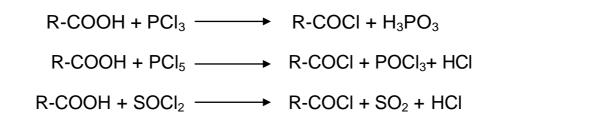
# CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT Based Notes of Chapter - 11) GANESH KUMAR DATE:- 12/11/2020

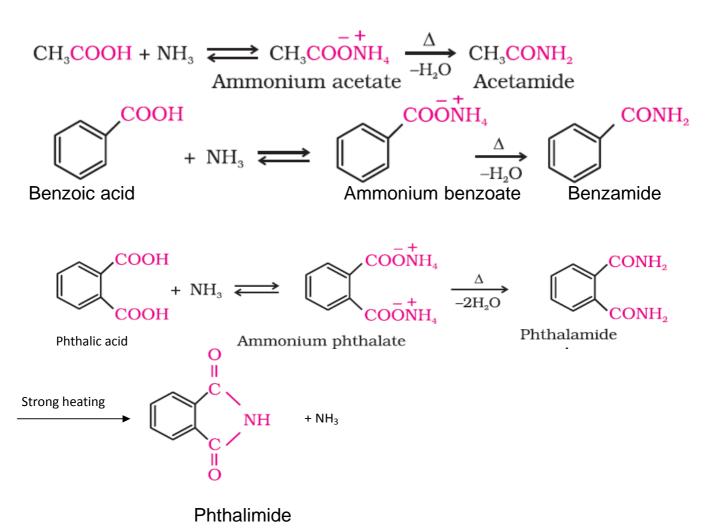
# Aldehyde, Ketones and Carboxylic Acid

3. Reactions with PCl<sub>3</sub>, PCl<sub>5</sub> and SOCl<sub>2</sub>: Carboxylic acids on treating with PCl<sub>3</sub>, PCl<sub>5</sub> or SOCl<sub>2</sub>, we get acid chlorides. Reaction with thionyl chloride (SOCl<sub>2</sub>) is preferred because the byproducts are gases and are easily escaped from the reaction mixture so that we get pure acid chloride.



**4. Reaction with ammonia**: Carboxylic acids react with ammonia to give ammonium salts which on further heating at high temperature give amides.

 $R-COO^{-}NH_{4}^{+} \xrightarrow{\Delta} R-CONH_{2} + H_{2}O$ 



## C. Reactions Involving –COOH Group

 Reduction: Carboxylic acids when reduced with lithium aluminium hydride or with diborane, primary alcohols are formed. Diborane does not reduce functional groups like ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

R-COOH 
$$\xrightarrow{(i) \text{ LiAlH4/ether or B2H6}}$$
 R-CH<sub>2</sub>OH  
(ii) H<sub>3</sub>O<sup>+</sup>  
CH<sub>3</sub>-COOH  $\xrightarrow{(i) \text{ LiAlH4/ether or B2H6}}$  CH<sub>3</sub>-CH<sub>2</sub>OH  
(ii) H<sub>3</sub>O<sup>+</sup>

#### 2. Decarboxylation:

(i) When sodium salts of carboxylic acid are heated with sodalime (a mixture of NaOH and CaO), they undergo decarboxylation (elimination of CO<sub>2</sub>) to form alkanes.

R-COONa + NaOH  $\xrightarrow{CaO/\Delta}$  R-H + Na<sub>2</sub>CO<sub>3</sub> CH<sub>3</sub>-COONa + NaOH  $\xrightarrow{CaO/\Delta}$  CH<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub>

(ii) Kolbe's electrolysis: When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, we get alkanes having twice the number of carbon atoms that present in the alkyl group of the acid. This reaction is known as Kolbe electrolysis.

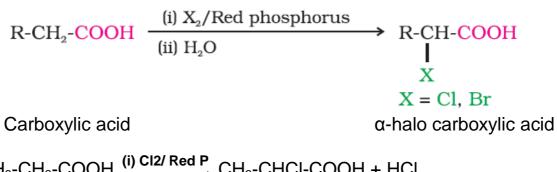
$$2 \text{ R-COOK} + 2 \text{H}_2 \text{O} \xrightarrow{\text{electrolysis}} \text{R-R} + 2 \text{KOH} + \text{H}_2 + 2 \text{CO}_2$$

 $2 \text{ CH}_3$ - COOH + 2 H<sub>2</sub>O  $\xrightarrow{\text{electrolysis}}$  CH<sub>3</sub>-CH<sub>3</sub> + 2KOH + H<sub>2</sub> + 2CO<sub>2</sub>

### D. Substitution Reactions in the Hydrocarbon Part:

#### 1. Halogenations [HVZ Reaction]

Carboxylic acids having an  $\alpha$ -hydrogen atom, when treated with halogen (chlorine or bromine) in the presence of red phosphorus, we get  $\alpha$ -halocarboxylic acids. This reaction is known as Hell-Volhard-Zelinsky(HVZ) reaction.



 $CH_{3}-CH_{2}-COOH \xrightarrow{(i) Cl2/ Red P} CH_{3}-CHCI-COOH + HCI$   $(ii) H_{2}O$ 

Propanoic acid 2-chloropropanoic acid

This reaction is synthetically important since the halogen atom

can be replaced by other groups.

### 2. Electrophilic substitution reactions:

The –COOH group is a deactivating group and meta-directing. So on electrophilic substitution reactions, we get meta derivatives.



But carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group to form salts.

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