

Aldehydes, Ketones and Carboxylic Acid...

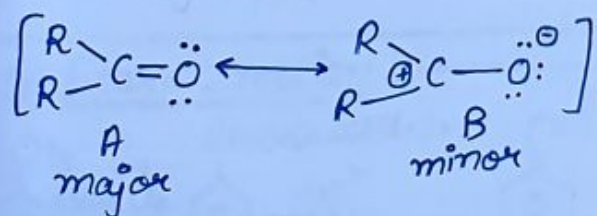
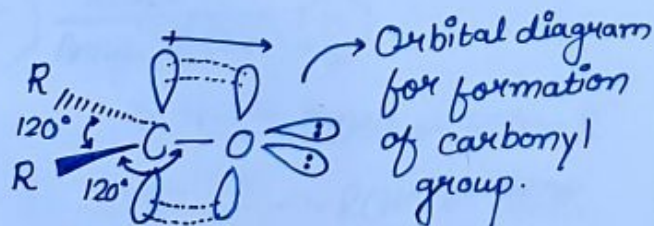
Introduction

- Aldehydes and Ketones have general formula $C_nH_{2n}O$ and contains $>C=O$ grp.
- Thus, aldehydes ($R-CHO$) and Ketones ($R-CO-R$) are collectively called as carbonyl compounds.
- Aldehyde \rightarrow Terminal positions
- Ketone \rightarrow Never at terminal position.

Nomenclature and Structure Of Carboxyl Group..

Structure and bonding in aldehydes and Ketones.

- Carbonyl carbon atom is sp^2 hybridized.
- Unhybridized p-orbital overlaps with a p-orbital of oxygen to form π bond.
- Double bond b/w carbon and oxygen is shorter, stronger and polarized.

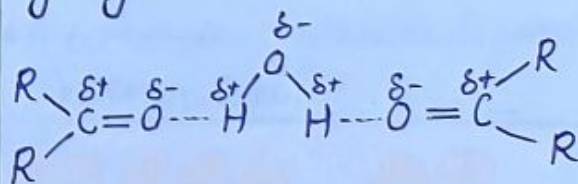


- Neutral and dipolar.

- This polarity confirms that there is nucleophilic addition rx.ⁿ take place in carbonyl compound.
- Double bond of carbonyl group has a large dipole moment becoz oxygen is more electronegative than carbon.
- Carbonyl carbon act as an electrophile. (Lewis acid).
- Carbonyl oxygen act as an nucleophile. (Lewis Base).

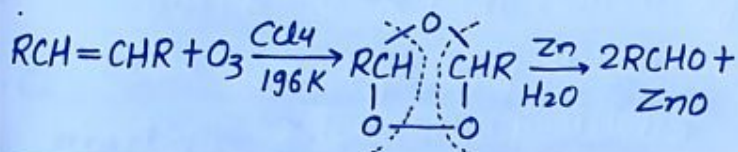
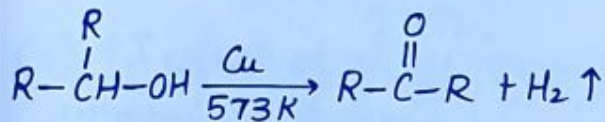
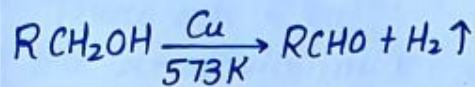
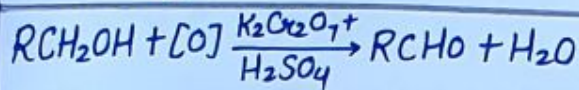
Physical Properties Of Aldehydes and Ketones..

- Boiling points of aldehydes and Ketone are higher than those of hydrocarbons and ethers of comparable molecular masses. As weak molecular association in aldehydes and Ketones, arising out of the dipole-dipole interactions.
- Boiling points of aldehydes and Ketones are lower than those of alcohols of similar molecular masses as absence of intermolecular hydrogen bonding.
- Lower members of aldehydes and Ketones are miscible with water. As they form hydrogen bonds with water.

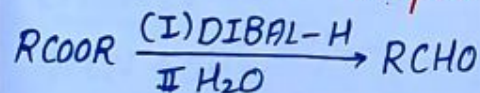
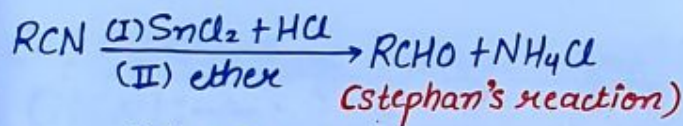
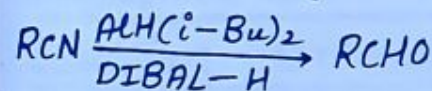
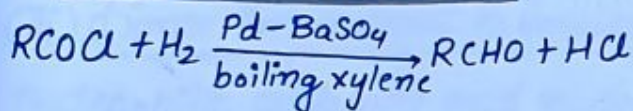


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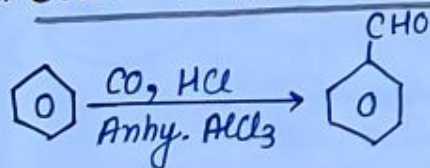
Preparation Methods Of Aldehydes and Ketones..



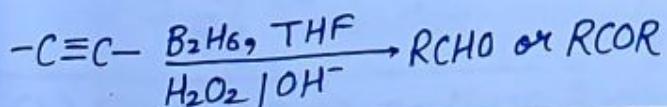
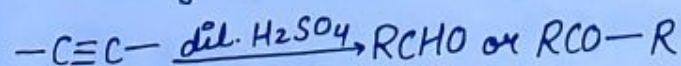
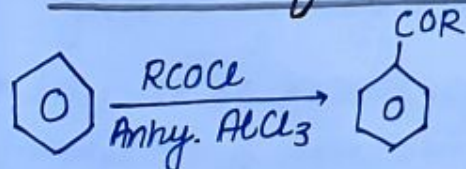
Rosenmund reduction :



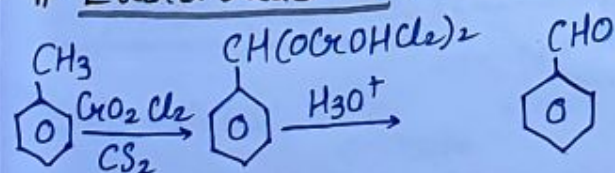
Gratterman-Koch reaction :



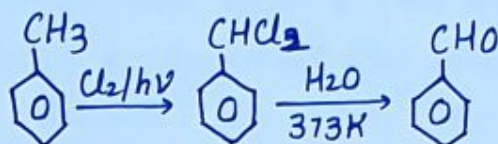
Friedel-Craft reaction :



Etard reaction :



> Side chain chlorination :



Chemical Reactions Of Aldehydes and Ketones :

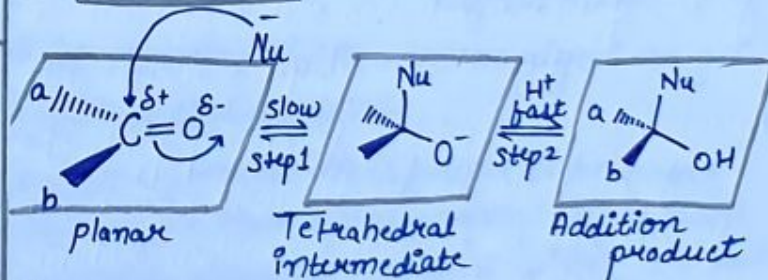
1. Nucleophilic addition Reactions :

- Addition of a nucleophile and a proton across the $C=O$ double bond.

The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarizatiⁿ of the carbon-oxygen double bond.

- The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, leaving it relatively unhindered and open to attack from either face of the double bond.

(i) Mechanism :

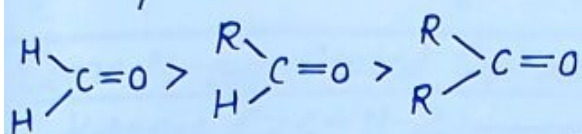


↳ Nucleophilic attack on carbonyl carbon.

- In process, hybridisation of carbon changes from sp^2 to sp^3 .
- A tetrahedral alkoxide is formed as intermediate.

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(ii) Reactivity: Aldehydes are more reactive than Ketones in nucleophilic addition reactions.



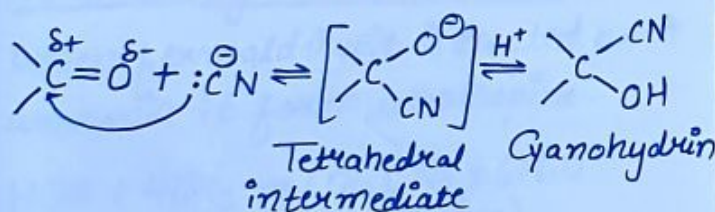
There are 2 factors which influence the reactivity of Ketone and aldehyde.

(1). +I effect of alkyl group decreases amount of charge on C^+ (C^+-O^-) in Ketones.

(2). Steric effect also causes the less reactivity of carbonyl group.

(iii) Some important examples of nucleophilic addition and nucleophilic addition elimination reaction:

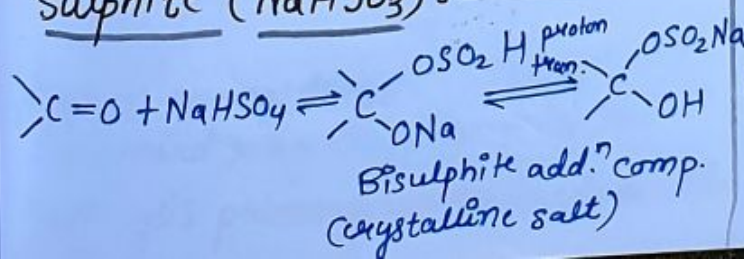
(a) Addition of hydrogen cyanide (HCN):



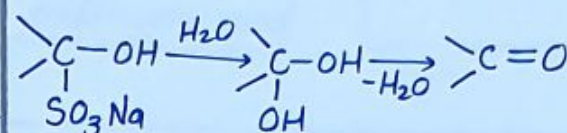
• Cyanohydrin on acid hydrolysis gives α -hydroxy acid.

• In case of Ketone, cyanohydrin formation is reversible due to bulky group of Ketone which hinders the formation.

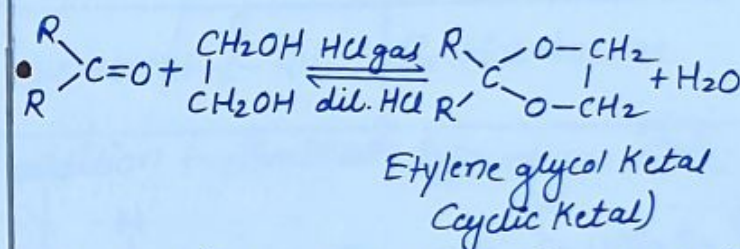
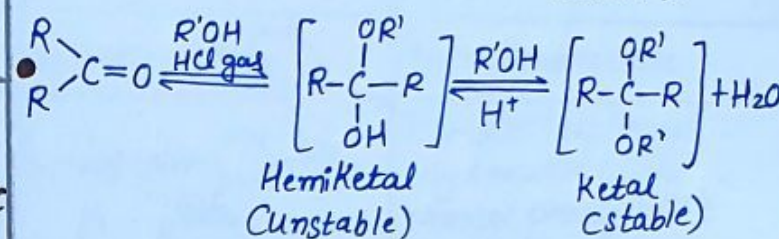
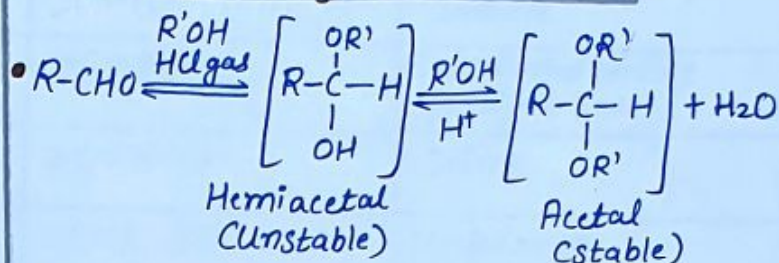
(b) Addition of sodium hydrogen sulphite (NaHSO_3):



• Salt on hydrolysis gives carbonyl compounds again, this reaction is used to separate the aldehydes from mixture.



(c) Addition Of Alcohols (ROH):

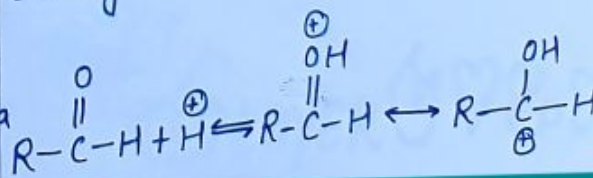


• On treating with ethylene glycol we get cyclic acetal or Ketal.

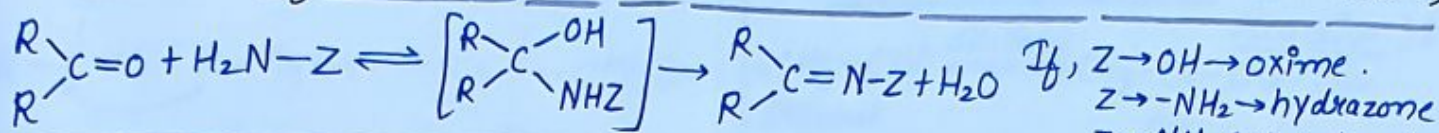
• Acetal formation is found to be more favourable than Ketal formation if both carbonyl groups are present within molecule.

(d) Addition Of Water:

Aldehyde or Ketones reacts with water to form gem-diols. Water is a poor nucleophile and therefore adds relatively slowly to the carbonyl group, but rate of reaction can be increased by an acid catalyst.

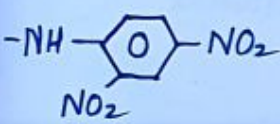


(e) Addition of ammonia and its derivatives (addition elimination rxn):



If, $Z \rightarrow OH \rightarrow$ oxime.
 $Z \rightarrow -NH_2 \rightarrow$ hydrazone
 $Z \rightarrow NH-C_6H_5 \rightarrow$ phenylhydrazone

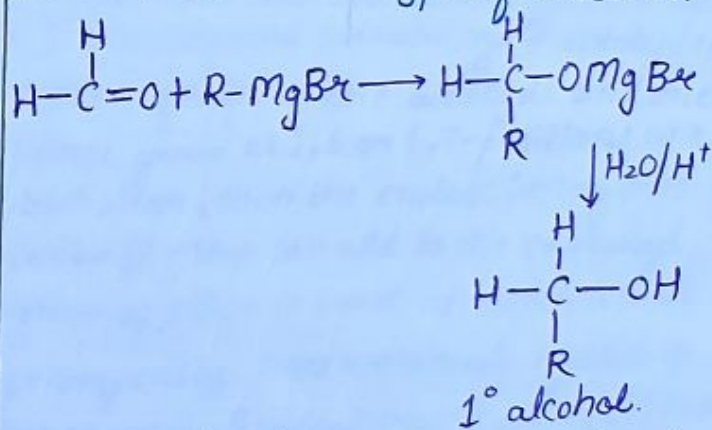
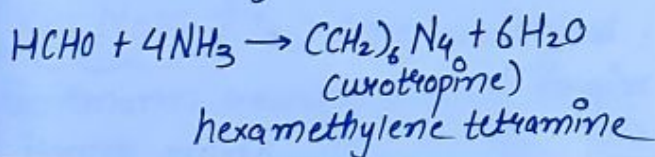
Some N-substituted Derivatives of Aldehydes and Ketones ($>C=N-Z$)

If Z are	Reagents name	Carbonyl derivative	Products.
-H	Ammonia	$>C=NH$	Imine
-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$>C=N-OH$	Oxime
-NH ₂	Hydrazine	$>C=N-NH_2$	Hydrazone
-NH-C ₆ H ₅	Phenylhydrazine	$>C=N-NH-\text{C}_6\text{H}_5$	Phenylhydrazone
	2,4-DNP (Brady's reagent)	$>C=N-NH-\text{C}_6\text{H}_3(NO_2)_2$	2,4-dinitrophenyl hydrazone (Solid orange precipitate)
$-NH-\overset{O}{\parallel}C-NH_2$	Semicarbazide	$>C=N-NH-\overset{O}{\parallel}C-NH_2$	Semicarbazone

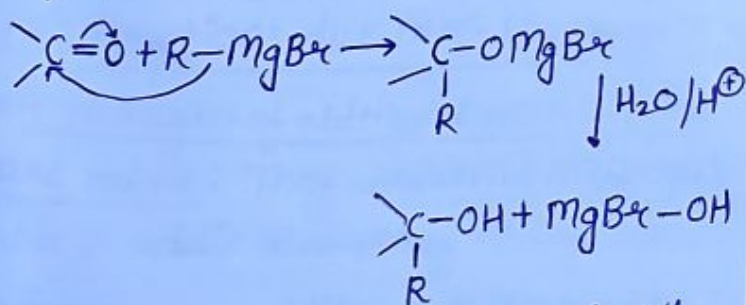
These reaction are nucleophilic addition + eliminate type of reaction.

Reaction of HCHO with NH₃:

When formaldehyde is treated with ammonia it form urotropine.



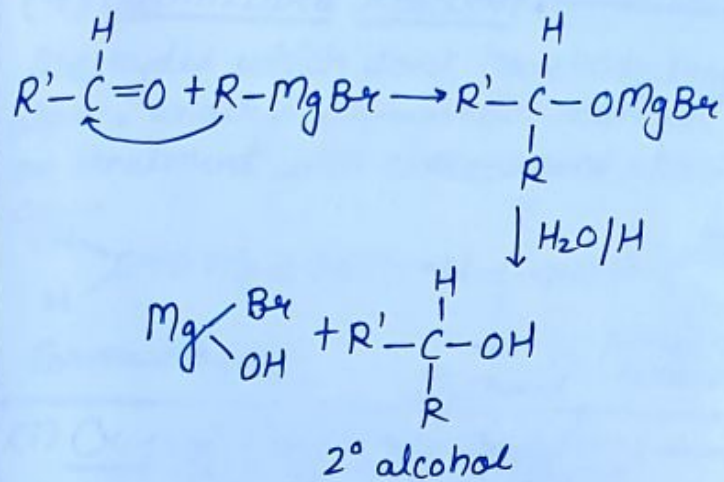
(f) Addition of Grignard reagents (preparation of alcohol):



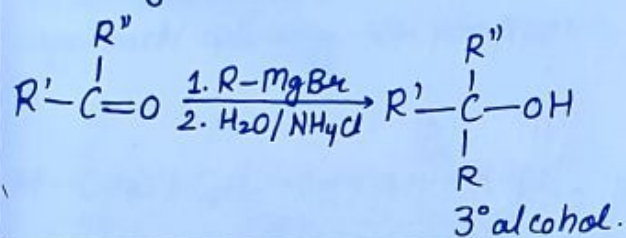
• When formaldehyde is treated with Grignard reagent followed by acid hydrolysis **primary alcohol** is obtained.

• When aldehyde except formaldehyde is treated with Grignard reagent followed by hydrolysis **2° alcohol** is obtained.

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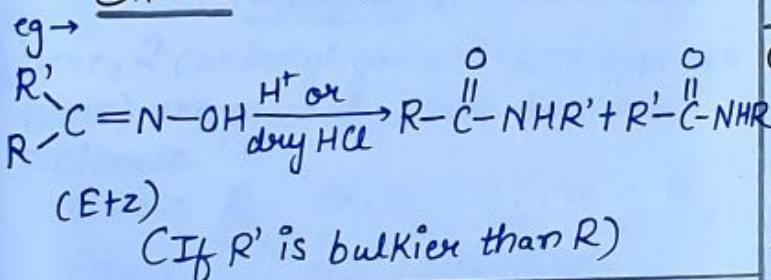


• When Ketone is treated with Grignard reagent followed by acid hydrolysis 3° alcohol is obtained.



(2) Beckmann rearrangement in

Oximes : \longrightarrow



Key Note • Oxime undergoes Beckmann rearrangement to give its isomer amide.

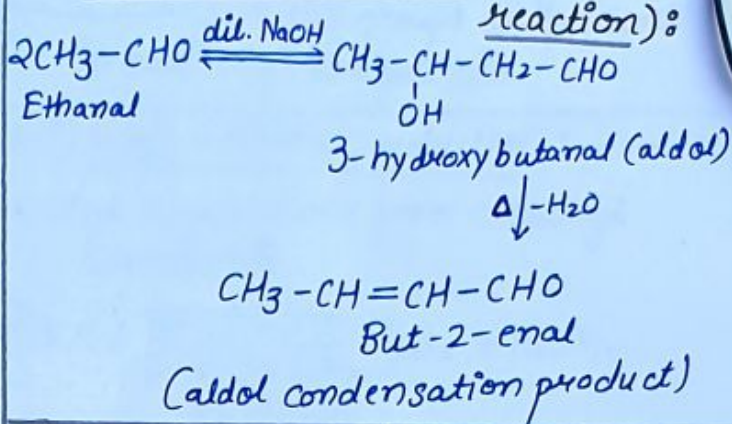
• In this rxn group which is anti to -OH group migrates.

(3) Reactions due to α-Hydrogen.

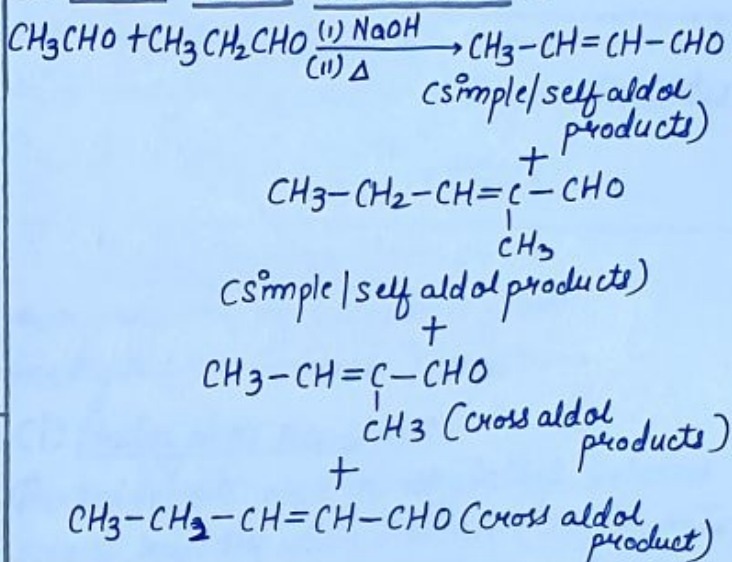
• α-Hydrogen of aldehydes and Ketones are acidic: They undergo no. of rxns due to acidic nature of α-hydrogen.

• Reason for acidity of α-hydrogen: Strong electron withdrawing effect of the carbonyl group, and resonance stabilization of conjugate base.

(i) Aldol condensation (or aldol reaction):

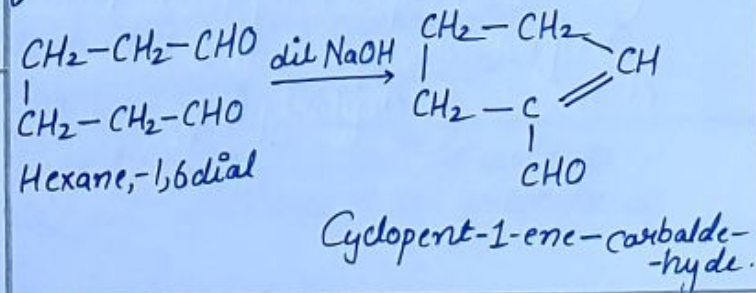


(ii) Cross-Aldol condensation : \longrightarrow



(iii) Intramolecular aldol Condensation

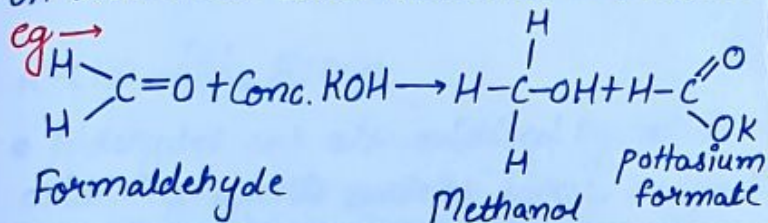
It's a compound containing 2 aldehyde/Ketone groups or one aldehyde and one Ketone group at 1,6 or 1,7-positions w.r.t. each other, then the enolate ion of one carbonyl group can add to the carbonyl group of other to form an aldol which subsequently loses a molecule of H₂O to form an α,β-unsaturated aldehyde/Ketone



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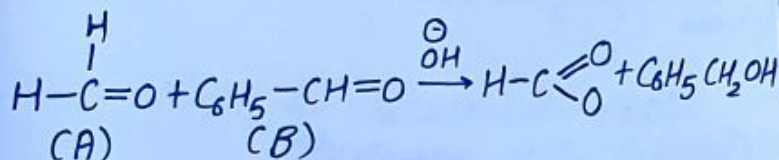
(4) Cannizzaro reaction:

Aldehydes which don't have α -hydrogen atom, undergo disproportionation rxn on treatment with concentrated alkali.



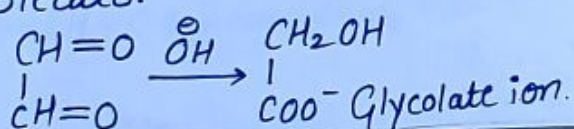
(i) Crossed Cannizzaro reaction:

On using 2 types of carbonyl compounds not having α -hydrogen atom, acid salt will be corresponding to that aldehyde over which OH will approach w/o any hindrance.



(ii) Intramolecular Cannizzaro Reaction:

Here, 2 carbonyl groups (w/o α -hydrogen atom) are present within the same molecule.



(5) Reduction reactions:

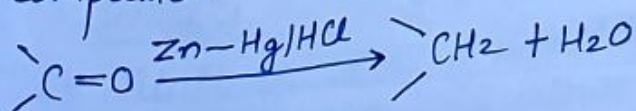
(i) Reduction to Alcohols \rightarrow

Aldehydes $\xrightarrow[\text{catalytic hydrogenat.}]{\text{NaBH}_4 \text{ or } \text{LiAlH}_4}$ 1° alcohols.

Ketones $\xrightarrow[\text{catalytic hydrogenat.}]{\text{NaBH}_4 \text{ or } \text{LiAlH}_4}$ 2° alcohols.

(ii) Clemmensen reduction \rightarrow

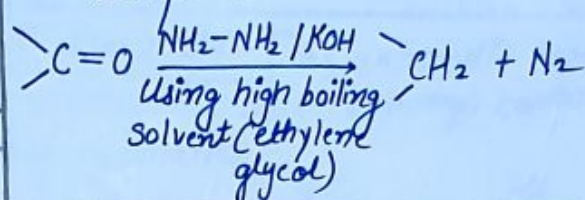
• Used to get alkane from carbonyl compounds.



Key Note \rightarrow avoid this rxn if acid sensitive groups are present in carbonyl compounds.

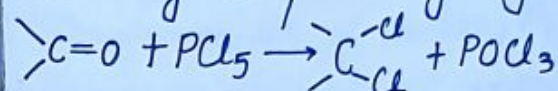
(iii) Wolff-Kishner reduction \rightarrow

• Used to get alkane from carbonyl compounds.



(iv) Reaction with PCl₅ \rightarrow

• Carbonyl compounds give gemdihalides.

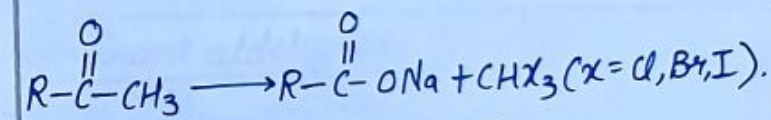


(6) Oxidation reactions \rightarrow

• preparation of haloform from methyl ketone involves 2 steps \rightarrow

(i) Haloform reaction.

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

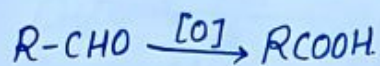


• In this rxn $-\text{CH}_3$ of $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ group is converted into haloform, as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

Key Note \rightarrow This rxn is used to distinguish the presence of $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ group.

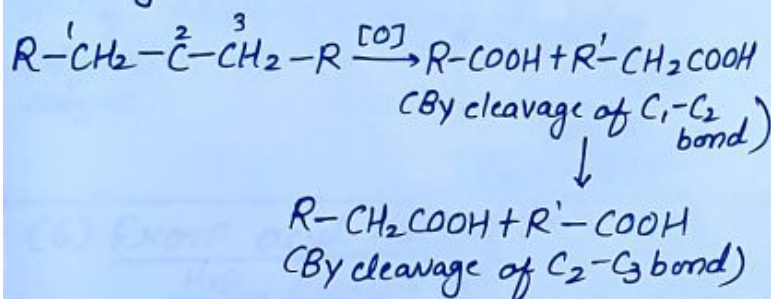
cii) Oxidation Of Aldehydes: →

- Aldehydes are oxidised to carboxylic acids by common oxidising agents such as KMnO_4 , HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc..



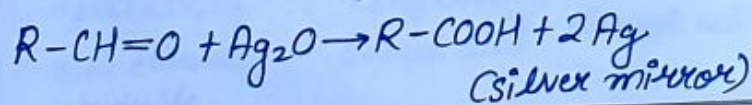
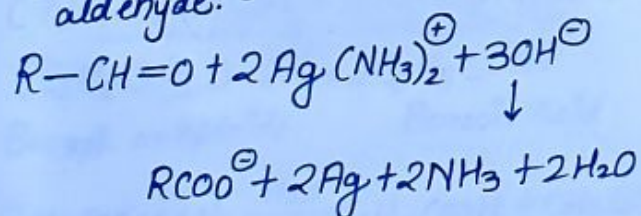
- Aldehydes are also oxidised by mild oxidising agents such as Tollen's reagent and Fehling's reagent. On other hand, Ketones are not oxidised by mild oxidising agents.

- It involves carbon-carbon bond cleavage.



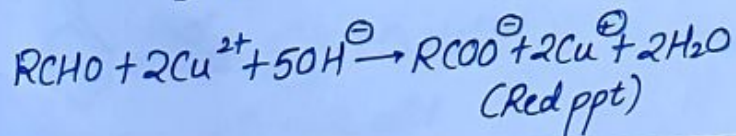
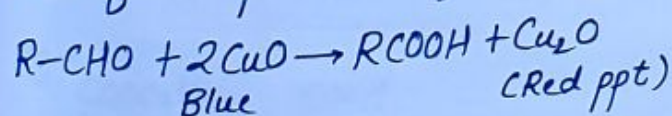
(a) Tollen's reagent: →

- Tollen's reagent is weak oxidising agent. It gives Ag mirror test with aldehyde.



(b) Fehling's solution: →

- Confirms presence of aldehyde.



(c) Schiff's reagent: →

It's dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2 .

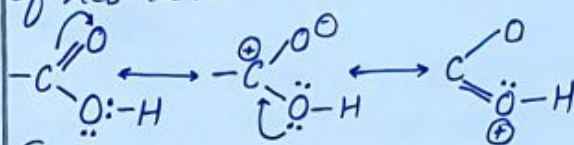
Aldehyde restores pink colour when treated with Schiff's reagent.

(Magenta solution in H_2SO_3).

Carboxylic Acids and acid Derivatives..

Structure.

- Carboxylic carbon is less electrophilic than carbonyl carbon bcoz of resonance.

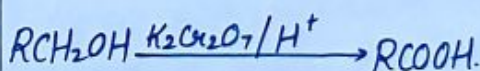
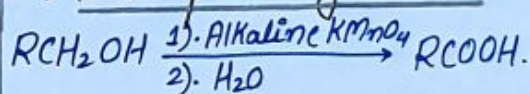


→ Resonance str. of carboxylic acid.

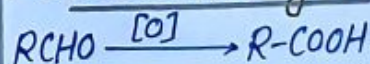
- Bonds to the carboxyl carbon lie in one plane and are separated by about 120° .

Methods Of Preparation Of Carboxylic Acids..

(1) From primary alcohols.



(2) From aldehydes.

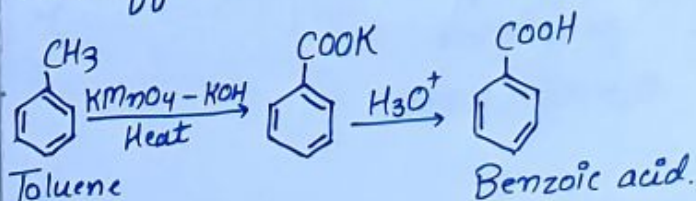


Oxidising agents - HNO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$.

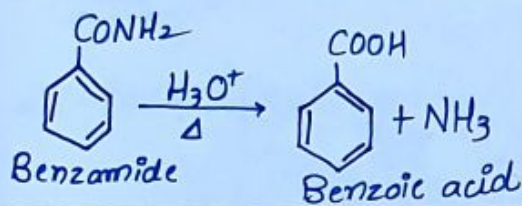
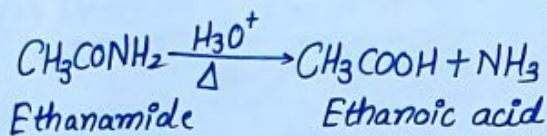
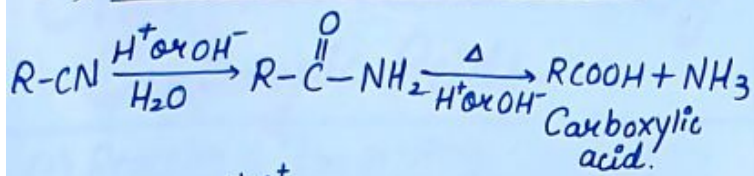
(3) From alkyl benzenes.

Alkyl benzenes $\xrightarrow[\text{alkaline or acidic KMnO}_4]{\text{Chromic acid or}} \text{Aromatic Carboxylic acids}$

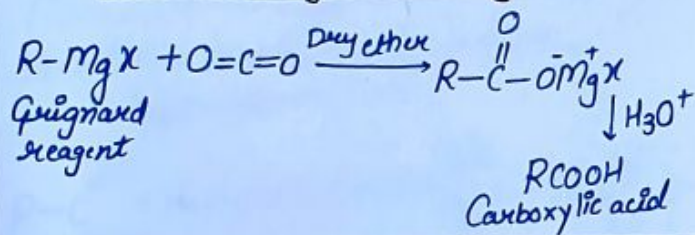
- 1° and 2° alkyl benzene are oxidised in this manner. Tertiary group is not affected.



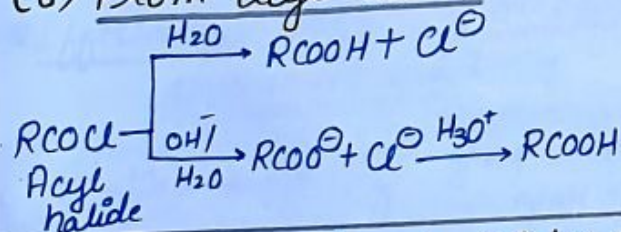
(4) From nitriles and amides \rightarrow



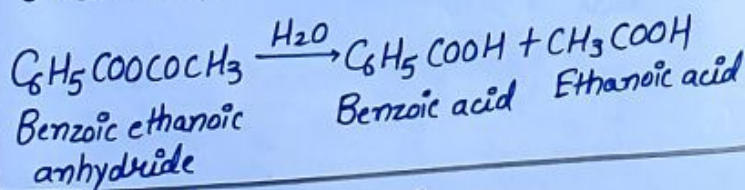
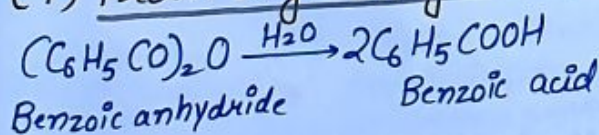
(5) From Grignard reagents \rightarrow



(6) From acyl halides \rightarrow

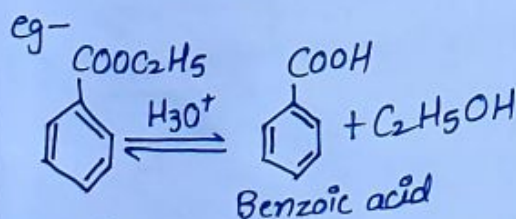


(7) From acyl anhydrides \rightarrow

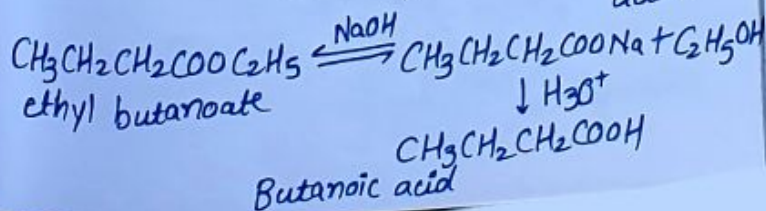


(8) From esters \rightarrow

Ester $\xrightarrow{\text{Acidic hydrolysis}}$ Carboxylic acid



Ester $\xrightarrow{\text{Basic hydrolysis}}$ Carboxylate $\xrightarrow{H_3O^+}$ Carboxylic acid.



Physical Properties Of Carboxylic Acids..

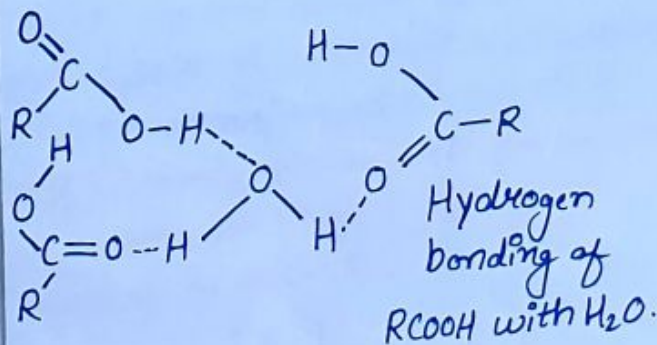
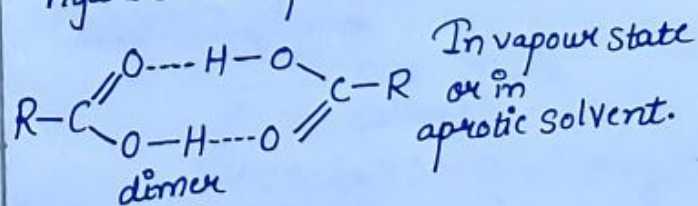
- Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

Hydrogen bonds are not broken completely even in vapour phase.

- In fact, most carboxylic acid exist as dimer in vapour phase or in the aprotic solvents.

- Simple aliphatic carboxylic acids having upto 4 carbon atoms are miscible in water due to the formation of hydrogen bonds with water.

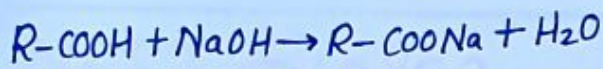
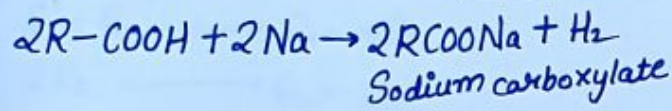
- Solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to increased hydrophobic interaction of hydrocarbon part.



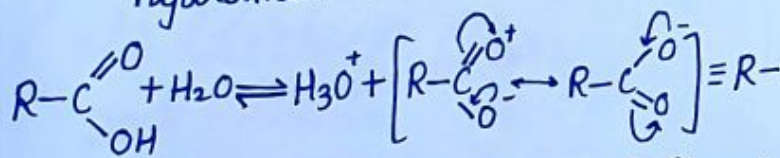
Chemical Reactions Of Carboxylic Acids..

(1) Reactions Involving Cleavage of O-H bond (Acidity of Acids)

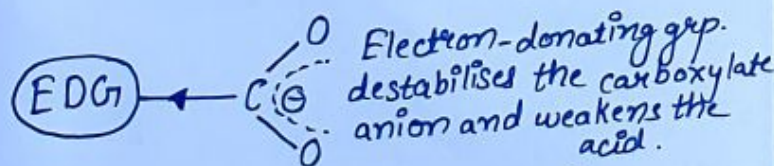
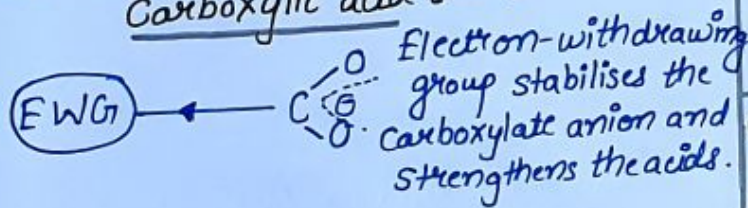
- Reactions with metals and alkalis: \rightarrow



Dissociate in water to give resonance-stabilised carboxylate anions and hydronium ion.



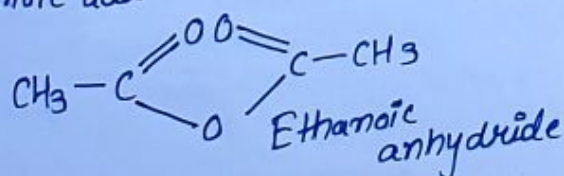
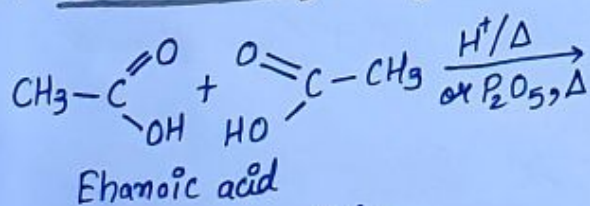
- Effects of substituents on acidity of carboxylic acid: \rightarrow



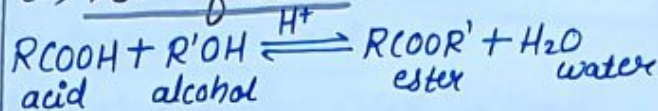
- Order of effect of groups in increasing acidity \rightarrow
 $Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

(2) Reactions Involving Cleavage of C-OH bond: \rightarrow

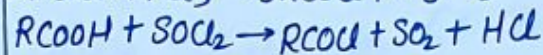
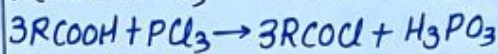
(i) Formation of anhydride.



(ii) Esterification.

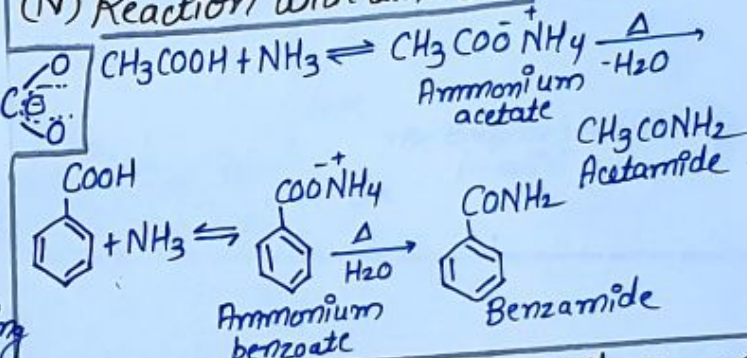


(iii) Reactions with PCl_5 , PCl_3 and $SOCl_2$: \rightarrow



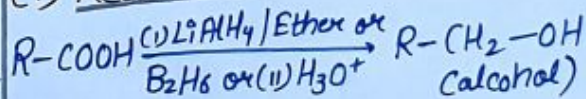
Key Note \rightarrow $SOCl_2$ is preferred bcoz the other 2 products are gaseous and escape the reaction mixture making the purification of products easier.

(iv) Reaction with ammonia: \rightarrow

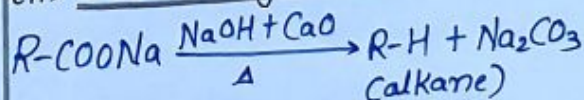


(3) Reactions Involving $-COOH$ groups:

(i) Reduction.



(ii) Decarboxylation: \rightarrow



- Kolbe's Electrolysis:** \rightarrow On electrolysis of an aqueous solution of alkali metal salts of carboxylic acids, salts undergo decarboxylation, forming hydrocarbons containing twice the number of carbon atoms present in alkyl group of the acid.





At anode




If mix. of 2 acid is taken, then



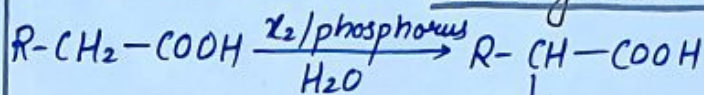
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Let's Unlock Our
potential,
Together... 

(4) Substitution reactions in the hydrocarbon part: \longrightarrow

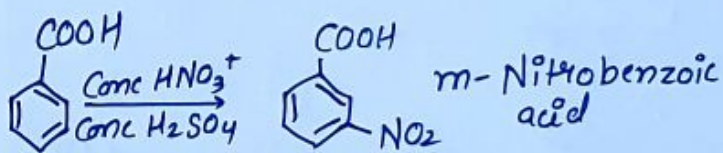
(i) Halogenation (Hell-Volhard-Zelinsky reaction)



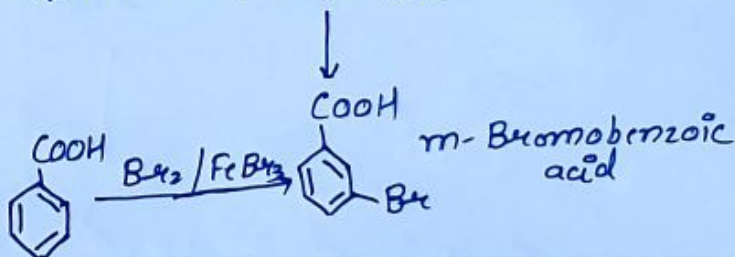
α -Halocarboxylic acid

(ii) Ring Substitution ($X = Cl, Br$)

Undergo electrophilic substitution rxn.
(except Friedel-Craft reaction)



m-Nitrobenzoic acid



m-Bromobenzoic acid



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