

Unit:- Carboxylic acid and its derivatives

Carboxylic acid :-

Organic compound containing COOH group are called carboxylic acid. It may be aliphatic or aromatic.

$\text{R}-\text{COOH}$
aliphatic carboxylic acid

$\text{Ar}-\text{COOH}$
Aromatic carboxylic acid

Carboxylic acid and ester are functional isomers of each other.

for $\text{C}_3\text{H}_6\text{O}_2$

$\text{CH}_3-\text{CH}_2-\text{COOH}$
Carboxylic acid

$\text{CH}_3\text{COOCH}_3$
ester.

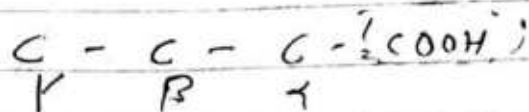
→ ~~Fatty acid~~ Aliphatic carboxylic acid
are commonly called fatty acid because some of their higher members ^(C_{12} to C_{18}) are obtained by hydrolysis of Natural fat.

Nomenclature of carboxylic acid.

→ Common system:-

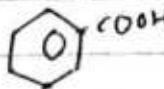
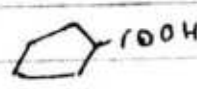
Common name of carboxylic acid is derived from their source of origin. position of substituent is shown by Greek letter α , β , γ etc as

as show below.



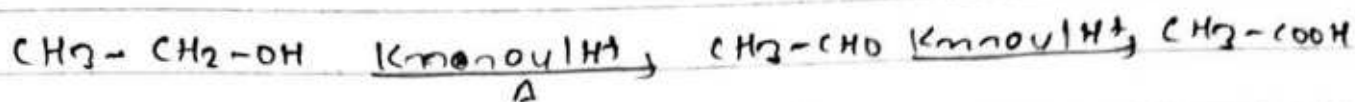
IUPAC system :- prefix + wordroot + pri. suffix + carboxylic acid

~~Eg formula~~ when carbonyl group is attached to carbon atom of a ring then secondary suffix carboxylic acid is used.

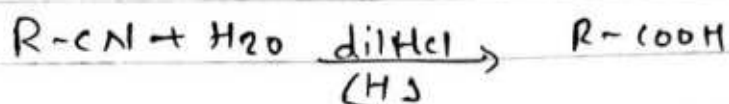
Eg	Formula	Common Name	IUPAC Name.
①	HCOOH	= Formic acid	Methanoic acid
②	$\text{CH}_3\text{-COOH}$	= Acetic acid	Ethanoic acid
③	$\text{CH}_3\text{-CH}_2\text{-COOH}$	propionic acid	Propanoic acid
④	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$	n-Butyric acid	Butanoic acid
⑤	$\text{CH}_3\text{-CH}(\text{CH}_3)\text{-COOH}$	iso-Butyric acid	2-methylpropanoic acid
⑥	HOOC-COOH (COOH) (COOH)	= Oxalic acid	Ethanedioic acid
⑦	$\text{HOOC-CH}_2\text{-COOH}$	Malonic acid	propanedioic acid
⑧	$\text{CH}_2\text{-COOH}$ $\text{OH} - \text{C} - \text{COOH}$ $\quad $ $\quad \text{CH}_2\text{-COOH}$	citric acid	3-carboxy-3-hydroxypentadioic acid.
⑨		Benzoic acid	Benzoic acid (Benzene carboxylic acid)
⑩			cyclopentane carboxylic acid

General Method of preparation.

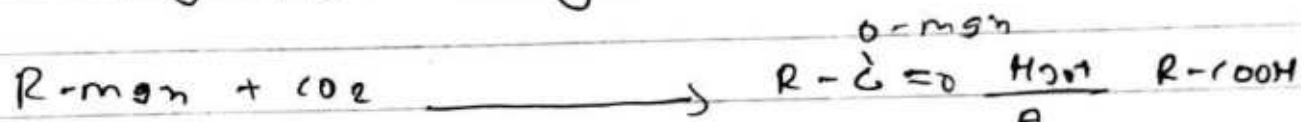
① By oxidation of 1-alcohol or aldehyde



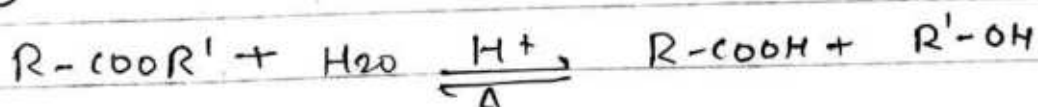
② By hydrolysis of alkanenitrile



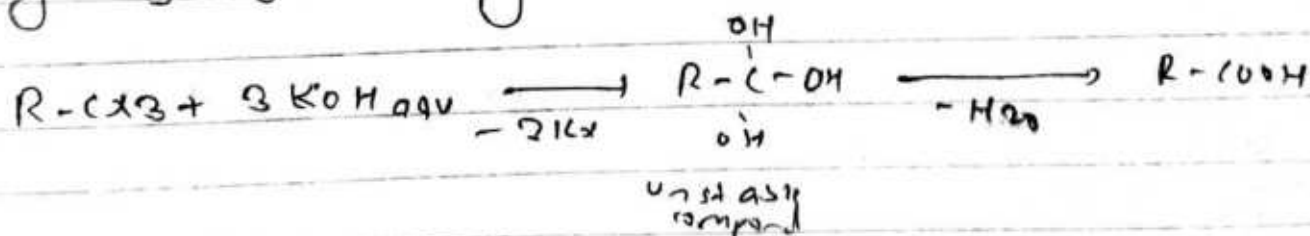
③ By using Grignard reagent



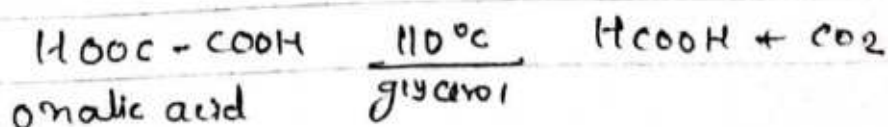
④ By hydrolysis of ester.

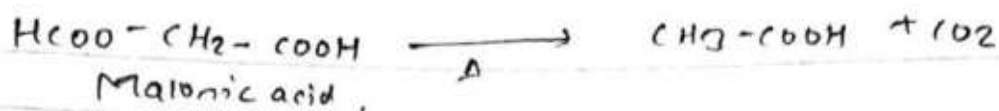


⑤ By hydrolysis of gemtrihalide.



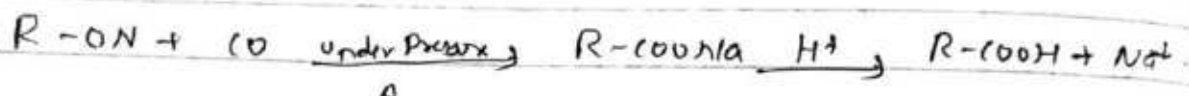
⑥ From dicarboxylic acid:-





⑦ From Sodium alkoxide:-

When Sodium alkoxide is heated with carbon monoxide under pressure then sodium salt of carboxylic acid is formed which on acidification gives carboxylic acid.



Physical properties of carboxylic acid.

(i) Physical states:-

Lower number of carboxylic acid upto 3 carbon atoms are colourless liquid, next six members are oily liquid with unpleasant smell more higher members are solid.

(ii) Solubility:-

Lower members of carboxylic acid upto 4 are soluble in water due to formation of intermolecular H-bond with water, but higher members are insoluble due to strong hydrophobic interaction shown by alkyl group.

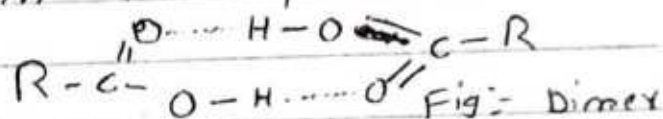
(iii) Boiling point:-

Carboxylic acid has high boiling point than alkane, haloalkane, ether, aldehyde and ketone having comparable molecular mass because carboxylic acid can form intermolecular H-bond but other cannot.

Carboxylic acid has high boiling point than alcohol having comparable molecular mass due to more extensive association of carboxylic acid molecule with intermolecular H-bond than alcohol.

(iv) Dimer of carboxylic acid:-

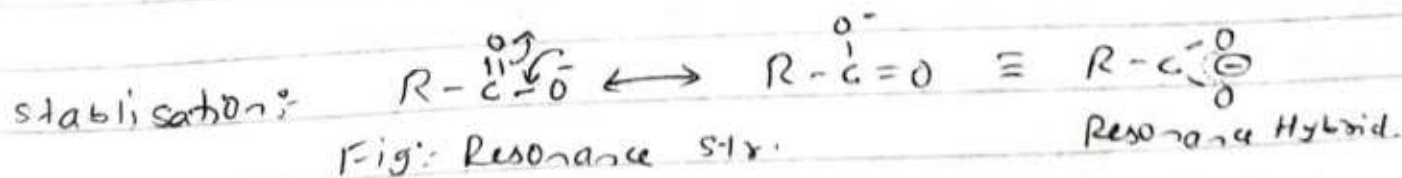
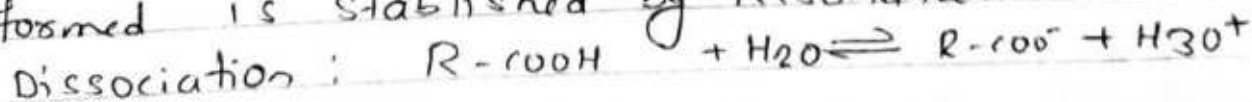
Each carboxylic acid can form two intermolecular H-bond with other carboxylic acid so they exist in dimer form in vapour state and in non-protic solvent.



Chemical properties of carboxylic acid.

(1) Acidic Nature:-

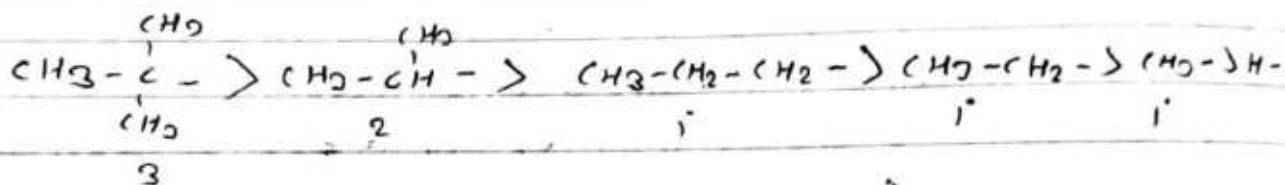
Carboxylic acid is acidic in nature because it releases H^+ in water and the carboxylate ion formed is stabilised by Resonance.



→ Factor affecting acidic strength of carboxylic acid.

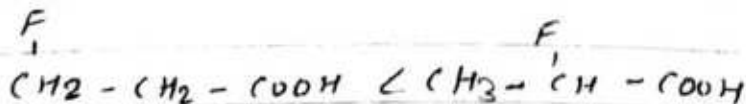
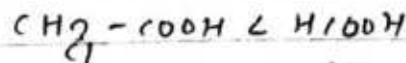
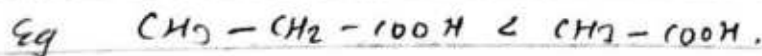
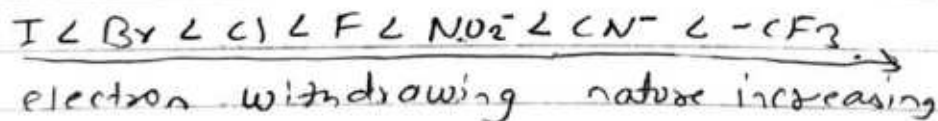
→ ~~Electron releasing group~~ ~~for and increased~~ ~~acidification~~.

Electron releasing group decreases acidic strength of carboxylic acid showing positive inductive effect.



Electron releasing nature decreasing

Electron withdrawing group increases acidic strength of carboxylic acid showing negative inductive effect.

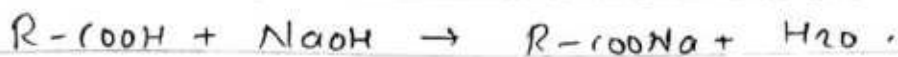


→ Reaction:-

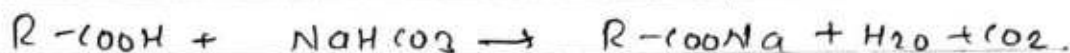
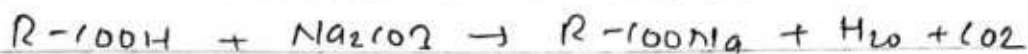
① Reaction with active metal releases H_2 gas



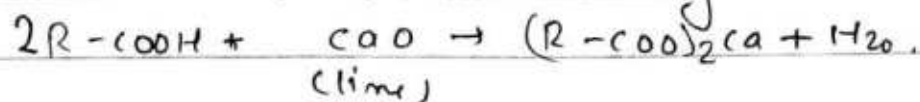
② Reaction with alkali form salt and water



③ Reaction with metal carbonate and bicarbonate releases CO_2 gas.

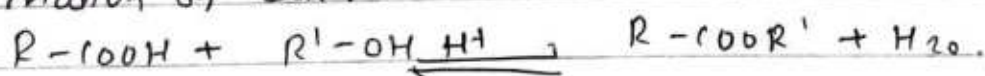


④ Reaction with metal oxide gives salt and water.

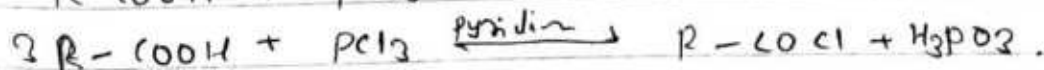


⑤ Reaction due to cleavage of $R-\overset{O}{\underset{||}{C}}-OH$ bond:

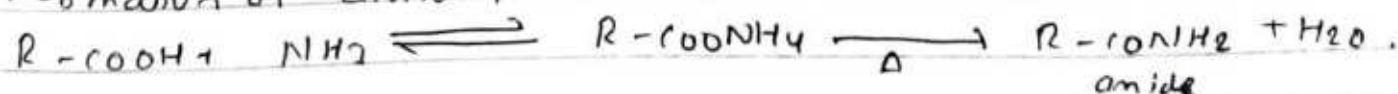
① Formation of ester.



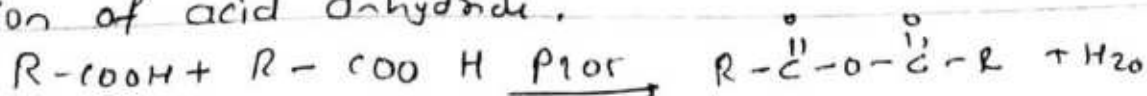
② Formation of acid halide.



③ Formation of amide.



④ Formation of acid anhydride.

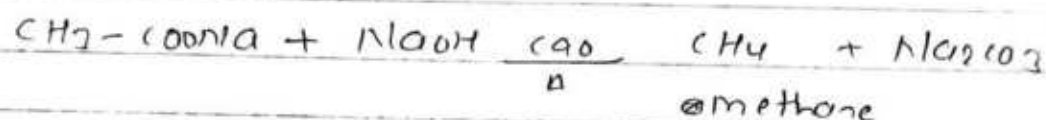
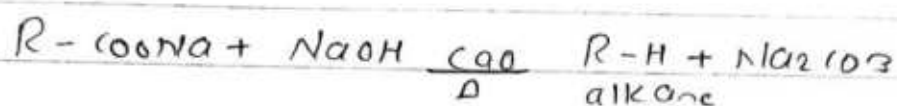


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Decarboxylation reaction (Removal of carbonyl group).

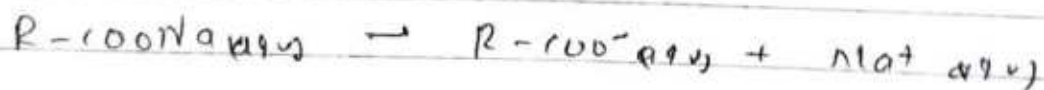
(i) Soda lime decarboxylation reaction:-

When anhydrous sodium salt of carboxylic acid is heated with soda lime ($\text{NaOH} + \text{CaO}$), it undergoes decarboxylation reaction producing alkane with one carbon atom less than carboxylic acid.

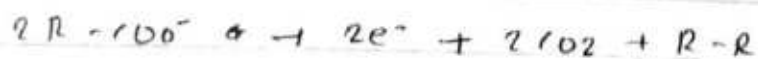


ii) Kolbe's electrolysis:-

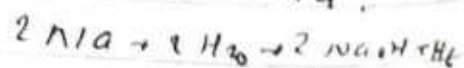
Electrolysis of aqueous sodium or potassium salt of carboxylic acid gives alkane with double the number of carbon atom present in alkyl group of carboxylic acid.

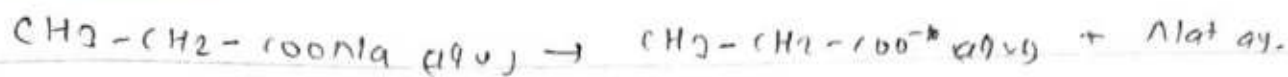


at anode,



at cathode,

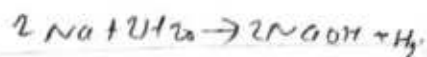
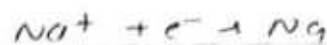




at anode.

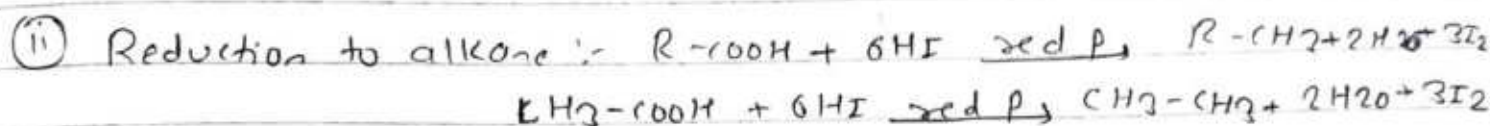
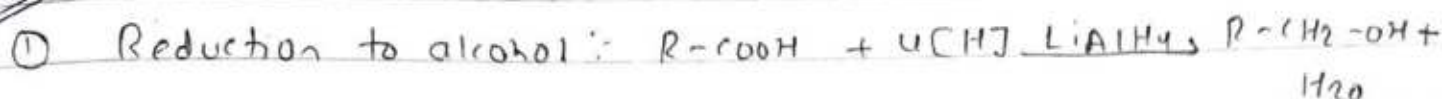


at cathode



Q. 4

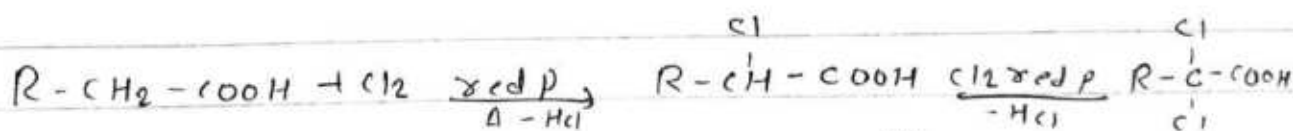
(u) Reduction



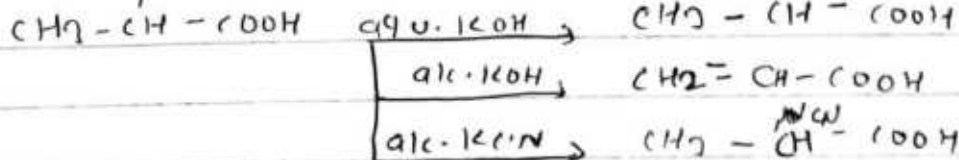
Q. 5

(u) Hell Volhard Zelinsky reaction:-

When carboxylic acid is treated with chlorine or bromine in presence of red phosphorus, α -chloro or bromo substituted carboxylic acid is formed



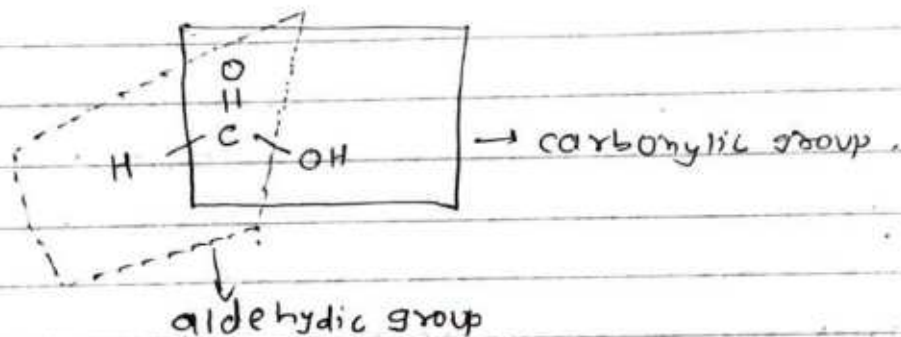
Q. complete the reaction of



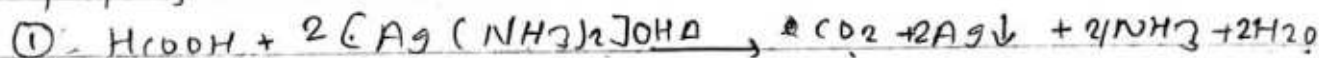
* Anomalous behaviour of formic acid :-

Formic acid is unique member of its homologous series because it

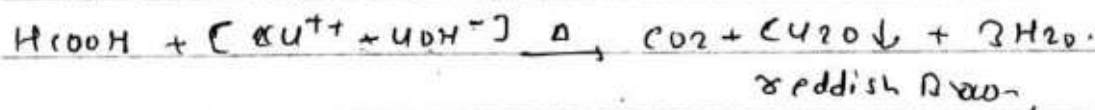
behaves as carboxylic acid as well as aldehyde due to presence of carbonyl group and aldehydic group in its structural formula.



* Properties



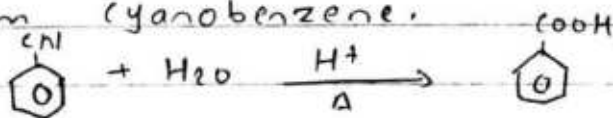
(ii) It reduces Fehling's solution.



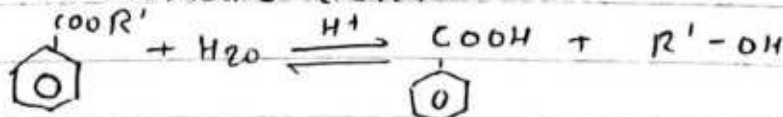
* Benzoic acid.

⇒ General method of preparation.

(i) From cyanobenzene.



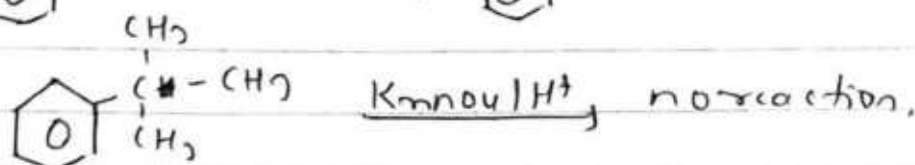
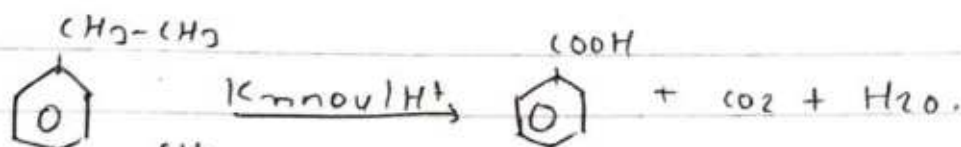
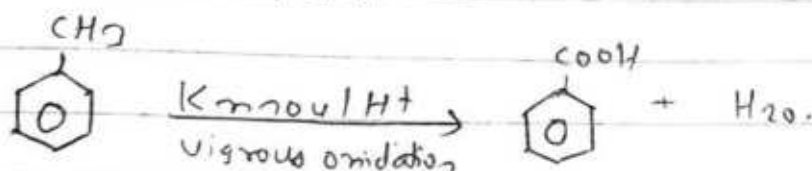
(ii) From aromatic ester.



(iii) From alkyl benzene:-

Alkyl benzene on vigorous oxidation

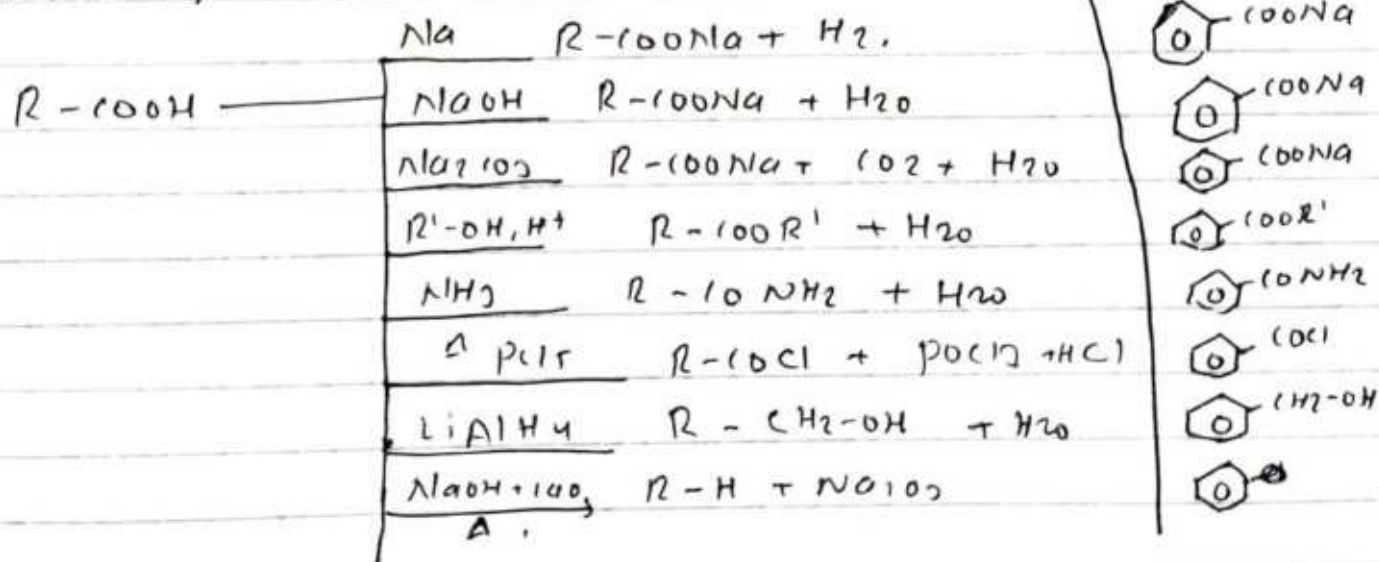
with KMnO_4/H^+ or $\text{KMnO}_4/\text{OH}^-$ or $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ etc gives benzoic acid. During this oxidation i.e. entire chain of alkyl group get oxidised but tertiary alkyl group remains unaffected.



* Properties:

(i) Benzoic acid is white coloured crystalline solid.

(ii) Reaction.

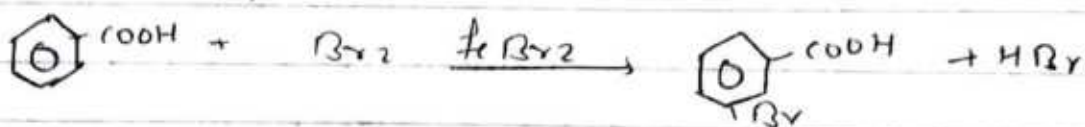


Electrophilic substitution reaction

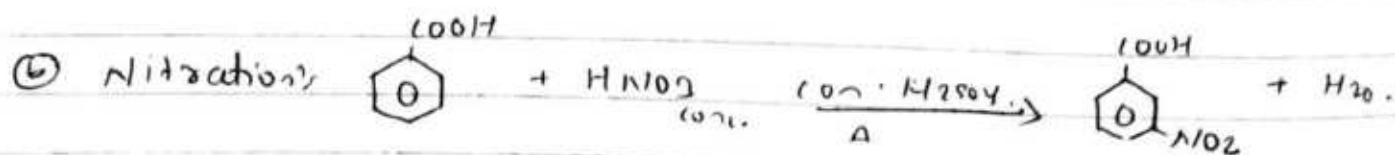
In Benzoic acid substitution reaction takes at meta position because resonance caused by electron drawing carbonyl group generates positive charge at ortho and para position, so electron density is comparatively higher at meta position. Therefore ~~it is called~~ carboxy group in benzoic acid is ~~not~~ called meta directing and ring deactivating group.

Reaction

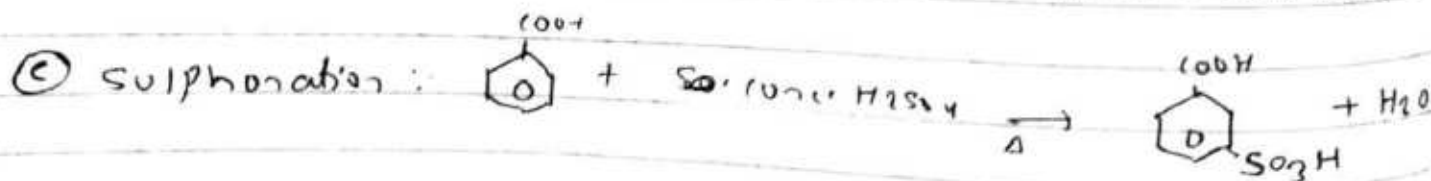
(i) Halogenation:



m-Bromobenzoic acid

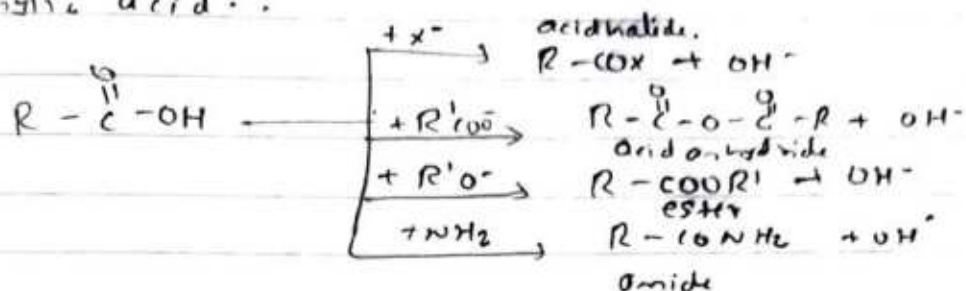


m-nitro benzoic acid



Derivatives of carboxylic acid:

The organic compound obtained by replacing hydroxy part of carboxylic acid with some other group is called derivative of carboxylic acid.



2. Acid halide: $R' - COX$

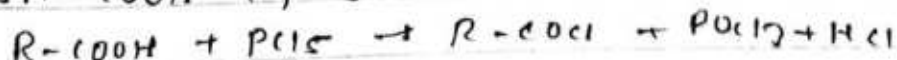
* Nomenclature:-

Common and IUPAC Name of acid halide can derive from the name of corresponding carboxylic acid by replacing ic acid with yl halide

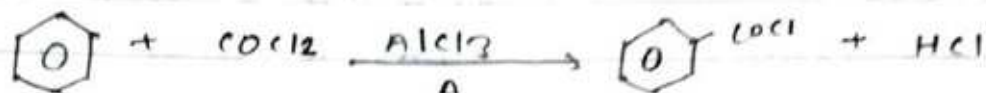
Eg	$CH_3 - COCl$	$CH_3 - CH_2 - COBr$
Common name:-	Acetyl chloride	propionyl bromide.
IUPAC Name:-	Ethanoyl chloride	propanoyl bromide.

* General method of preparation.

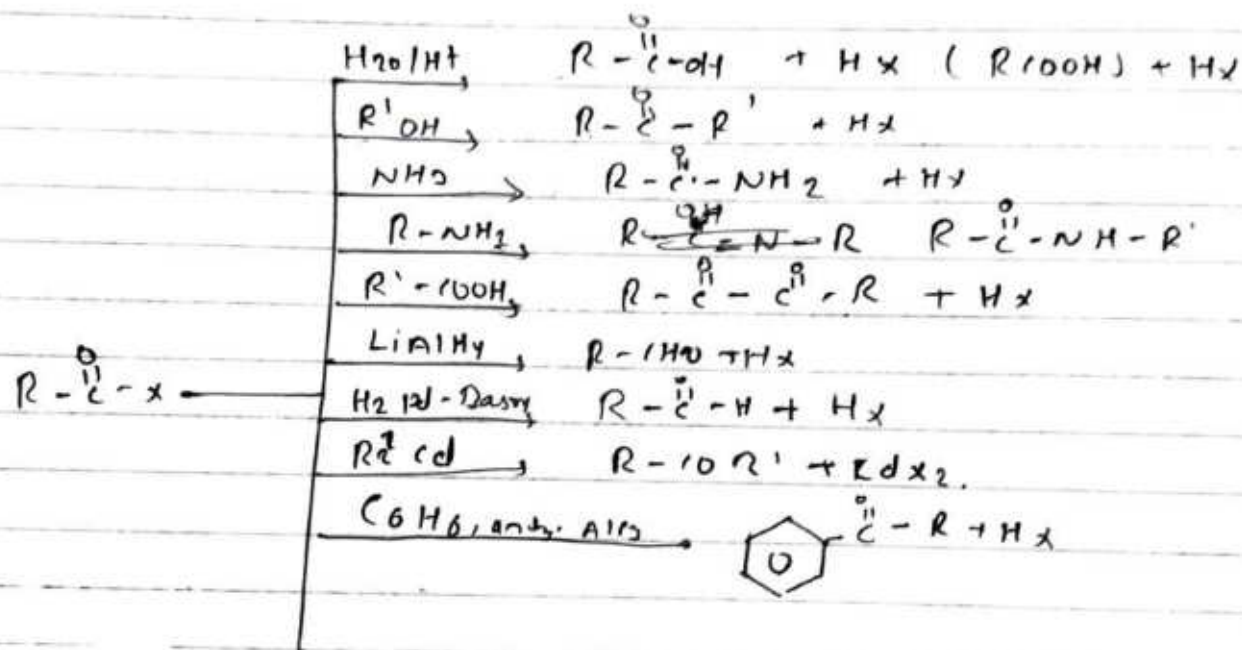
① From carboxylic acid.



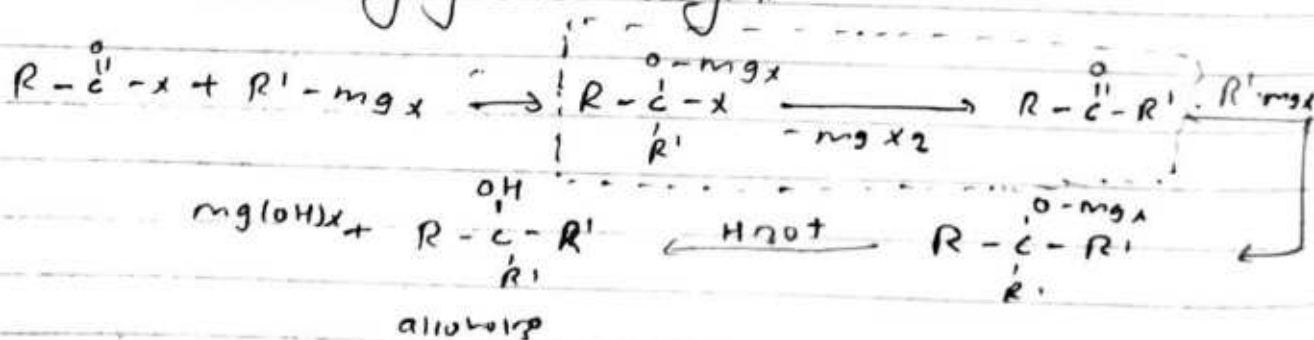
Q (ii) From Benzene and phosgene.



Reaction.



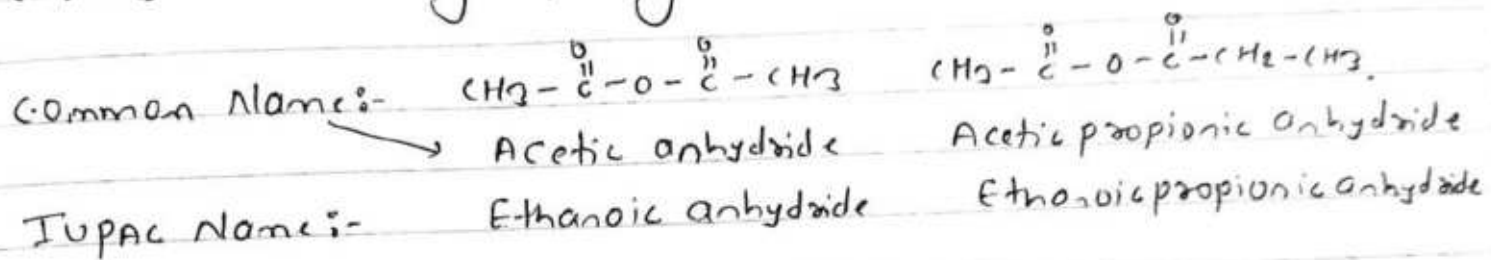
Reaction with grignard-reagent.



II Acid anhydride ($R-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R'$)

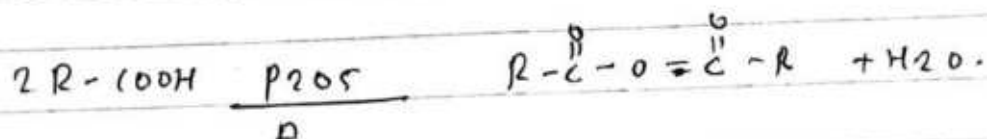
Nomenclature:-

Common and IUPAC Name of acid anhydride can derive from the name of corresponding carboxylic acid by replacing acid with anhydride.

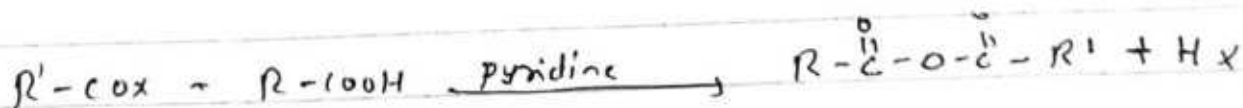


General method of preparation.

① From carboxylic acid:-

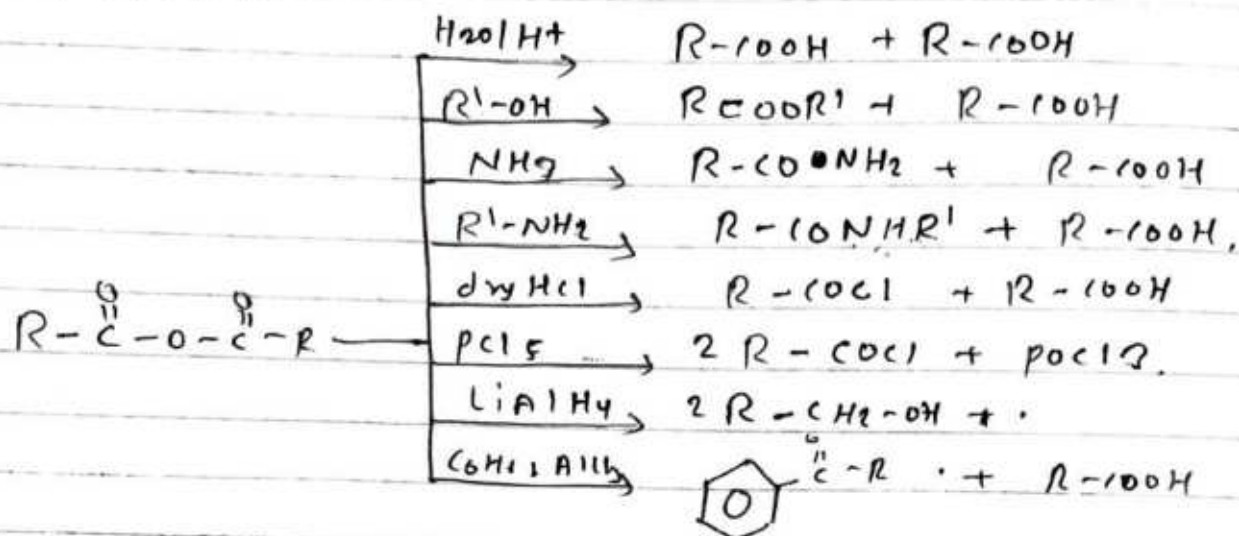


② From acid halide and carboxylic acid.



==>

Reaction:-



③ Ester ($RCOOR$)

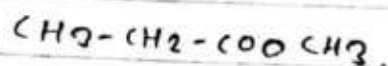
Nomenclature:-

Common and IUPAC Name of ester can derive from the name of corresponding carboxylic acid by replacing ic acid with ate and writing the name of alkyl group word root.



Common Name:- Ethylacetate

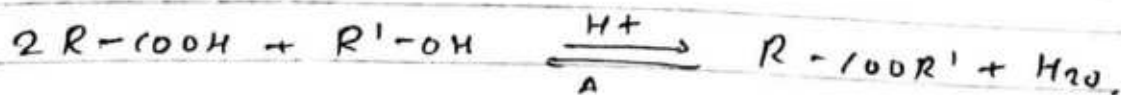
IUPAC Name:- Ethylethanoate



Methyl propionate.

Methyl propanoate.

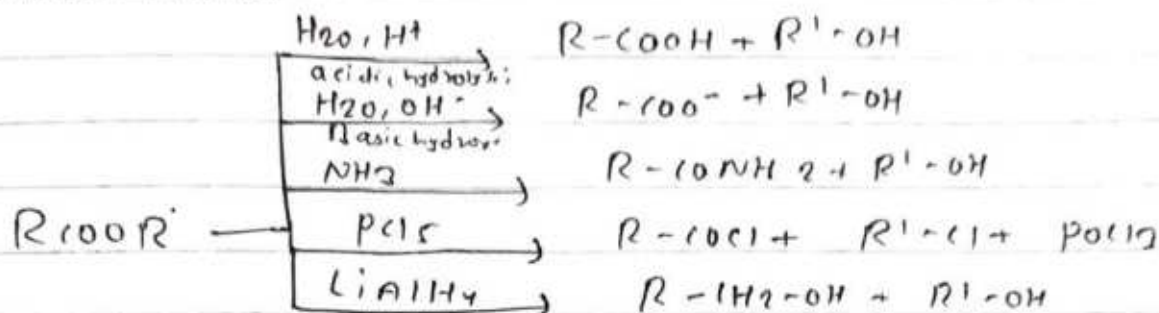
General method of preparation.



⑪ From acid halide and alcohol

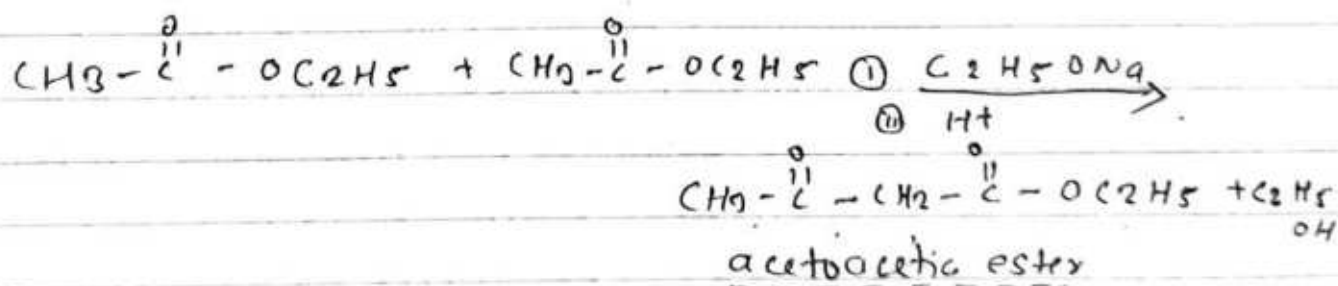


General reaction:

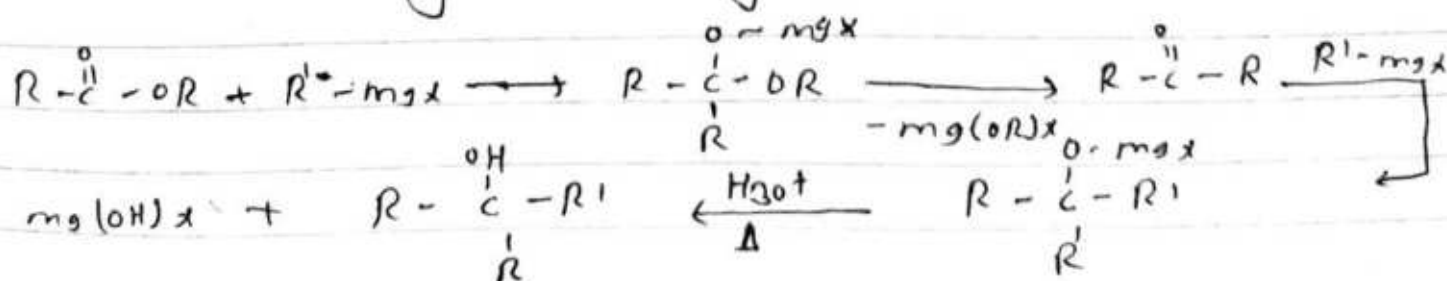


Claisen condensation reaction:-

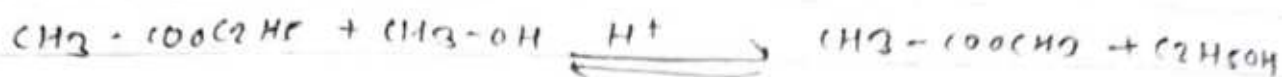
When ester containing alpha hydrogen is treated with strong alkali like sodium ethoxide (C_2H_5ONa) followed by acidification, gives β -keto ester. This reaction is called claisen condensation reaction.



① Reaction with grignard reagent.



Q # Trans-esterification.



→ alkoxy part of ester get exchanged with alkoxy part of alcohol

IV Amide:- $\text{R}-\text{CONH}_2$

Nomenclature:-

Common and Iupac Name of amide can derive from the name of corresponding carboxylic acid by replacing ic acid ~~with~~ from common name and oic acid from Iupac name with amide



common :- Acetamide

Iupac :- Ethanamide

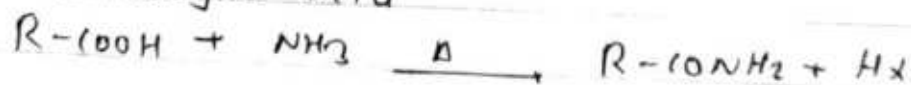


N-Methylacetamide

N-Methylethanamide

General Method of preparation.

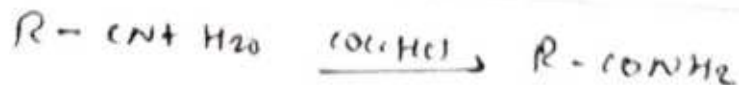
(i) From carboxylic acid



(ii) From acid halide

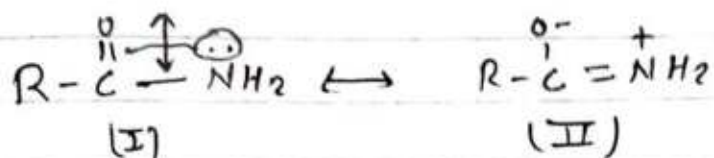


(iii) From alkoxamide



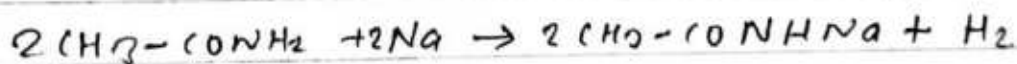
properties.

① Amphoteric Nature



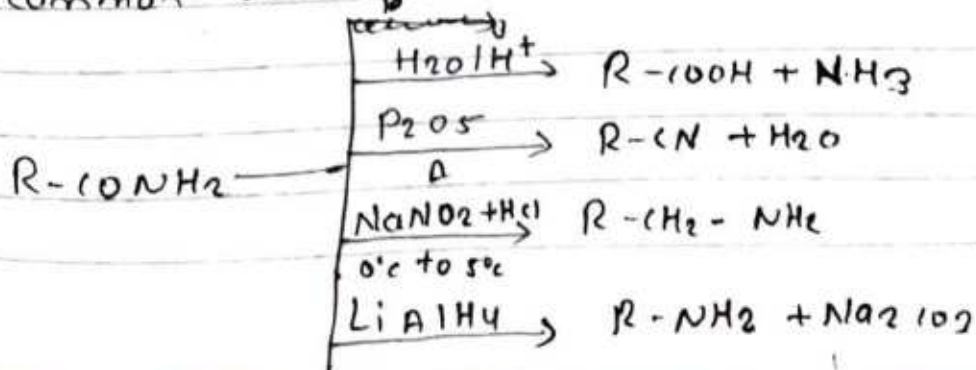
Amide behaves as acid as well as so, it is Amphoteric Nature.

Generation of positive charge on nitrogen as shown in resonance str. second facilitates release of H^+ showing acidic nature of amide.



In amide Nitrogen posses donateable lone pair of electron so it is basic in nature. But the lone pair of electron is involved in resonance so, it is not easily available for donation. Therefore amide is less basic than amine and even ammonia.

common reaction.



✓✓
✓✓ # Hoffmann's Bromide rxn or Decarboxylation reaction #

