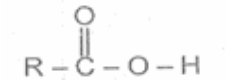
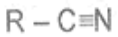
Carboxylic Acids & Acid Derivatives

Introduction :



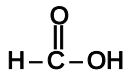
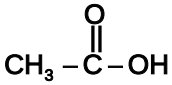
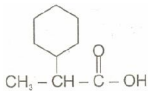
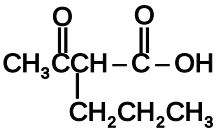
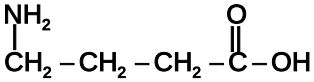
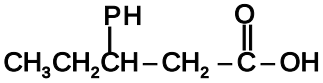
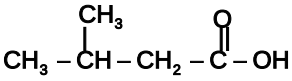
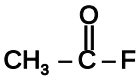
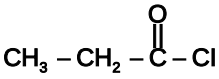
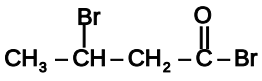
Carboxylic acid

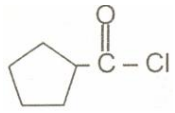
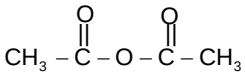
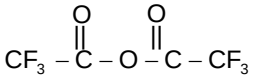
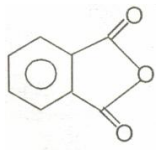
Acid halide anhydride ester amide

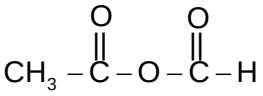
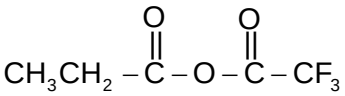
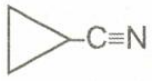
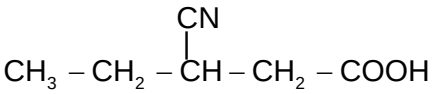
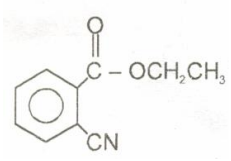
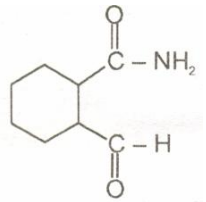
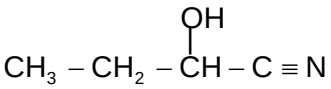


nitrile

Table – 1 : IUPAC Nomenclature of Acid derivatives :-

Compound	IUPAC Name
(1) 	Methanoic acid
(2) 	Ethanoic acid
(3) 	2- Cyclohexylpropanoic acid
(4) 	3- Oxo-2- propylbutanoic acid
(5) 	4- Aminobutanoic acid
(6) 	3- Phenylpentanoic acid
(7) 	3- Methylbutanoic adic
(8) 	Ethanoylchloride
(9) 	Propanoylchoride
(10) 	3- Bromobutanoylbromide

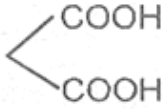
(11) 	Cyclopentanecarbonyl chloride
(12) 	Ethanoid anyhydride
(13) 	Trifluoroethanoic anhydride
(14) 	1,2- Benzenedicarboxylic anhydride

	Ethanoic methanoic anhydride
	Trifluoroethanoic propanoic anhydride
	Cyclopropane carbonitrile
	3- Cyanopentanoci acid
	Ethyl o-cyanobenzoate
	2- Formylcyclohexane carboxamide
	2- Hydroxyutane nitrile

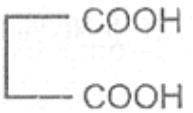
Dicarboxylic acids

If the subsituent is a second carboxyl gropu, we have a dicarboxylic acid. For example :

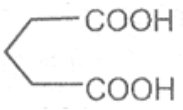
Oxalic acid
Ethanedioic acid



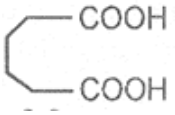
Malonic acid -1, 3-dioicacid



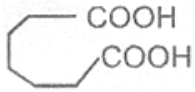
Succinic acid -1, 4-dioic acid



Glutaric acid
Pentane-1, 5-dioicacid



Adipic acid
Hexane-1, 6-dioicacid



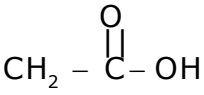
Pimelic acid
Heptane-1, 7- dioci acid

$HOOCCH_2COOH$ $HOOCCH_2CH_2COOH$ $HOOCCH_2CH_2CH_2CH_2COOH$

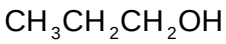
Malonic acid Succinic acid Adipic acid
Propanedioic acid Butanedioic acid Hexanedioic acid

Physical properties of acids and acid derivatives :

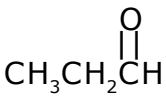
(1) Boiling point :



Acetic acid,
bp 118^{0}C

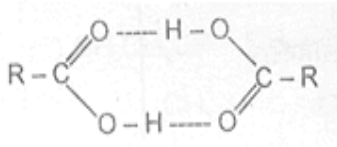


1-propanol
bp91^{0}C



Propionaldehyde
bp49^{0}C

The high boiling points of carboxylic acids is the result of formation of a stable hydrogen-bonded dimer.



Hydrogen bonded acid dimer

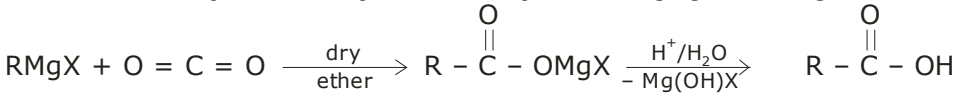
(2) Solubility :

Carboxylic acids form hydrogen bonds with water and the lower molecular –weight carboxylic acids (upto 4 carbon atoms) are miscible with water.

Acid derivatives (esters, acid chlorides, anhydride, nitriles and amides) are soluble organic solvents such as alcohols, ethers, chlorinated alkanes and aromatic hydrocarbons.

Methods of preparation of carboxylic acids

1. **Synthese of carboxylic acids by the carboxylation of grignard reagents**



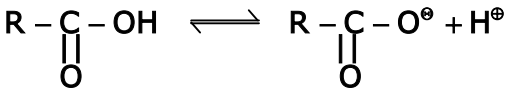
2. Synthesis of Carboxylic acids by the hydrolysis of nitriles Mechanism :

Nitrile carboxylic acid

Chemical Reactions

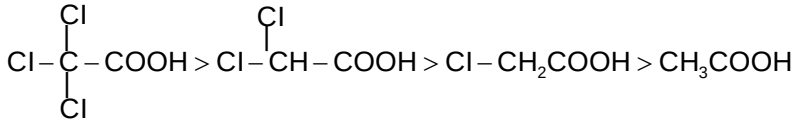
1. Acidic strength :

Acidity of carboxylic acids :-



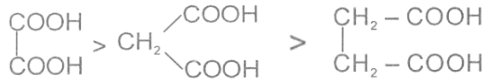
Ex. $F\text{-}CH_2\text{-}COOH > Cl - CH_2COOH > Br - CH_2COOH > 1 - CH_2COOH$

Increasing acid strength

Ex. 

Increasing acid strength

Ex. $HCOOH > CH_3COOH > CH_3\text{-}CH_2\text{-}COOH$

Ex. 

Ex. Relative acid strength is:-
$RCOOH > HOH > ROH > HC \equiv CH > NH_3 > RH$

Note:- Acidity of acids is compared by compairing stability of conjugate base

2. **Reaction involving removal of proton from –OH group.**

(1) Action with blue litmus : All carboxylic acids turn blue litmus red.

(2) Reaction with metals :

$$2\,CH_3\,COOH + 2Na \rightarrow 2CH_3\,COONa + H_2$$

Sodium acetate

$$2CH_3\,COOH + Zn \rightarrow (CH_3COO)_2\,Zn + H_2$$

Zinc acetate

(3) Reaction with alkalies :

$$CH_3\,COOH + NaOH \rightarrow CH_3\,COONa + H_2O$$

(4) Reaction with carbonates and bicarbonates :

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3\,COONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$$

Reaction of carbroxylic acid with aqueous sodium carbonatge solution produces brisk efferuescnce. However most phenols do not produce effervescence. Therefore, the reaction may be used to distinguish between carboxylic acids and phenols.

(5) Reaction with grignard reagent :

$$R\text{-}CH_2\,MgBr + R'COOH \xrightarrow{ether} R\text{-}CH_3 + R'COOMgBr$$

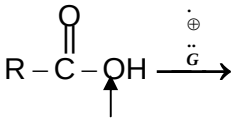
Note : A stronger acid displaces a weaker acid from salt of the weaker acid.

Ex. CH_3COOH (Stronger acid) + $CH_3ONa \rightarrow CH_3\,COONa + CH_3$ —OH (WeakerAcid)

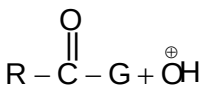
Ex. CH_3COOH (stronger acid) + $NaHCO_3 \rightarrow CH_3\,COONa + H_2\,CO_3$ (Weaker acid) $\rightarrow H_2O + CO_2$ t

(lab, test of carboxylic acide)

3. Reaction involving replacement of –OH group

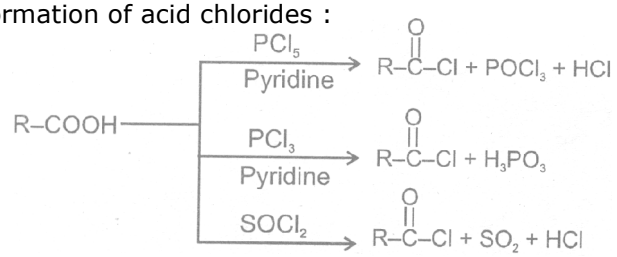


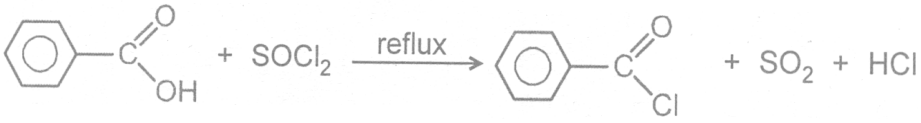
Strong bases so not a Good leaving group



basicity must be less then basicity of G–

(1) Formation of acid chlorides :

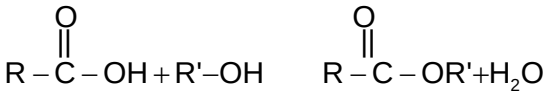




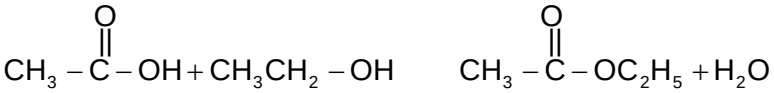
(2) Fisher Esterification

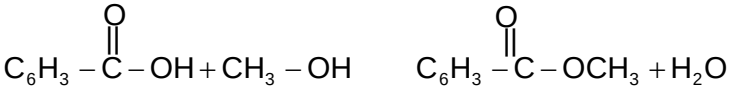
Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

General Reaction :

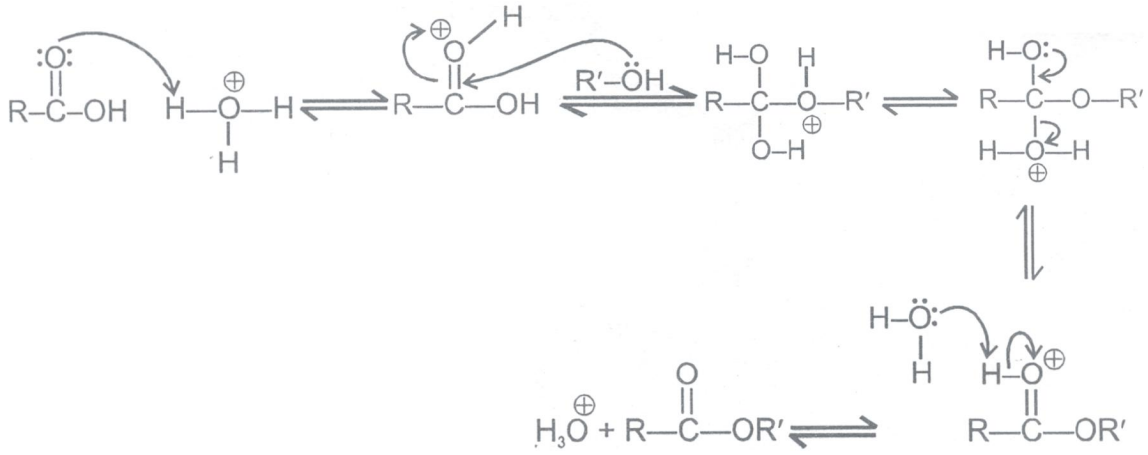


Specific Example:

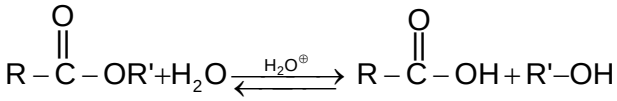




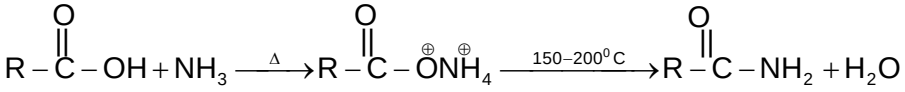
Mechanism : (Acid catalysed esterfication)



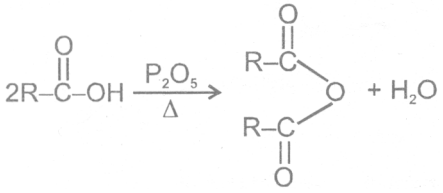
If we follow the forward in this mechanism, we have the mechanism for the acid catalysed esterification fo an acid. If however, we follow the reverse reactions, we have the meachanism for the acid catalysed hydrolysis of an ester. Acid catalysed ester hydrolysis.



(3) Formation of amides :



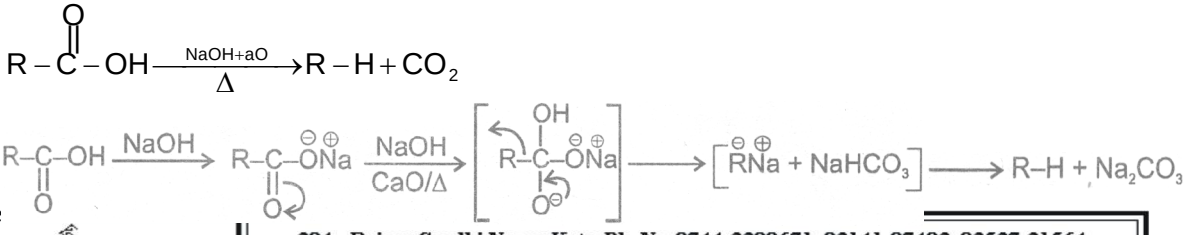
(4) Formation of acid anhydride :



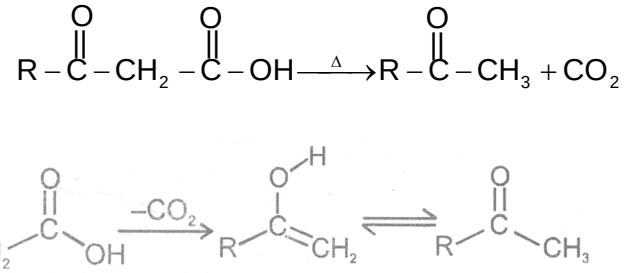
4. Decarboxylation reactions:

(1) **Soda-lime decarboxylation :**

General reaction:



(2) Decarboxylation of β- keto carboxylic acids :



β - keto acid

(3) Kolb's electrolysis

$$2RCOOK + 2HOH \xrightarrow{\text{Electrolysis}} R - R + 2CO_2 + H_2 + 2KOH$$

Mechanism $R\,CO_2K \rightleftharpoons R\,CO_2^- + K^+$

At Anode :– $R\,CO_2^- \rightarrow R\,CO_2 + e^-$ (oxidation)

(I)

$R\,CO_2 \rightarrow R^{\cdot} + CO_2$

(II)

$R^{\cdot} + R^{\cdot} \rightarrow R - R$

If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed 2(n-1) carbon atoms.

Ex. $2CH_3 — COOK + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3CH_3 + 2CO_2 + H_2 + 2KOH.$

(4) Hunsdiecker Reaction (Brome-decarboxylation):

$$R\text{-}COOAg + Br_2 \longrightarrow R\text{-}Br + CO_2 + AgBr$$

Mechanism:

Step 1: $R.COOAg + X_2 \longrightarrow R - \overset{\overset{O}{\|}}{C} - O - X + AgX$

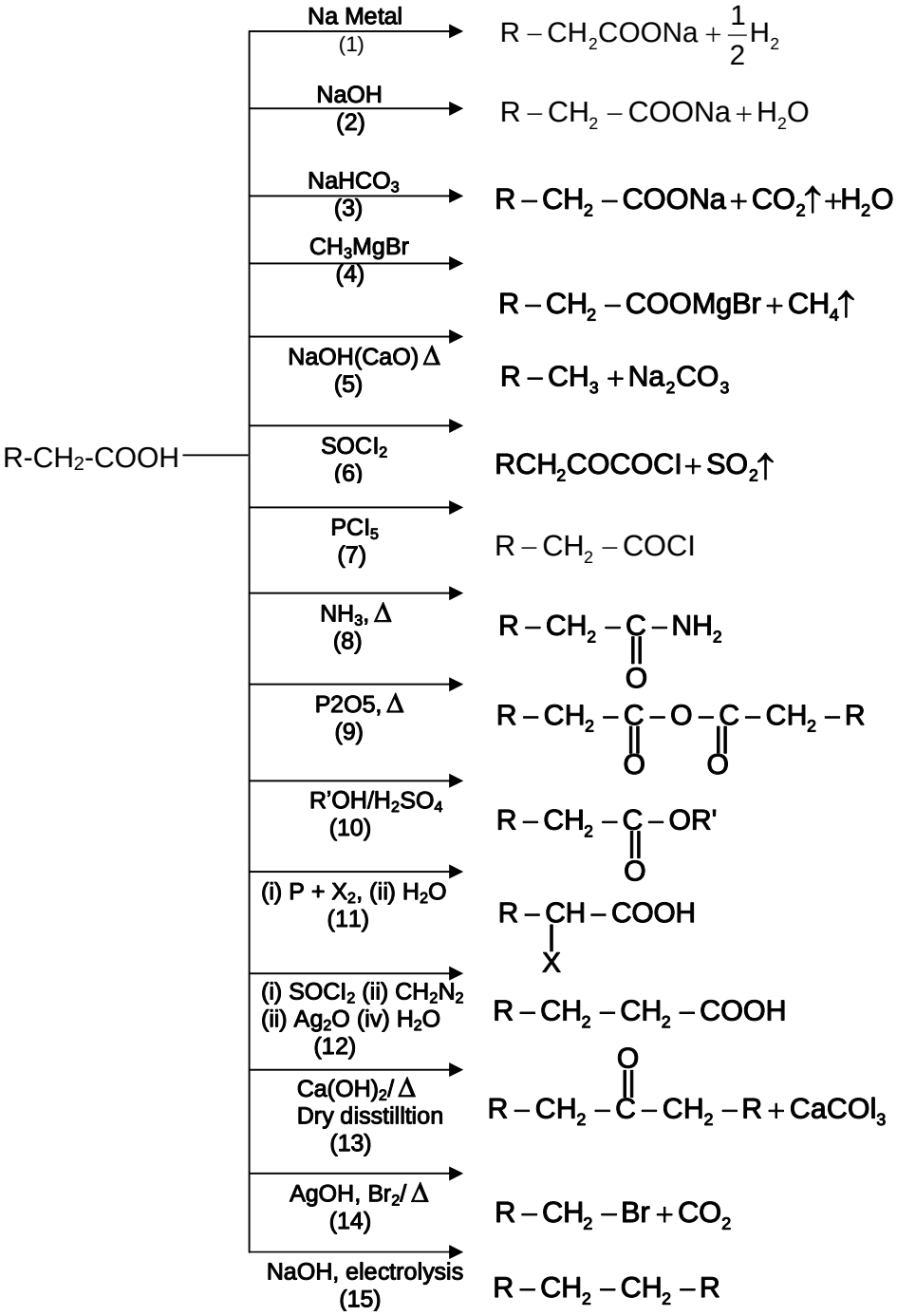
Step 2: $R - \overset{\overset{O}{\|}}{C} - O - X \longrightarrow RCOO^{\bullet} + \dot{X}$ (initiation)

Step 3: $R - \overset{\overset{O}{\|}}{C} - O^{\bullet} \longrightarrow R^{\bullet} + CO_2$

Step 4: $R^{*\cdot} + RCOOX \rightarrow R—X + RCOO^{*}$ (Propagation)

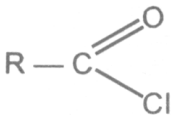
5. HVZ Reaction (Halogenation of aliphatic acids and Substituted acids)

$$CH_3COOH \xrightarrow{Cl_2,P} ClCH_2COOH \xrightarrow{Cl_2,P} Cl_2CHCOOH \xrightarrow{Cl_2,P} Cl_3CCOOH$$

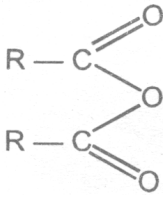


Carboxylic Acid Derivatives

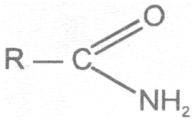
Closely related to the carboxylic acids and to each other are a number of chemical families known as functional derivatives of carboxylic acids : acid chloride, anhydrides, amide, and esters, These derivatives are compounds in which the -OH of a carboxyl group has been replaced by–Cl, -OOCR, $-NR_2$ or –OR



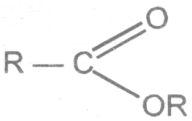
Acid chloride



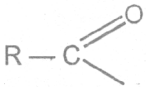
Anhydride



Amide



Ester

They all contain the acyl group , 

(A) Acid halides

Methods of preparations of Acyl halides

(i) $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

(ii) $3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$

(iii) $RCOOH + SOCl_2 \xrightarrow{\text{Pyridine}} RCOCl + SO_2 + HCl$

Ex. $3CH_3COONa + PCl_3 \xrightarrow{\text{Distil}} 3CH_3COCl + Na_3PO_3$

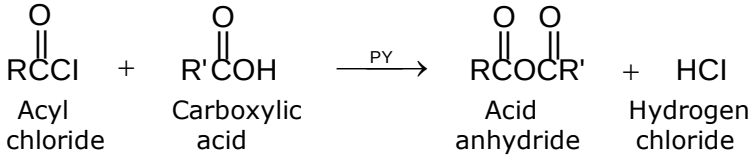
Acetyl chloride

Ex. $2C_6H_5COONa + POCl_3 \xrightarrow{\text{Distil}} 2C_6H_5COCl + NaCl + NaPO_3$

Sod. benzoate Benzoyl chloride

Chemical Reactions

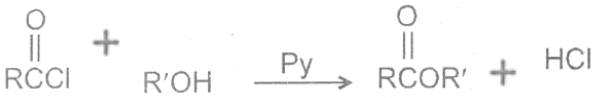
(1) **Reaction with carboxylic acids**



Acyl chloride | Carboxylic acid | Acid anhydride | Hydrogen chloride

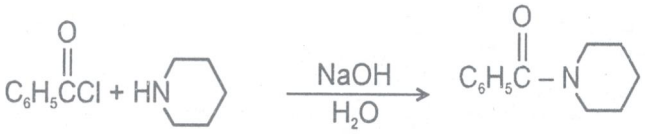
(2) Reaction with alcohols

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



Acyl Alcohol Ester Hydrogen

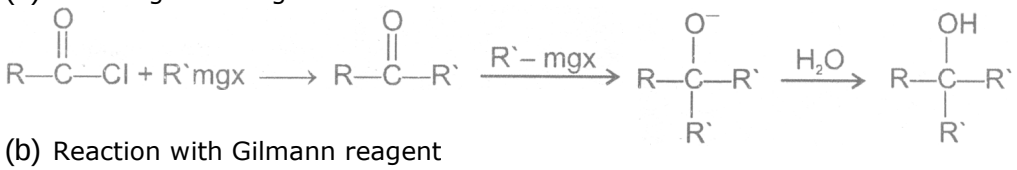
choride chloride



(3) Hydrolysis

(4) Reaction of acid halide with organometallic

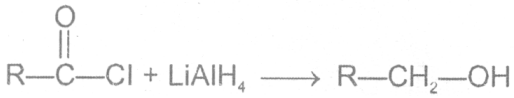
(a) with Grignard reagent



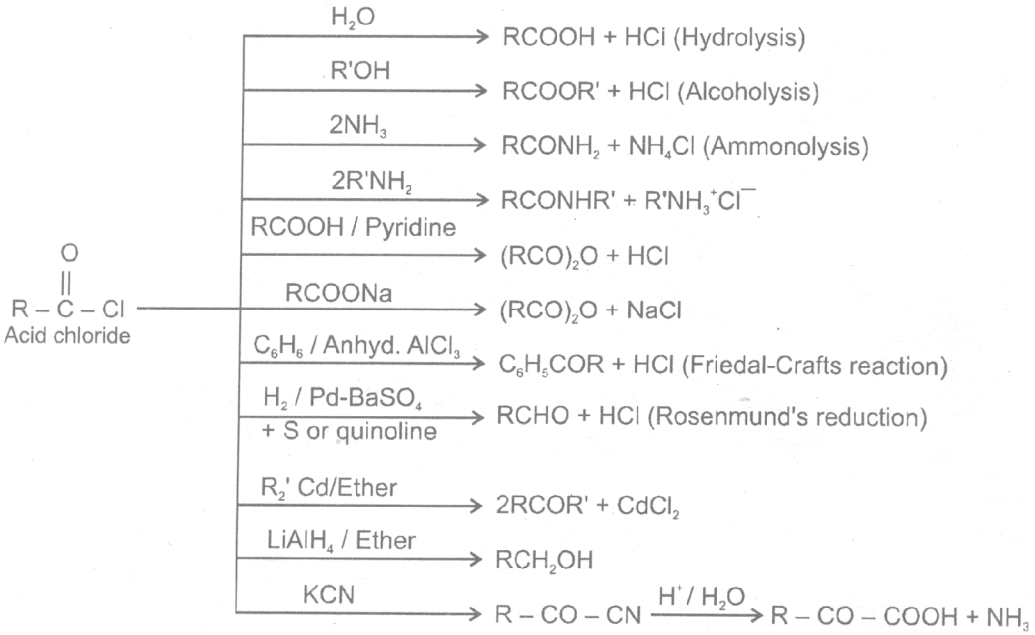
(b) Reaction with Gilmann reagent

(5) Reduction of acid halided

(a) Reduction $LiAlH_4$



(b) Reduction with $H_2/Pd/BaSO_4$ (Rosenmund reduction)



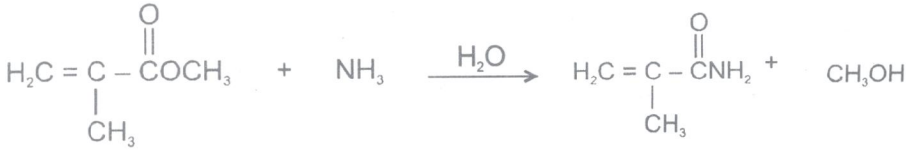
(B) Acid amides

Methods of preparation of acids amides

1. By reaction of esters with ammonia and amines

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

Ex.



2. From acid halides

$RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$

3. From anhydride

$(RCO)_2O + 2NH_3 \rightarrow RCONH_2 + RCOO\ NH_4$

4. From esters

$RCOOR + NH_3 \rightarrow RCONH_2 + R'OH$

5. From ammonium salt of carboxylic acid

$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$

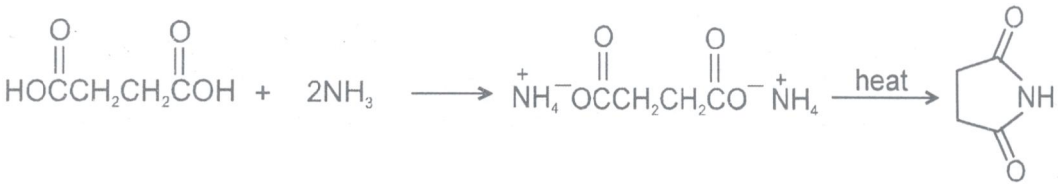
$CH_3\ COONH_4 \xrightarrow{\Delta} CH_3CONH_2$

6. From cyanides

$R - C = N + H_2O \xrightarrow[\text{or } H_2O_2\ -\ NaOH]{\text{Conc. HCl}} R - CONH_2$

$CH_3C = N + H_2O \xrightarrow{\text{Conc. } H_2SO_4} CH_3 - CONH_2$

7.



Chemical Reactions

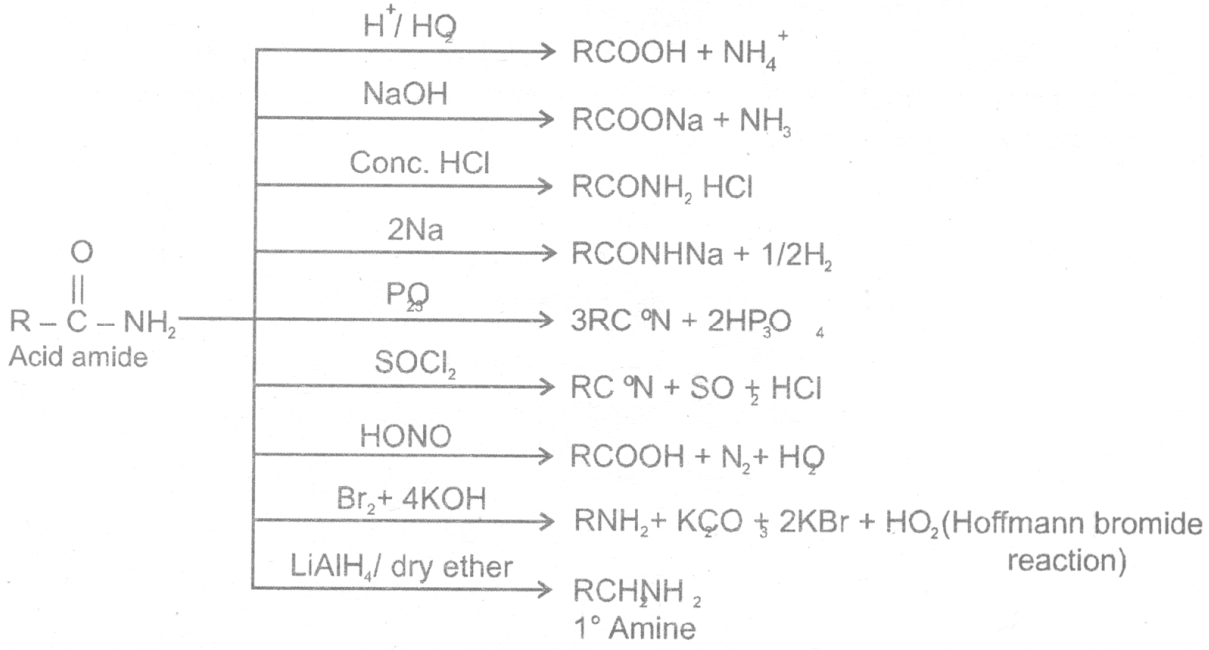
(1) Hoffmann rearrangement

General reaction

(2) Hydrolysis of amides

In acid, however, the amine is protonated, giving an ammonium ion, $R_2' \overset{+}{N}H_2$

Summary of reaction of amide:



(C) Esters

Mathods of Preparation

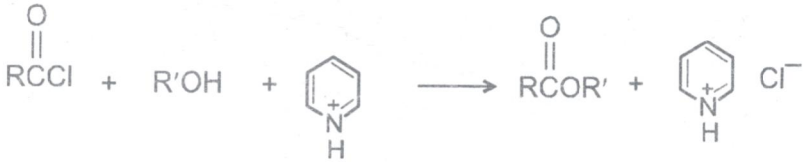
(i) $CH_3COOH + C_2H_5OH \xrightarrow{H^+} CH_3COOC_2H_5 + H_2O$

Acetic acid

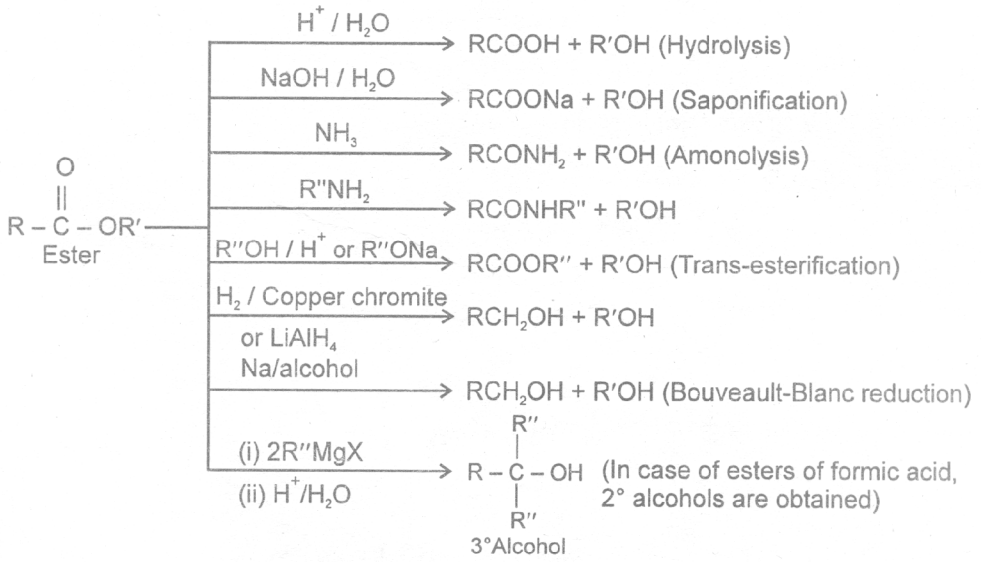
$C_6H_5COOH + CH_3OH \xrightarrow{H^+} C_6H_5COOCH_3 + H_2O$

(ii) $CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} CH_3COOC_2H_5 + HCl$

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



Summary of reaction of esters :



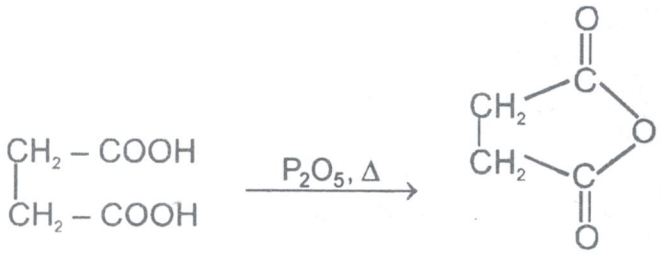
(D) Acid anhydrides

Methods of Preparation of acid anhydrides

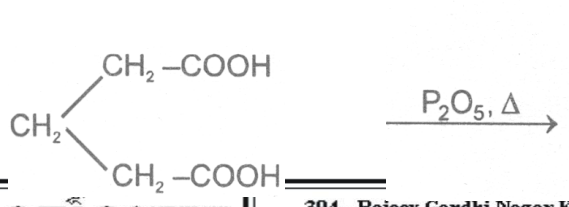
1. From carboxylic acids

Ex. $CH_3COOH + HOOCCH_3 \xrightarrow{P_2O_5,\Delta} CH_3CO.O.COCH_3 + H_2O$
Acetic acid — Acetic anhydride

Ex.



Ex.



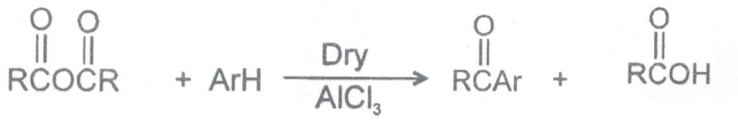
2. From acid and acid halide

Ex. $CH_3COOH + CH_3COCl \xrightarrow{\text{Pyridine}} CH_3\,CO.O.COCH_3 + HCl$

Ex. $CH_3COCl + CH_3COONa \xrightarrow{\Delta} CH_3CO.O.COCH_3 + NaCl$

Chemical Reactions

(1) Reaction with aromatic compounds (Friedel crafts acylation)



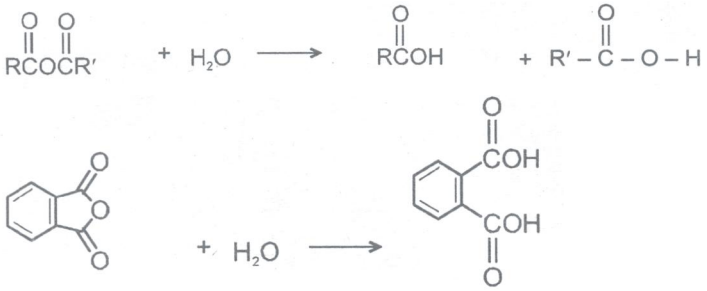
(2) **Reaction with alcohols**

Ex.

(3) **Reaction with ammonia and amines**

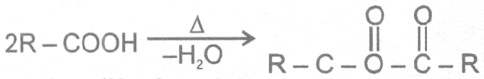
(4) **Hydrolysis**

Acid anhydrides react with to yield two carboxylic. Cycylic anhydides yield dicarboxylic acids.

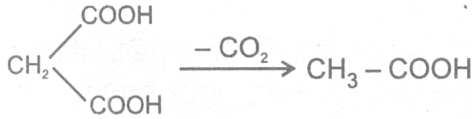


5. Heating Effects :

(a) Heating effect on monocarboxylic acid

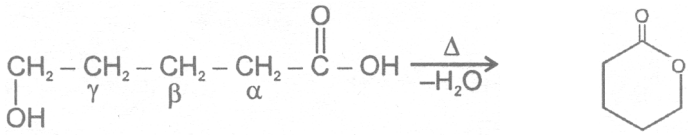


(b) Heating effect on dicarboxylic acid

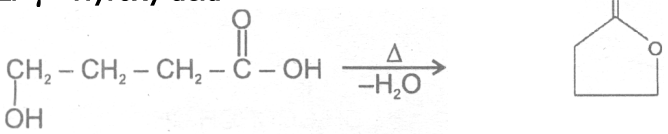


(c) Heating effect on Hydroxy acids

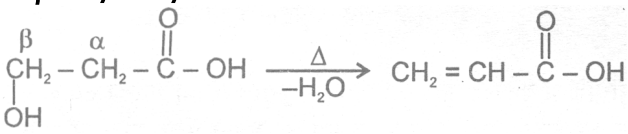
1. δ – Hydroxy acid



2. γ – Hyroxy acid

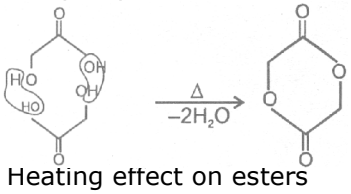


3. β – Hydroxy acid

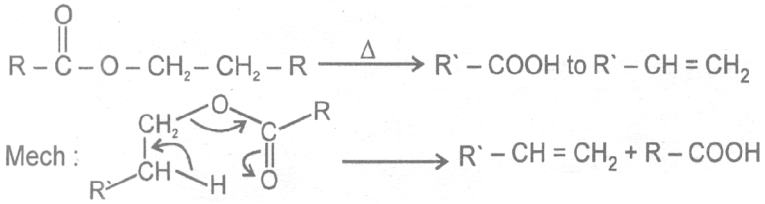


Since 4 or 8 membered rings are less stable the refore β-Hydroxy acids on heating produce α, β unsaturated carboxylic acid.

4. a-Hyroxy acid



• Heating effect on esters



This reaction follows syn elimination & hoffman product is formes.