Carboxylic Acid Synthesis and Reactions

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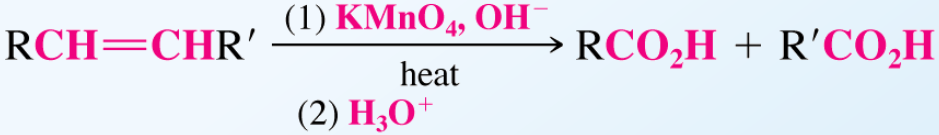
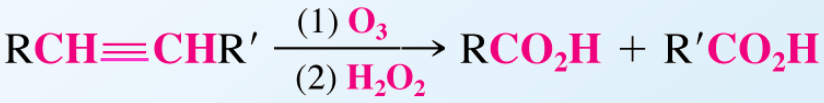
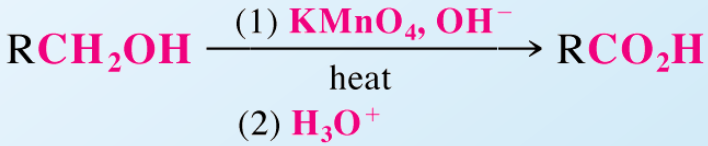
Synthesis of Carboxylic Acids

1) By Oxidation of Alkenes and Alkynes

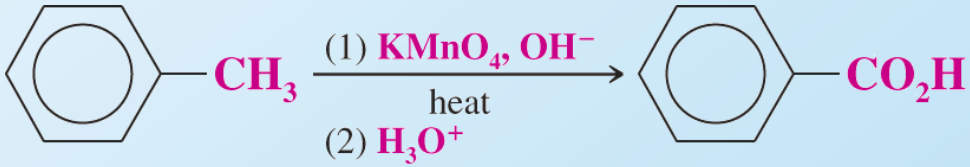




2) By Oxidation of Aldehydes and Primary Alcohols

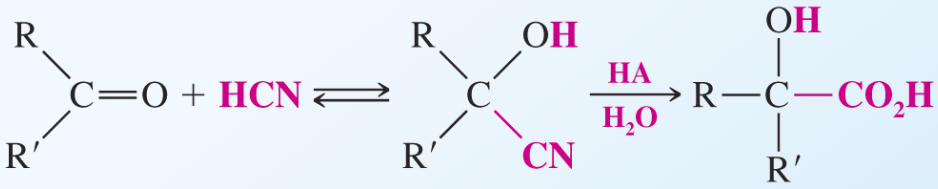


3) By Oxidation of Alkylbenzenes



Hydrolysis of Nitriles

4) By Hydrolysis of Cyanohydrins and Other Nitriles



$$HOCH_2CH_2Cl \xrightarrow[(80\%)]{NaCN} HOCH_2CH_2CN \xrightarrow[(2)\ H_3O^+\ (75\text{–}80\%)]{(1)\ OH^-,\ H_2O} HOCH_2CH_2CO_2H$$

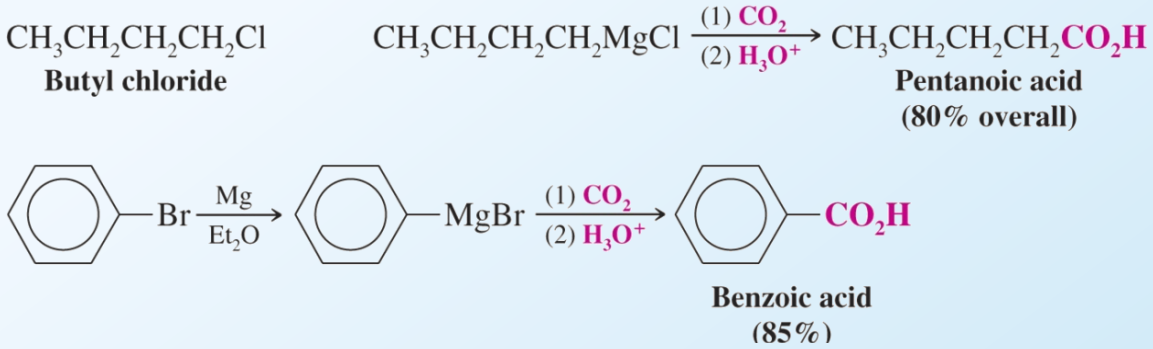
3-Hydroxypropanenitrile — 3-Hydroxypropanoic acid

$$BrCH_2CH_2CH_2Br \xrightarrow[(77\text{–}86\%)]{NaCN} NCCH_2CH_2CH_2CN \xrightarrow[(77\text{–}86\%)]{H_3O^+} HO_2CCH_2CH_2CH_2CO_2H$$

Pentanenitrile — Glutaric acid

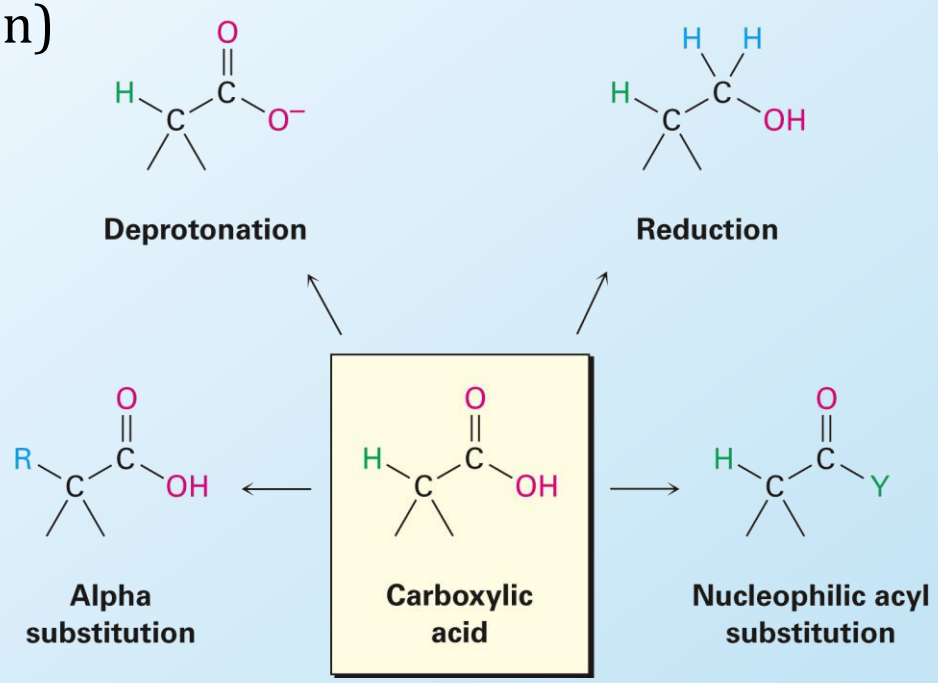
From Grignard Reactions

5) From Carbonation of Grignard Reagent



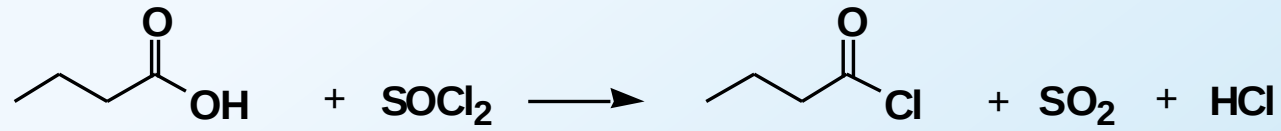
Reactions of Carboxylic Acids

- Acid – base reaction (see intro power point)
- Nucleophilic additions, just like all carbonyls.
- In some conditions carboxylic acids can also undergo nucleophilic substitution where – OH is the leaving group.
- Reactions can also occur on the alpha carbon (carbon next to carbonyl carbon)



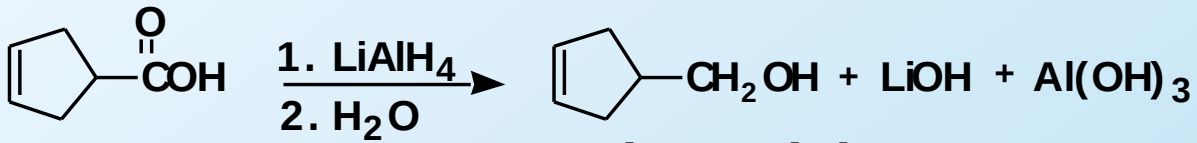
Reactions of Carboxylic Acids

1) **Acid chlorides** are most often prepared by treating a carboxylic acid with thionyl chloride or PCl_3 or PCl_3.



Butanoic acid Thionyl chloride Butanoyl chloride

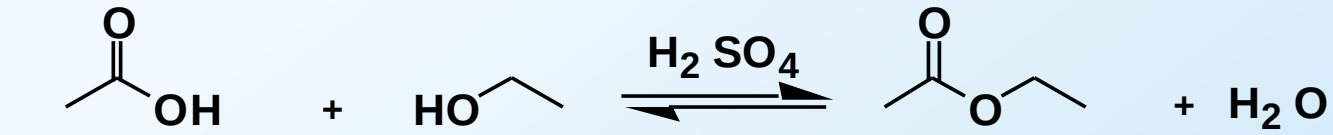
2) **Reduction**: Lithium aluminum hydride reduces a carboxyl group to a 1° alcohol. Usually done by converting acid to acyl chloride first.



4-Hydroxymethyl-cyclopentene

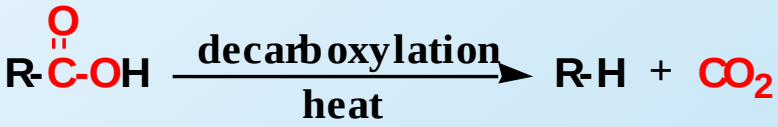
Reactions of Carboxylic Acids

3) **Esterification**: Esters can be prepared by treating a carboxylic acid with an alcohol in the presence of an acid catalyst, commonly H_2SO_4 or gaseous HCl. (Mechanism will be covered later.)



Ethanoic acid (Acetic acid) + **Ethanol (Ethyl alcohol)** → **Ethyl ethanoate (Ethyl acetate)** + H_2O

4) **Decarboxylation**: loss of CO_2 from a carboxyl group. Most carboxylic acids, if heated to a very high temperature, undergo thermal decarboxylation.



Key Concepts

- Synthesis
  - Oxidations
  - Hydrolysis of nitriles
  - Carboxylation using Grignard
- Reactions
  - Acid base reactions
  - Reductions
  - Esterification