

Carboxylic Acids and their derivatives Part 4

Acid Derivatives.

The compounds which are obtained by replacing the $-OH$ of the carboxylic group by other atoms or groups such as X^- , $-NH_2$, $-OR$ and $O-\overset{\overset{O}{\parallel}}{C}-R$ are known as acid derivatives.

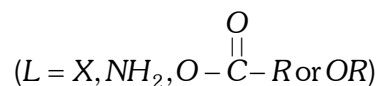
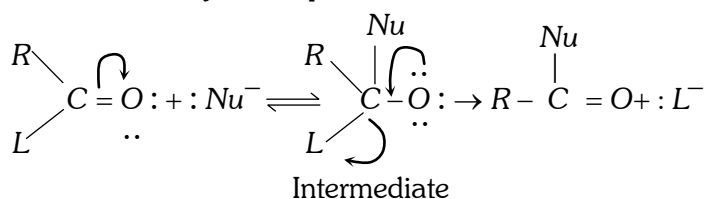
- $R-\overset{\overset{O}{\parallel}}{C}-$ group is common to all the derivatives and is known as acyl group and these derivatives are termed as acyl compound.

- The important derivatives are given below :

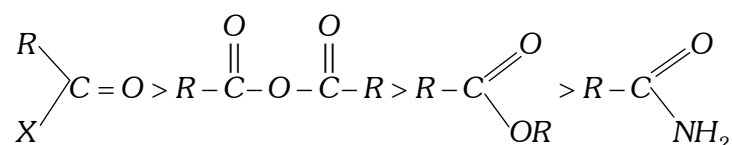
Group replacing $-OH$	Name	Structure
$\overset{X}{\text{---}}$ ($X = F, Cl, Br, I$)	Acyl halide	$R-\overset{\overset{O}{\parallel}}{C}-X$
$-NH_2$	Amide	$R-\overset{\overset{O}{\parallel}}{C}-NH_2$
$-OR'$	ester	$R-\overset{\overset{O}{\parallel}}{C}-OR'$ (R' may be R)
$-OOCR$	anhydride	$R-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R$

Reactivity

Acyl derivatives are characterised by nucleophilic substitution reactions.



The relative reactivities of various acyl compounds have been found to be in the following order:



Out of acid halides, the acid chlorides are more important ones.

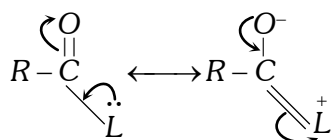
The overall order of reactivity can be accounted for in terms of the following three factors:

(i) Basicity of the leaving group (ii) Resonance effects and (iii) Inductive effects.

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(i) **Basicity of the leaving group** : Weaker bases are good leaving groups. Hence, the acyl derivatives with weaker bases as leaving groups are more reactive. Chloride ion is the weakest base while $-NH_2$ is the strongest base. Thus, acyl chlorides are most reactive and amides are least reactive.

(ii) **Resonance effect** : The leaving group in each case has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.

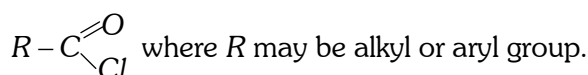


This makes the molecule more stable. The greater the stabilization, the smaller is the reactivity of the acyl compound.

However, acyl chlorides are least affected by resonance. Due to lower stabilization, the acid chlorides are more reactive as the loss of $-Cl$ is easier. Greater stabilization is achieved by resonance in esters and amides and thus, they are less reactive.

(iii) **Inductive effect** : Higher the $-I$ effect, more reactive is the acyl compound. Inductive effect of oxygen in ester is greater than nitrogen in amide, hence ester is more reactive than an amide.

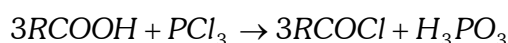
Acyl Halides



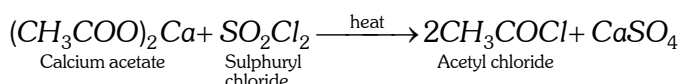
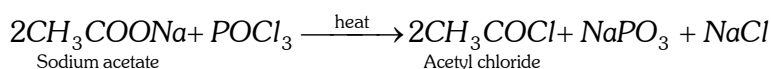
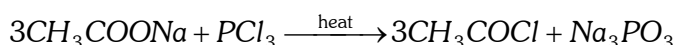
Nomenclature: The common names as well as IUPAC names of the acid halides are derived by replacing ic acid by yl halide.

Acyl chloride	Common name	IUPAC name
$HCOCI$	Formyl chloride	Methanoyl chloride
CH_3COCl	Acetyl chloride	Ethanoyl chloride
CH_3CH_2COCl	Propionyl chloride	Propanoyl chloride
C_6H_5COCl	Benzoyl chloride	Benzoyl chloride

(1) Methods of Preparation



(ii) **Industrial method** : By distilling anhydrous sodium acetate



This is the best method because SO_2 and HCl are gases and easily escape leaving behind acyl chloride.

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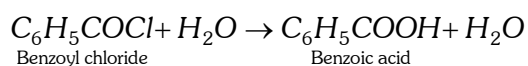
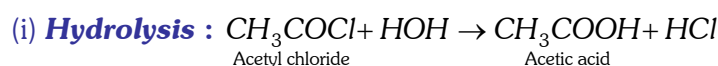
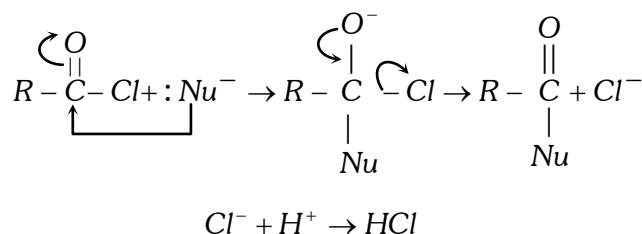
(2) **Physical properties** : The lower acyl chloride are mobile, colourless liquid while the higher members are coloured solids.

Acyl chloride have very pungent, irritating order and are strong lachrymators (tears gases)

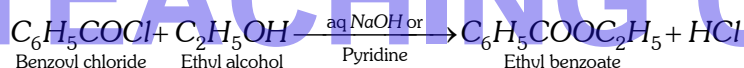
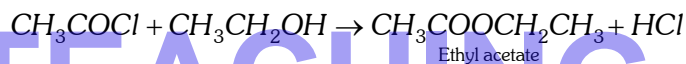
The fume in air due to the formation of hydrochloric acid by hydrolysis.

They are readily soluble in most of the organic solvent. Acyl chloride don't form intermolecular hydrogen bonding. Therefore, their boiling points are lower than those of their parent acids.

(3) Chemical properties

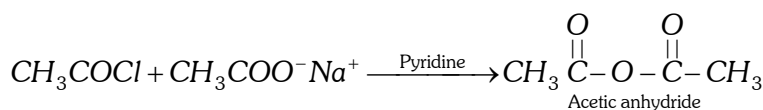


(ii) Reaction with alcohols (alcoholysis)

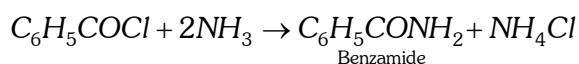
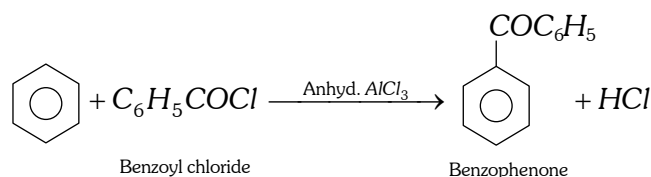
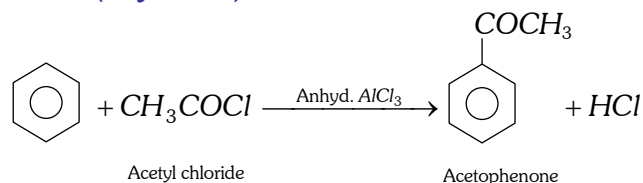


This reaction is called **Schotten Baumann reaction**.

(iii) Reaction with salts of carboxylic acid

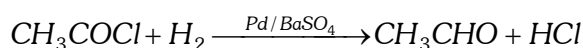
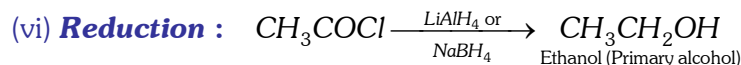
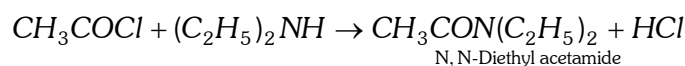
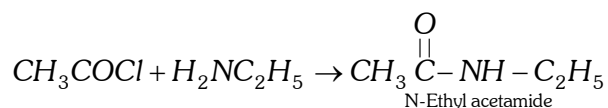


(iv) Reaction with benzene (acylation) : This reaction is called friedel craft reaction.



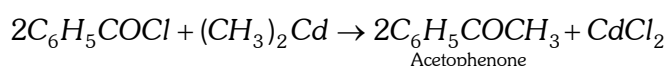
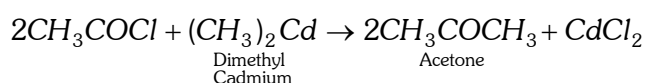
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However, acyl chlorides react with amines to form substituted amides.

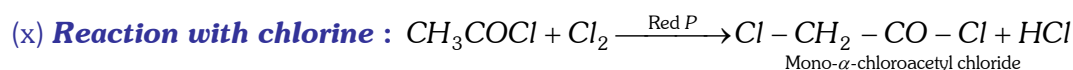
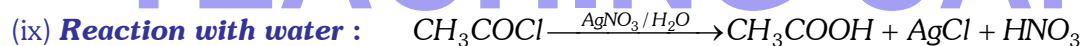
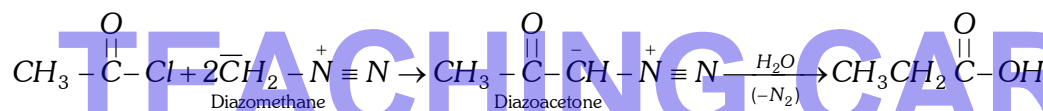


This reaction is called **Rosenmund reaction**.

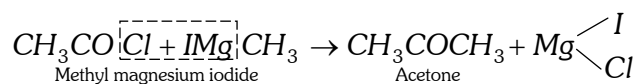
(vii) **Reaction with organocadmium compounds (formation of ketones)**



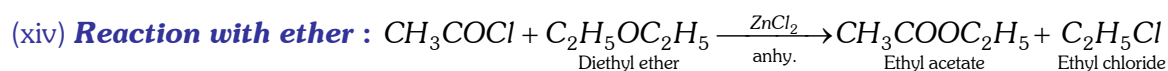
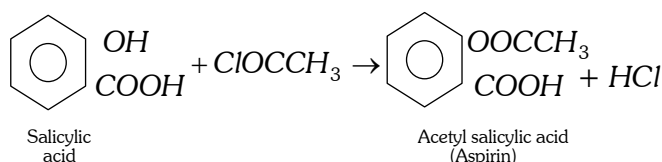
(viii) **Reaction with diazomethane**



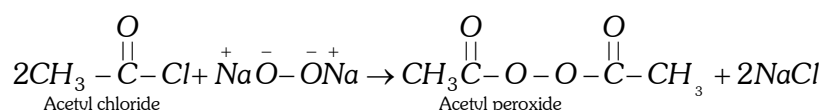
(xi) **Reaction with Grignard reagent**



(xiii) **Reaction with Salicylic acid**

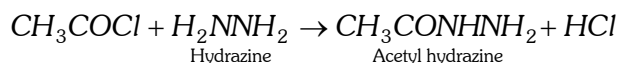
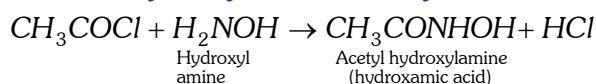


(xv) **Reaction with sodium peroxide (Peroxide formation)**



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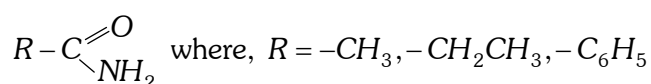
(xvi) Reaction with hydroxylamine and hydrazine



(4) Uses

- (i) As an acetylating agent.
- (ii) In the estimation and determination of number of hydroxyl and amino groups.
- (iii) In the preparation of acetaldehyde, acetic anhydride, acetamide, acetanilide, aspirin, acetophenone etc.

Acid Amides



Nomenclature

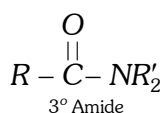
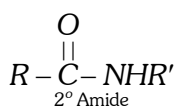
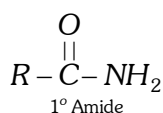
- ✱ In common system, -i.c., acid is replaced by amide.
- ✱ In IUPAC system, e of parent hydrocarbon is replaced by amide.

Acyl amides	Common name	IUPAC name
HCONH_2	Formamide	Methanamide
CH_3CONH_2	Acetamide	Ethanamide
$\text{C}_2\text{H}_5\text{CONH}_2$	Propionamide	Propanamide
$\text{C}_6\text{H}_5\text{CONH}_2$	Benzamide	Benzamide

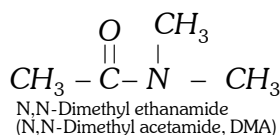
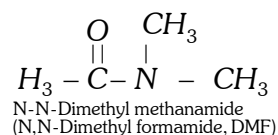
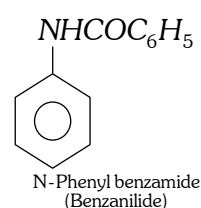
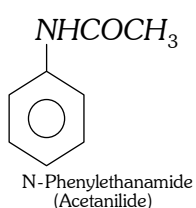
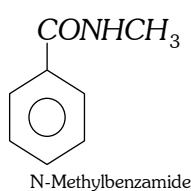
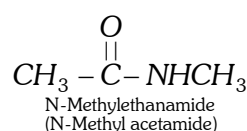
- ✱ The hydrogen atom of the acid may also be replaced by alkyl groups.



Therefore, the acid amides are classified:



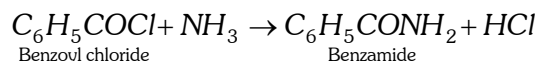
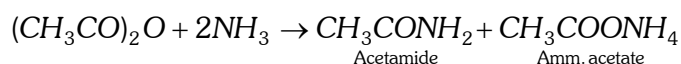
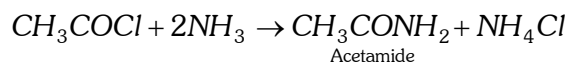
Similarly



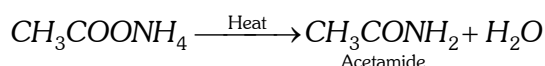
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(1) Methods of preparation

(i) Ammonolysis of acid derivatives



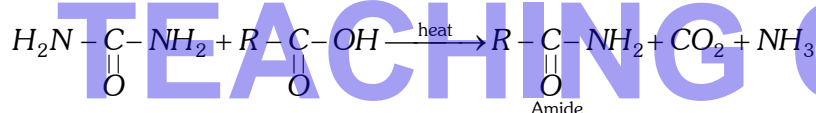
(ii) From ammonium salts of carboxylic acids (Laboratory Method)



Note : * Ammonium acetate is always heated in presence of glacial acetic acid to avoid the side product (CH_3COOH).



(iv) By heating carboxylic acid and urea



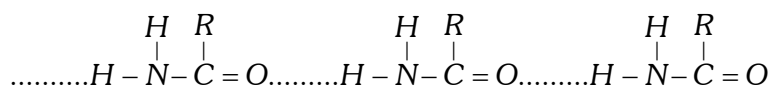
(2) Physical properties

(i) **Physical state :** Formamide is a liquid while all other amides are solids.

(ii) **Boiling points :** Amides have high boiling points than the corresponding acids.

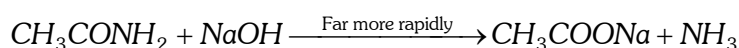
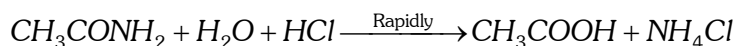
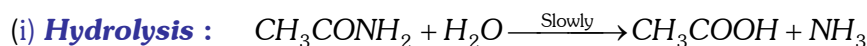
Acetic Acid	Acetamide
b.p. 391 K	b.p. 494 K
Benzoic acid	Benzamide
b.p. 522 K	b.p. 563 K

The higher boiling points of amides is because of intermolecular hydrogen bonding

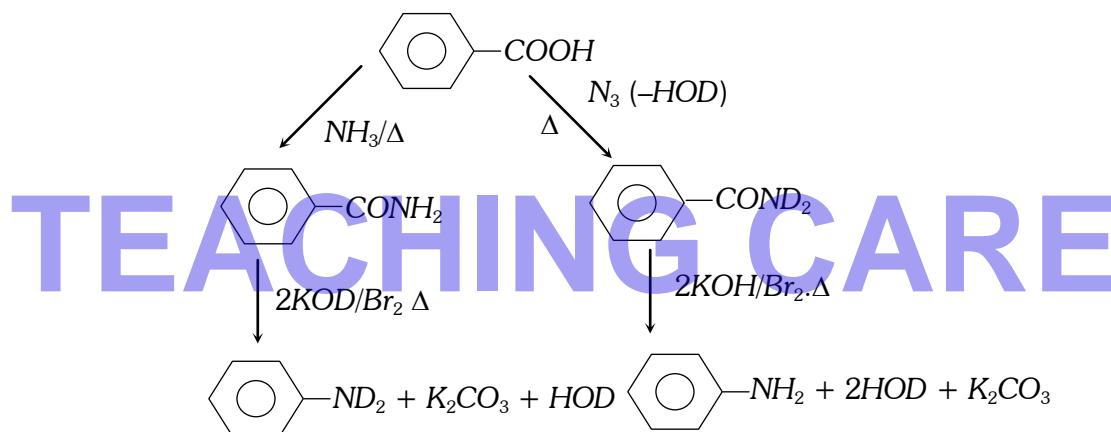
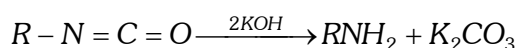
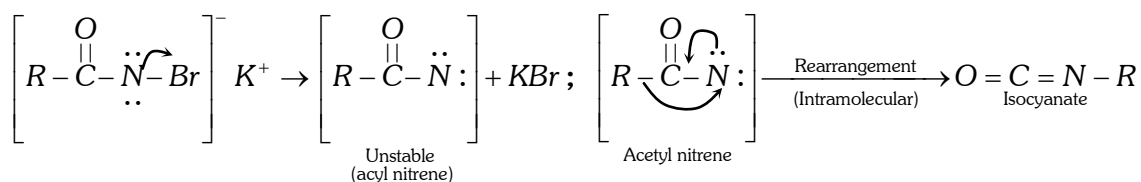
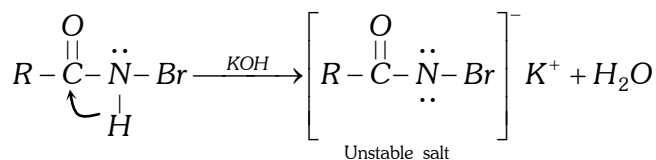
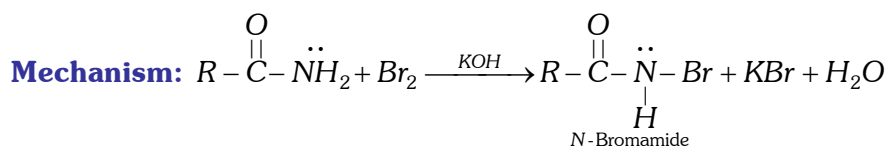


(iii) **Solubility :** The lower members of amide family are soluble in water due to the formation of hydrogen bonds with water.

(3) Chemical properties

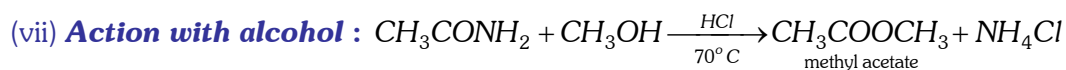


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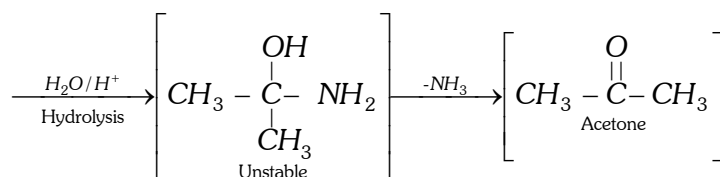
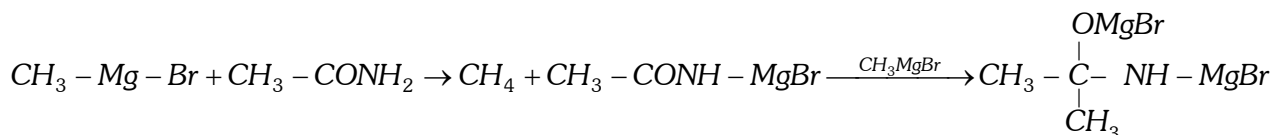


Note : * In this reaction a number of intermediates have been isolated; *N*-bromamides, $R\text{CONHBr}$; salts of these bromamides $[R\text{CONBr}^-] \text{K}^+$; Isocyanates, RNCO .

* Nitrene rearranges to form isocyanate.



(viii) **Reaction with grignard reagent**

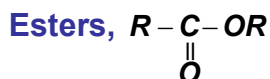


Carboxylic Acids and their derivatives Part 4

(4) Uses

- (i) In organic synthesis. The compounds like methyl cyanide, Methylamine and ethylamine can be prepared.
- (ii) In leather tanning and paper industry.
- (iii) As a wetting agent and as soldering flux.

Amides such as dimethyl formamide (DMF), dimethyl acetamide (DMA) are used as solvents for organic and inorganic compounds.

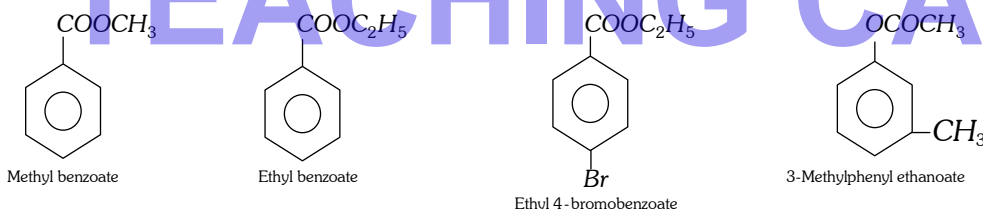


These are the most important class of acid derivatives and are widely distributed in nature in plants, fruits and flowers.

Nomenclature : In common names and IUPAC system, change the suffix ic acid by ate.

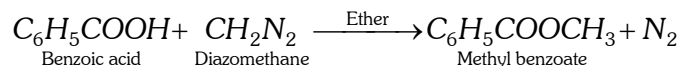
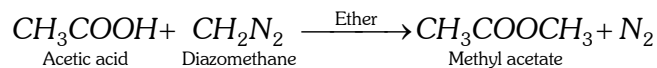
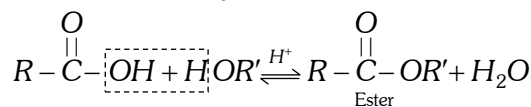
Ester	Common name	IUPAC name
$HCOOCH_3$	Methyl formate	Methyl methanoate
CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$CH_3COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
$CH_3COOC_6H_5$	Phenyl acetate	Phenyl ethanoate
$\begin{array}{c} \gamma \quad \beta \quad \alpha \\ CH_3CH_2\overset{\alpha}{C}HCOOC_2H_5 \\ \\ CH_3 \end{array}$	Ethyl α-methyl butyrate	Ethyl 2-methylbutanoate

The name of some aromatic esters are given below :



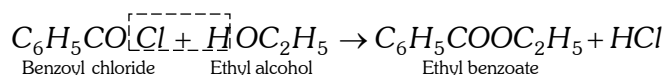
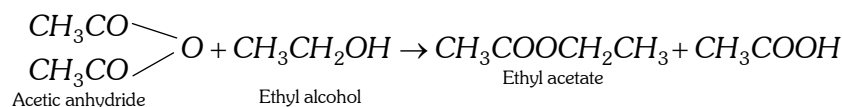
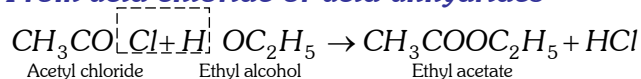
(1) Methods of preparation

(i) **From carboxylic acid [Esterification]** : Laboratory method.

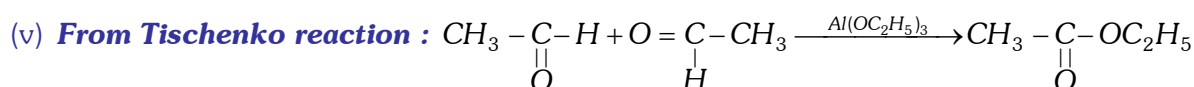
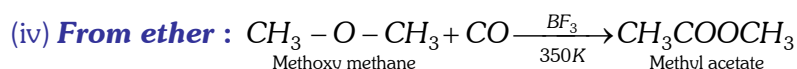
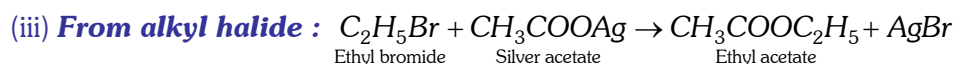


✱ With diazomethane is the best method.

(ii) **From acid chloride or acid anhydrides**



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(2) Physical properties

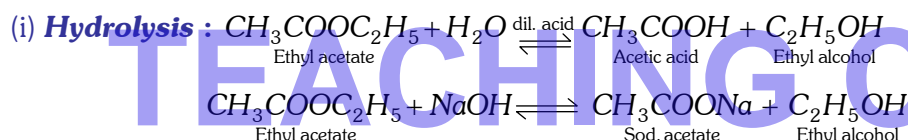
(i) **Physical state and smell** : Esters are colourless liquids (or solids) with characteristic fruity smell. Flavours of some of the esters are listed below :

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pineapple
Amyl butyrate	Apricot	Octyl acetate	Orange

(ii) **Solubility** : They are sparingly soluble in water but readily soluble in organic solvents such as alcohol, ether etc.

(iii) **Boiling points** : Their boiling points are lower than the corresponding acids because of the absence of hydrogen bonding. i.e., ethyl acetate = 77.5°C.

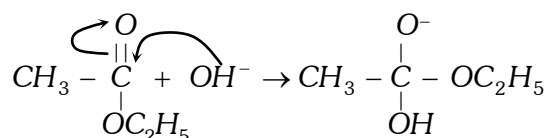
(3) Chemical properties



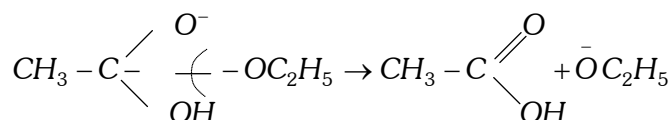
Hydrolysis of ester by alkalis (NaOH) is known as saponification and leads to the formation of soaps

Mechanism : It follows three steps :

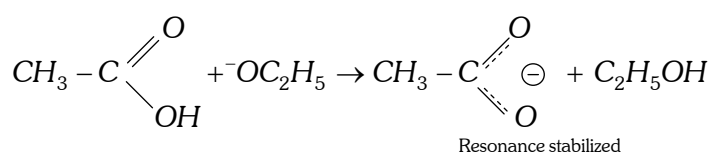
Step I : The nucleophile, OH^- ion from the alkali attacks the carboxyl carbon to form an intermediate.



Step II : The intermediate, then loses a molecule of ethoxide ion to form acetic acid as:



Step III : Ethoxide ion abstracts the acidic proton from acetic acid to form acetate ion.

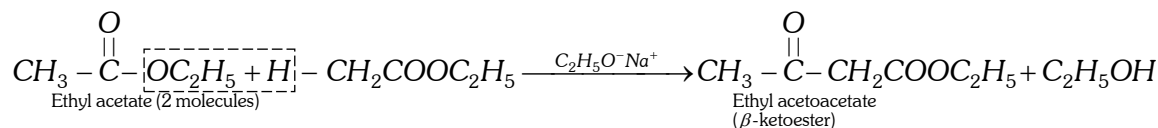


Note : * This reaction is irreversible because a resonance stabilized carboxylate (acetate) ion is formed.

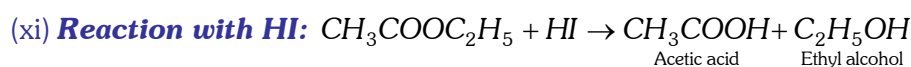
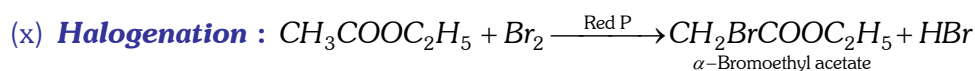
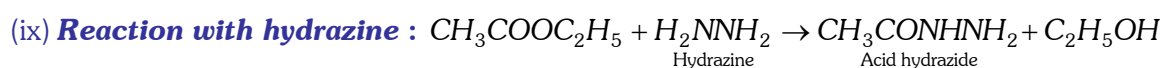
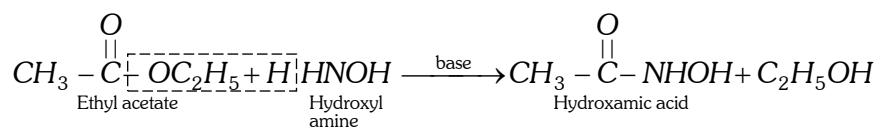
* The acid hydrolysis of esters is reversible.

Carboxylic Acids and their derivatives Part 4

(vii) Claisen condensation



(viii) Reaction with hydroxyl amine

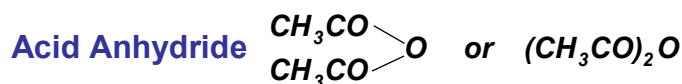


(4) Uses

- (i) As a solvent for oils, fats, cellulose, resins etc.
- (ii) In making artificial flavours and essences.
- (iii) In the preparation of ethyl acetoacetate.

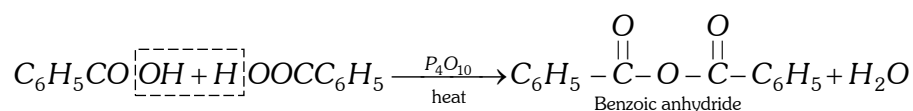
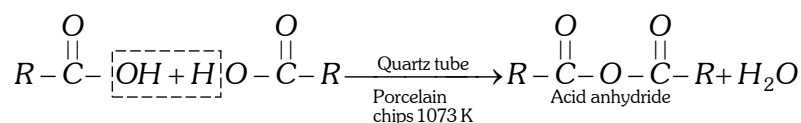
(5) General Tests

- (i) It has sweet smell.
- (ii) It is neutral towards litmus.
- (iii) A pink colour is developed when one or two drops of phenolphthalein are added to dilute sodium hydroxide solution. The pink colour is discharged when shaken or warmed with ethyl acetate.
- (iv) Ethyl acetate on hydrolysis with caustic soda solution forms two compounds, sodium acetate and ethyl alcohol.
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$



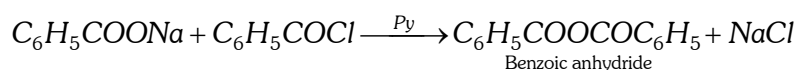
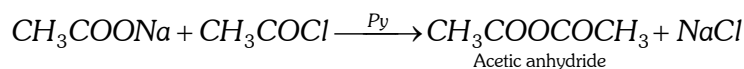
(1) Method of preparation

(i) From carboxylic acid

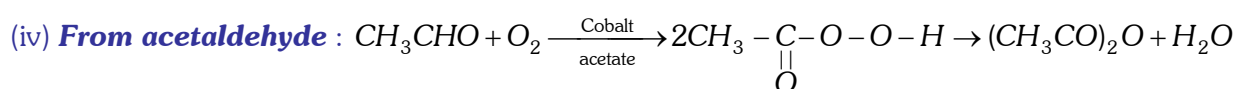


Carboxylic Acids and their derivatives Part 4

(ii) From carboxylic acid salt and acyl chloride [Laboratory method]



(iii) From acetylene



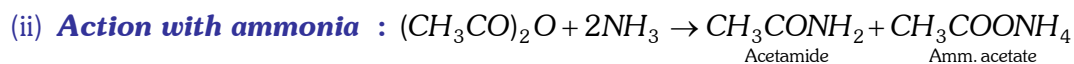
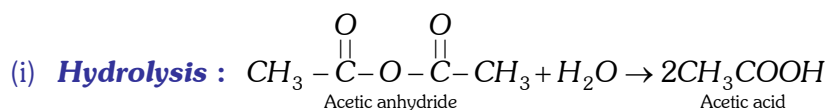
(2) Physical properties

(i) **Physical state** : Lower aliphatic anhydrides are colourless liquids with sharp irritating smell. The higher members of the family as well as the aromatic acid anhydrides are solids in nature.

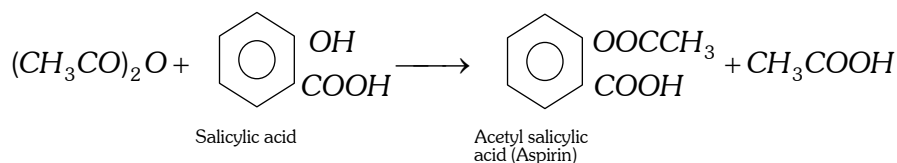
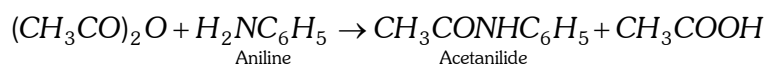
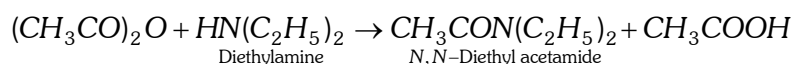
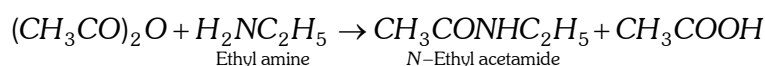
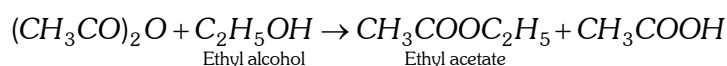
(ii) **Solubility** : They are generally insoluble in water but are soluble in the organic solvents such as ether, acetone, alcohol, etc.

(iii) **Boiling points** : The boiling points of acid anhydrides are higher than those of carboxylic acids because of the greater molecular size.

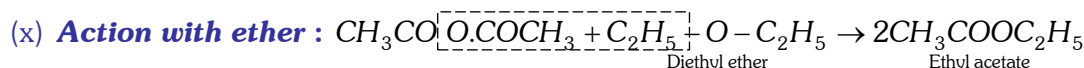
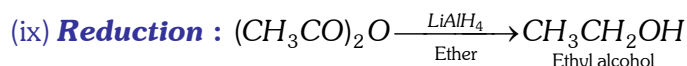
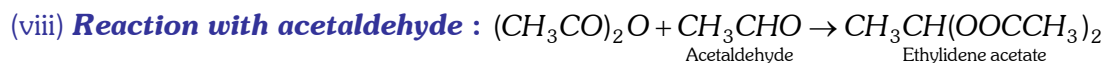
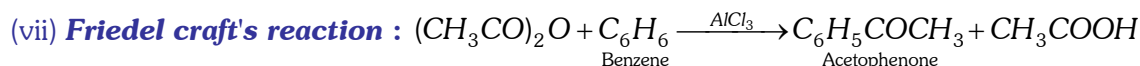
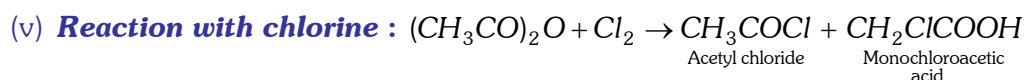
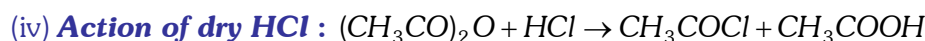
(3) Chemical Properties



(iii) **Acetylation** : Acetic anhydride react with compound having active hydrogen.



Carboxylic Acids and their derivatives Part 4

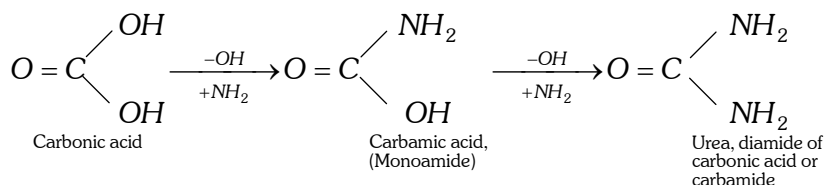


(4) **Uses** : Acetic anhydride is used

- (i) as an acetylating agent.
- (ii) For the detection and estimation of hydroxyl and amino group.
- (iii) in the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, acetophenone, etc.



Urea may be considered as diamide of an unstable and dibasic carbonic acid from which both the hydroxyl groups have been replaced by $-NH_2$ groups.



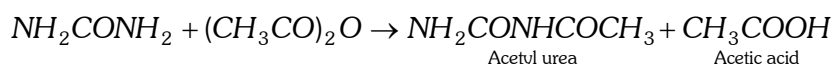
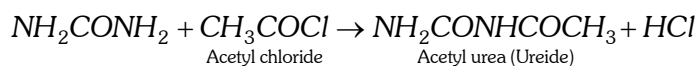
- ✱ Urea in 1773 by Roule and hence the name urea was given.
- ✱ It was the first organic compound synthesised in the laboratory from inorganic material (by heating a mixture of ammonium sulphate and potassium cyanate) by Wohler in 1828.
- ✱ This preparation gave a death blow to *Vital force theory*.
- ✱ It is the final decomposition product of protein's metabolism in man and mammals and is excreted along with urine.
- ✱ Adults excrete about 30 grams of urea per day in the urine.

(1) Method of preparation

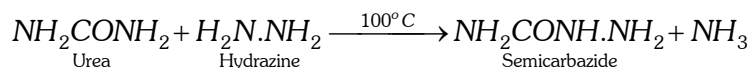
(i) **From urine** : Urine is treated with conc. nitric acid where crystals of urea nitrate $CO(NH_2)_2.HNO_3$ are obtained.

Carboxylic Acids and their derivatives Part 4

(vi) **Reaction with acetyl chloride or acetic anhydrides**

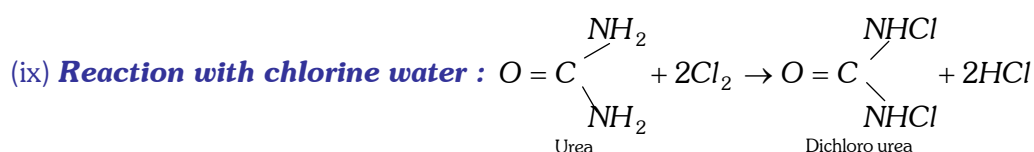


(vii) **Reaction with hydrazine**



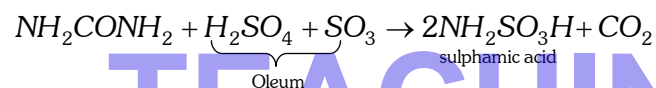
(viii) **Reaction with ethanol** : $\text{H}_2\text{NCO}\text{---}\text{NH}_2 + \text{H}\text{---}\text{OC}_2\text{H}_5 \xrightarrow{\text{heat}} \text{H}_2\text{NCOOC}_2\text{H}_5 + \text{NH}_3$

Ethanol Urethane

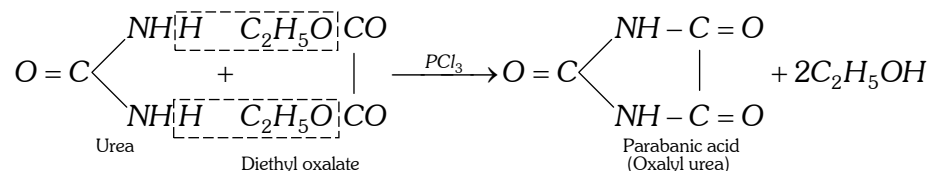
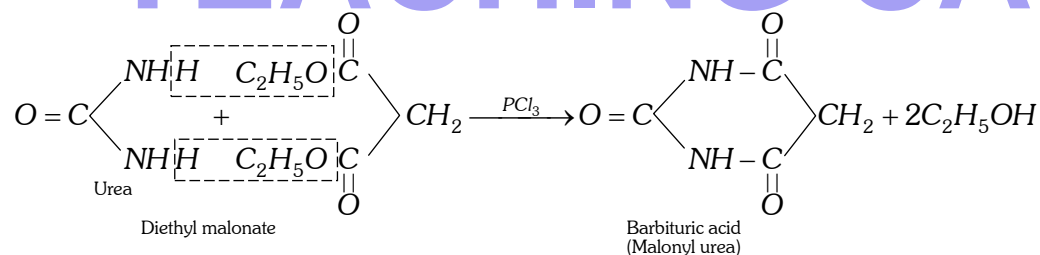


(x) **Dehydration** : $\text{NH}_2\text{CONH}_2 + \text{SOCl}_2 \rightarrow \text{H}_2\text{N}-\text{C}\equiv\text{N} + \text{SO}_2 + 2\text{HCl} + \text{H}_2\text{O}$

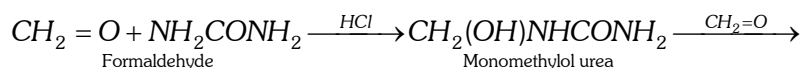
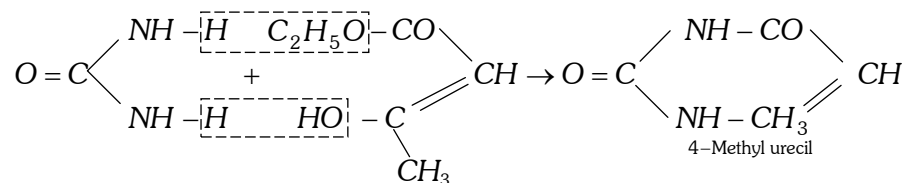
(xi) **Reaction with fuming sulphuric acid**



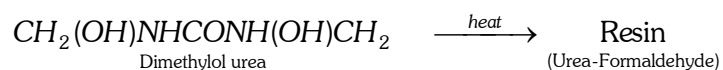
(xii) **Formation of cyclic ureides**



(xiii) **Reaction with formaldehyde**



Carboxylic Acids and their derivatives Part 4



(4) Uses

- (i) Mainly as a nitrogen fertilizer. It has 46.4% nitrogen.
- (ii) In the manufacture of formaldehyde-urea plastic and semicarbazide.
- (iii) As animal feed.
- (iv) For making barbiturates and other drugs.
- (v) As a stabilizer for nitrocellulose explosives.

(5) General Tests

- (i) When heated with sodium hydroxide, ammonia is evolved.
- (ii) When heated gently, it forms biuret which gives violet colouration with sodium hydroxide and a drop of copper sulphate solution.
- (iii) Its aqueous solution with concentrated nitric acid gives a white precipitate.
- (iv) On adding sodium nitrite solution and dil. HCl (i.e., HNO_2) to urea solution, nitrogen gas is evolved and gives effervescence due to carbon dioxide.

TEACHING CARE