UNIT: 14
CARBOXYLIC ACID

NEB Syllabus:
[A] Aliphatic and Aromatic Carboxylic Acid:

Introduction, Nomenclature and Isomerism
Preparation of Monocarboxylic acids from
a) Aldehydes
b) Nitriles
c) Grignard reagents
d) Dicarboxylic acid
e) Sodium alkoxide
f) Trihaloalkanes
Preparation of Benzoic acid from Alkyl benzene
Physical Properties of Monocarboxylic acids
Chemical properties of Aliphatic and Aromatic Carboxylic acids:
1. Acidic Nature
a) Action with metals
b) Action with alkalies
c) Action with metal oxides
d) Action with metal carbonates and bicarbonates
2. Action with PCl3 , PCl5 , SOCl2
3. Action with LiAlH4
4. Dehydration of carboxylic acid
5. Decarboxylation reaction
6. Esterification reaction
7. Hell-Volhard-Zelinsky reaction
Electrophilic Substitution reaction of Benzoic acid (Bromination, Nitration and Sulphonation)
Effect of Substituents on the acidic strength of carboxylic acid
Abnormal behavior of Methanoic acid (Formic acid)

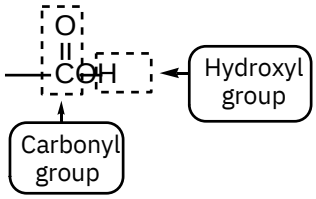
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[B] Derivatives of Carboxylic Acids (Acid halides, Amides, Esters and Anhydrides)

Preparation of acid derivatives from Carboxylic acid
Comparative Physical Properties of acid derivatives
Comparative Chemical Properties of acid derivatives(Hydrolysis, Ammonolysis, Reaction with primary amine, Alcoholysis and Reduction)
Claisen condensation
Hofmann-Bromamide reaction
Amphoteric nature of Amide
Relative reactivity of acid derivatives

Introduction

Organic compounds containing carboxyl group (-COOH) as a functional group are called carboxylic acid. The carboxyl group is the combination of carbonyl & hydroxyl group.



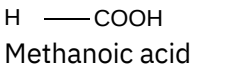
General representation:
R— COOH or Ar — COOH

Where, R= alkyl groups (in aliphatic carboxylic acids) and Ar = aryl group usually Phenyl group (in aromatic carboxylic acid)

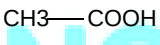
Nomenclature

IUPAC format: Alkanoic acid

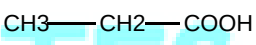
Aliphatic Carboxylic acids



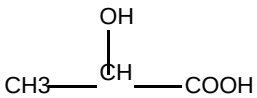
Methanoic acid (Formic acid)



Ethanoic acid (Acetic acid)

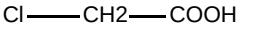


Propanoic acid

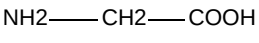


2-Hydroxy propanoic acid

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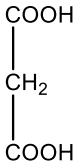
2-Chloro ethanoic acid -Chloroacetic acid)



2-Amino ethanoic acid -aminoacetic acid)

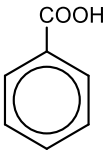


Ethanedioic acid (Oxalic acid)

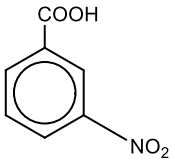


Propane-1,3-dioic acid (Malonic acid)

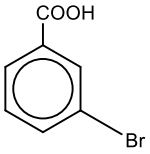
Aromatic Carboxylic acid



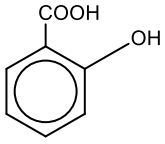
Benzoic acid



m-nitrobenzoic acid



m-bromobenzoic acid



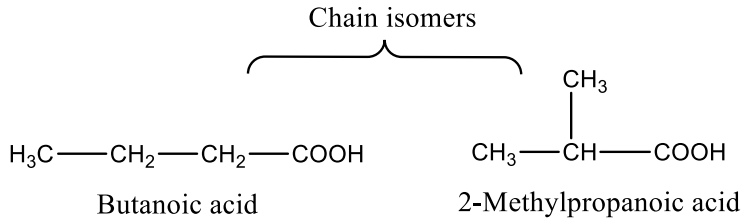
o-hydroxybenzoic acid (Salicylic acid)

Isomerism

Carboxylic acid shows following types of isomerism.

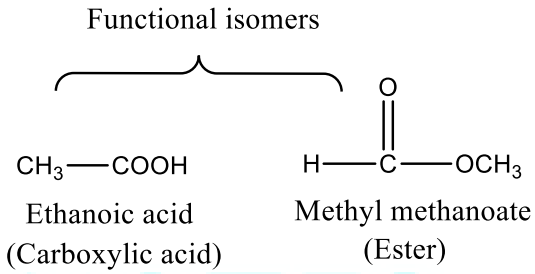
1) Chain Isomerism:

Example: Isomers of C4H8O2



2) Functional Isomerism:

Example: Isomers of C2H4O2



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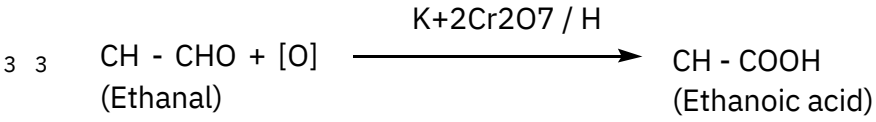
Question: *Write the functional isomer of ethanoic acid & its IUPAC names.*

General Methods of Preparation of Monocarboxylic acids

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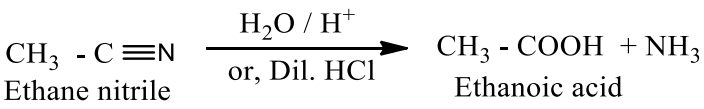
1) From Oxidation of Aldehydes

Aldehydes are easily oxidized into carboxylic acids by using oxidizing agents under normal condition.



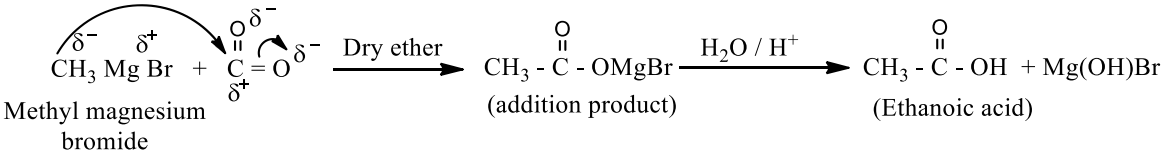
2) From Nitriles (or Cyanides)

Alkane nitrile undergoes acidic hydrolysis to give carboxylic acid.



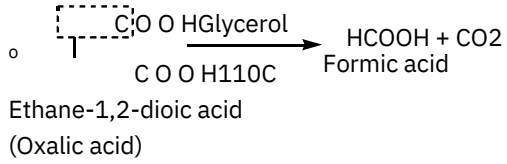
3) From Grignard's reagent (Carboxylation reaction)

Grignard reagent reacts with carbon dioxide in presence of dry ether to form addition product, which on acid hydrolysis gives carboxylic acid.

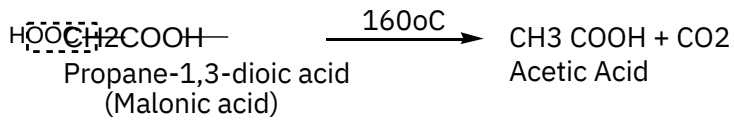


4) From Dicarboxylic Acid

When dicarboxylic acid is heated with glycerol, forms monocarboxylic acid.



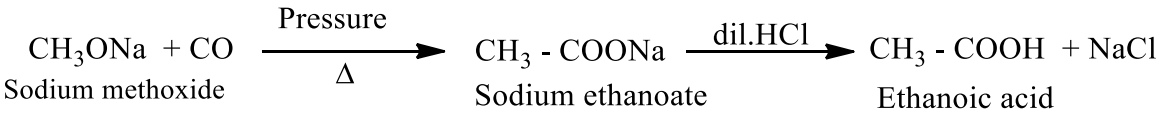
Ethane-1,2-dioic acid
(Oxalic acid)



Propane-1,3-dioic acid
(Malonic acid)

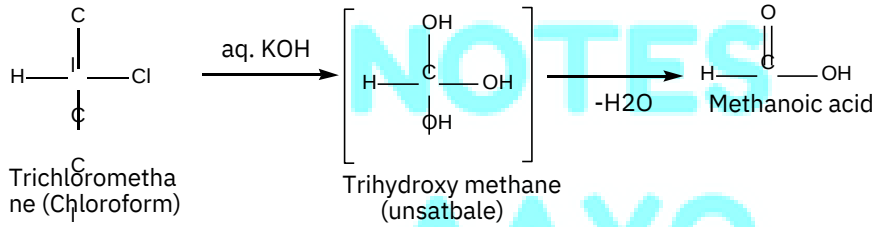
5) From Sodium Alkoxide

When sodium alkoxide reacts with carbon monoxide in presence of temperature and pressure, gives sodium alkanoate, which on acidification with dil. HCl forms carboxylic acid.



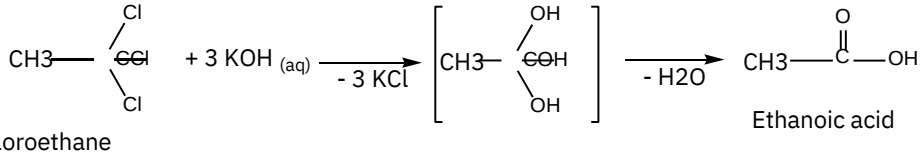
Sodium methoxide — Sodium ethanoate — Ethanoic acid

6) From Trihaloalkanes



Trichloromethane (Chloroform)

Trihydroxy methane
(unsatbale)



1,1,1- trichloroethane

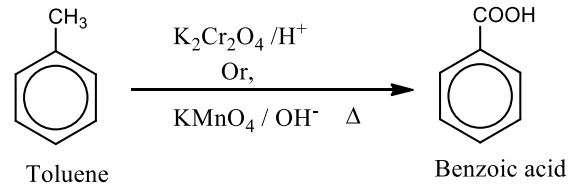
Unstable

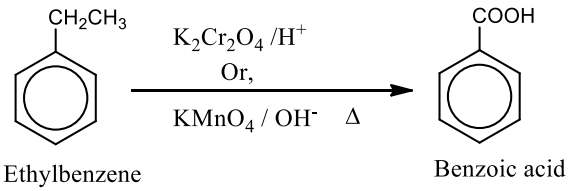
Question. *What is meant by carboxylation reaction? Write an example of it.*

Question. *Give the chemical reaction for the preparation of ethanoic acid from*
i) Sodium ethoxide ii) Ethane nitrile iii) Methyl magnesium iodide
iv) 1,1,1-Trichloroethane

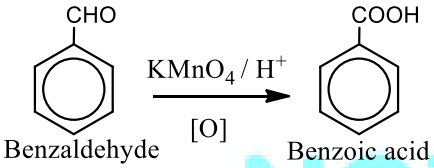
Preparation of Benzoic acid from Alkyl benzene

By Oxidation of Toluene





By Oxidation of Benzaldehyde

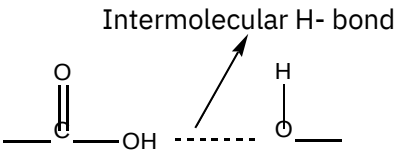


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Physical Properties of Monocarboxylic acid

a)**State, color and odor:** Lower members of carboxylic acids up to C10 are colorless unpleasant smelling liquid while higher members are colorless, odorless waxy solids.

b) **Solubility:** The first four members are completely soluble in water because they can form intermolecular hydrogen bond with water molecule whereas higher members are insoluble in water due to increase in hydrophobic nature of hydrocarbon portion.



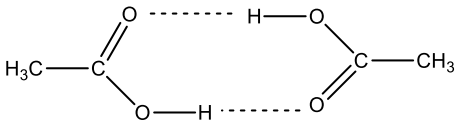
Carboxylic acidWater

c) Boiling point:

Carboxylic acids have higher boiling point than alcohol, ether etc. of comparable molecular mass because carboxylic acid can form two intermolecular hydrogen bonds & forms stable cyclic dimer structure whereas alcohol can form only one intermolecular hydrogen bond with each other & ether cannot form such H-bonds with themselves.

Example:

Acetic acid	Butanol	Ethoxyethane
CH3COOH MW= 74 B.pt= 141oC	CH3CH2CH2CH2OH MW= 74 B.pt= 118oC	CH3CH2 O CH2CH3 MW= 74 B.pt= 34.6oC



Dimer structure
(Two intermolecular H-bonds
between two acetic acid molecules)



Only one intermolecular H- bond
between two butanol molecules

Question: *The boiling point of Methanoic acid is higher than ethanol though they have same molecular mass. Explain.*

Boiling increases with the increase in molecular mass in homologous series of carboxylic acid due to increase in size and strength of force held between the molecules.

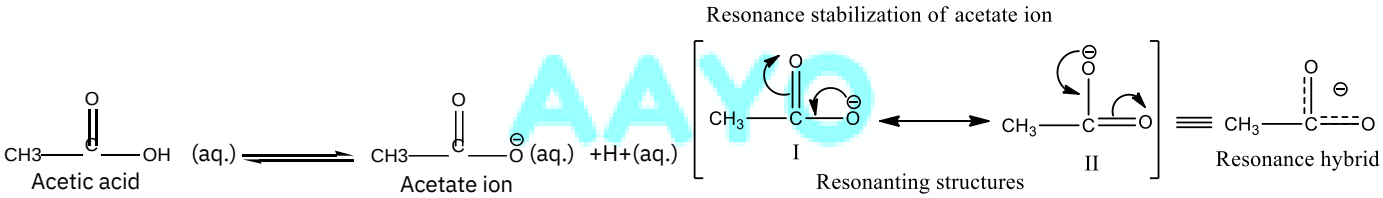
Example: HCOOH < CH3COOH < CH3CH2COOH

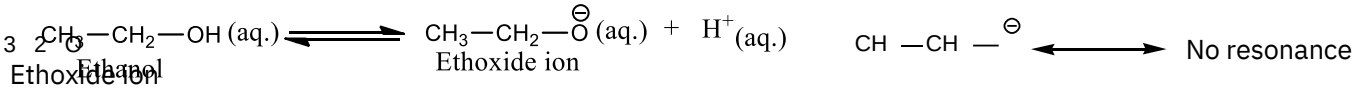
Chemical Properties of Aliphatic and Aromatic carboxylic acids

1)Acidic nature:

Carboxylic acids are more acidic in nature than aliphatic alcohols because the carboxylate ion forme after the ionization of carboxylic acid is resonance stabilized whereas alkoxide ion formed after the ionization of alcohol is not resonance stabilized. More the stability of ion in aqueous solution higher will be the acid strength.

Example: Acetic acid (Ethanoic acid) is stronger acid than Ethanol

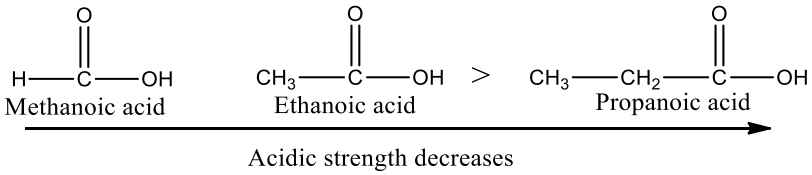




Effect of Substituent on acidic strength of Carboxylic acid

i) Electron donating groups such as –CH3, –OH, –NH2, etc. donates the electrons and **shows + I effe** which destabilize the carboxylate anion by intensifying the negative charge on oxygen atom & decrease the acid strength of carboxylic acid.

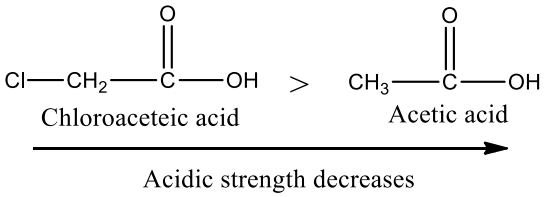
Example:



Question: *Why is ethanoic acid (acetic acid) weaker acid than Methanoic acid (Formic acid)?*

ii) Electron withdrawing groups such as –F, –Cl, –Br, –I, –CN, –NO2, etc. withdraws the electrons and shows **– I effect,** which stabilize the carboxylate anion by dispersing the negative charge on oxygen atom & increase the acid strength of carboxylic acid.

Example:

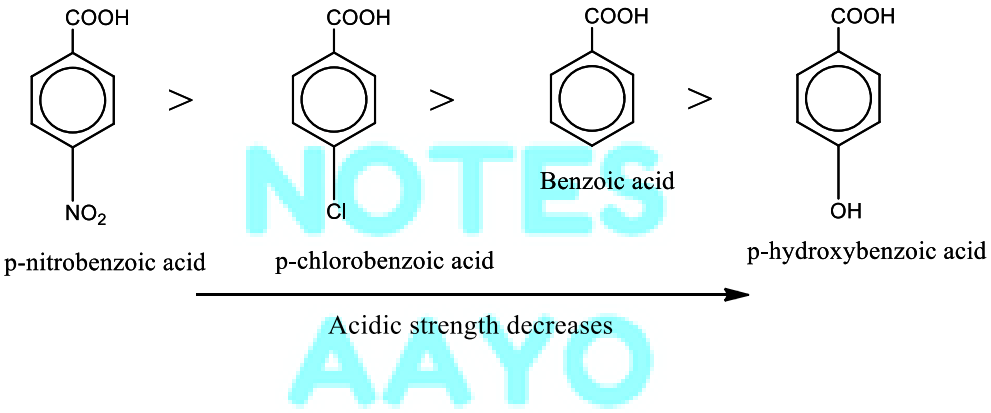


***Question**: Why is Chloroacetic acid stronger acid than acetic acid?*

Effect of Substituent on acidic strength of Benzoic acid

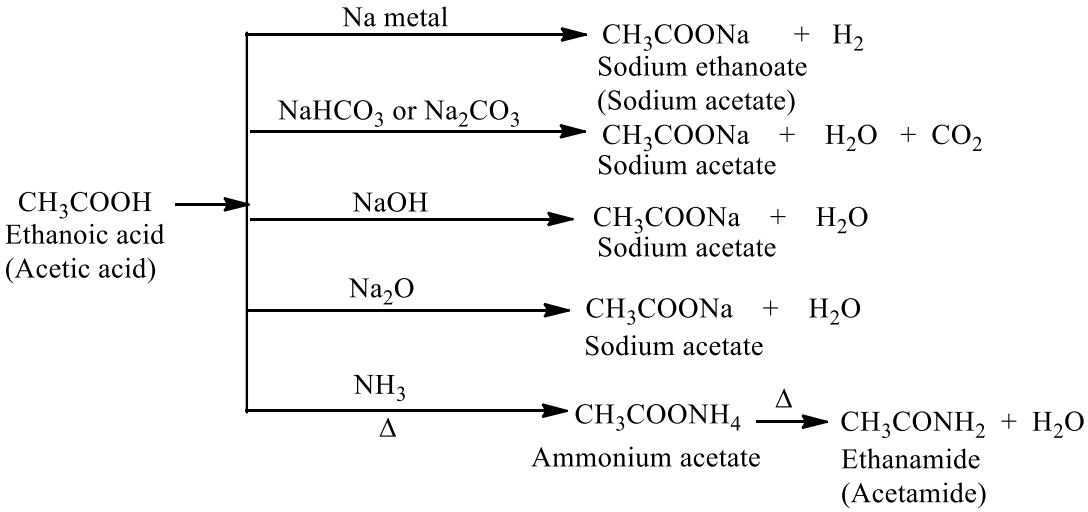
Benzoic acid is less acidic than formic acid but more acidic than acetic acid because phenyl group (–C6H is weak electron releasing group than –CH3 group of acetic acid. –CH3 group intensify the negative char more in acetate ion and destabilize than –C6H5 group in benzoate ion.
Example:
Decreasing Order of acidic strength: HCOOH > C6H5COOH> CH3COOH

Electron donating substituent (-OH, -NH2, -CH3, etc.) decreases the acidic strength of benzoic acid whereas **electron withdrawing substituent** (-NO2, -Cl, -Br, -I, -CN, etc.) increases the acidic strength benzoic acid.
For example:



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Reactions to show the acidic nature of carboxylic acid



Laboratory Test of Carboxylic acid

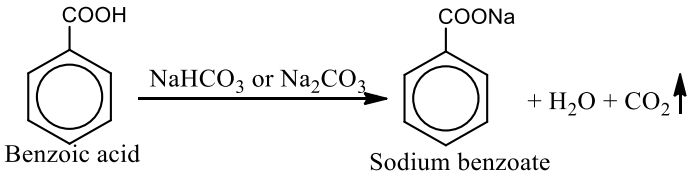
Carboxylic acid reacts with sodium carbonate or sodium bicarbonate & produce brisk effervescence of carbon dioxide gas whereas other weak acids like alcohol & phenols does not reacts with sodium carbonate or sodium bicarbonate.

2 3

NaCO
RCOOH3 or NaHCO → RCOONa + CO_2↑ + H2O
Carboxylic acid

Na2CO3 or NaHCO3 →
ROHNo reaction
Aliphatic alcohol

Na →
C2CO3 or NaHCO36H5OHNo reaction
Phenol



Other Important reactions:

3

PCl /
CH3COCl + H3PO3
Ethanoyl chloride

PCl/ (Acetyl chloride)5 → Formation of acid Chlorides
CH3COCl + POCl3 + HCl

SOCl2 / Pyridine / →
CH3COCl + SO2 + HCl

P2O5 /
CH3COOCOCH3 + H2OFormation of acid anhydride
Ethanoic anhydride
(Acetic anhydride)

C+2H5OH / H
CH3COOC2H5 + HOFormation of ester (Esterification)2
Ethyl ethanoate
(Ethyl acetate)

CH3COOH → Ethanoic acid (Acetic acid)

NaOH/ CaO /
CH4 + Na2CO3 + H2ODecarboxylation
(Soda lime)Methane

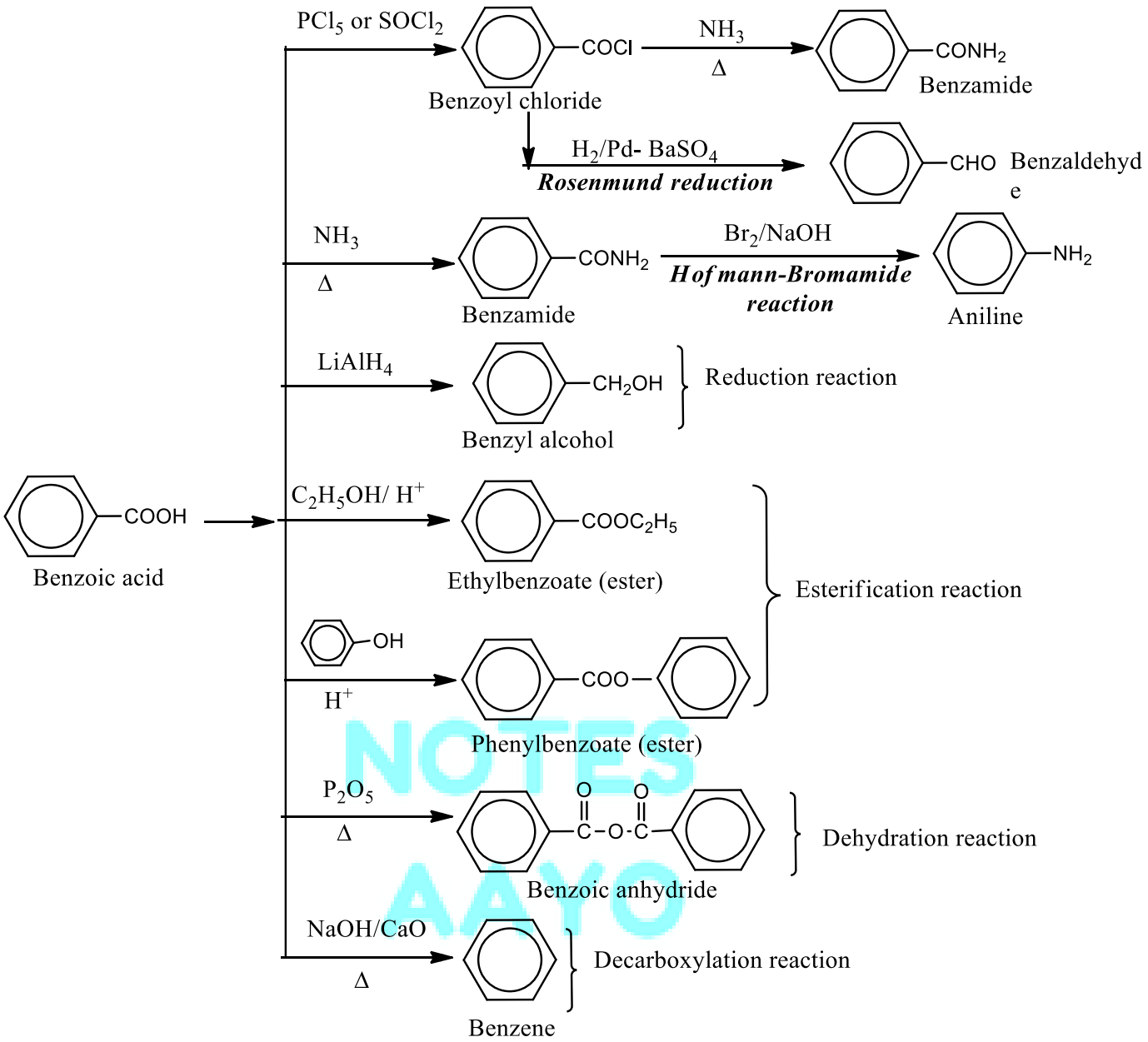
LiAlH4 →
CH3CH2OH + H2O
EthanolReduction

red P / HI →
CH3-CH3 + H2O + I2
Ethane

red P / Cl2red P / Cl2red P / Cl2 → → →
Cl-CHCOOH (-HCl)2Cl2CHCOOHCl3CCOOHHell-Volhard-Zelinsky RxnCl)
Dichloroacetic (-HCl) halogenation)Chloroacetic acid(-HTrichloroacetic acidacid

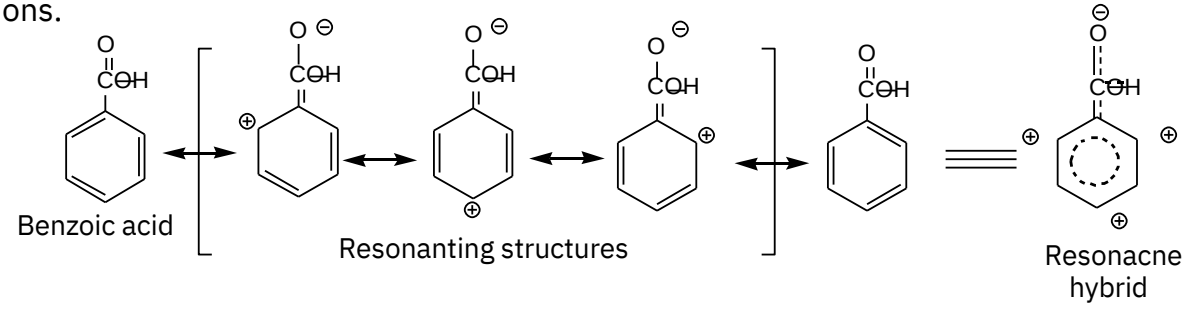
MnO/ 300oC
CH3COCH3 + CO2 + H2OFormation of carbonyl compound
Propanone
(Acetone)

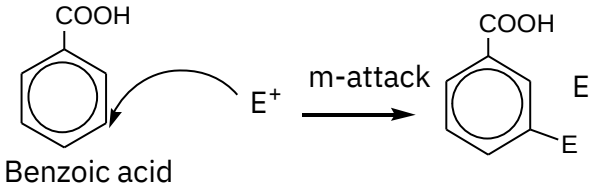
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Electrophilic Substitution Reaction of Benzoic acid

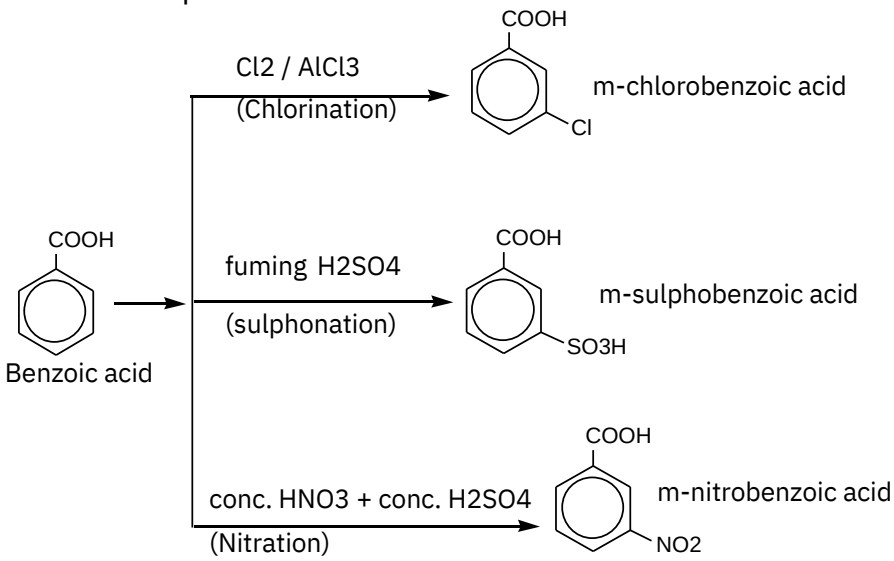
–COOH group is meta directing group. Due to resonance in benzoic acid, electron density decreases more at ortho and para positions as compared to meta position. Hence, the incoming electrophile will prefer to attack the meta position during the electrophilic substitution reactions.





E+ = electrohile (e.g. Cl+, NO+2, SO3, etc

Some examples of electrophilic substitution reaction are as follows:



Uses of Benzoic acid

Salt of benzoic acid i.e. sodium benzoate is used as food preservatives.

Esters of benzoic acid are used in perfumery.

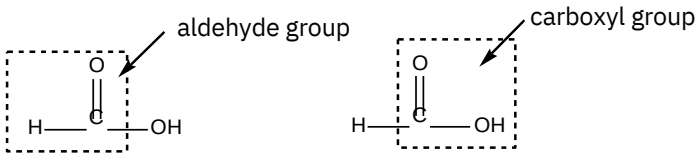
Used in organic synthesis (dyes, drugs).



Aspirin
(Analgesics & antipyretic drug)

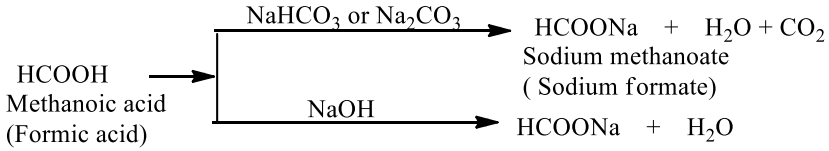
Formic acid (Methanoic acid)

Formic acid differs from other carboxylic acid because it contains both carboxyl group (–COOH) and aldehyde (–CHO) group. So, it behaves as both acid as well as aldehyde.

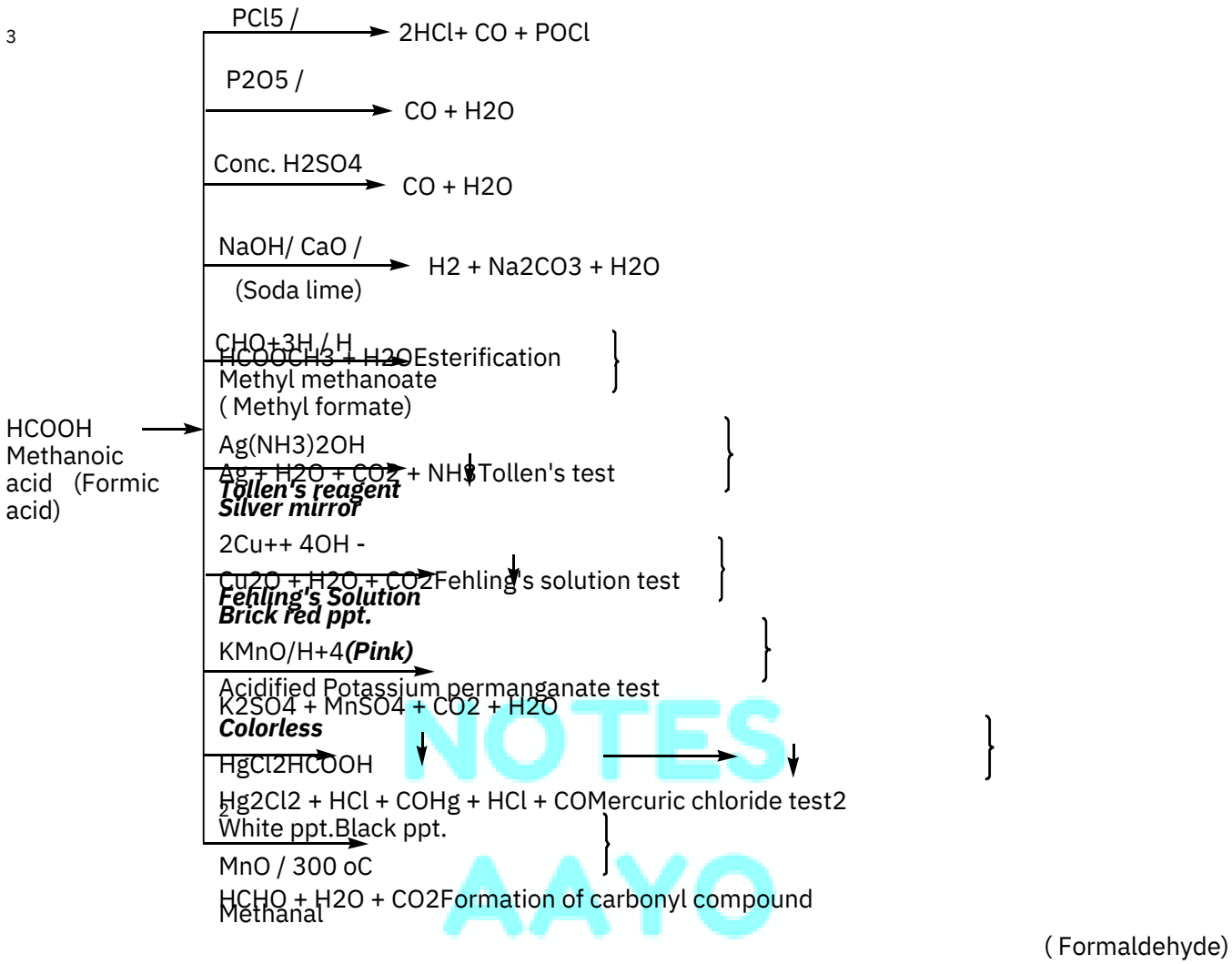


Methanoic acid (Formic acid)

Acidic Nature:



Abnormal behavior of Methanoic acid (or Formic acid):



NOTES
AAYO

Difference between properties of HCOOH & CH3COOH

3 HCOOH	CHCOOH
1. Gives positive Tollen's test	1.Does not gives positive Tollen's test
2. Gives positive Fehling solution test	2.Does not give positive Fehling solution test
3. Reacts with acidified KMnO4	3.Does not reacts with acidified KMnO4
4. Gives CO & H2O When heated with P2O5	4. Gives ethanoic anhydride or acetic anhydride when heated with P2O5
5. Gives CO & H2O when reacts with conc. H2SO4	5. Does not reacts with conc. H2SO4

USES:

1. Formic acid is used in leather tanning, textile industry for dying process,
2. It is used in preparation of carbon monoxide.
3. It is used in medicine for treatment of gout.
4. Acetic acid is used in plastic and rubber industries, as coagulant in manufacture of rubber from latex and casein from milk, as vinegar, as solvent.

Past Questions

Q.1*. Write an example of Decarboxylation reaction.*

Q.2.*What happens when ethanoic acid is heated with i) P2O5 ii) Alcohol in presence of H2SO4?*

Q.3*.How does ethanoic acid reacts with i) ethanol ii) PCl5?*

Q.4*.What products are obtained when CH3COOH is allowed to reacts with a) NaOH b) NaOH/CaO c) PCl5 d) P2O5 e) LiAlH4 f) SOCl2 g) HI in presence of red Phosphorous h) passed over heated MnO i) warmed with ethanol in presence of conc. H2SO4?*

Q.5*.Write the suitable chemical reaction to convert ethanoic acid into a) methane b) Methyl ethanoate c) ethanoic anhydride*

Q.6*. Write a chemical test to distinguish ethanoic acid from Methanoic acid.*

Q.7*. Methanoic acid gives Tollen's test but ethanoic acid does not. Give reason.*

Q.8*. How is ethanoic acid distinguished from Methanoic acid?*

Q.9*.What happens when Methanoic acid is warmed with Ammoniacal silver nitrate?*

Q.10*. How would you convert Methanoic acid into ethanoic acid and vice versa?*

Some Organic Conversion

NEB 2072 supp.

$CH_3COOH \xrightarrow{P_2O_5} A \xrightarrow{LiAlH_4} B$

NEB 2070

$NH_3Br/\ aq \longrightarrow \longrightarrow \longrightarrow$ A2. KOHHNO2NaOH / IC2BDE

Compound E produce ethyne when heated with silver powder.

NEB 2069

$NH_3Br \longrightarrow \longrightarrow \longrightarrow \longrightarrow$

2/ aq. KOHHNO2KMnO4/ H

A B C D E

Compound E can be obtained by heating oxalic acid in presence of gylcerol.

NEB 2068

$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow{H_2/\ Pd\text{-}BaSO_4} B \xrightarrow{HCN} C \xrightarrow{H_2O/\ H} D$

NEB 2057

i) PCl_5

$\longrightarrow \longrightarrow$ Br2/ NaOHHNO2 $\longrightarrow$

A B C D

ii) NH 3

Compound A is carboxylic acid & calcium salt of A on heating gives acetone.

NEB 2053

SOCl2NH3Br/ KOHNaNO/ HCl

AC22B $\longrightarrow \longrightarrow \longrightarrow \longrightarrow$

D E

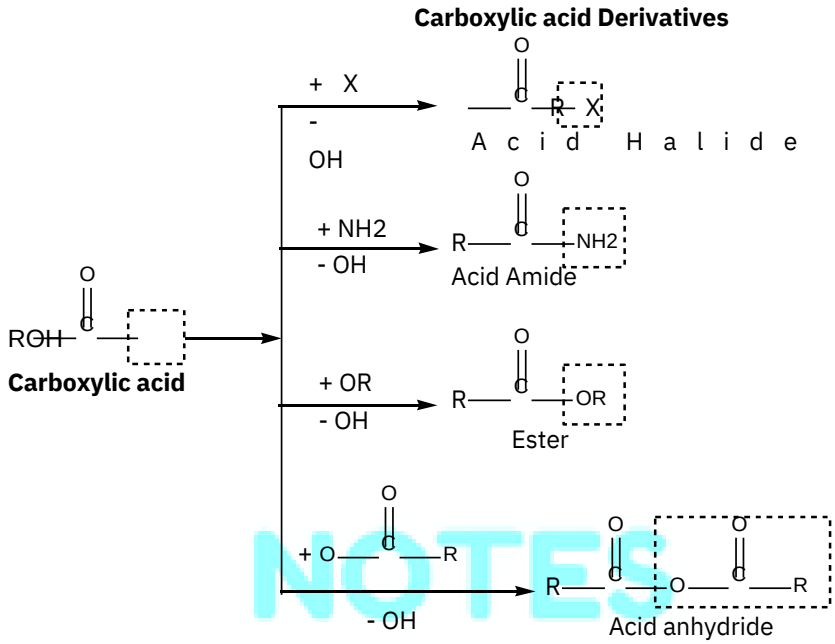
Compound E is primary alcohol which gives positive iodoform test.

Aliphatic and Aromatic Derivatives of Carboxylic Acid

The organic compounds formed by the replacement of –OH group of carboxylic acid by electron rich species like -X (halo), -NH2 (Amino), -OR (Alkoxy) and –OCOR group are known as derivatives of
carboxylic acid.

These derivatives are either aliphatic or aromatic in nature.

i.e.



NOTES AAYO

[A] Acid Halide or Acyl halide

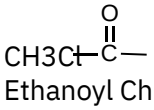
IUPAC Nomenclature:

Functional Group: –COCl

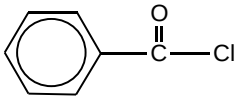
Aliphatic Derivative: “Alkanoyl halide”

Aromatic derivative: “Benzoyl halide”

Examples:

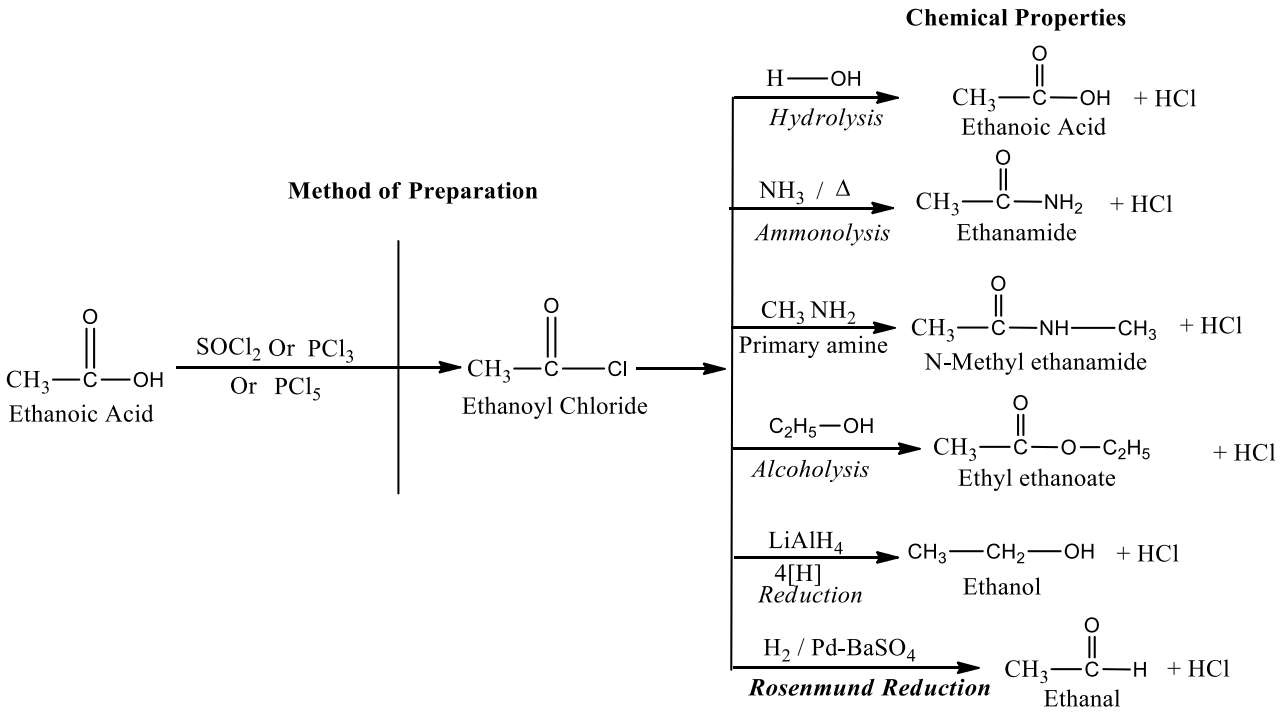


Ethanoyl Chloride
Aliphatic

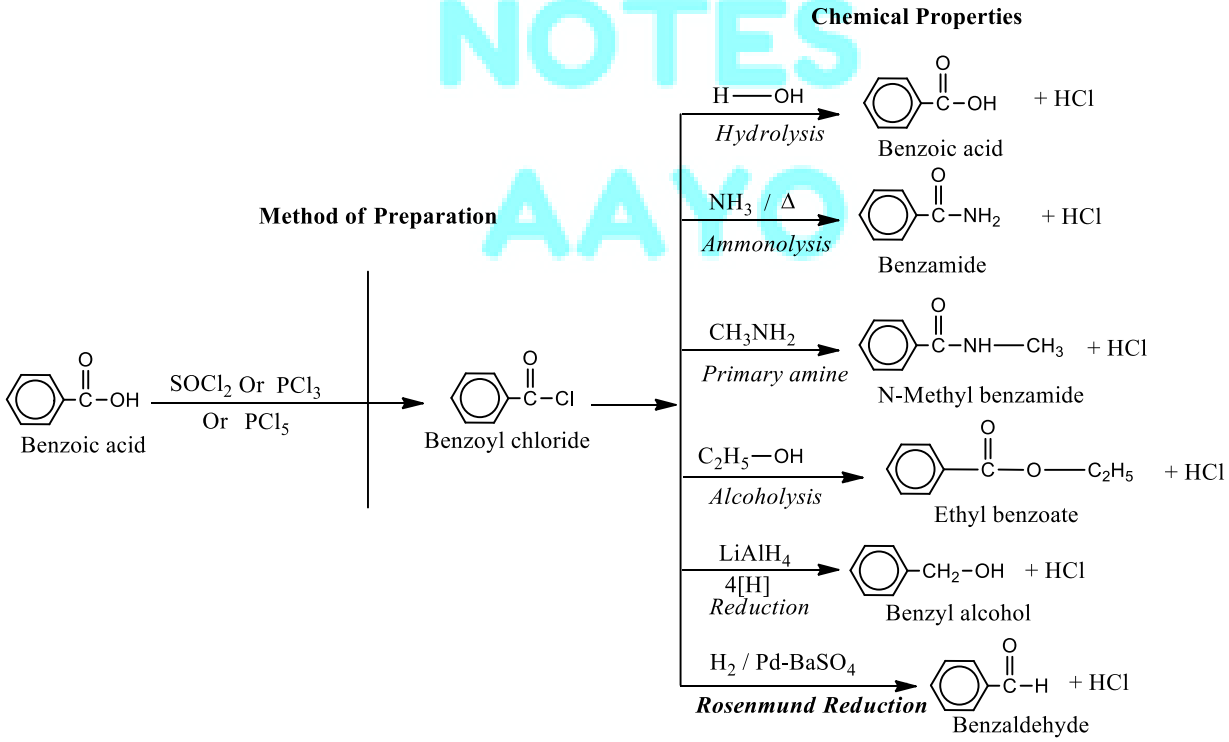


Benzoyl Chloride
Aromatic

Aliphatic Acid halide



Aromatic Acid halide



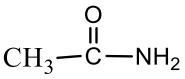
[B] Acid Amides

IUPAC Nomenclature: Functional Group: —C(=O)—NH2

Aliphatic Derivative: “Alkanamide”

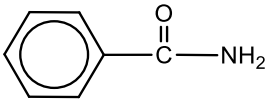
Aromatic derivative: “Benzamide”

Examples:



Ethanamide

Aliphatic

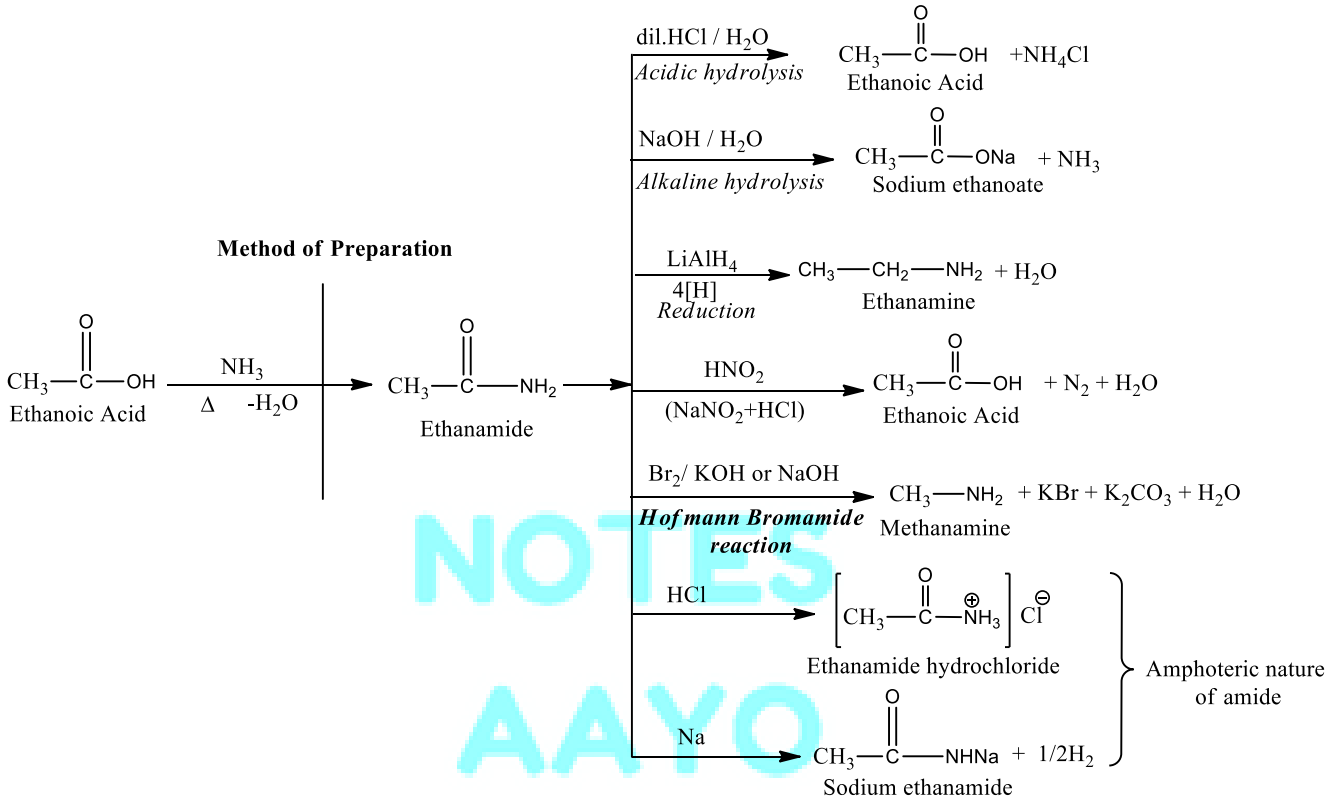


Benzamide

Aromatic

Aliphatic Acid Amide

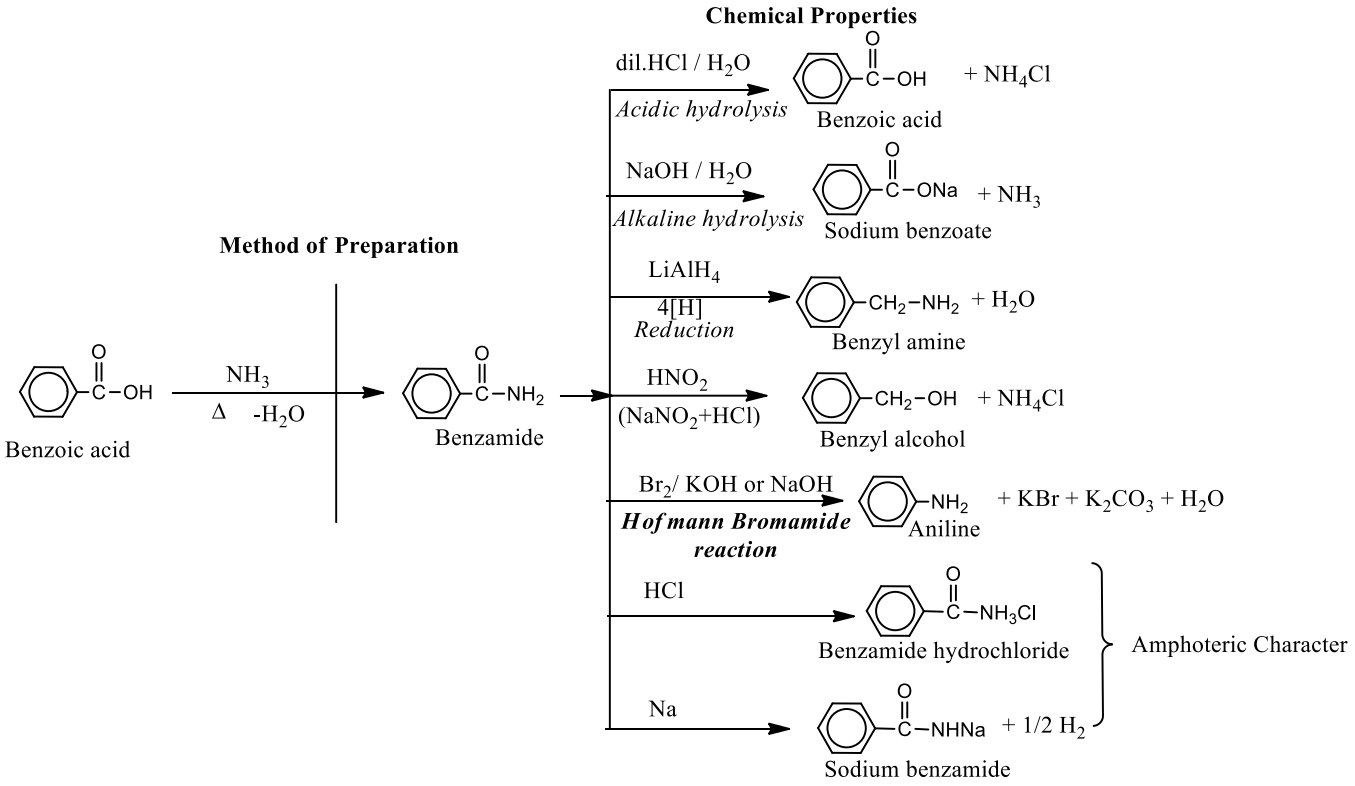
Chemical Properties



NOTES AAYO

Aromatic Acid Amide

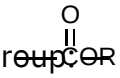
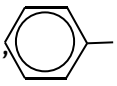
Chemical Properties



[C] Esters

IUPAC

Nomenclature:

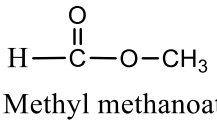
Functional Group  Where R = CH3, C2H5,  etc.

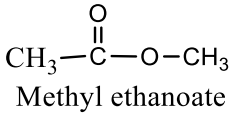
Secondary suffix: -oate

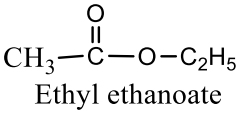
Aliphatic Derivative: "..... alkanaote"

Aromatic derivative: ".....benzoate"

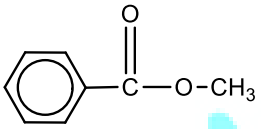
Examples:

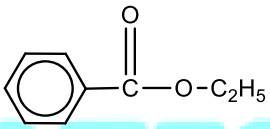

Methyl methanoate

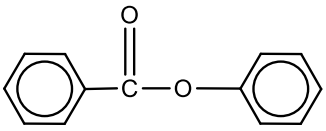

Methyl ethanoate


Ethyl ethanoate

Aliphatic Esters


Methyl benzoate


Ethyl benzoate


Phenyl benzoate

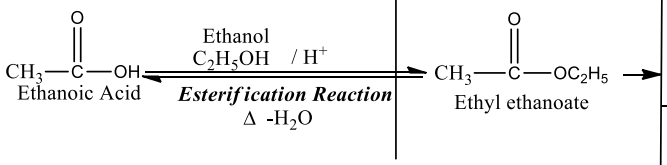
Aromatic Esters

NOTES

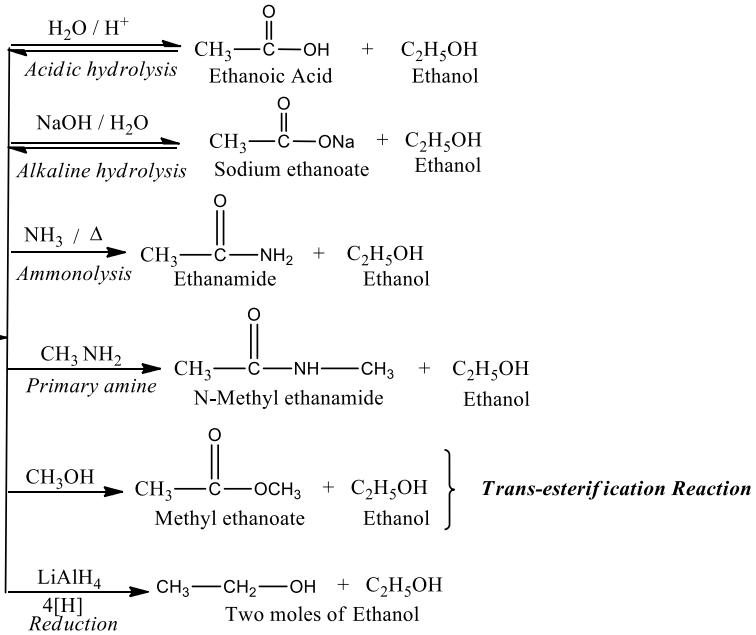
Aliphatic Esters

AAYO

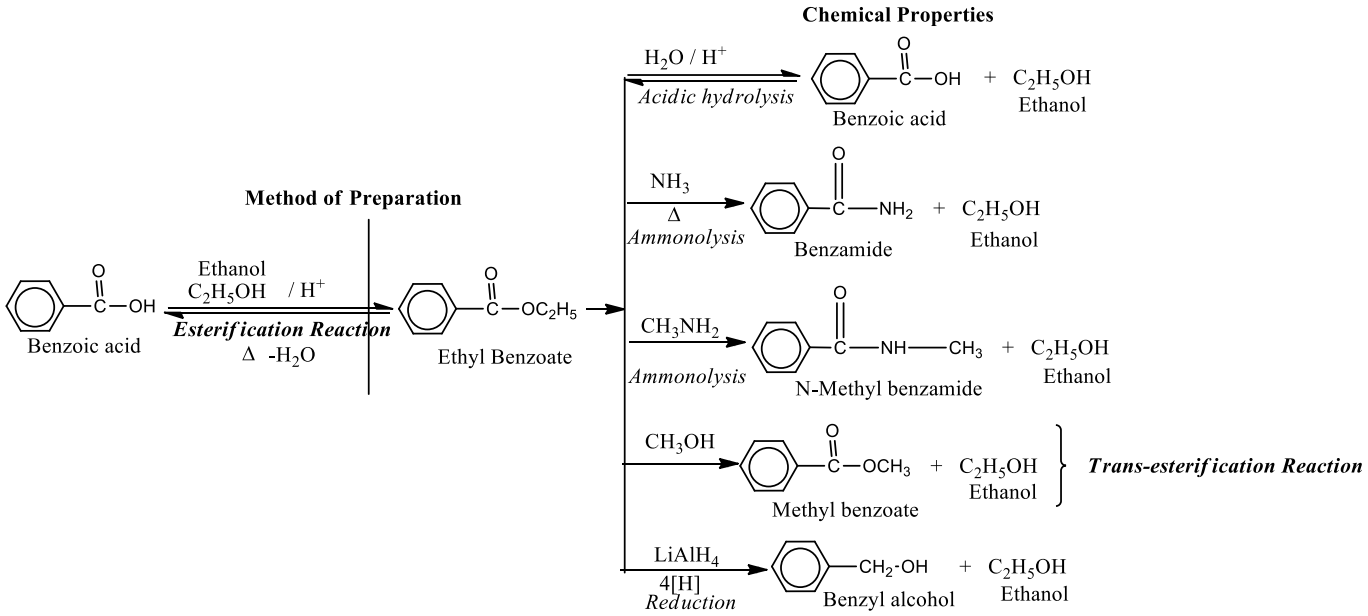
Method of Preparation



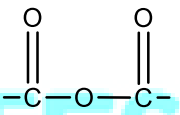
Chemical Properties



Aromatic Esters



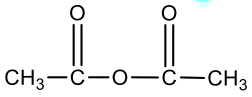
[D] Acid Anhydrides

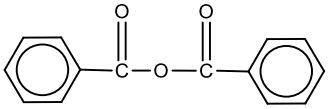
IUPAC Nomenclature: Functional 

Group: Secondary suffix: -oic anhydride

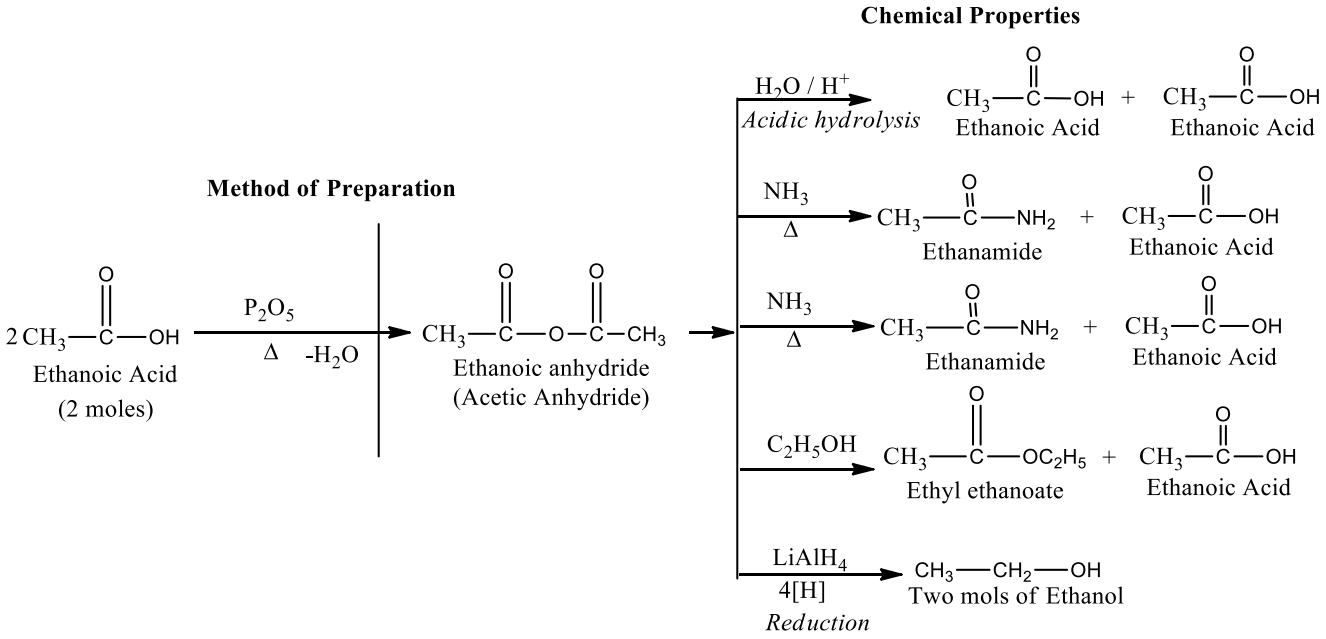
IUPAC Name: "….. oic anhydride"

Examples:


Ethanoic anhydride

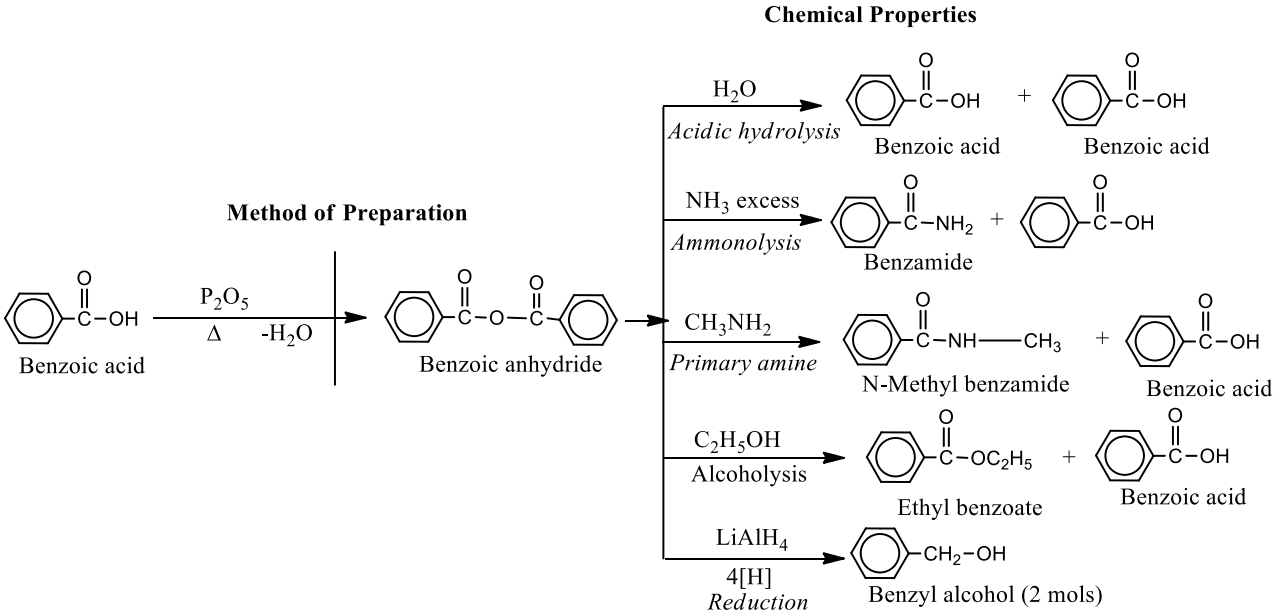

Benzoic anhydride

Aliphatic Acid Anhydride



© NOTES.AAYO TEAM

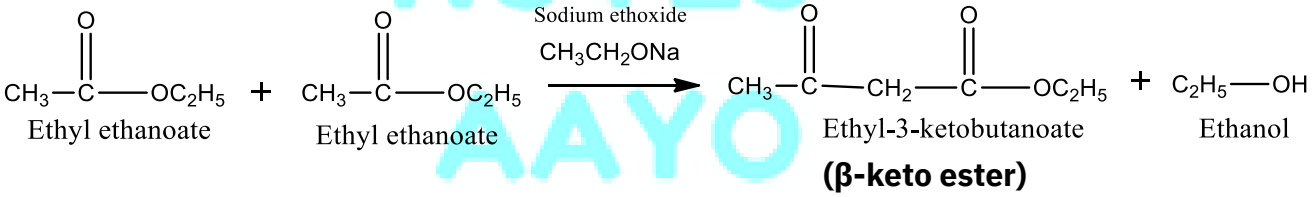
Aromatic Acid Anhydride



Claisen Condensation

When α-hydrogen containing esters undergoes condensation reaction in presence of strong base like sodium ethoxide, then β-keto ester is formed. This reaction is called Claisen condensation reaction.

For example:



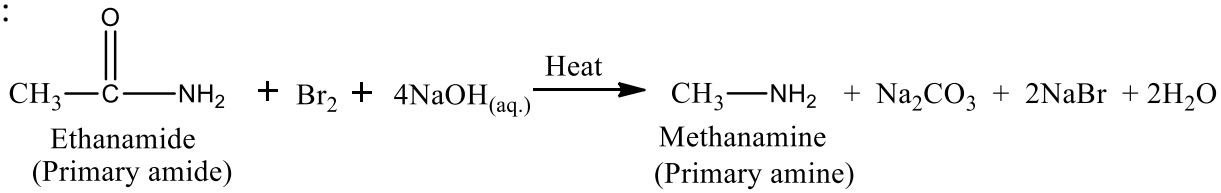
(β-keto ester)

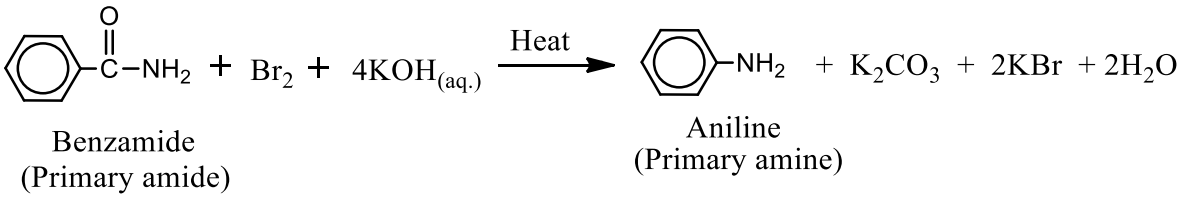
Hofmann-Bromamide reaction(Decarbonylation reaction)

When primary amide is heated with bromine in presence of aqueous NaOH or KOH solution, then primary amine is formed having one carbon less than parent amide. This reaction is called Hofmann-Bromamide reaction.

In this reaction, carbonyl group is removed during the reaction. Thus, this reaction is also called **decarbonylation reaction**.

Example:





Note: This reaction is used to decrease the carbon chain by one carbon atom.

Comparative Study of Physical Properties of Acid Derivatives

S.N	Physical Properties	Acid Chlorides	Amides	Esters	Anhydrides
1	**State/Color/ Odour**	Lower members are colourless liquids and higher members are colourless solids having irritating odour.	Formamide is liquid but other members are colourless, odourless crystalline solids.	Lower members are colourless pleasant smelling liquids while higher members are colourless, smell odourless solids.	Lower aliphatic members are colourless liquids with sharp irritating while aromatic members are colourless solids.
2	**Boiling Point**	Lower b.pt. than parent acid due to absence of intermolecular H-bonds.	Higher b.pt. than parent acid due to presence of strong intermolecular H-bonds.	Lower b.pt. than parent acid due to absence of intermolecular H-bonds.	Higher b.pt. than parent acid due to larger size and greater van der Waal's force of attraction.
3	**Solubility in water**	Insoluble in water but slowly dissolves due to hydrolysis.	Lower amides are soluble in water due to formation of intermolecular H-bond between amide and water molecules.	Generally insoluble in water. They are themselves excellent solvent.	Generally insoluble in water.

NOTES AAYO

Relative reactivity of Acid derivatives

The reactivity order of acid derivatives towards nucleophilic substitution follows the order;

