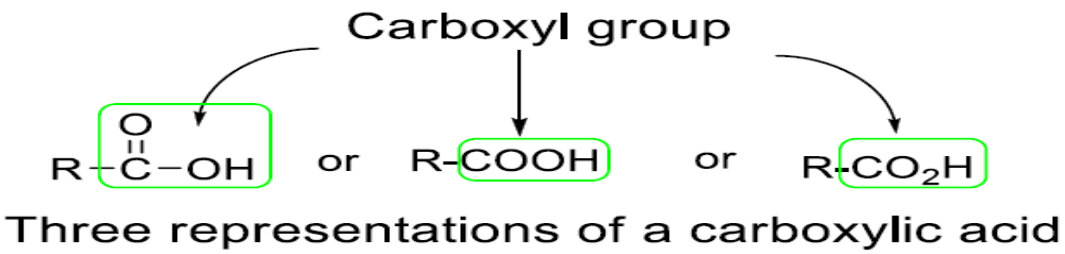
Chapter 6

Carboxylic Acids

1. Structure

Carboxylic acids are organic compounds containing the carboxyl group (-COOH), where in the hydroxyl group (-OH) is directly attached to the carbonyl (C=O) group.



Three representations of a carboxylic acid

Nomenclature of Carboxylic Acids

The common names of some basic carboxylic acids are derived from Latin names that indicate the first original natural source of the carboxylic acid.

Structure of Acid	Natural Source	Common Name
$H-\overset{O}{\overset{\|}{C}}-OH$	Ants (Formica)	Formic acid
$CH_3-\overset{O}{\overset{\|}{C}}-OH$	Vinegar (Acetum)	Acetic acid
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH$	Basic Fat (Propio)	Propionic acid
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$	Rancid butter (Butyrum)	Butyric acid
$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$	Present in aValerian herb	Valeric acid
$CH_3CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$	Goat (Caper)	Caproic acid

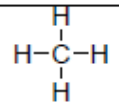
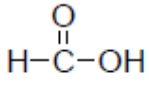
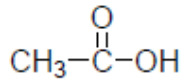
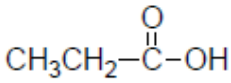
Common Names of Carboxylic Acids

The common name of a carboxylic acid (R-COOH) is derived by adding the suffix–**ic acid** to a prefix representing the chain length of the carboxylic acid.

# of Carbons	Prefix	Common Name of Acid
1	Form-	Formic acid
2	Acet-	Acetic acid
3	Propion-	Propionic acid
4	Butyr-	Butyric acid
5	Valer-	Valeric acid
6	Capro-	Caproic acid
Aromatic acid	Benzo-	Benzoic acid

IUPAC Nomenclature of Aliphatic Carboxylic Acids

IUPAC names of straight chain aliphatic carboxylic acids are derived by adding the suffix **–oic acid** to the systematic name of the parent hydrocarbon. They are named as alkanoic acids.

# of Carbons	Structure & IUPAC Name of Alkane	Structure & IUPAC Name of Acid
1	 Methane	 Methanoic acid
2	CH_3-CH_3 Ethane	 Ethanoic acid
3	$CH_3CH_2-CH_3$ Propane	 Propanoic acid

Systematic Nomenclature of Substituted Carboxylic Acids

The systematic names of substituted aliphatic carboxylic acids are derived by:

(i) First identifying the parent chain that contains most, if not all, the carboxyl groups.

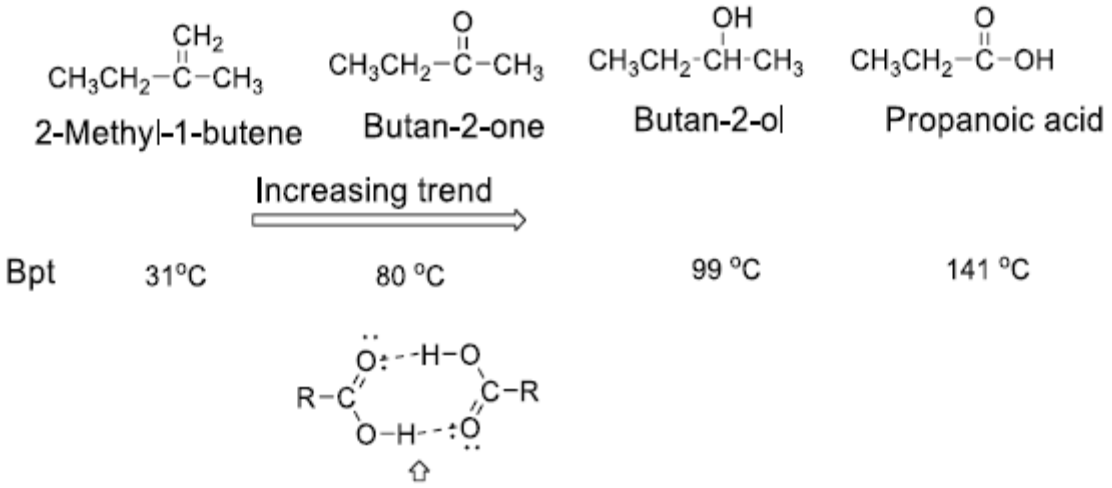
(ii) Number the parent chain from the carbon of the carboxyl group i.e the carboxyl carbon is C-1.

(iii) Identify the substituents and assign each substituent a locator/address number (2,3,4…etc.) consistent with the numbering in the parent chain.

(iv) Arrange the names of the substituents in alphabetical order in the systematic name of the poly-substituted carboxylic acid.

Physical properties of Carboxylic Acids

The physical properties of carboxylic acids can be explained from the perspective of the bond polarization in the carboxyl group and its capacity to engage in hydrogen-bonding. Carboxylic acids boil at considerably higher temperatures than alcohols, ketones, or aldehydes of similar molecular weight.

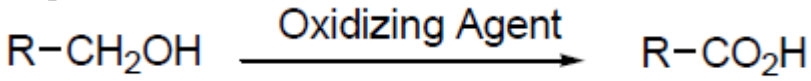


The high boiling point of carboxylic acids is attributed to their capacity to readily form stable, hydrogen-bonded dimers.

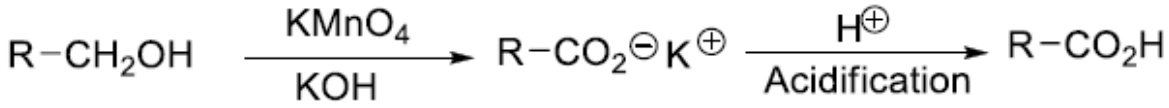
Preparation of Carboxylic Acids

1. Oxidation of Primary Alcohols

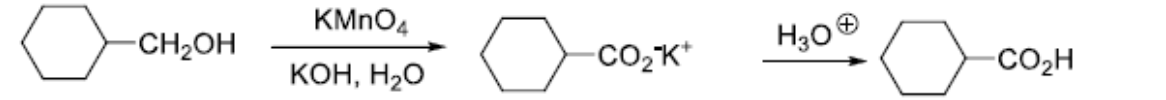
The synthesis of carboxylic acids requires the generation or incorporation of the carboxyl group in a substrate.



The best conditions for the oxidation of primary alcohols to carboxylic acids is under the basic conditions employing potassium permanganate.



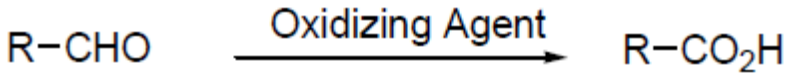
Example



Cyclohexylmethanol

Cyclohexanecarboxylic acid

2. Oxidation of Aldehydes



Aldehydes can be oxidized to carboxylic acids by a variety of oxidizing agents. Both strong and mild oxidizing agents may be employed successfully.

Strong Oxidizing Agents

(a) CrO_3
Oxidations in water or dilute mineral acid

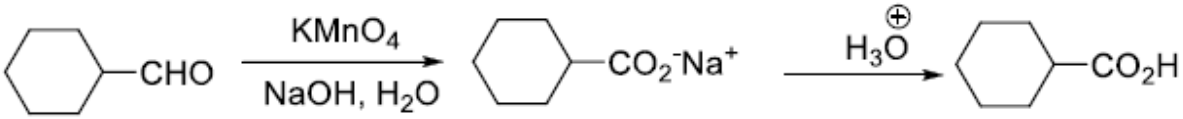
(b) $Na_2Cr_2O_7$ or $K_2Cr_2O_7$
Oxidation in dilute mineral acid

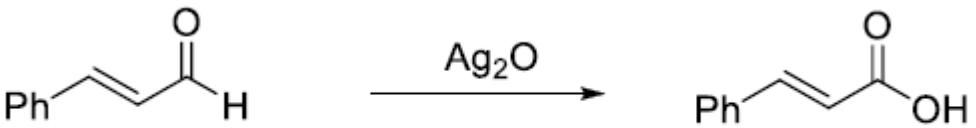
(c) $KMnO_4$
Oxidations in basic media in the presence of KOH

Mild Oxidizing Agents

(a) Ag_2O

Note that Ag_2O does not oxidize alcohols

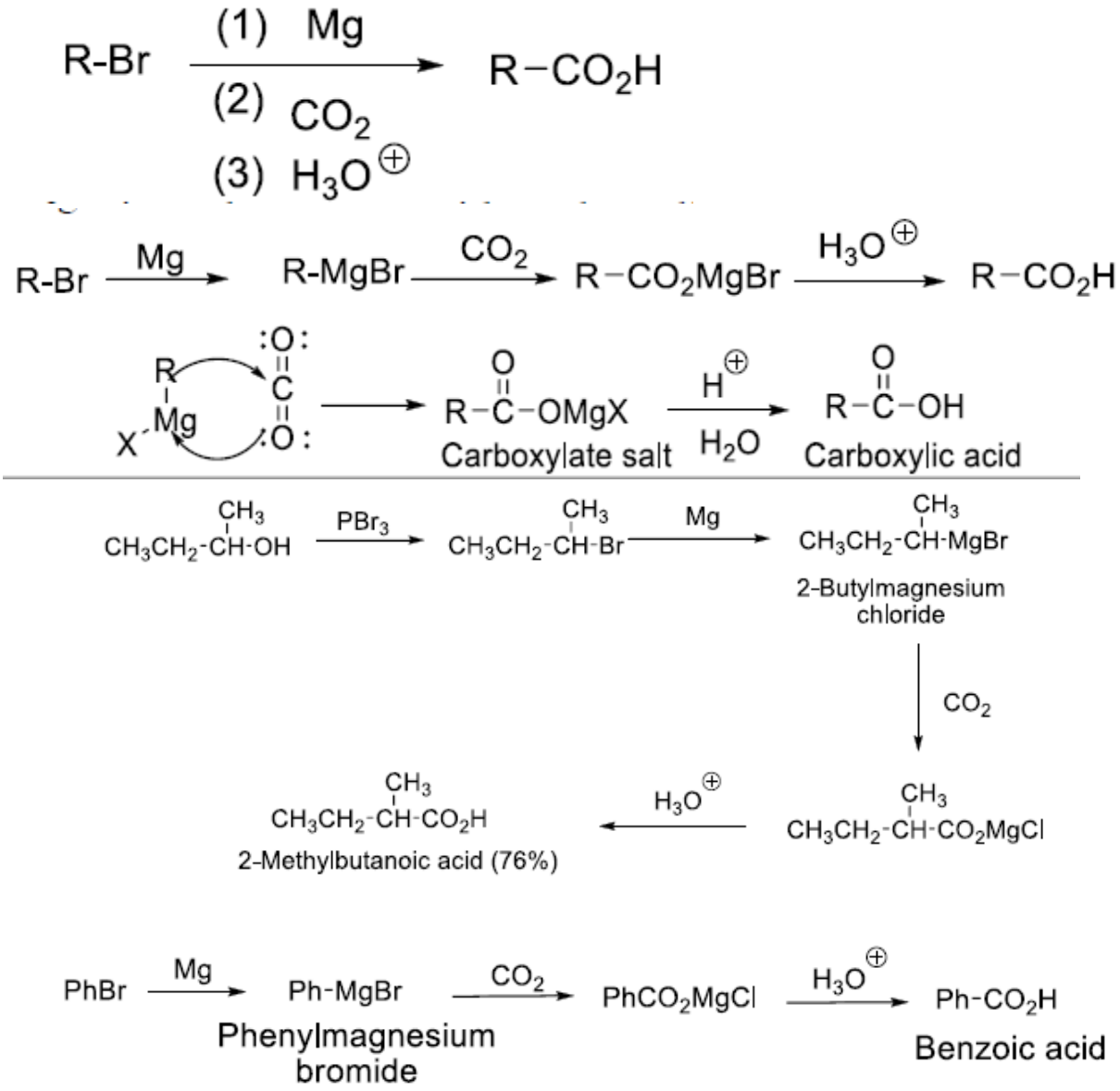




Cinnamaldehyde

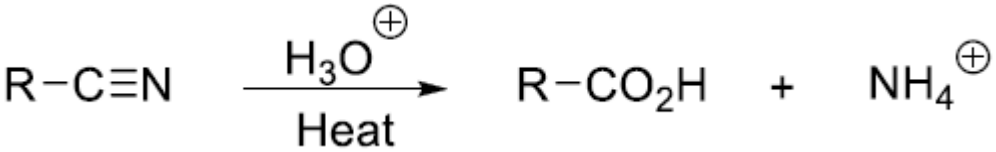
Cinnamic acid

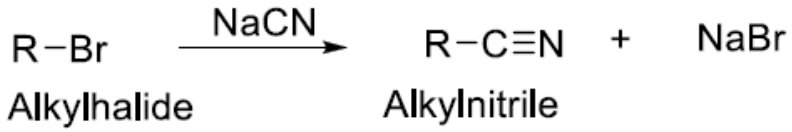
3. Carboxylation of Grignard Reagents



4. Hydrolysis of Nitriles

Acid-catalyzed hydrolysis of nitriles provides carboxylic acids.





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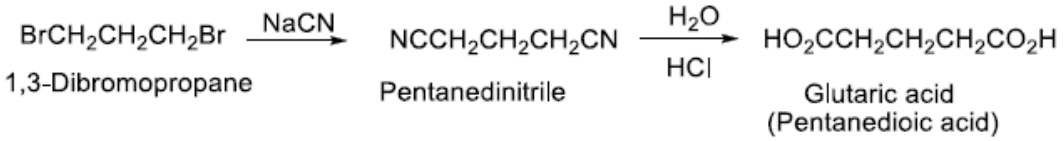
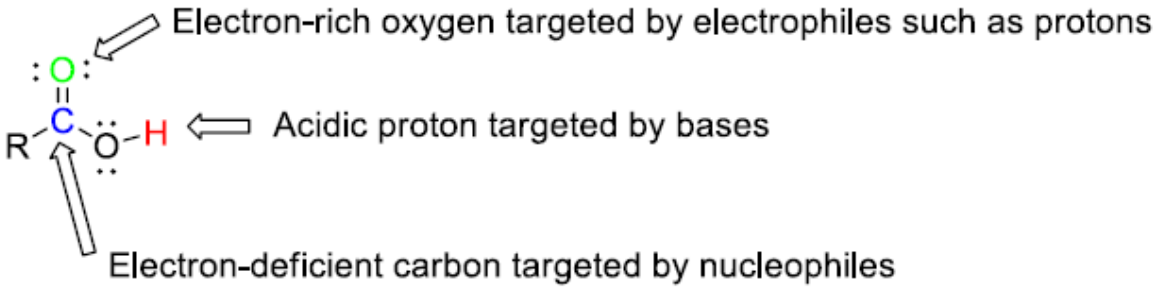


Reactions of Carboxylic Acids

The reactions of carboxylic acids can be directed to various sites on the carboxyl group.

Reaction sites on the carboxyl group of Carboxylic Acids



Reactions of carboxylic acids can be placed into four categories:

(1) Reactions at the acidic hydrogen on the carboxyl group.

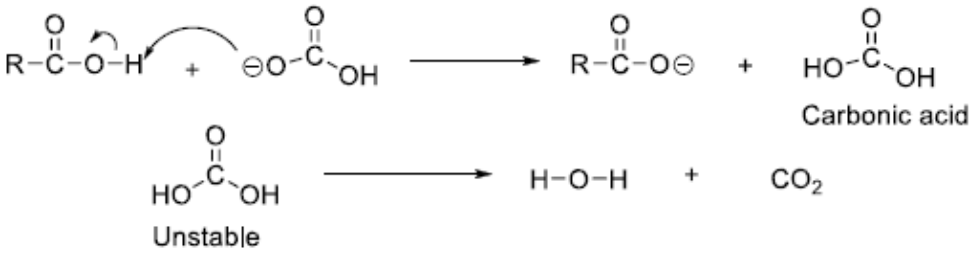
(2) Reactions at the carbonyl group

(3) Reactions at the carboxylate oxygen

(4) Reactions that lead to loss of the carboxyl group as CO_2

a) Reaction of Carboxylic Acids with Sodium Bicarbonate

The most reliable test for carboxylic acids employs $NaHCO_3$ leading to evolution of CO_2. This is commonly called the bicarbonate test for carboxylic acids.



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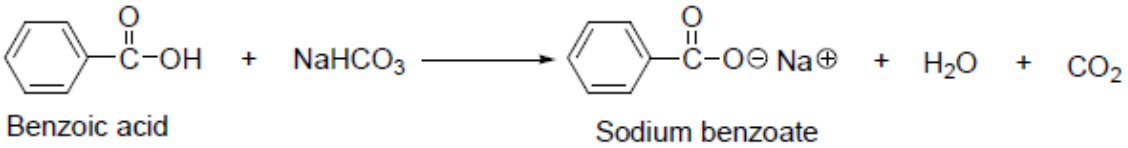
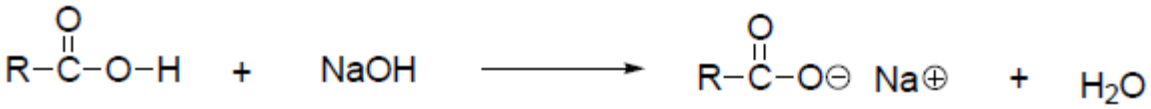
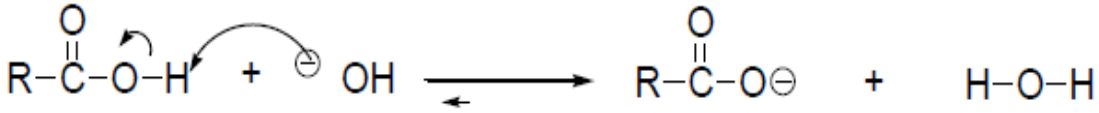


b) Reactions of Carboxylic Acids with Strong Bases



Bases such as metal hydroxides (NaOH and KOH) and amines abstract the acidic proton on carboxylic acids to form carboxylate salts.

Mechanism



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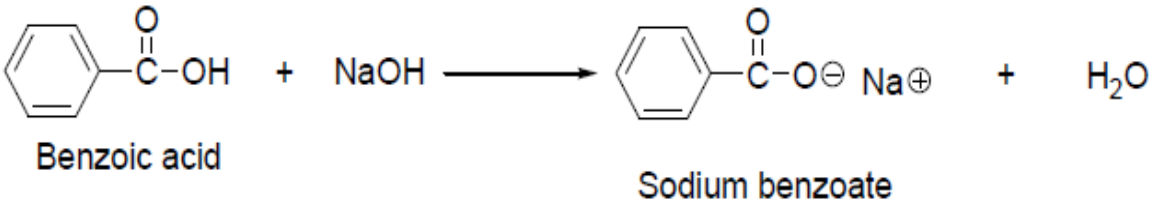
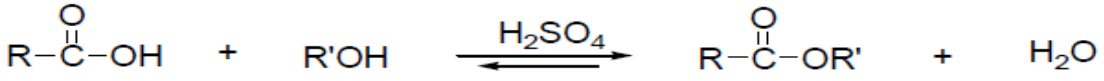


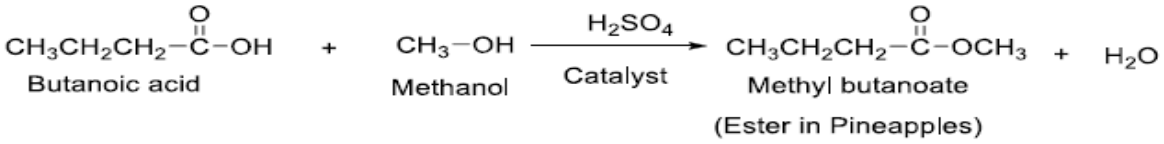
c) Acid-Catalyzed Esterification of Carboxylic Acids

The traditional method for converting carboxylic acids to esters is through an acid-catalyzed esterification in the presence of an alcohol: Commonly referred to as the Fischer esterification.



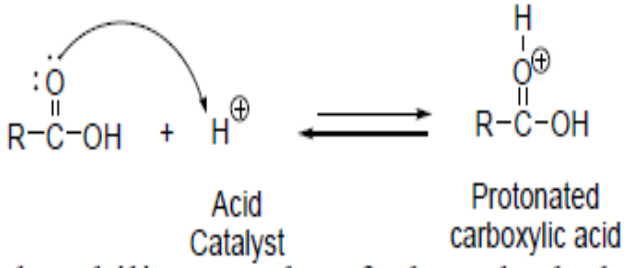
The acid-catalyst can be provided by strong mineral acids such as H_2SO_4, HCl and H_3PO_4 or organic acids such as benzenesulphonic acid or *p*-toluenesulphonic acid.

Example

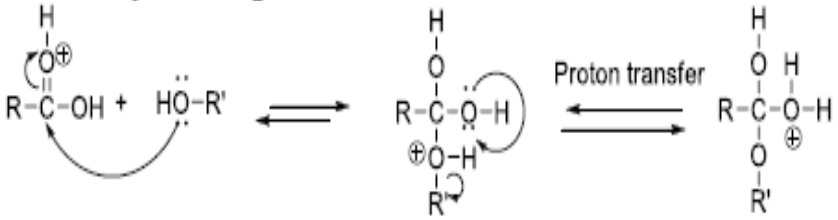


Mechanism of the Acid-Catalysed Esterification of Carboxylic Acids

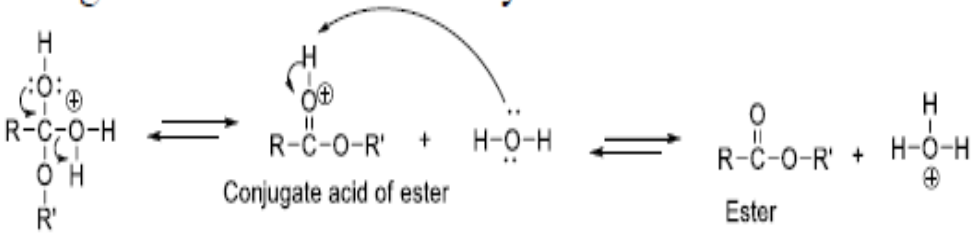
Step 1: Protonation of the carbonyl oxygen of the carboxylic acid (activation of the carbonyl carbon).



Step 2: Nucleophilic attack of the alcohol to the activated carbonyl and proton tranfer



Step 3: Loss of water to give the conjugate acid of the ester and regeneration of acid catalyst.



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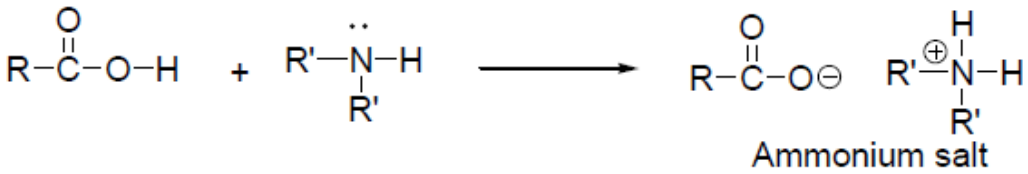
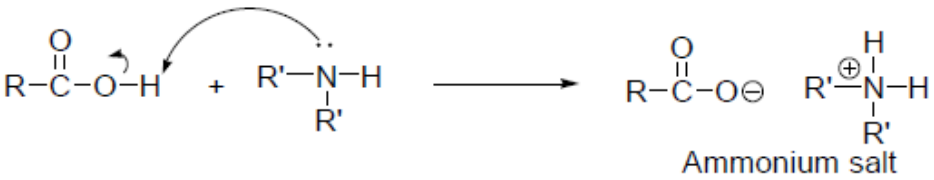
d) Reaction of Carboxylic Acids with Amines

Amines, being organic bases, react with carboxylic acids to form ammonium salts.



Mechanism



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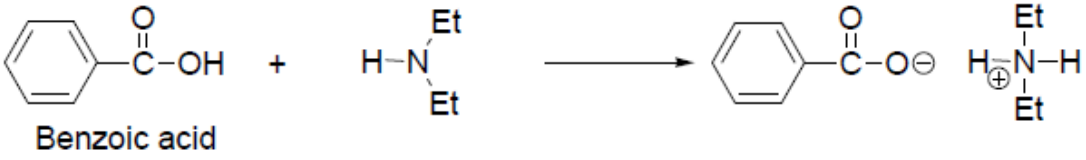
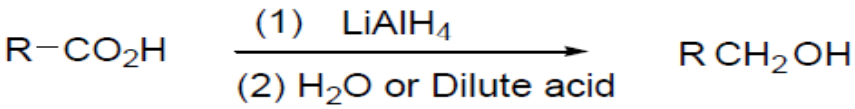


e) Reduction of Carboxylic Acids to Primary Alcohols

Carboxylic acids are reduced to primary alcohols when treated with a strong reducing agent such as $LiAlH_4$.



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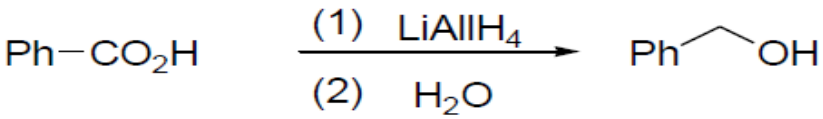

Medium strength reducing agents such as sodium borohydride ($NaBH_4$) that reduce aldehydes and ketones are not sufficiently strong to reduce carboxylic acids.