of rotations is called Rotational axis.Ex:Rotation of earth on its own axis.

Intensities of spectral lines :-

The pure rotational spectrum of a diatomic molecule consists of a series of equally space lines corresponding to the transitions $J=0 \rightarrow J=1, J=1 \rightarrow J=2, J=2 \rightarrow J=3$.We now esti. mate the relative intensities of these spectral lines.The important factor that decides the intensity of lines will be the number of molecules present in each level.This depends on the boltzmann factor and the degeneracy of the level which is (2J+1).

If NO is the no.of molecules in the J=0 level.The numbers in the jth leves is

$$N_J = No.e^{\left(\frac{-EJ}{KT}\right)} \qquad = No.e^{\left[\frac{-BhcJ(J+1)}{KT}\right]}$$

Taking degeneracy into account,the number actually available in a state.

$$N_J = No(2J+1).\ e^{\left[\frac{-BhcJ(J+1)}{KT}\right]}$$

To find the value of'J'for which the populaticn is maximum,we have to set dNJ/dJ=0.

This leads to $J = \sqrt{\frac{KT}{2Bhc}} - \frac{1}{2}$

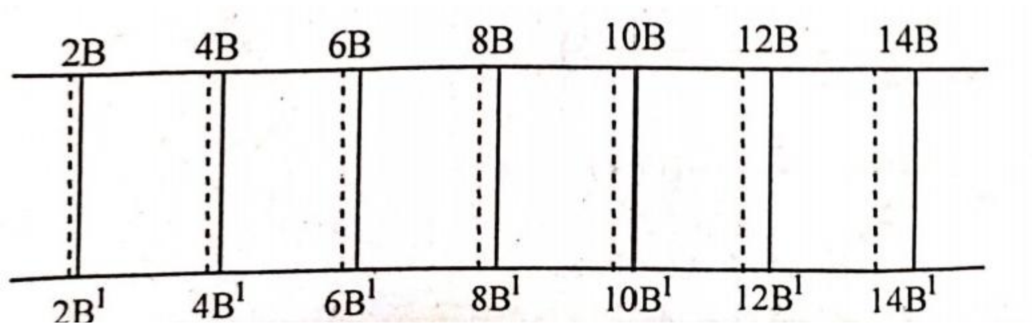
That is the level nearest to this'J'value will have the maximum population.Hence trans tion originating from the level having this 'J'value will have the maximum intensity. Isotope effect in rotational spectra /Isotopic substitution :-

increase in mass of atom in the molecule-increases reduced mass (u).

$$I = \mu r_0^2$$

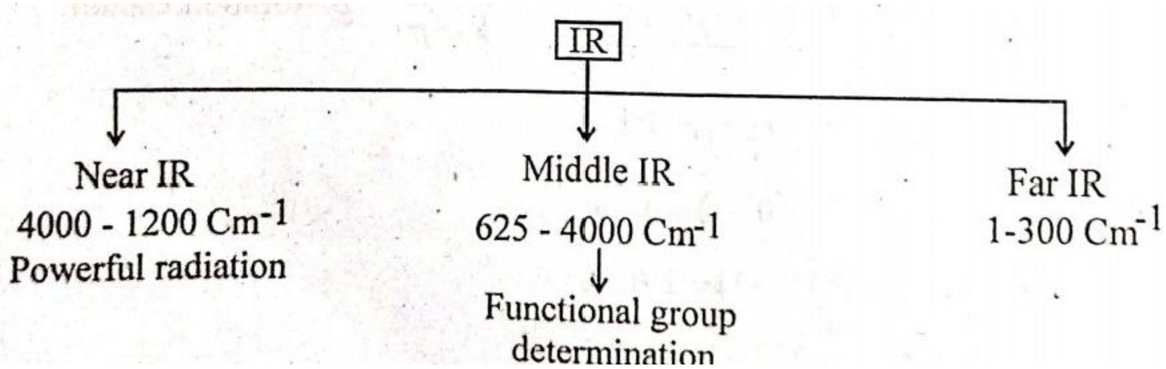
The change in mass not changes the bond length,with increase in μ the T also increase

Isotopic substitution decreases energy as well as wave numbers of rotational energy levels.i.e.,energies of energy levels of cl^{3}ol6 smaller than energies of energy levels of cl^{2}ol6. The effect of cl3 Isotope substitution on the rotational spectrum of diatomic molecule cl^{2}ol^6
is



INFRA RED SPECTROSCOPY

Radiation::



For organte molecules absorptlon energy is 625-4000cm^2(or)2.5n-154(1u=10cm).

Principle

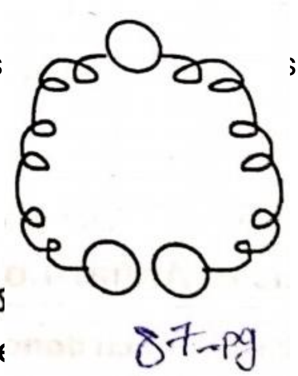
When sample irradlatedwlthIR-range of radiation,ltbli-pbout changes vibrational levels of molecules.lte,molecule vibrates from one vib level to another due to this change the dipolemoment of the molecules are detected by detector and information pass to the recorder,and give a spectrum.

There are two type of molecular vibrations due to IR-radiation

1)Stretching vibrations 2)Bending vibrations

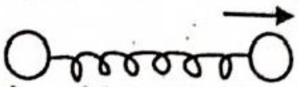
1.Stretching vibrations:-

In these vibrations the bond length of the molecules increases se are high energetic vibrations.

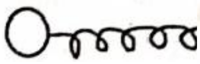


87-pg

Ex:For a diatomic molecule



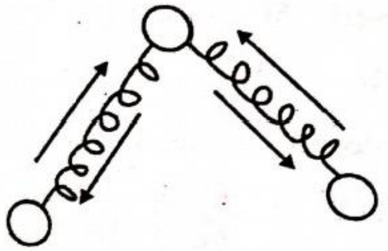
bond length=x



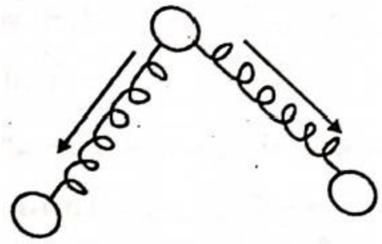
stretche

For triatomic molecule

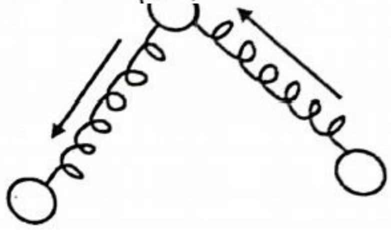
109-pg



(Bond stretchings)



(Symmetrical stretching)

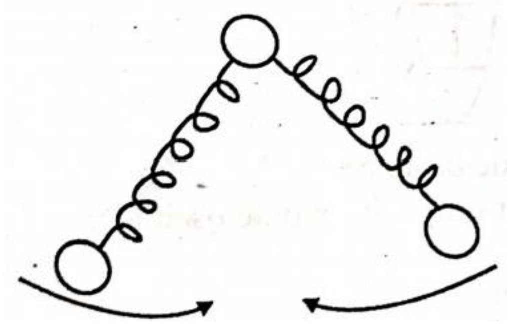


Asymmetrical (Stretching)

For a diatomic molecules only stretching vibrations are possible

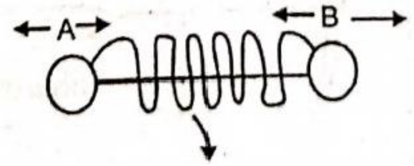
2.Bending vibrations:-

This is also called Deformation of molecule.These vibrations taking place with change in Bond angle of the molecule.These are low energetic vibrations.



Energy levels of simple harmonic oscillator:-

Ex:Diatomic molecule.



(spring)simple harmonie oscillator

The oscillator which takes in equal distance is called simple harmonic oscillator.

Frentoncw nf mnlartlla is in simple harmonic motion is qiven by Hook's Law.

m=Reduced

DIvide the equatlon (1)with 'C'(velocity of light)

$$\frac{\nu}{C} = \bar{\nu} = \frac{1}{2\pi C}\sqrt{\frac{K}{\mu}}\ cm^{-1}$$ y-=wave number

LIke other molecular energylevels,the vibrational energies also quantised.Vibrationa enegles of systems are calculated by using schrodinger's wave equation

For a simple harmonic osclllator

$E_V = (V+\frac{1}{2})h\nu_{osc}$ Jouls V=Vib.quantum no.

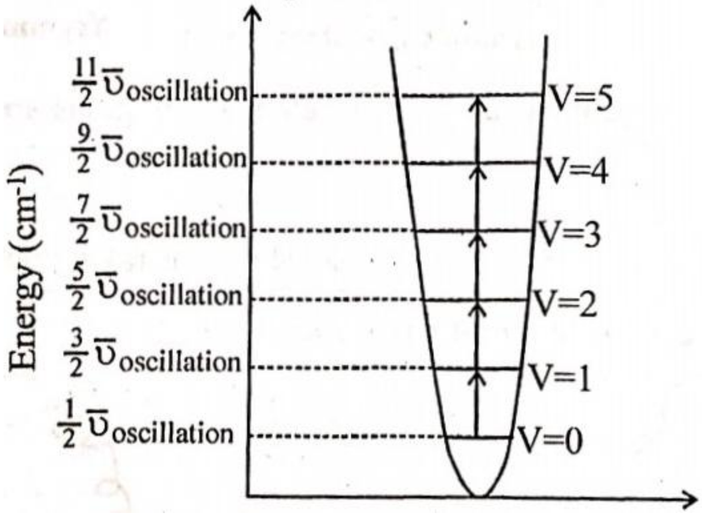
E=-((+3)αcm¹N=0.4.23...)

V=O → E_0=÷Toscilation(Zero vib-level)

V=~~1>&$_1$=2Toscillation~~(Fist vib-level)

V=2 → E_2=号Doscilation(Secound vib-level)

V=3 → e_2=2Gosilation(Thard vib-level)

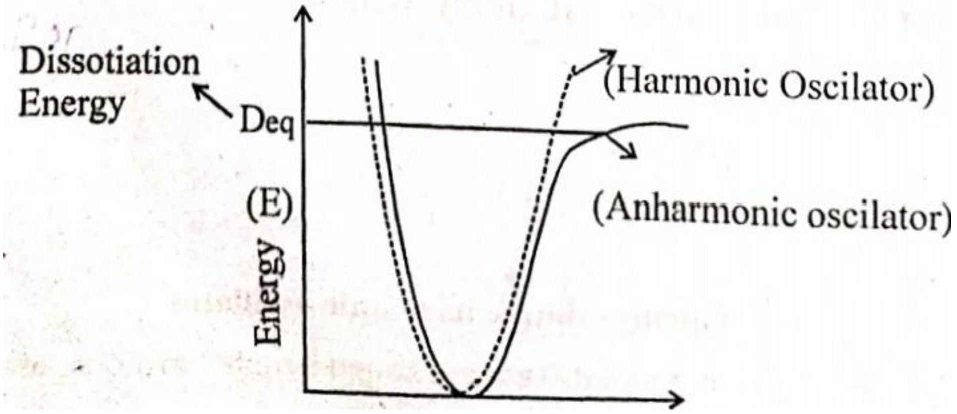


Inter atomic distance

Vibrational energy level of simple hormonic oscillator

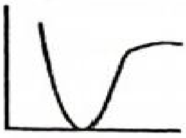
Energy levels of Anharmonic Oscillator:-

"The osclIator which donot takes equal distances is called Anharmonic oscillator.“



Inter nuclear distance(r)

Real molecules do not follow laws of simple harmonic motion They donot obey Hook's Law at all internuclear separation. In real molecules simple compression & elangations are perfectly elastic, but for longer compressions and elongations they deviate. experimentally it is observed that the molecule is stretched beyond 10% of it's bond length, the molecule dissociates into atoms (or) ions. The energy of real molecule as a function of internuclear separations is given by morse curve

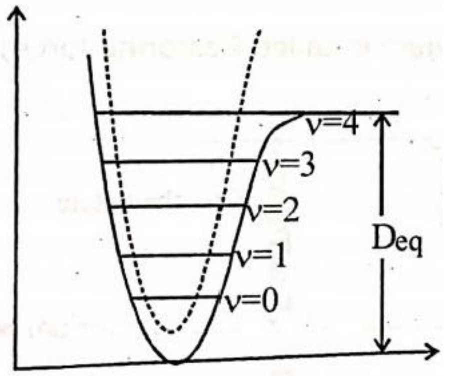


Sub.equation(1)in schrodinger wave equation and solve it.We get equation four Anharmonic oscillator

$$\boxed{\varepsilon_v = \left(v+\frac{1}{2}\right)\bar{\omega_e} - \left(v+\frac{1}{2}\right)^2 \bar{\omega_e} xe\ Cm^{-1}}$$

xe=Anharmonicity constant

$xe=0.001(0<xe<<1)$



E<u>nergy levels:</u>

$$If\ \ v=0 \Rightarrow \varepsilon_0 = \left(0+\frac{1}{2}\right)\bar{\omega_e} - \left(0+\frac{1}{2}\right)^2 \bar{\omega_e} x_e Cm^{-1}$$

$$\varepsilon_0 = \frac{1}{2}\bar{\omega_e} - \frac{1}{4}\bar{\omega_e}\ x_e\ Cm^{-1}$$

$$v=1 \Rightarrow \varepsilon_1 = \frac{3}{2}\bar{\omega_e} - \frac{9}{4}\bar{\omega_e}\ x_e\ Cm^{-1}$$

$$v=2 \Rightarrow \varepsilon_2 = \frac{5}{2}\bar{\omega_e} - \frac{25}{4}\bar{\omega_e}\ x_e\ Cm^{-1}$$

$$v=3 \Rightarrow \varepsilon_3 = \frac{7}{2}\bar{\omega_e} - \frac{49}{4}\bar{\omega_e}\ x_e\ Cm^{-1}$$

Selectlon rules for Anharmonic. osclllator(1)μ≠0,(2)△v=±1,±2,±3..

Er:(1) $\varepsilon_0 \rightarrow \varepsilon_1$, $\Delta v = \pm 1$

$$\Delta\varepsilon = \varepsilon_1 - \varepsilon_0 = \left(\frac{3}{2}\bar{\omega_e} - \frac{9}{4}\bar{\omega_e}xe\right) - \left(\frac{1}{2}\bar{\omega_e} + \frac{1}{4}\bar{\omega_e}xe\right)$$

Selection rules:

1.molecule should be with permenant (or) induced dipole moment i.e u=o(or) $\frac{d\mu}{dr} = 0$

Ex:H_2molecule. $\frac{d\mu}{dr} = 0$:Rinactive

All Homo atomic molecule(H_2 ,Cl_2 ,O_2 ,N_2...)are IR inactive

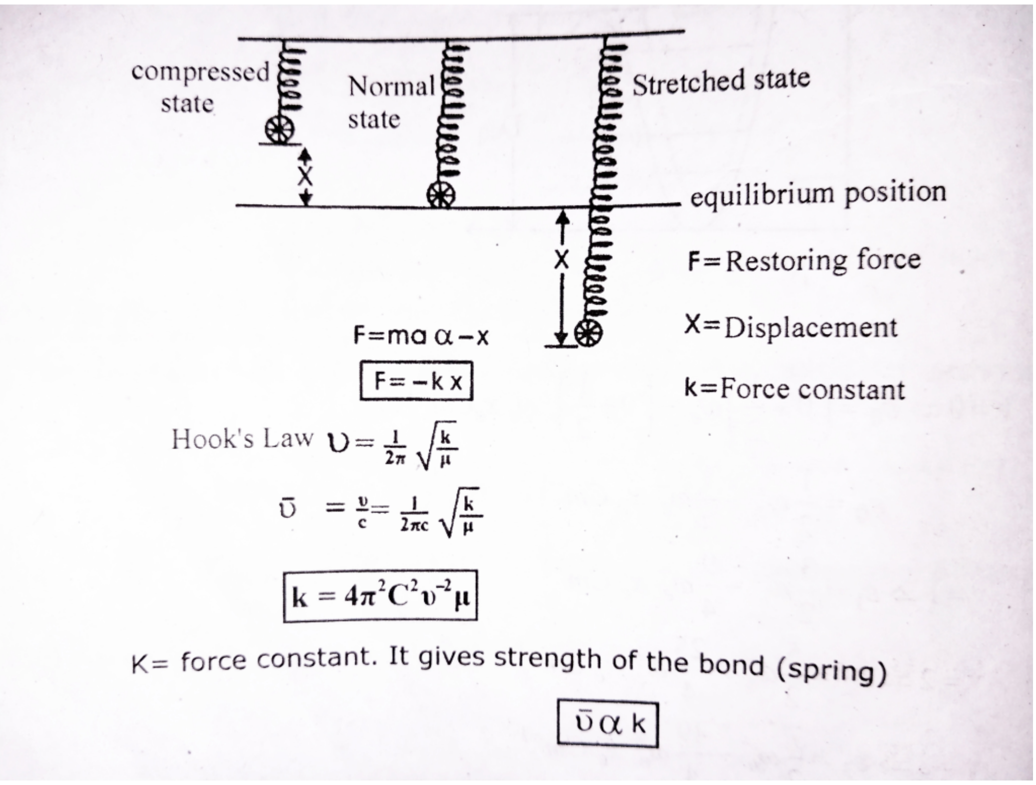
Hetero atomic molecules dipole moment change with vibration so they are IR active.

(2) △V=±1 △V:Diff b/w vibrational quantum number.

Force constant(K):

Force constant (K)is the measure of elasticity (or)strength of the bond.

Object with mass 'm'is hanging to the spring and pull downward takes simple'hormonic oscillations.In this process the Restoring force of the object taking the object to original position. (Force responsible for taking back of object is called Restoring force).



$F = ma \alpha -x$

$\boxed{F = -kx}$

Hook's Law $\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

$\boxed{k = 4\pi^2 C^2 \bar{\upsilon}^2 \mu}$

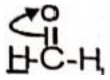
K= force constant. It gives strength of the bond (spring)

$\boxed{\bar{\upsilon} \alpha k}$

a

Force constant is directly proportional to the vib.frequency.I.e molecules witi large force constant value high frequency radiation.

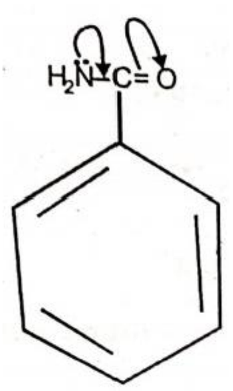
Ex:-



chH chcH

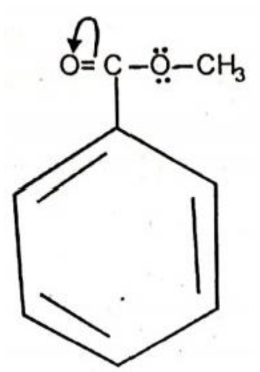
Fe=o-1kFocm^2 c=o=17$_{k4↓5}$^{cm} D=o=1715cm kJ↓

Due to +I effect of -CHʒgroup the C=0 bond is weakend and value of K is decreases. Therefore absorption frequency also decreases.



Bonzamide

c=o=1693cm



Phenyl acetate

De=o=1730cm'$^{-1}$

Oxygen is more E.N than Nitrogen.So for oxygen there is less chance to donate eO pair.due to thin C=0 absorption frequency is more.

Force constant values of some molecules are given in the below table.

Molecules	force constant (k)(Nm	vibration(cm
HF	966	4138.5
HCl	516	2990.6
HBr	412	2649.7
HI	314	2309.5
CO	1902	2169.7
NO	1595	1904.0
ICL	238	384.2

grees of freedom for polyatomic molecules:-

In 3D-space for a molecule total number of degrees of freedom =3N

N =No.of atoms in a molecule.

out of 3N-degrees of freedom the trans lattonal degrees offreedoms are three (for both linear &Non -linear)

Fora non-inear molecutle rotational degrees offreedoms are three =(3N-3-3)

Fundamental vibrations of 'N'atoms molecules
For linear molecule=3N-5

Over tones:

The transitions between v=0. v=2,3,4..............results overtones with weak intensity. i.e.transitions from ground state to higher vibrational levels.

Hot bands:-

The bands due to vibrational transitions such as v=1 → v=2,v=2 → v=3........in presence of high temperature only are called hot bands

.

Selection Rules:-

1.Molecules should pocess a permenant dipole moment.

μ≠0 (∵μ=Dipole moment)

Ex:HCl,CO,NH_3,H_2O...(Hetero atomic molecules)

For H_2,Ci_2,O_2,N_2......Homo atomic molecules μ=0.So rotational spectrum is not possible.

2.△J=±1 △J=Energy diff-b/w rotational levels.

Characterstic absorption bands of various functional groups:

In organic compounds there are various types of functional groups.Each functional group has its characterstic absorption frequency in IR-range.based on these absorption frequency bands it is possible to detect nature of the functional group in the compound.

Some functional groups and their absorption frequencies are given below.

Functional group	Absorption frequency region(cml)
C-H(Akane)	2960-2850
C-C	1300-800
C=C	1650-1600
C=C	2260-2100
C=C(aeromatic)	1660 -1500
O-H(Hydrogen Bond)	3400-3200
O-H(Fee)	3600-3400
C=0	1750-1650
C=N	3210-2280
$-NO_2$	1540
$-NH_2$(1°)	3500 - 3300 () Two peaks
¬N+(2°)	3500 - 3300 () one peak

ELECTRONIC SPECTROSCOPY

Uv-Spectroscopy is the study of electronic transitions or rearrangement in the molecule produced from irradiation with UV-Vissible light.

- O UV-Vissible radiation brings about changes in electronic levels of molecules,also reffered as electronic spectroscopy,mainly valence electrons are involved in Transitions.

Bonding,Anti bonding molecular orbitals:

- O Linear combination of Atomic orbitals(LCAO)produces molecular orbitals.(M.O.S)

$$AO'S \xrightarrow{LCAO} MO'S$$

- O Number of molecular orbitals produced are equal to no.of atomic orbitals mixed.

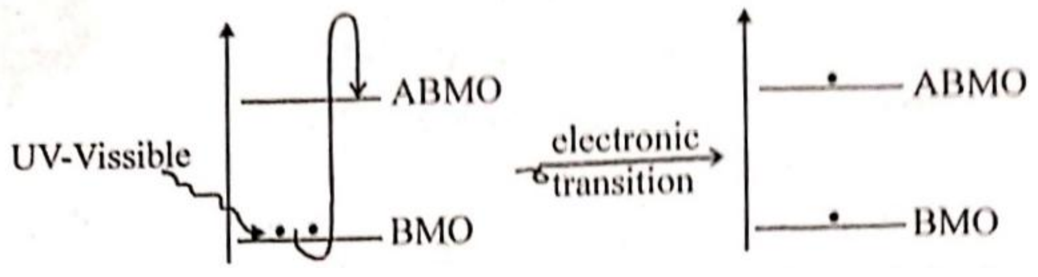
$$n.A.O'S \xrightarrow{LCAO} n.M.O'S$$

- O Half of the molecular orbitals posses low energy than Atomic orbitals and produced by addi - tion method are called Bonding molecular orbitals.

- O Half of the molecular orbitals posses High energy than the Atomic orbitals and produced by subtraction method are called Antibonding molecular orbitals.

ELECTRONIC TRANSITION:

Promoton of electron from lowereneryy M.O to Highereneray M.O by nteractlng wilthradn tion is called electronic transition.



(Ground state) (excited state)

The Range of UV-Vissible radiation is 200 -800 nm

λ=200-400nm -UV -radiatlon
400-800nm -Vissible light

Energy levels of molecules:-

Generally molecules pocess 4 types of energy levels.In molecules certain quantity d energy is stored internally,this energy is called Internal energy.It is associated with the following 4 types of energies.

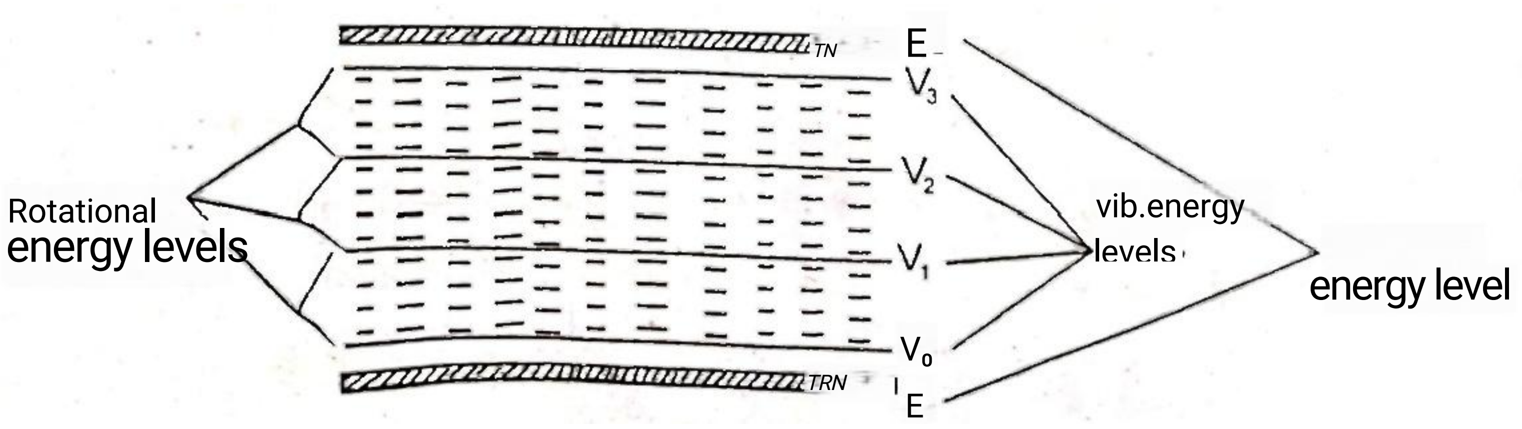
1)Translational Energy 2)Vibration Energy

3)Rotational Energy 4)Electronic Energy

In the above four types of energies except translational energy remaining are quantised.The order of various energies is Electronic energy>Vib.energy >Rotation energy.

In b/w every two electronic energy levels,a number of vib.energy levels are present simillarly in b/w every two vib.energy levels,a number of rotational energy levels are present.

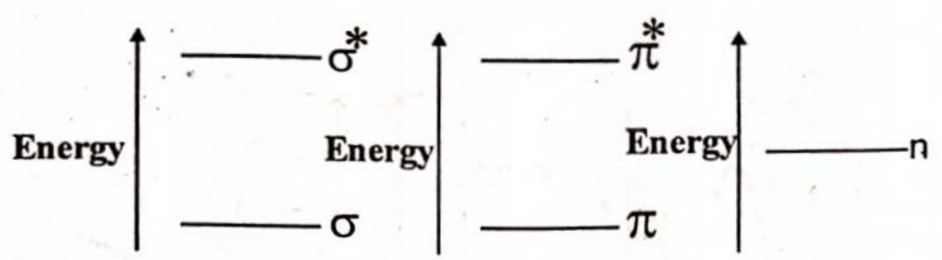
When electronic transiton occurs that can leads to change in vib.and rotational energy levels of the molecules.



Types of electrons:

In organic compounds mainly there are three types of electron(bonds)

(1)o-bonded electrons -Ex:All org-molecules
(2)π-bonded electrons -Ex:Unsaturated compound
(3)non-bonded electrons -Ex:Compound with Lone pair of electrons



σ,π—Less energy σ* 光 — More energ)

Based on nature of the electrons there are total six types of electronic transitions are possible inorg. Compound they are

(2)分-o”Transition σ-π”Transition

5)π-π*Transition 6)n-π*Transition

Allthough six transitions are posslble but in reallty only two types of transition (π-π',n-n') are detectable,remaining are ruled out because they occur in out of range of radiation.

(<200mm(or)>400mm)

1)σ-g*Transition:

Promotion of electron from o-bonding M.O to o*antibonding M.O in the absorption of UV - light..

Ex:-Alkanes(CH_3-CH_3),Cyclo alkanes,All org-compounds

2)π-π*Transiton:

Promotion of e9 from π-bonding M.O to π'-Antibonding M.O by absorbing light

Ex:Unsaturated compounds (Alkenes,Alkynes,Carbonyl etc...Compounds)

3)n-π*Transiton:

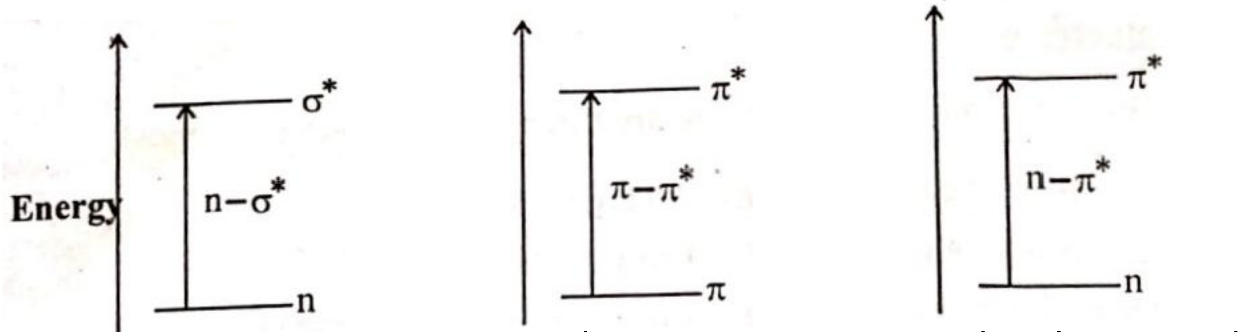
Promotion of e9 from Non-bonding M.O toπ*-Antibonding M.o.

Ex:Unsaturated compounds with Lone pair of electrons (Carbonyl compounds)

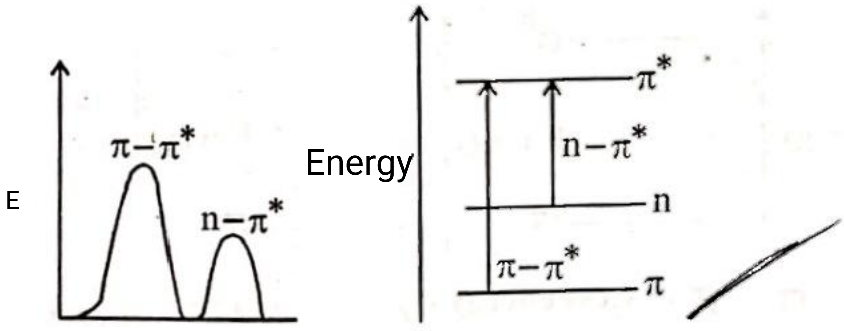
4)n-g”Transition:

Promotion of ee from Nonbonding M.O to c*-Antibonding M.o.

Ex:Saturated comp.With lone pair of ees (Alcohols,Amines...)

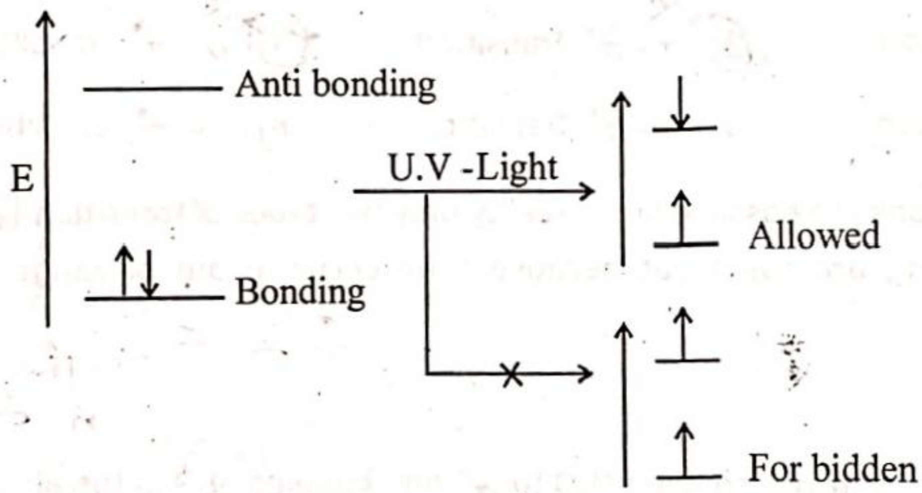


Electron Transitions on carbonyl compounds

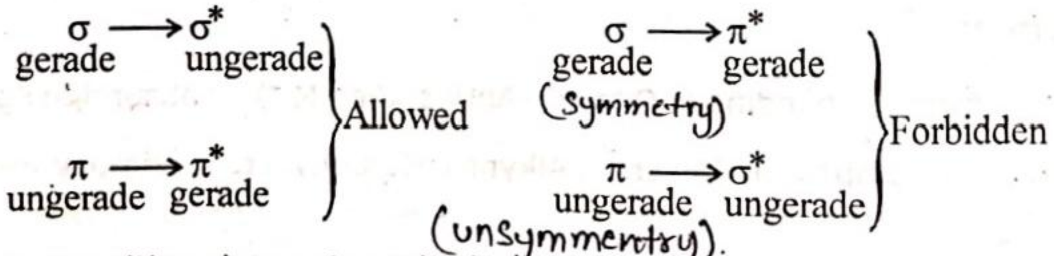


Selection Rules:

1.During the electronic transitions Retention of spin of electron is Allowed,Inversion of spint electron in Forbidden.

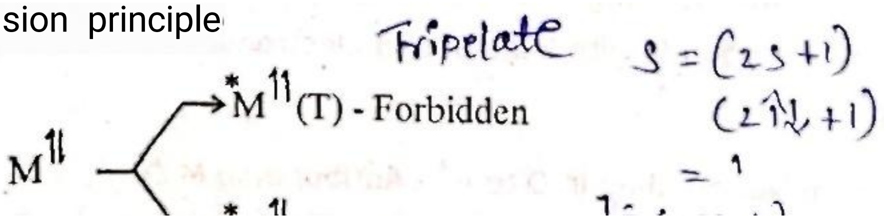


2.In electronic Transitions involved orbitals with different symmetry are allowed and orbitas wth samesymmetry areforbiuden.



3.In electronictransttion change in multipleity is forbidden,Retention in mutiplicity is Alowe

(multiplicit exclusion principle

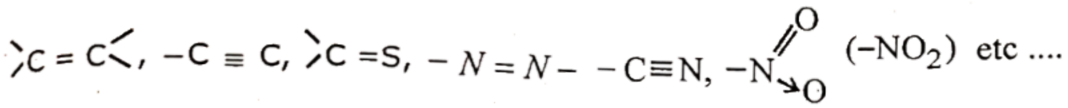


Terminology:-

chromophore·

The group which is responsible for absorption of UV-Vissible range of radiation is called tnomophore.These groups imparts colour to the molecules.

Ex:All unsaturated groups are chromophores



Nitro (-NO_2)group imparts yelow colour to the compound

Azo(-N=N)-group imparts Colour to the compounds

2.Auxo chrome:

Groups which cannot absorbs UV-vissible range of radiation it self,but enhances absorption wavelengths of chromophores are called auxochromes.

Ex:-Group with lone pair of electrons.

-OH,-OCH_3,-NH_2,-NHR,-NR_2,-X:etc.

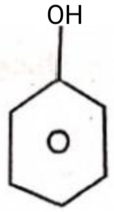
Auxo chromes are called colour intensifiers.

3.Batho chromic shift /Red shift:

Shiftting of UV-Vissible band towards longer wave lengths(or)Right side in a spectrum is called Batho chromic shift (or)Red shift.

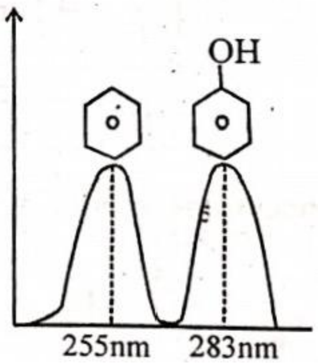
benzen

λmax =255 nm



phenol

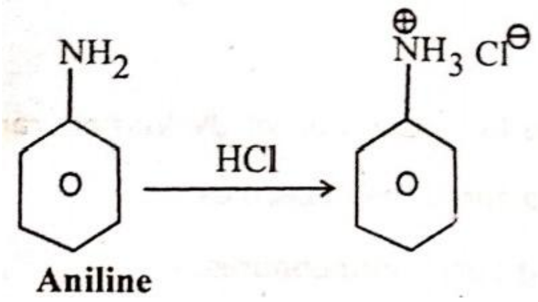
λmax=283 nm



4.Hipsochromic shift /Blue shift:

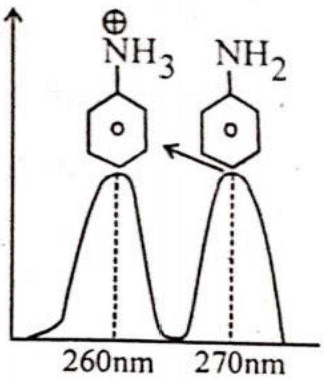
Shifting of UV-Vissible band towards shorter wavelength(or)Left side in a spectrum is ualed Hypsochromic shift (or)Blue shift.

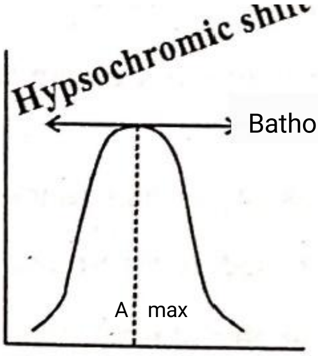
2 Ex:



λmax =270 nm λmax =260 nm

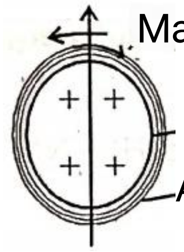
Hypsochromic shift





P. ROTON MAGNETIC RESONANCE SPECTROSCOPY

Nature of nucleus

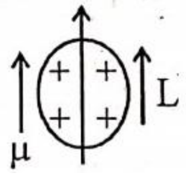


Spinning nucleus

Rotation of particle around it's own axis called spinning.

Spinning nucleus produces magnetic field,Therefore nucleus act as tiny bar magnet.Useful: for NMR spectroscopy.

Spinning nucleus associates with magnetic moment vector(μ)and Angular momentum vector (L)Both are parallel to each other at nucleus.



Angular mormentumL/F_1 =√TC+1).

I=sum of spin Quantum members

)Spin quantum number zero -nucleus is non-magnetic.

S.No	No.of.'P'S	No.of.'n'S	At.No	Man No.	Spin Q.No(1)	Example
	Even	Even	Even	Even	Zero	$^{12}_{6}C$. $^{32}_{16}S$. $^{16}_{8}O$
2	Even	Odd	Even	Odd	Non Integer Non Integ ($\frac{1}{2}$,$\frac{3}{2}$......)	$c^{13}4$=5).g^{7} (=3)
3	Odd	even	Odd	Odd	Non -Integer	$^{15}_{7}N(I=\frac{1}{2})$, $^{19}_{9}F(I=\frac{1}{2})$
4	Odd	Zero	Odd	Odd	Non-Integer	$?^{3'}$(=5).H(=5)
5	Odd	Odd	Odd	Even	Integer(1,2,3...	N(t=1).D(I=1)

Principle:-

Din the absence of external magnetic field spin orientation of nuclei are random:once ·magnetic field is applied at the nuclei disorder /random arrangement of nuclei disappears ang nuclei orients in two possible directions.

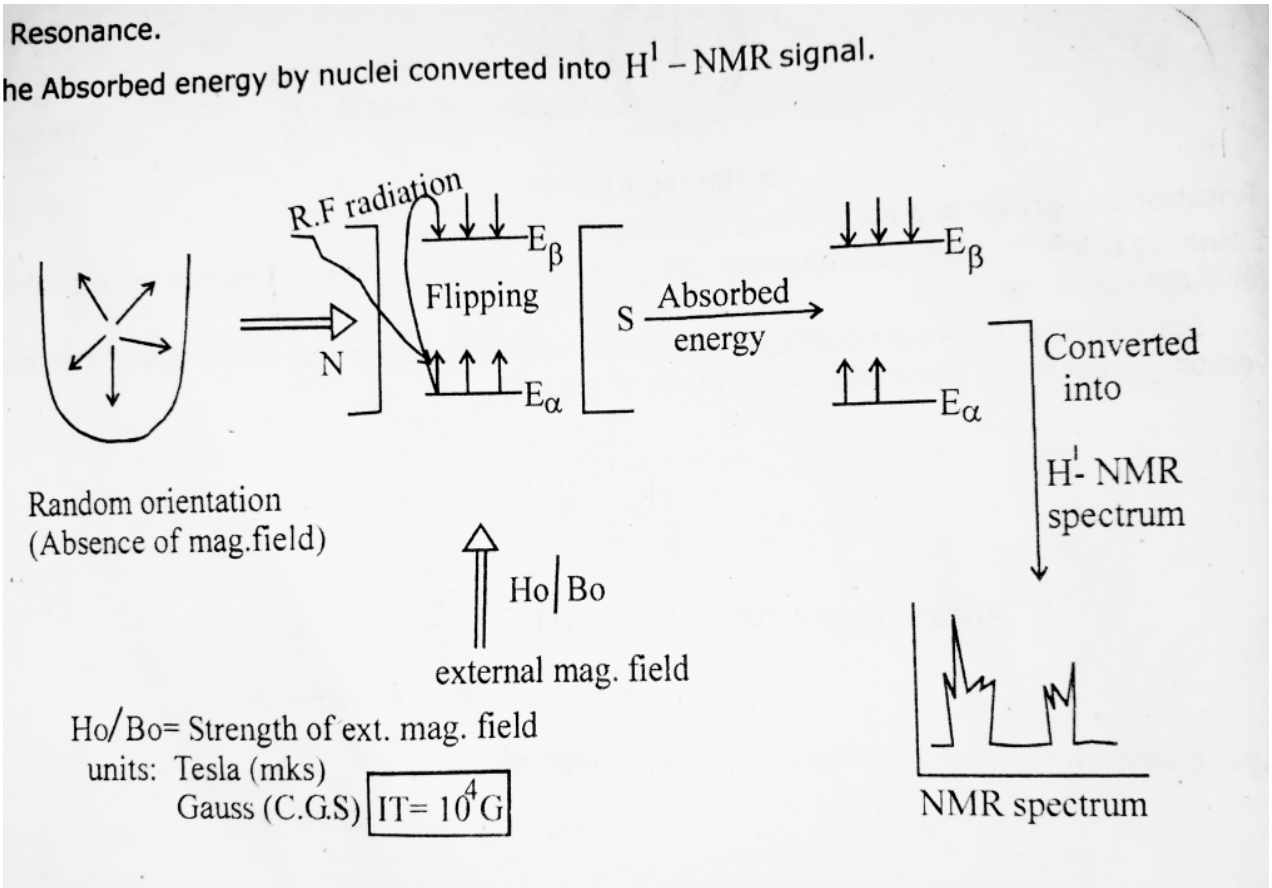
In one orientation nuclear spins are parallel to direction of external magnetic field(Aligne orientation Ea),In another orientation nuclear spins are Ir to direction of external magneticfie:
(opposed orientation Eg).Little excess of nuclei with aligned arrangment,then opposed arranment.

Under resonance condiuon,if nuclei irradiated with Radio frequency(RF)radiation nucle absorbs energy and participate in upward transitions with change in spin orientations are calleda

Flipping of nuclei.

Resonance:- Matching of energy of R.F.radiation and energy gap of two nuclear energy levels called Resonance.

The Absorbed energy by nuclei converted into H^1-NMR signal.



Resonance.

he Absorbed energy by nuclei converted into H^1 – NMR signal.

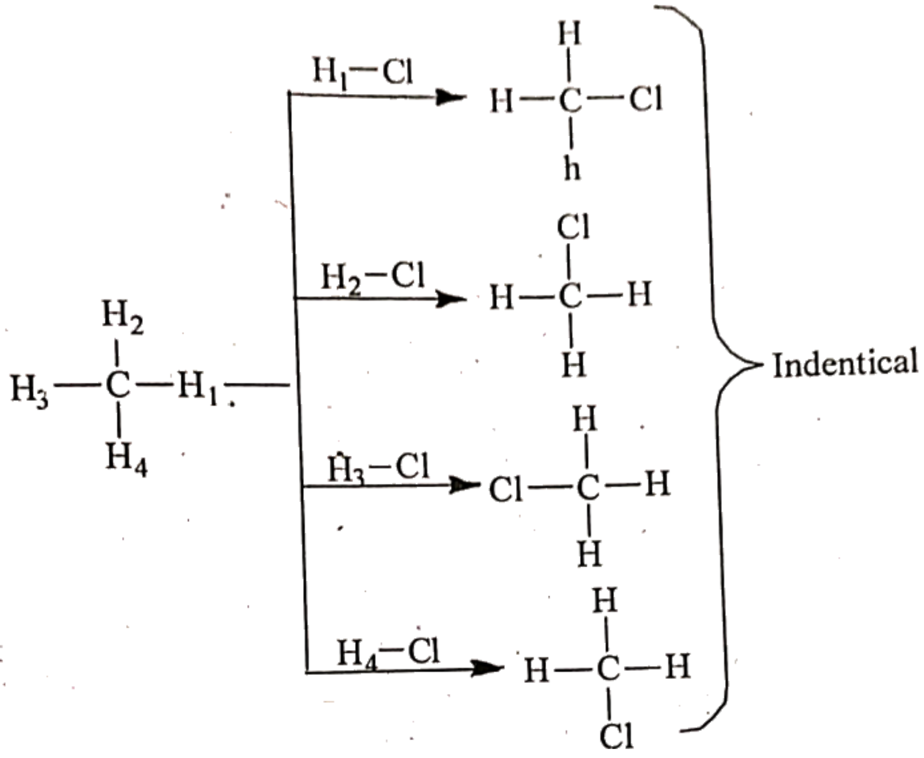
Ho/Bo= Strength of ext. mag. field
units: Tesla (mks)
Gauss (C.G.S) $\boxed{1T = 10^4 G}$

Equivalent and Non-equivalent protons:-

Equivalent protons:-

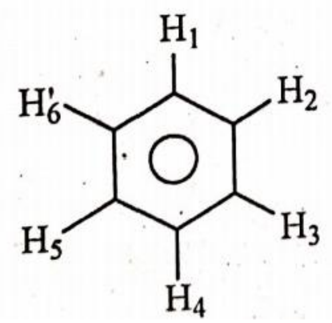
protons which possesses same chemicalenvironmentsandsimilar chemicalshift(ö)values are called equivalent protons.

Ex:-(1)CH_4 → 4-protons of methane are equivalent i.c.1 sct



∴H_1,H_2,H_3,H_4**Protons are equivalent =1 set**

(2 2)

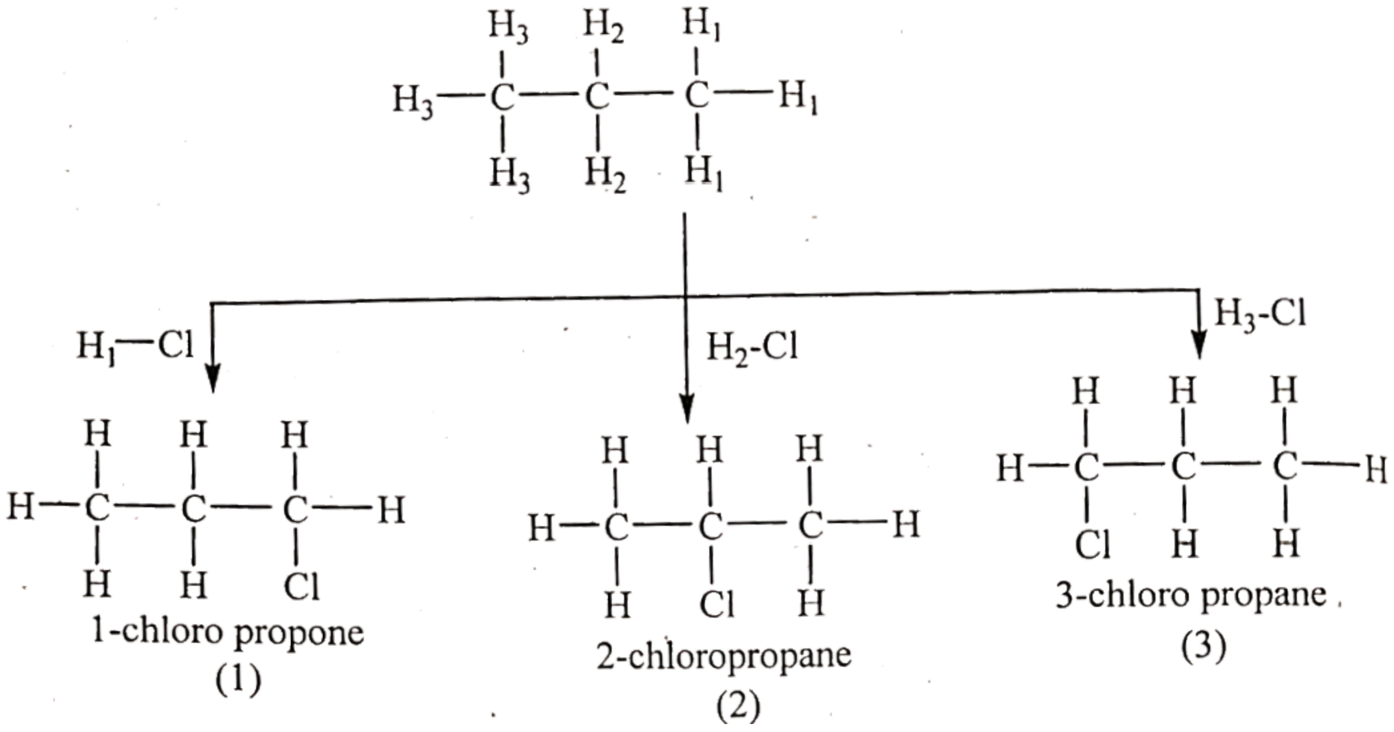


All the 6-H of benzene are equivalent

Non-equivalent protons:-

Protons which possesses different chemical environments and shows different chemical shift (δ)values are called Non-equivalent protons.

Ex--$CH_3-CH_2-CH_3$--Propane



1-chloro propone
(1)

2-chloropropane
(2)

3-chloro propane
(3)

(1),(3)are Identical →equivalent

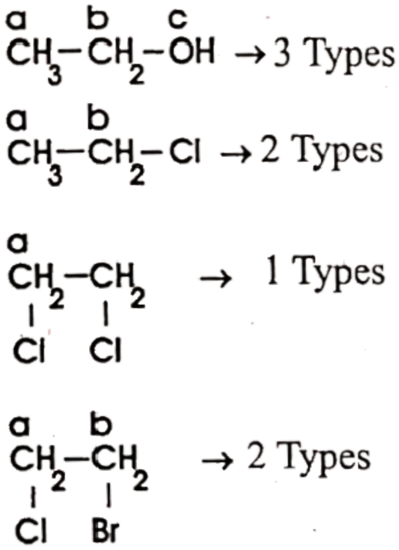
(2)→different

∴.Two types of protons =2 sets

(2)cH_3-Ch_2-oH-Ethanol

Ethanol pocess three Non-equivalent sets of protons.

Examples:



$\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{OH}$ → 3 Types

$\overset{a}{CH_3}-\overset{b}{CH_2}-Cl$ → 2 Types

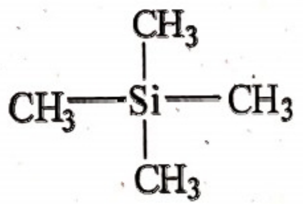
$\overset{a}{\underset{Cl}{CH_2}}-\underset{Cl}{CH_2}$ → 1 Types

$\overset{a}{\underset{Cl}{CH_2}}-\overset{b}{\underset{Br}{CH_2}}$ → 2 Types

The change in the position of nmr signal when compared with reference compound due to shielding(or)deshielding effect of protons is called chemical shift (δ)

$$\text{Chemical shift}(\delta) = \frac{\nu_{\text{Sample (Hz)}} - \nu_{\text{Reference (Hz)}}}{\nu_{\text{Instrument}}}$$

The reference compound used in NMR spectroscopy is TMS (Tetramethyl silane)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3$$

δ=0

0 Chem.shift of equivalent protons is always same.

0 Chem.shit of non-equivalent protons is always different

$$\boxed{\text{Chemical shift }(\delta)\ \alpha\ \text{E.N}}$$

Ex:--CH_3,-OH,-NH_2protons

E.N=O>N>C

δ=-OH>-NH_2>-CH_3

Type of proton	Chemical shitt (δ)
Alcohols H-C-OH	3.4$_\circ$ 4.0
AldelydesR-CHO	9.0-10.0
Acids H-C-COOH	2.0 -2.5
Armomatic Ar-H	6.0-9.0
Acetylenic -C=CH	2-3
Ethers H-C-OR	3.3 -4.0
Esters H-C-COOR	2-2.2
Hvdroxy R-OH	1-5.5
Alkane R-CH_3	0.9

Spin multiplicity:

Total number of lines in a nmr signal is called multiplicity

nmr-Signal	Namg	Symbol	Spin multiplicity
 One line	Singlct	S	1
 Two lines	Doublet	d	2
 Three lines	Triplet	t	3
 Four lines	Quartet	q	4
	Pentet	P	5
	Multiplet	m	5

Splitting of nmr-signal:-

Due to interaction of spin of one partcular set of protons with the spin of Nelghboun protons leads to splitting of nmr-signals.

O Splitting of nmr signal is due to spin-spin coupling process.

Spin -Spin coupling:-

The process of spin of one partcular set of protons coupled with the spin of netghounms protons is called spin-spin coupling.

c b a

Eg:-CH_3——CH_2—OH -

Ethyl alcohol

spin multiplicity of proton = n + 1

n =no.of neighbouring protons

for—ÖH proton =no.ofneighbourng protons (n)=2

muliplicity of -OH proton=n+1

=2+1

= 1

(Triplet)

or-&tz protons no ofneghtouring poos (yltt

∴multiplicity of —CHz protons =n+1

=4+t 3+

=g4

Pente

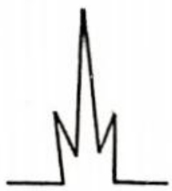
quartet

for—&t$_3$protons =no.of neighbouring protons(n)=2 (-CH_2)

:multiplicity of -CH_3 protons =n+1

=2+1

=3

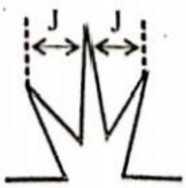


Triplet)

Coupling constant)(J):

The distance between the two adjacent peaks in a multiplet is called coupling constant. The value of the coupling constant is independent of the external field.

>itis measured in Hertz(HZ)(or)in cycles per second (CPS).

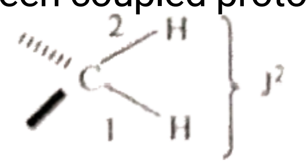


Types of coupling in h1-NMR

1.Geminal coupling Jeem(or)]J_2

---

j* x no.o! ntervening bonds between coupled protons,

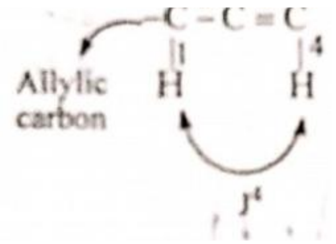


Couplng Inlteracuonsot protons attachedto same carbon are geminal couplnqs(N)

2. Vicinal coupling

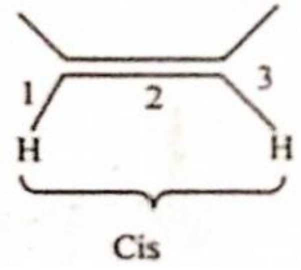
Coupling between adjacent carbon atom protons

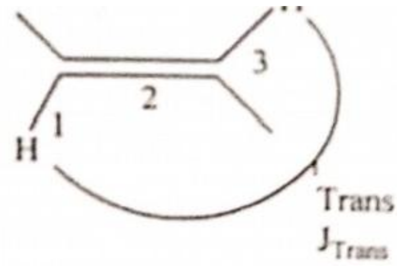
3. Allylic coupling



Cis-transcoupiling

Coupling between cis-protons/trans protons





Jay

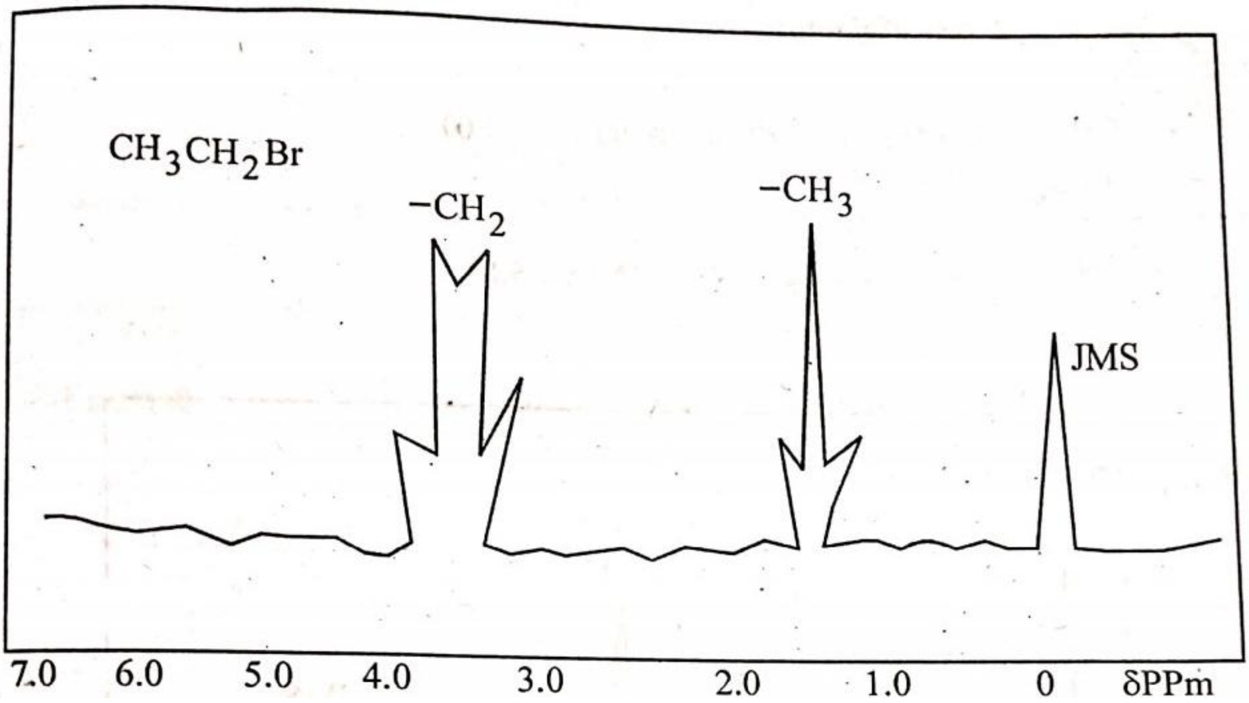
H1-NMR spectras ot some org.compounds:-

1)Ethylbromide:-

$\overset{b}{\text{-CH}_2} \rightarrow n=3$

from n+1 rule

3+1=4(Quartet)(δ=3.3)



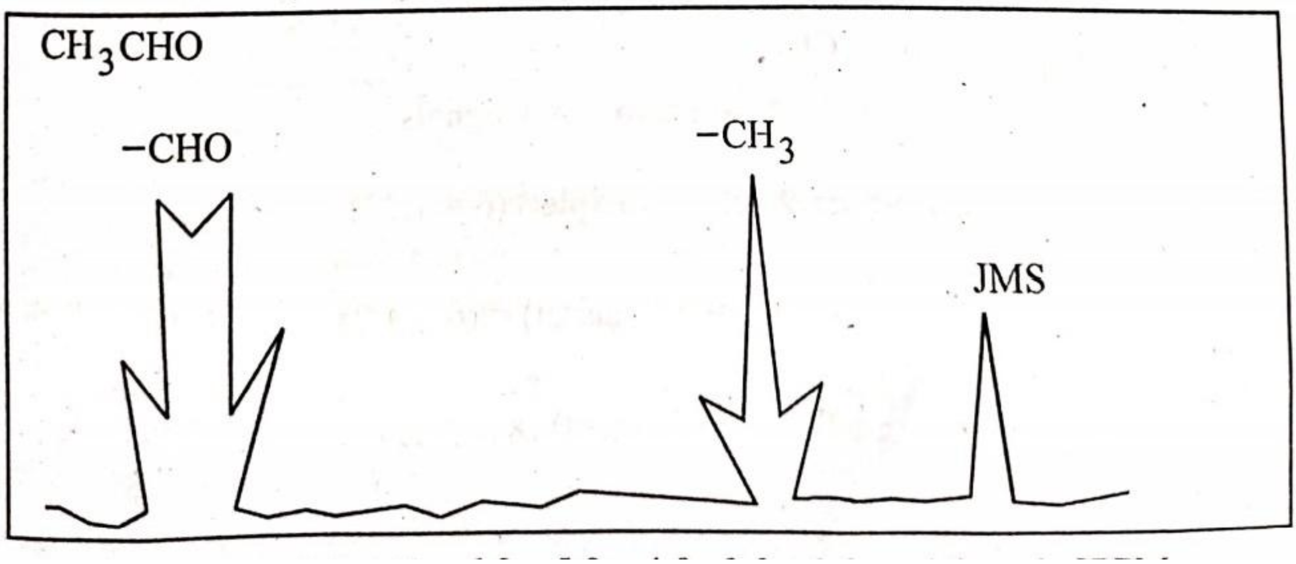
2)Acetaldelyde:-

ch_1;

2-sets of protons

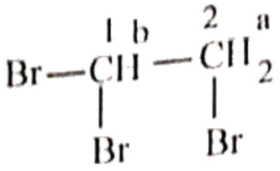
$\text{-C\&}_2$ n=1 → 1+1=2(Doublet)(δ=2.2)

-CHO → n=3 → 3+1=4(Quartet)(δ=9.5)



10.0 9.08.07.0 6.0 5.0 4.03.0 2.0 1.0 0 δPPM

(3)1_,2-Tribromo ethane:

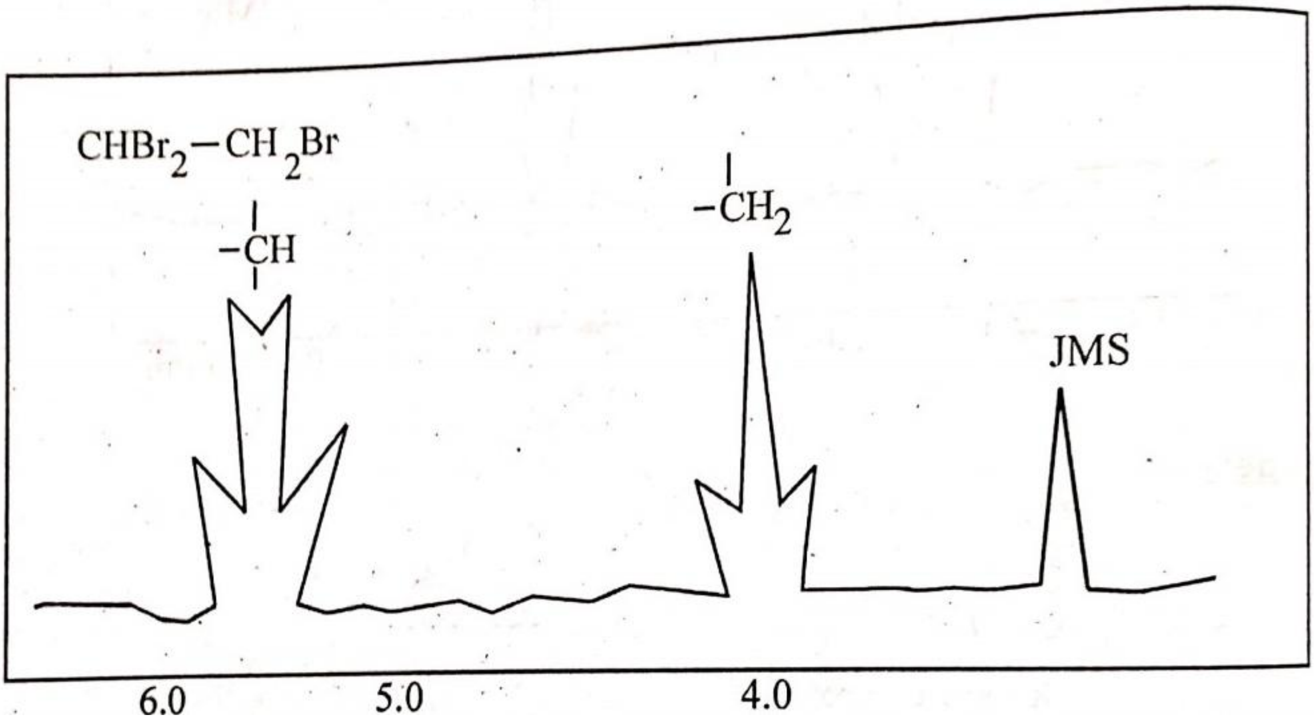


$Br-\underset{Br}{\overset{1\ b}{CH}}-\underset{Br}{\overset{2\ a}{CH_2}}$

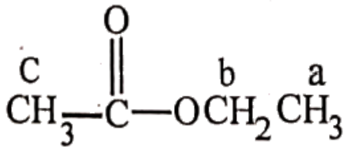
2-sets of protons

-C2>n=1=1+1=2(doubet)(6=4.0)

-H²=n-2=2+1-3 y(8-5)



Ethyl acetate



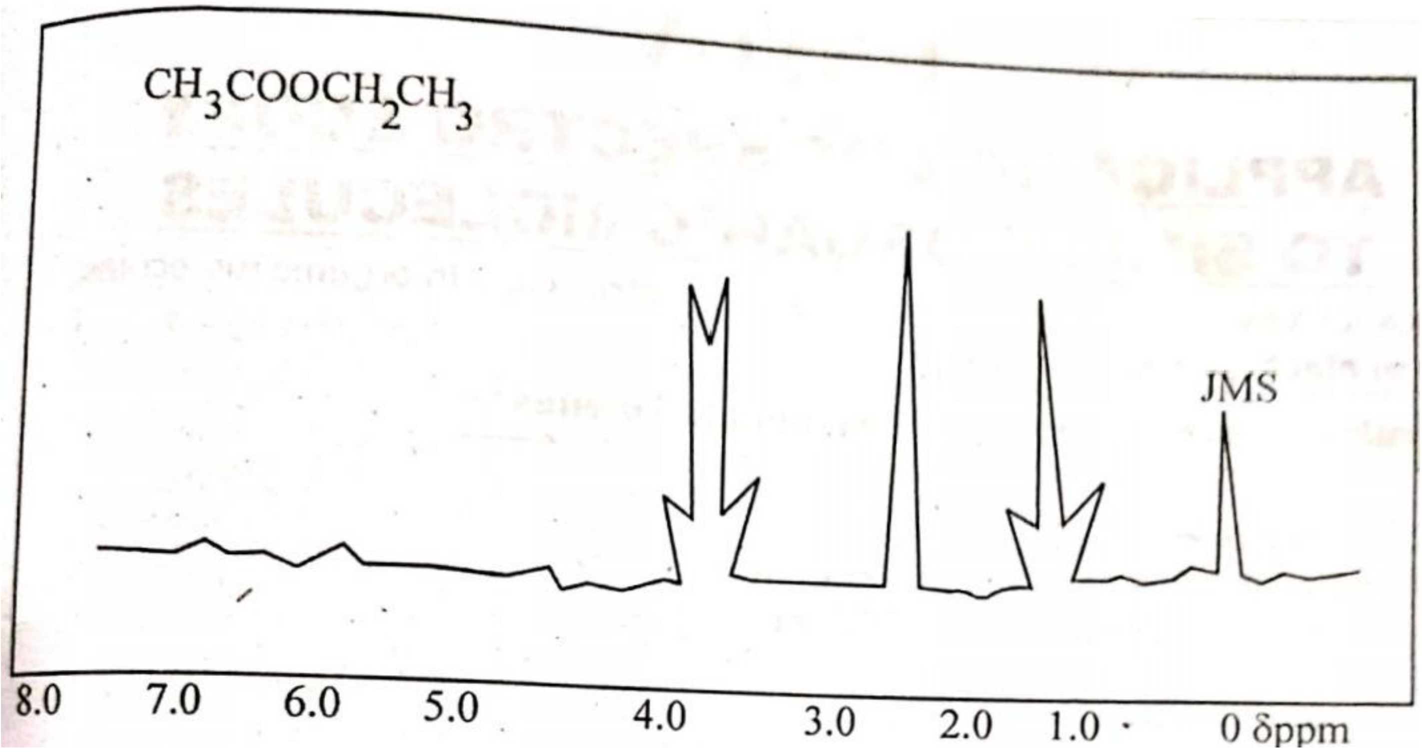
$\overset{c}{CH_3}-\overset{O}{\overset{\|}{C}}-O\overset{b}{CH_2}\overset{a}{CH_3}$

→3 sets of protons =3 signals

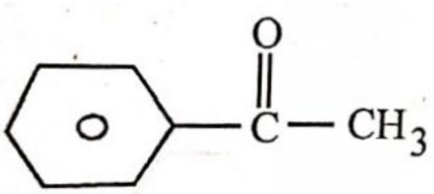
$\overset{a}{-CH_3} \Rightarrow n=2 \Rightarrow 2+1=3$ (Triplet) ($\delta = 1.21$)

$\overset{b}{-CH_2} \Rightarrow n=3 \Rightarrow 3+1=4$ (Quartet) = ($\delta = 4.2$)

$\overset{c}{-CH_3} \Rightarrow n=0 \Rightarrow 0+1=1$ (singlet) ($\delta = 2.09$)



Acetophenone:-

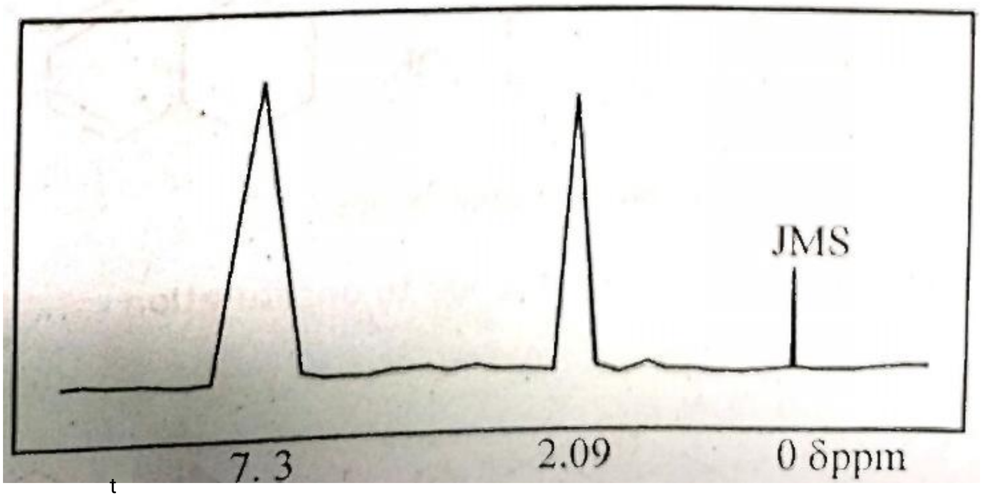


(or $\overset{b}{C_6H_5}\text{-}\overset{a}{C}\text{-CH}$

2-sets of protons=2 signals

$-Ci_3 \rightarrow n=0 \rightarrow 0+1=1$(Single)(6=2.09)

$-C_6H_5=n=0 \geq 0+1=1$(Singlet)(δ=7.3)



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APPLICATION OF SPECTRO SCOPY TO SIMPLE ORGANIC MOLECULES

Appllcation of visible ultraviolet and infrared spectros copy in organic molecules.

Application of electronic spectroscopy:

Woodward rules for calculating Xmax of conjugated dienes :-

Rules:

1.For a cyclic diene base value =217 nm

2.For hetero annular diene base value =214 nm

3.·For homo annular diene base value =253 nm

Increments:-

1.Per alkyl group/Ring residue =+5 nm

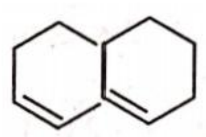
2.Per exo double band =+5 nm

3..Per extended conjugation =+30 nm'

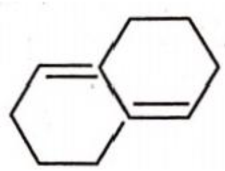
4.Per Halo group =+5 nm

→extended conjugation

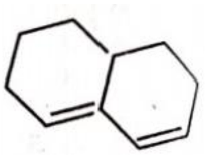
Acyclic diene



(OR)

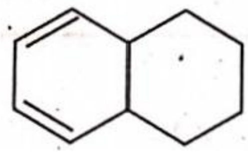


(OR)

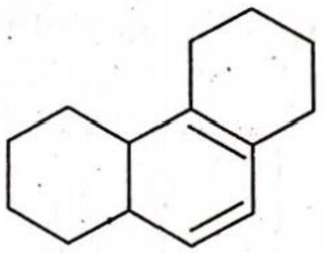


Hetero annular dienes

(OR)



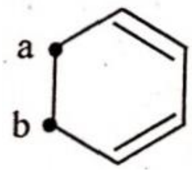
(OR)



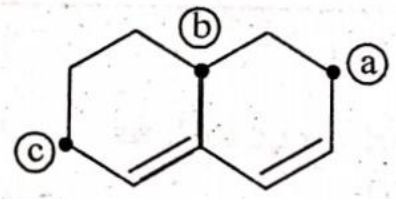
Homo annular dien

Ring residue

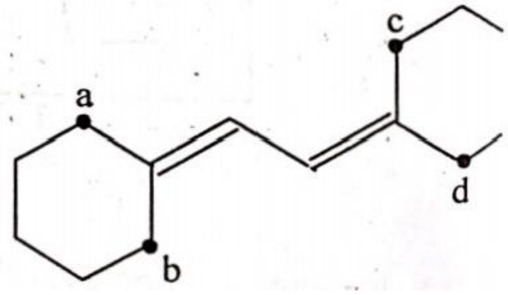
Saturated ring carbon groups directly attached to unsaturation



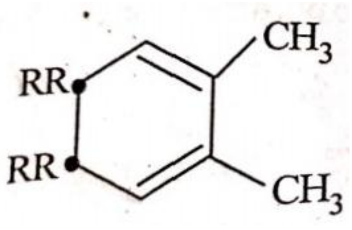
a &⑥→Ring residue



a,b,c→RR's



4-Ring residue

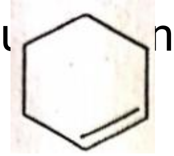


→2-RR's

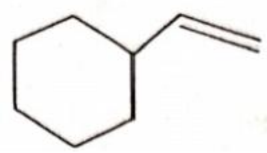
2-Alkyl su

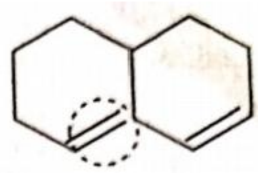
EXO CYCLIC DOUBLE BOND

Dou nd arranged out of ring,with one temiptaf

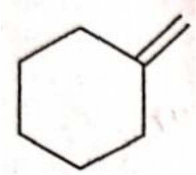


Not exocyclic

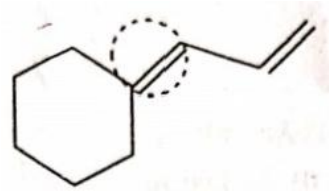




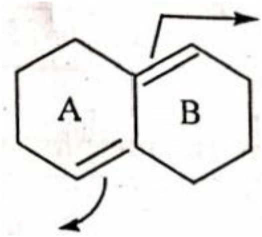
exo cyclic db



exo cyclic db



exo cyclic

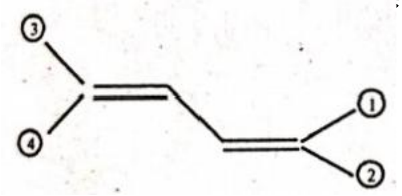


exo to A-

ring exo to B-ring

→ If molecules having both homo annular and hetero annular dienes to apply woodward rules, Homo annulas should be selected.

Ex:1.



Acyclic diene

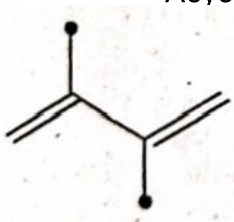
Base value =217nm

4-Alkl gps =+20nm

(4×5nm)

λmax =237 nm

2.



Acyclic diene

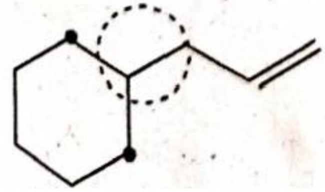
Base value =217nm

2-Alkyl gps =+10nm

(2×5nm)

λmax =227 nm

3.



Acyclic diene

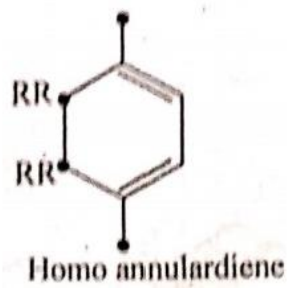
Base value =217nm

2-Ring residue =+10nm

1-exodouble bond =+ m 5nm

λmax =232 nm

4,



Homo annulardiene

Base valuc =253nm

2-Aikyl gpn +10nm

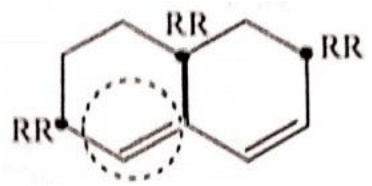
(2×5nm)

2-Ring residue s410nm

(2×5nm)

λmax =273 nm

5,



Hetero annular

Base value =215nm 214np

3Ring residue =+15nm

(3×5nm)

1-exocyclicdb =+5nm

λmax=234nm

.a,β-unsaturated compounds /enone chromophore :-

Rules:

1.Parent acyclic(or)sixmembered and higher membered ketones base value =215nm

2.Parent flve membered cyclic ketones base =202nm

3.Parent a,β-unsaturated aldehyde base value =207nm

4.Parent a,β-unsaturated acld /ester base value =195nm

Increments :-

1. Per alkyl /Ring residue at 'a¹=+10nm

'β'=+12nm

γ/higher =+18nm

2.Per exo-cyclic double bond =+5nm

3.Per extended conjugation =+30nm

4.Per-OH group at a=+35nm

β=+30nm

γ=+50nm

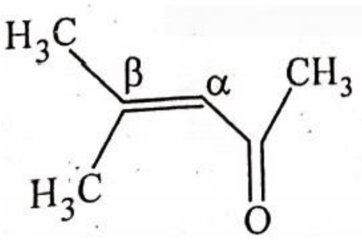
5.Per chloro at a =+15nm

β=+12nm

¥

Examples :-

1.



Acyclic

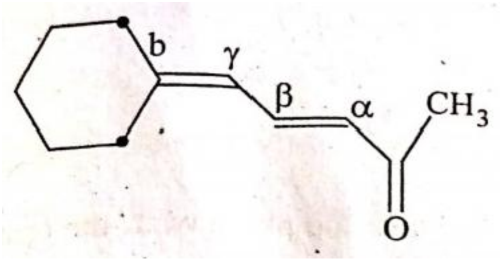
Base value=215 nm

Two alkyls at (β)(2×12nm)=+24nm

λmax =239nm

NATCANNA AAINIINA AAN

2.



Base value =215nm

1-extended conjugation =+30 nm

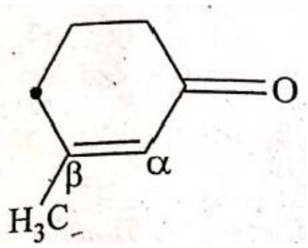
1-exo db =+5nm

aty/morethan'γ'2-RR's =+36nm

(2×18 nm)λmax=286nm

γ β

3.



Base value =215nm

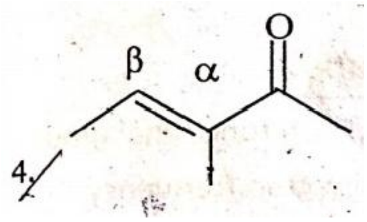
1-Alkyl at g=+12nm

1-RR at β=+12nm

Amax =239nm

6-membered enone

4.



Base value =215nm

1-Alkyl at a=+10nm

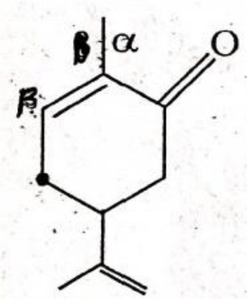
1-Alkyl at β=+12nm

$\lambda_{1\,max}$ =237nm

&15.
10
l2

acyclic enone

5



Base value =215nm

1-Alkyl at α=+10nm

1-RR at β=+12nm

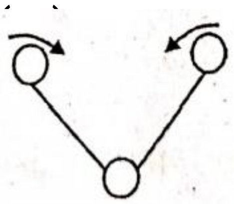
max =237nm

Cyclic 6-membered enone

Types of molecular vibration:

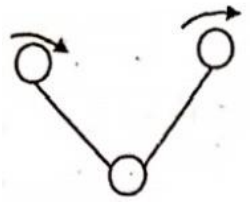
1.scissors

wo atoms approach each other ent of the atoms takes place in opposite direction.

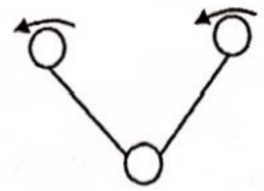


2.Rocking

In this type the movement of the atoms takes place in the same directi.

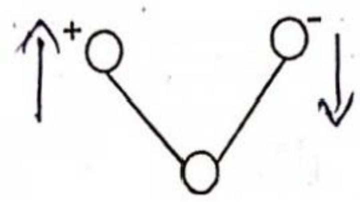


(or)



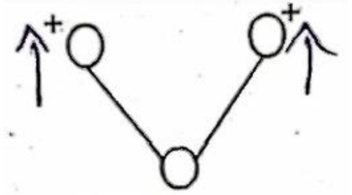
3.Twistting

the atom moves up the plane and the other moves down the plane w.kt.the ceng atom.



4.Wagging:

Two atoms move up and down the plane w.r.t.central atom.



Characterstic absorption bands of various functional groups:

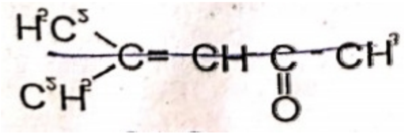
In organic compounds there are various types of functional groups.Each functional grou; has its characterstic absorption frequency in IR-range.based on these absorption frequency bands it is possible to detect nature of the functional group in the compound.

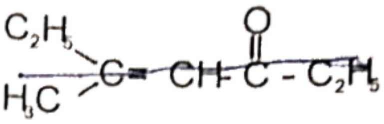
Some functional groups and their absorption frequencies are given

Functional group (cml)	Absorption frequency region
C-H(Akane)	2960-2850
C-C	1300 -800
C=C	1650-1600
C=C	2260-2100
C=C(aeromatic)	1660-1500
O-H(Hydrogen Bond)	3400-3200
O-H(Fee)	3600-3400
CC=0	1750-1650
C=N	3210-2280
$-NO_2$	1540
$-NH_2(1°)$	3500.-3300(V wo peaks)
-NH2)	3500-3300(one peak

Fingerprint region:

In IRspetroscopy the frequency range 1400-910cm-is caled fingerprint region,In t region each compound has some specific absorption bands. Functonal groupregloniniR cannot dlistngulsh the structurally ctoser



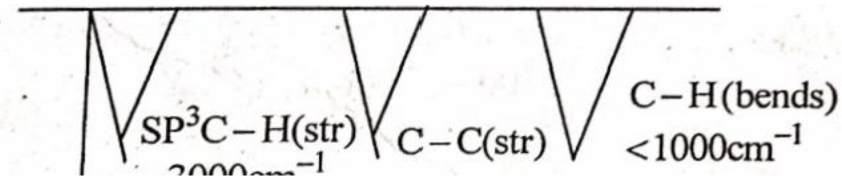


rR spectra of alkanes

таГкапез смо гурез оГ Ьапаз (С-Н апа С-Г
pectra can be Interpreted in terms of four vlbrations.

1. C-H stretchino
2. C-H bending

?с-н(bend)—>10001о 750 ст7'(<1000ст-!)

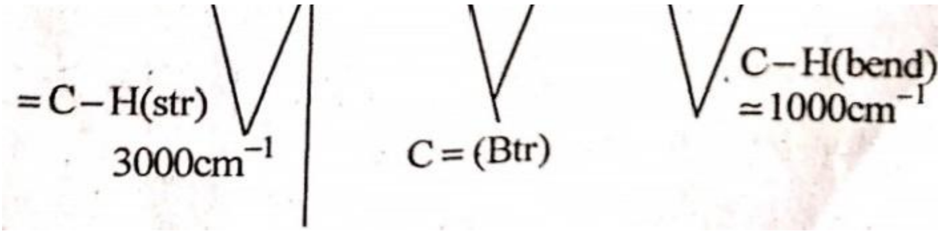


1100—1300ст—1

2.Alkenes

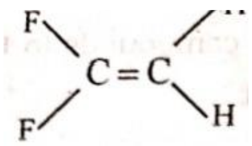
1

2

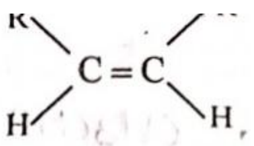


Prsence of substituents on double bonded carbons also influences vibrational

Presence of-I.E of gps increases vib,frequencncles and +M.E group decreases vibfrequencncles,



$H_2C=CH_2$

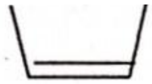


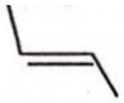
Vc=C=1730 cm-1

vc=c=1600-1580 cm-1

VC=c=1640 cm-1

In Cis &trans isomers cis vibrational frequency is larger than trans vib frequency





In alkynes

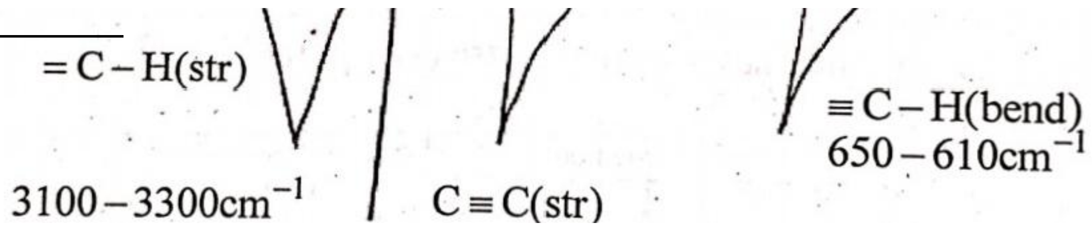
1.C=C(str)=v~=2100-

970cm-1 730-650cm-1

3.Alkynes:-

2.=C-H(str) v~=3100-3300cm-l

3.=C-H(bend) → v~=650-610cm-1



2100-2200cm-1

4.Alcohols(-OH):-

$\nu_{\substack{O\text{-}H\,(free)\\(Str)}} = 3600-3400\ cm^{-1}$

$\bar{\nu}_{\substack{O\text{-}H\,(H\text{-}bonded)\\(Str)}} = 3200-3400\ cm^{-1}$

Vc-o(Sr)=1000-1300 cm-¹

Alcohols ;-

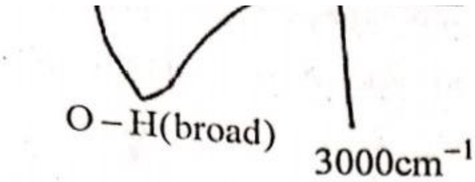
$\overset{\circ}{1}_{C-O(str)} \simeq 1050 \text{ cm}^{-1}$

2c-o(sr)=1100 cm-l

$\overset{\circ}{3}$C -O(str)=1200 cm

Phenolic C-O(str)=1250 cm-

ICATIANS.NALGONDA



helbqn gwinbs egus

Ex:-IR spectra of ethanol constis the following band

O-H(str) → 3330cm-1
C-H(str)- 2996cm~1

C-H(str)—→2924cm-l

.-0(str)(for-1-Aleohols) 1050cm²

The O-H stretching depends upon concentration,nature of the solvent and temperature 5.Aldehydes (-CHO)&Ketones (-COR):-

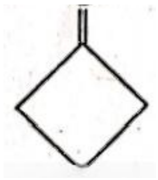
$R\text{-}\overset{H}{C}{=}o$ sr=2800cm*

Carbonyl carbon C-H(str)is highly characterstic of Aldehydes,appears at 2800cm-¹very intense.

The appearance of a strong band in the spectrum between 1650-1750cm-l shows the presence of as carbonyl (C=O)function.

The C=O(Str)absorption for formaldelyde (HCHO)is 1750cm-land for acetaldehyde is 1745cm-l and for acetone(CH_3-$COCH_3$)is 1718cm-1.

Aldehydes can be easily distinguished from ketones due to the presence of C-H(Str) absorption band at near 2820cm-1.



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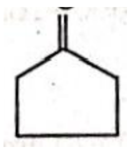
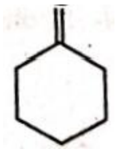


V
C=O(Sr)=1775c

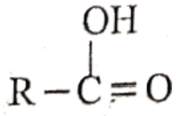
v~=1750cm-1



v~=1715cm-1

→ Ring size increases C=O(str)frequency decreases.

6.Carboxylic acids and their derivaties :



$R-\overset{OH}{\overset{|}{C}}=O$

Carboxyic group(-COOH)is the easiest functlonal group to detect by infrared spectros copy since this group can be considered as being formed from C=O and O-H units.

»The nbsorpUonolH(Slr) appearѕ аза broadband nеаг 3000—2500cm-1. Тпе у

stretching absorptlon in aliphatic acids occurs at 1725-1700cm-1

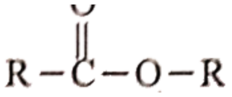
V o-wsu) = 3000—2500cm=1

Vc=osr) =1720-1750cm-1

Some ot the aclds Ike acetlc acld, benzolc ~~acld~~ exist as dlmers due to hydrogen bar..

Formatlon of brldge lowers the force constant and thus v c=o and v’o-н absorption occ.. lowerwave number.

Esters :-

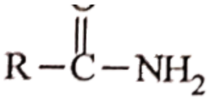


$R-\overset{O}{\overset{\|}{C}}-O-R$

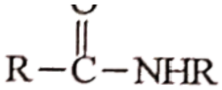
$\bar{\nu}_{C=O(Str)} = 1750-1725 cm^{-1}$

V c-otst) =1260-1160cm=]

Am Ides !-



$R-\overset{O}{\overset{\|}{C}}-NH_2$



$R-\overset{O}{\overset{\|}{C}}-NHR$

g-m,

.0— amide »0— amide з0—amide

10-amides:-

VC=0(sr) =169O ст-Т

Ум-нвну—э—3фООстТ ё—350Oст- (гмо реакз)

V n-нcsi—H-bondei)—) 2=3350cm-1 &~3180cm~1

VM-нtbondng) =1600—1650cm-1

90- amide5 !-

V’ c=o(st) ~1700—1670 cm-1

Vм-н(su) =3425(em71), (опереак)

VN-н(si-H-bondea) =3330—3140ст71

ao..amides..-

Пп Сео гедЮп опу опе ЬапааєТбБО—ТТООстТ аЬоуе ЗОООстТ Ьапдб аге аЬзепЕЬесоз д absence of N-H hydrogens

Anhydrides :-

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

characterstie vibratons of anhydrndes is V cac=1250-1350cm-in carbonyl region two bands are appery one IS from symm.stretching and another one is from asymmetritcal stretchires ,c=o(sym)=1755-1744cm-

, (osym)=1825-1815cm-

Imnortant nnactinne