241 Chem

CH-7

Carboxylic Acids and their derivatives

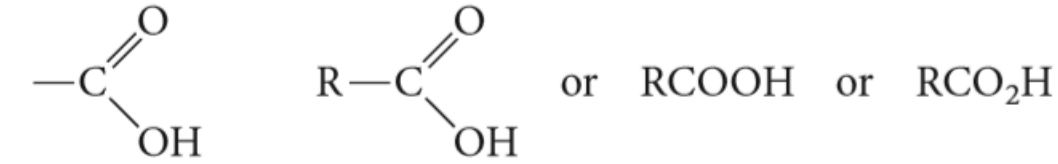
Learning Objectives

By the end of this chapter the student will:

- Structure of Carboxylic Acids and their derivatives
- Nomenclature Carboxylic Acids and their derivatives
- Physical Properties of Carboxylic Acids and their derivatives
- Preparation of Carboxylic Acids and their derivatives
- Reactions of Carboxylic Acids and their derivatives

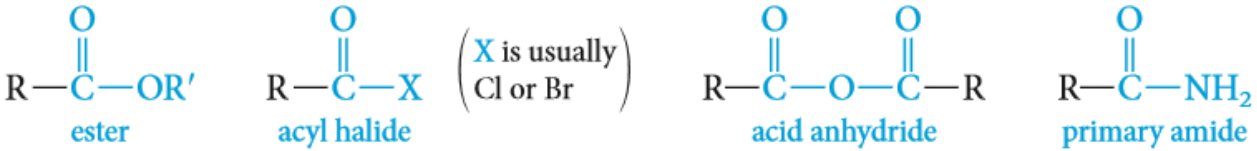
Structure of carboxylic Acids and their derivatives

- The combination of a carbonyl group and a hydroxyl on the same carbon atom is called a carboxyl group
- Carboxylic acids are strong organic acids which contain the carboxyl group.



carboxyl group — three ways to represent a carboxylic acid

- Carboxylic acid derivatives, in which the hydroxyl group of an acid is replaced by other functional groups.



- Carboxylic acids are classified as aliphatic or aromatic depending on whether R or an Ar is attached to the carboxylic group R-COOH or Ar-COOH

Nomenclature of carboxylic Acids

The IUPAC name:

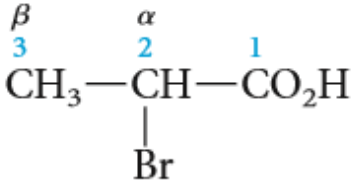
- The root name is based on the longest continuous chain of carbon atoms bearing the carboxyl group.
- The *-e* is replaced by *-oic acid*.
- The chain is numbered starting with the carboxyl carbon atom.
- Cycloalkanes with carboxyl substituents are named as *cycloalkanecarboxylic acids*.

The Common name:

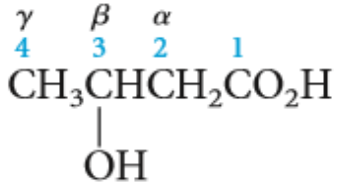
In common names, the positions of substituents are named using Greek letters (α, β, γ , δ…..) beginning with carbon next the carboxyl group.

Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, *formica*)	formic acid	methanoic acid
2	CH_3COOH	vinegar (Latin, *acetum*)	acetic acid	ethanoic acid
3	CH_3CH_2COOH	milk (Greek, *protos pion*, first fat)	propionic acid	propanoic acid
4	$CH_3(CH_2)_2COOH$	butter (Latin, *butyrum*)	butyric acid	butanoic acid
5	$CH_3(CH_2)_3COOH$	valerian root (Latin, *valere*, to be strong)	valeric acid	pentanoic acid
6	$CH_3(CH_2)_4COOH$	goats (Latin, *caper*)	caproic acid	hexanoic acid
7	$CH_3(CH_2)_5COOH$	vine blossom (Greek, *oenanthe*)	enanthic acid	heptanoic acid
8	$CH_3(CH_2)_6COOH$	goats (Latin, *caper*)	caprylic acid	octanoic acid
9	$CH_3(CH_2)_7COOH$	pelargonium (an herb with stork-shaped seed capsules; Greek, *pelargos*, stork)	pelargonic acid	nonanoic acid
10	$CH_3(CH_2)_8COOH$	goats (Latin, *caper*)	capric acid	decanoic acid

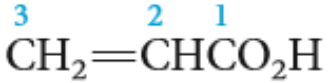
IUPAC name:
Common name:



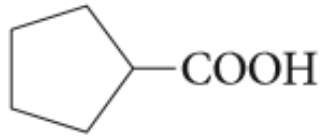
2-bromopropanoic acid
(α-bromopropionic acid)



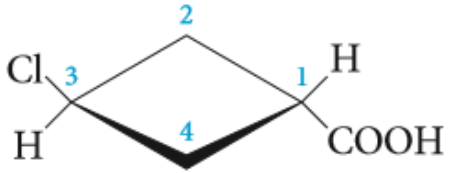
3-hydroxybutanoic acid
(β-hydroxybutyric acid)



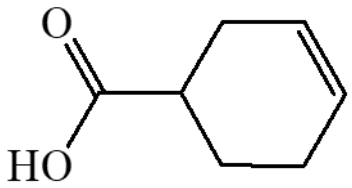
propenoic acid
(acrylic acid)



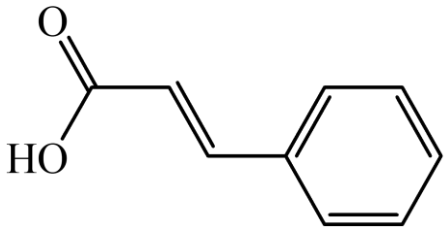
cyclopentanecarboxylic acid



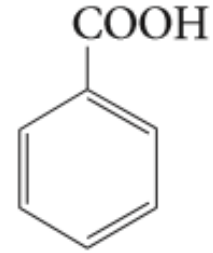
trans-3-chlorocyclobutanecarboxylic acid



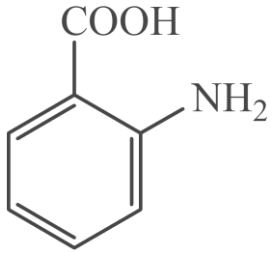
3-Cyclohexenecarboxylic acid



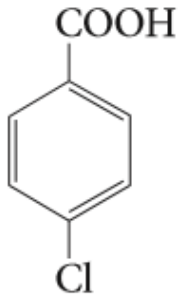
trans-3-Phenylpropenoic acid
(Cinnamic acid)



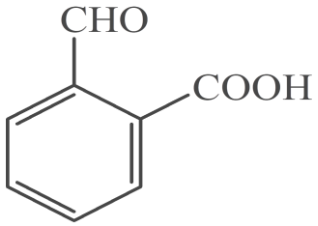
benzoic acid
Benzenecarboxylic acid



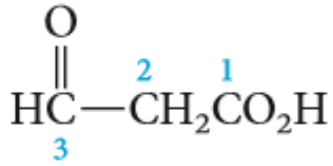
2-Aminobenzoic acid



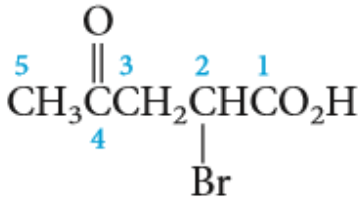
4-chlorobenzoic acid



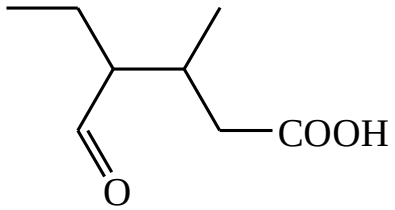
2-Formylbenzoic acid



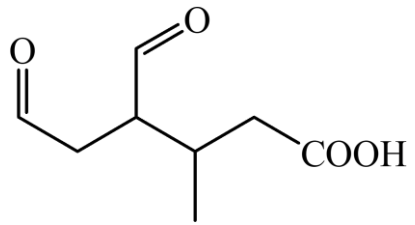
3-oxopropanoic acid



2-bromo-4-oxopentanoic acid



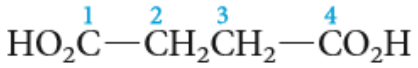
4-Formyl-3-methylhexanoic acid



4-Formyl-3-methyl-6-oxohexanoic acid

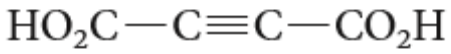
Dicarboxylic Acids:

- Dicarboxylic acids are named as *alkanedioic acids* in the IUPAC system.
- Many dicarboxylic acids occur in nature and go by their common names, which are based on their source.

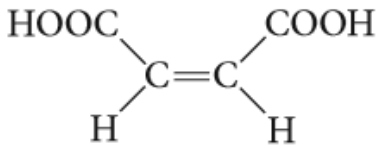


butanedioic acid

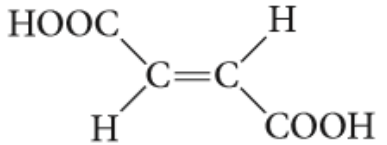
Formula	Common name	Source	IUPAC name
HOOC—COOH	oxalic acid	plants of the *oxalic* family (for example, sorrel)	ethanedioic acid
HOOC—CH_2—COOH	malonic acid	apple (Gk. *malon*)	propanedioic acid
HOOC—$(CH_2)_2$—COOH	succinic acid	amber (L. *succinum*)	butanedioic acid
HOOC—$(CH_2)_3$—COOH	glutaric acid	gluten	pentanedioic acid
HOOC—$(CH_2)_4$—COOH	adipic acid	fat (L. *adeps*)	hexanedioic acid
HOOC—$(CH_2)_5$—COOH	pimelic acid	fat (Gk. *pimele*)	heptanedioic acid



butynedioic acid



and



IUPAC name:

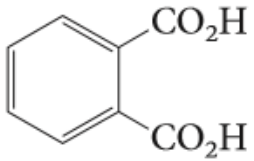
Common name:

cis-2-butenedioic acid

maleic acid

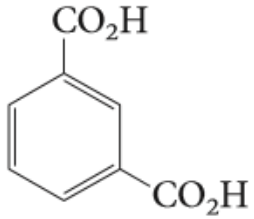
trans-2-butenedioic acid

fumaric acid



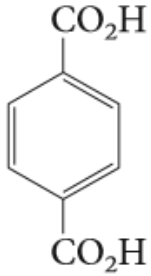
1,2-Benzenedicarboxylic acid

phthalic acid



1,3-Benzenedicarboxylic acid

isophthalic acid



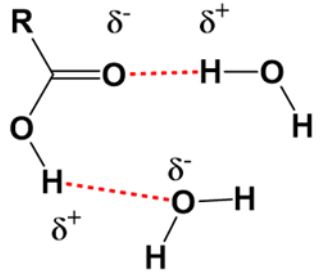
1,4-Benzenedicarboxylic acid

terephthalic acid

Physical Properties of Carboxylic acids

Solubility

- Carboxylic acids interact with water molecules by hydrogen bonding through both the carbonyl and hydroxyl groups. Because of greater hydrogen bonding interactions, carboxylic acids are more soluble in water than are alcohols, ethers, aldehydes, and ketones of comparable molecular weight.

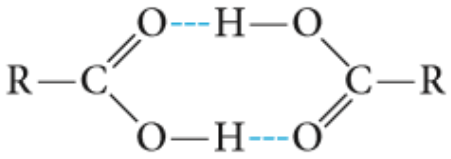


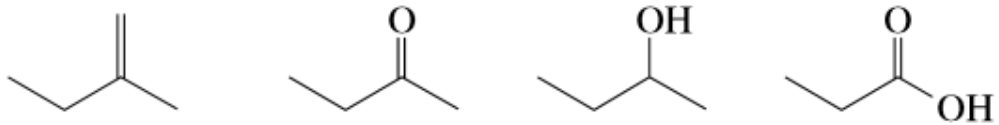
- A carboxylic acid consists of two regions of distinctly different polarity: a polar hydrophilic carboxyl group and, a nonpolar hydrophobic hydrocarbon chain. The hydrophilic carboxyl group increases water solubility; the hydrophobic hydrocarbon chain *decreases* water solubility.
- As the size of the hydrocarbon chain increases relative to the size of the hydrophilic group, water solubility decreases.

Physical Properties of Carboxylic acids

Boiling Point

- Carboxylic acids have significantly higher boiling points than other types of organic compounds of comparable molecular weight, such as alcohols, aldehydes, and ketones.
- The hydroxyl group of one carboxylic acid molecule acts as a proton donor toward the carbonyl oxygen of a second.
- The hydroxyl proton of the second carboxyl function interacts with the carbonyl oxygen of the first. The result is that the two carboxylic acid molecules are held together by two hydrogen bonds. So efficient is this hydrogen bonding that some carboxylic acids exist as hydrogen-bonded dimers even in the gas phase. In the pure liquid a mixture of hydrogen-bonded dimers and higher aggregates is present.



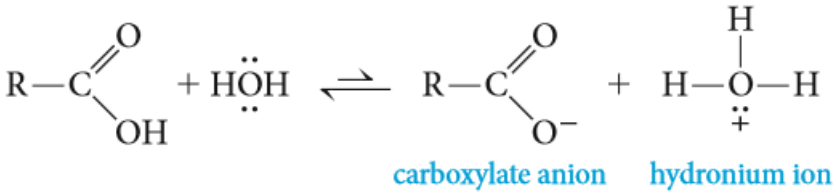


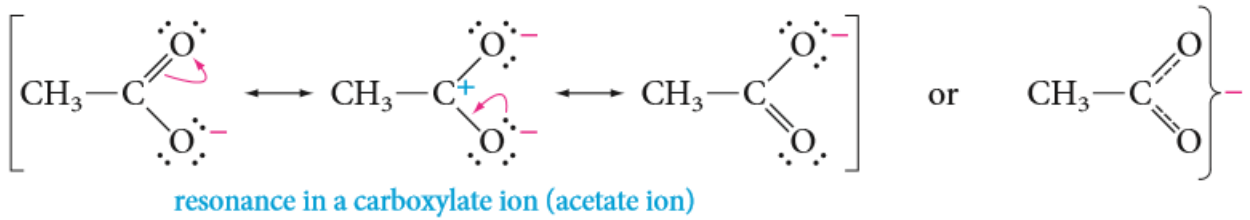
	2-Methyl-1-butene	2-Butanone	2-Butanol	Propanoic acid
bp (1 atm):	31°C	80°C	99°C	141°C

Physical Properties of Carboxylic acids

Acidity

- Carboxylic acids are the most acidic class of compounds, they are much stronger acids than water and alcohols.
- Dissociation of either an acid or an alcohol involves breaking an O-H bond, but dissociation of a carboxylic acid gives a carboxylate ion with the negative charge spread out equally over two oxygen atoms, compared with just one oxygen in an alkoxide ion .This charge delocalization makes the carboxylate ion more stable than the alkoxide ion; therefore, dissociation of a carboxylic acid to a carboxylate ion is less endothermic than dissociation of an alcohol to an alkoxide ion.

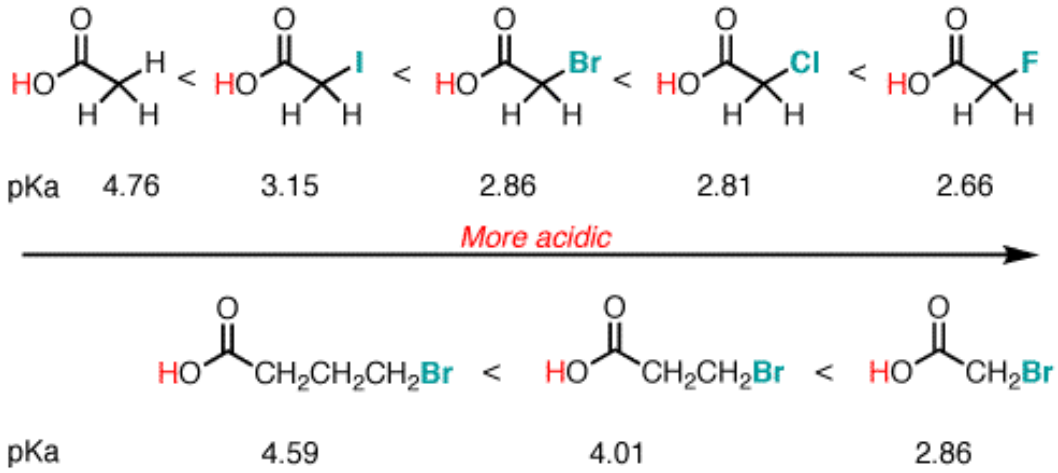




Physical Properties of Carboxylic acids

Effect of Structure on Acidity; the Inductive Effect Revisited

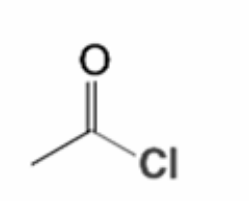
The most important factor operating here is the inductive effect of the groups close to the carboxyl group. This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms. Recall that electron-withdrawing groups enhance acidity, and electron-releasing groups reduce acidity.



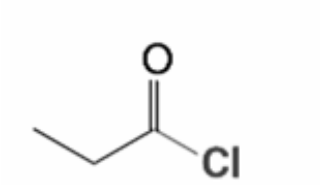
Nomenclature of carboxylic Acid derivatives

Nomenclature of Acyl Chlorides

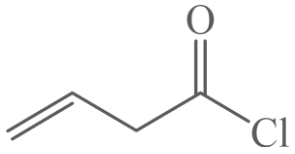
- Acyl chlorides are also called acid chlorides.
- They are named by dropping *-oic acid* from the name of the acid and then adding *-oyl chloride* or the *-e* is replaced by *-oyl chloride*.
- Cycloalkanes with Acyl chloride substituents are named as *cycloalkanecarbonyl chloride*.



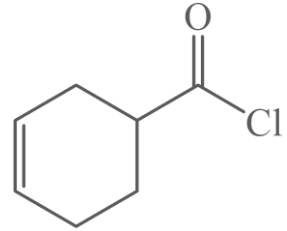
Ethanoyl chloride
Acetyl chloride



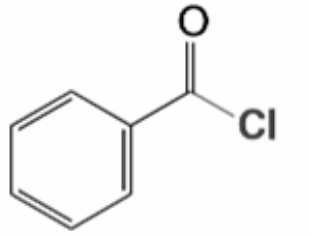
Propanoyl chloride



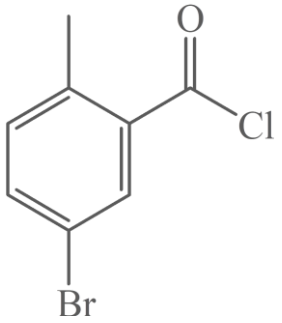
3-Butenoyl chloride



3-Cyclohexenecarbonyl chloride



Benzoyl chloride

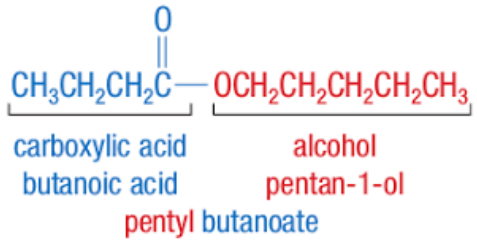


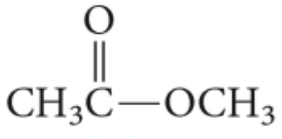
5-Bromo-2-methylbenzoyl chloride

Nomenclature of carboxylic Acid derivatives

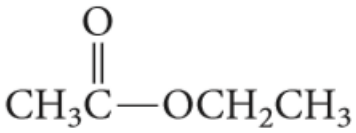
Nomenclature of Esters

- The names of esters are derived from the names of the alcohol (with the ending -yl) and the acid (with the ending *-oate* or the *-e* is replaced by *-oate* .

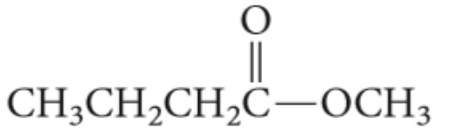




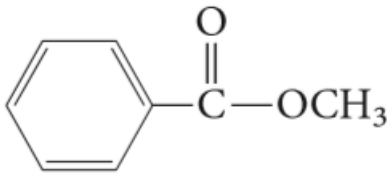
Methyl ethanoate
methyl acetate



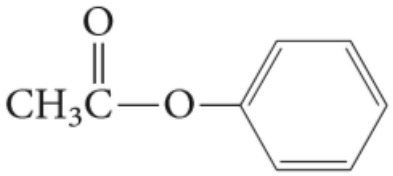
Ethyl ethanoate
ethyl acetate



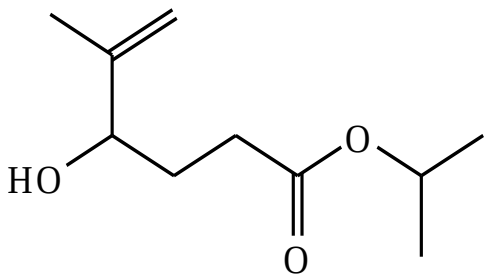
methyl butanoate



methyl benzoate



phenyl acetate

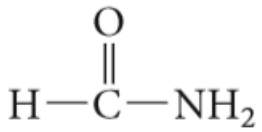


isopropyl-4-hydroxy-5-methyl-5-hexenoate

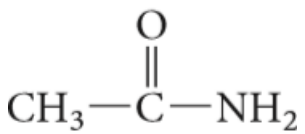
Nomenclature of carboxylic Acid derivatives

Nomenclature of Amides

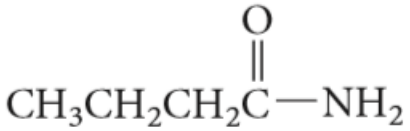
- Amides are named by replacing the *-ic* or *-oic acid* ending of the acid name, either the common or the IUPAC name, with the *-amide* ending or the *-e* is replaced by *-amide* .
- Alkyl groups on the nitrogen atom of amides are named as substituents, and the named substituent is prefaced by *N-* or *N,N-*



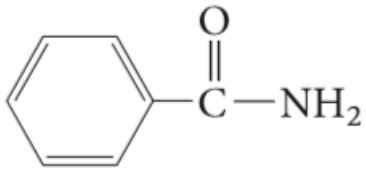
Methanamide
formamide



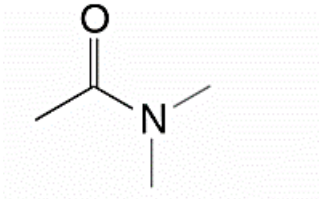
Ethanamide
actamide



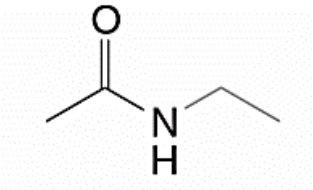
butanamide



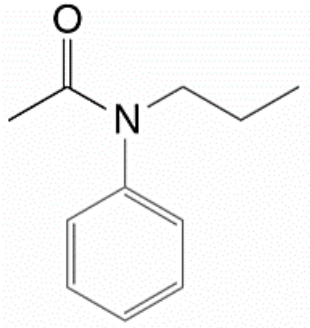
benzamide
(benzenecarboxamide)



N,N-Dimethylethanamide



N-Ethylethanamide

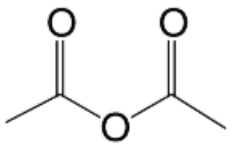


N-Phenyl-N-propylethanamide

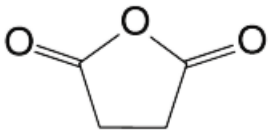
Nomenclature of carboxylic Acid derivatives

Nomenclature of Acid Anhydrides

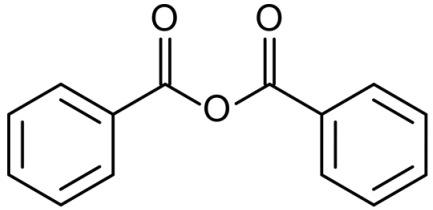
Most anhydrides are named by dropping the word *acid* from the name of the carboxylic acid and then adding the word *anhydride*



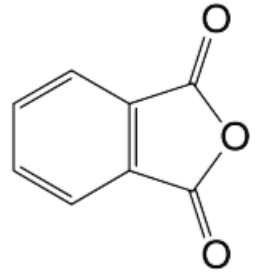
Ethanoic anhydride
acetic anhydride



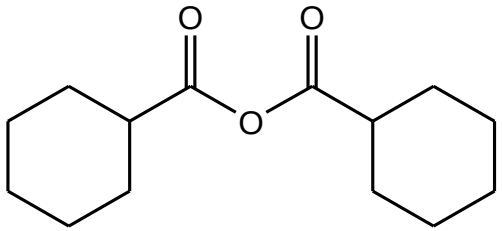
Butanedioic anhydride
succinic anhydride



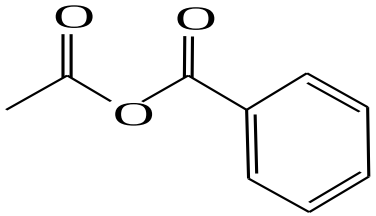
Benzoic anhydride



Phthalic anhydride



Cyclohexanecarboxylic anhydride



Benzoic ethanoic anhydride

Preparation of Carboxylic Acids

1- Oxidation of aldehydes and primary alcohols:

Strong oxidizing agent

Potassium permanganate $KMnO_4$,OH^-/ H_3O^+

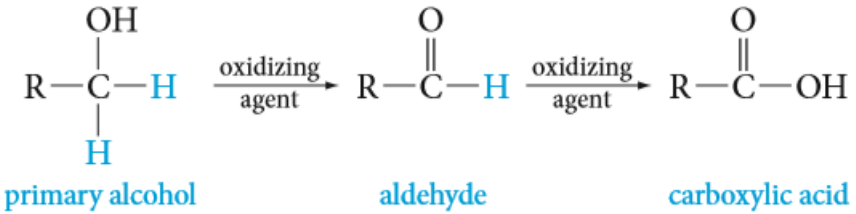
Chromic oxide CrO_3 / H_2SO_4 (H_2CrO_4 Jones' reagent)

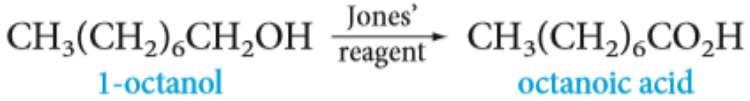
Weak oxidizing agent

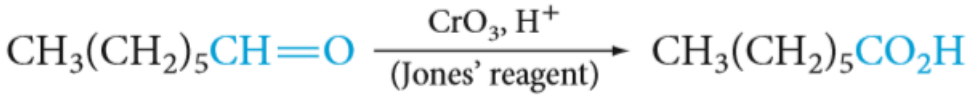
silver oxide Ag_2O

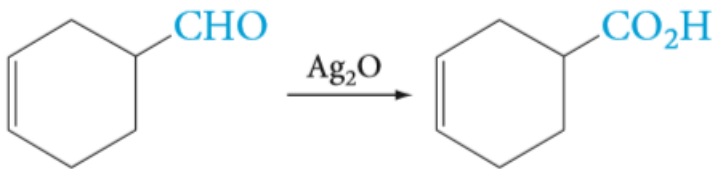
Chromic oxide CrO_3 / pyridine

Pyridinium chlorochromate PCC / methylene chloride CH_2Cl_2



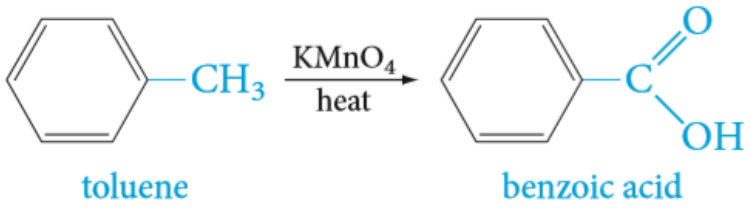




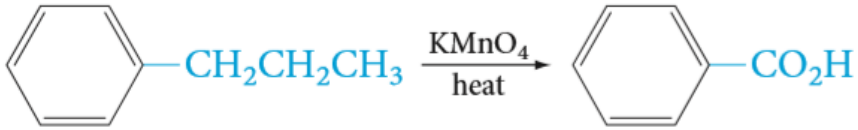


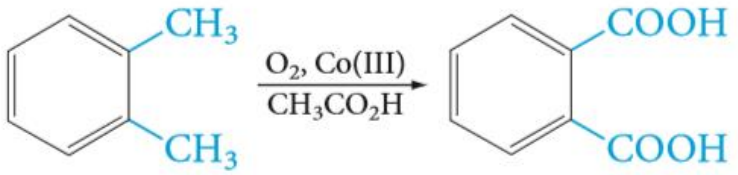
Preparation of Carboxylic Acids

2- Oxidation of Aromatic Side Chains:



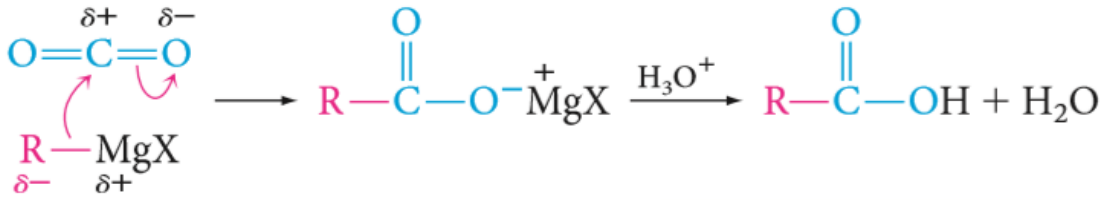
toluene benzoic acid

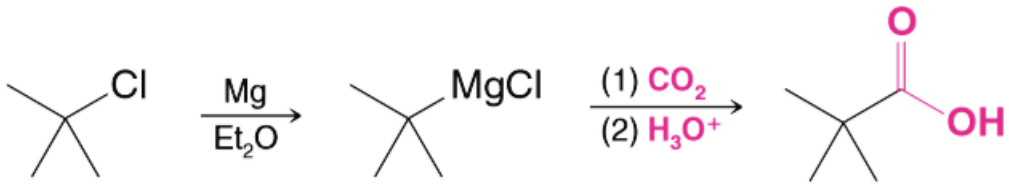




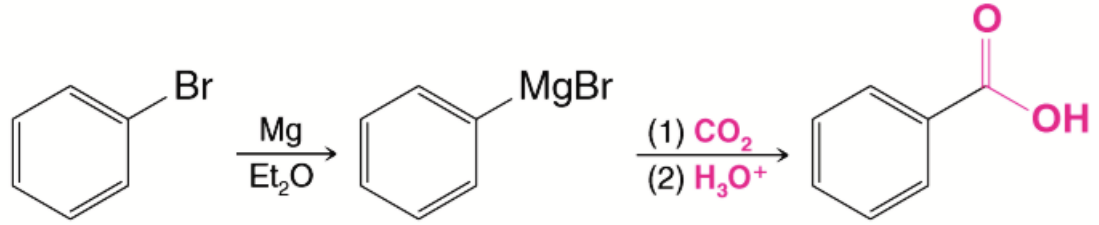
o-xylene phthalic acid

3- Reaction of Grignard Reagents with Carbon Dioxide:





***tert*-Butyl chloride** **2,2-Dimethylpropanoic acid (79–80% overall)**

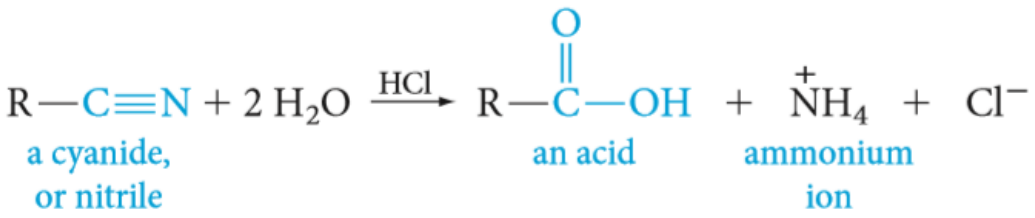


Bromobenzene **Benzoic acid (85%)**

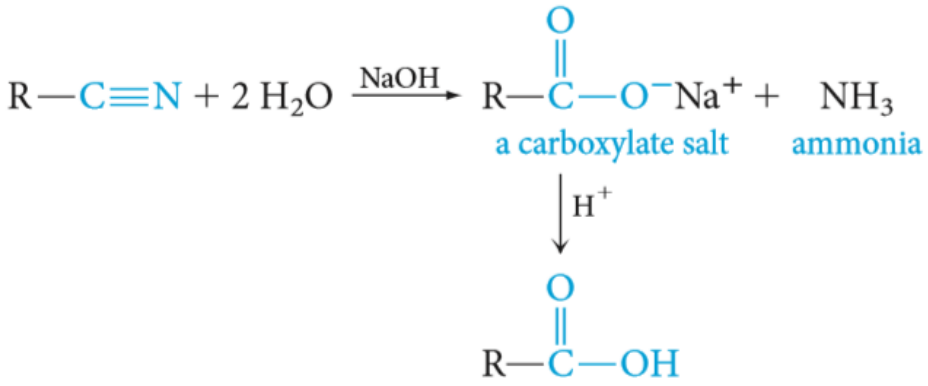
Preparation of Carboxylic Acids

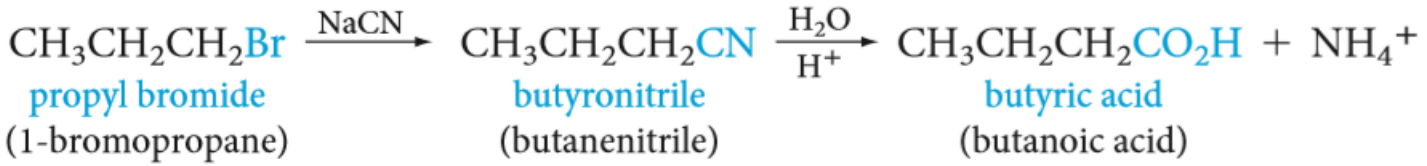
4- Hydrolysis of cyanohydrins and other nitriles:

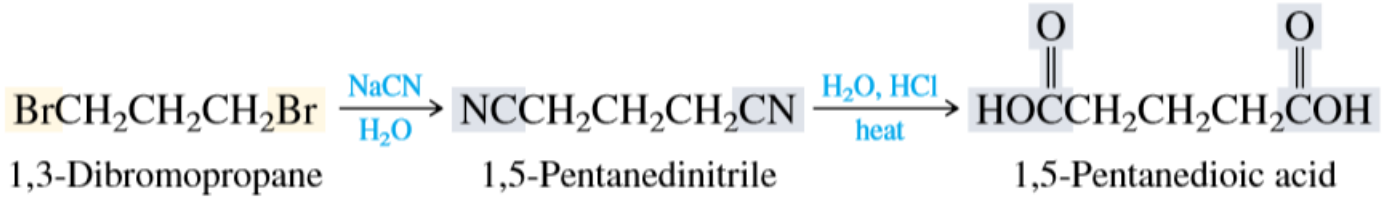
In Acid:



In Base:

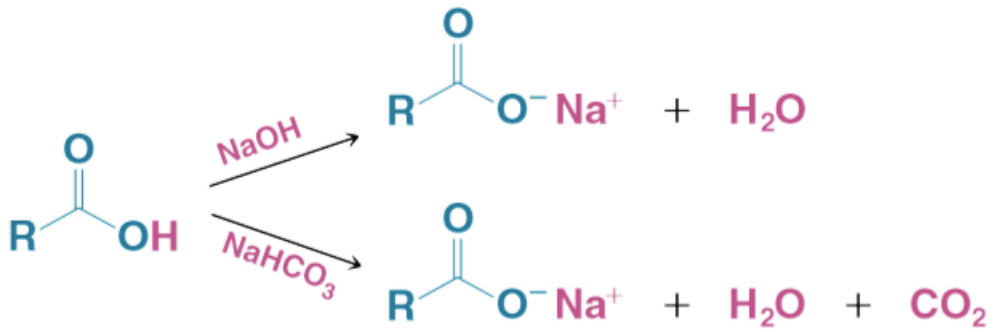


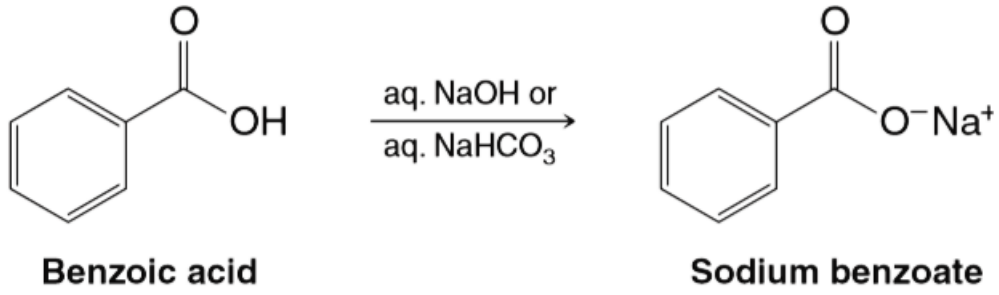




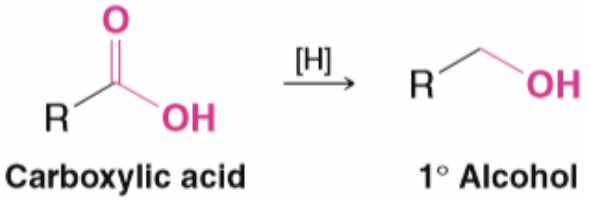
Reaction of Carboxylic Acids

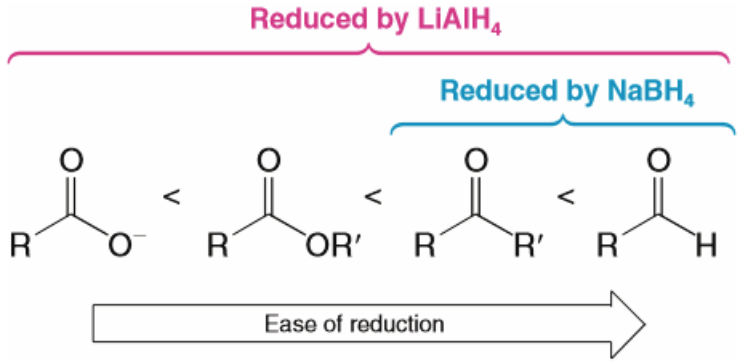
1- Reaction with Bases: NaOH or $NaHCO_3$



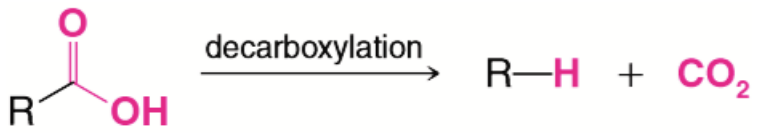


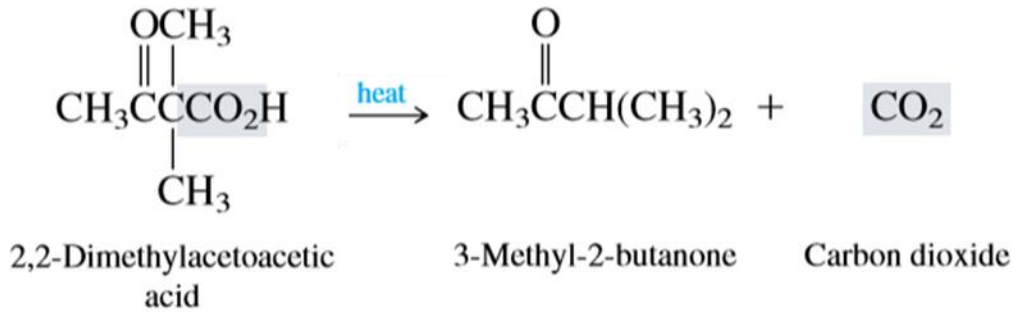
2- Reduction of carbonyl group: Addition of metal hydrides (formation of alcohol)





3- Decarboxylation of Carboxylic Acids: Carboxylic acid loses CO_2

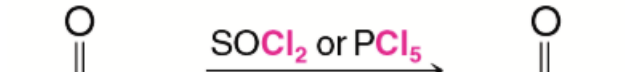


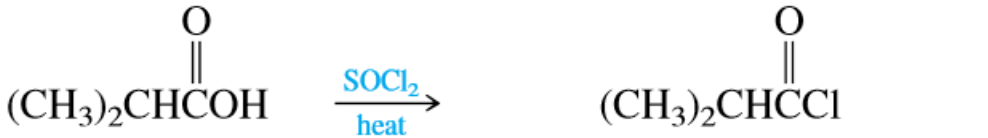


Reaction of Carboxylic Acids

3- Nucleophilic Substitution of Hydroxyl Group

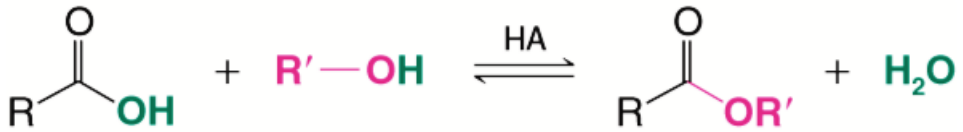
a) Conversion to acyl chlorides:

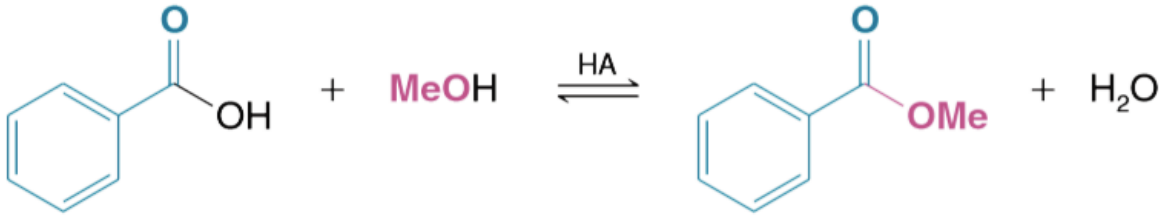




2-Methylpropanoic acid — 2-Methylpropanoyl chloride (90%)

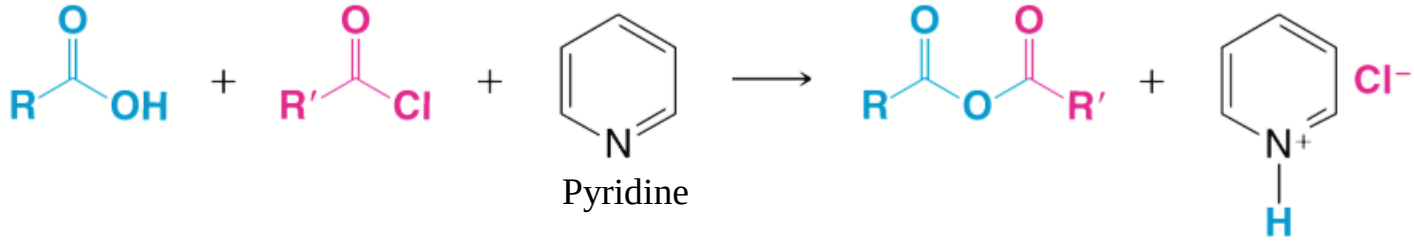
b) Conversion to esters:



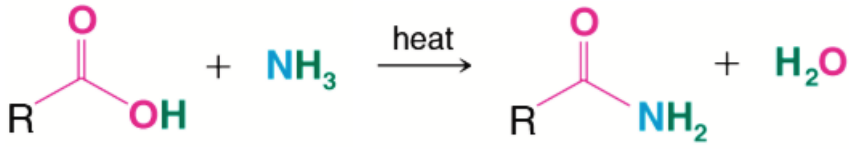


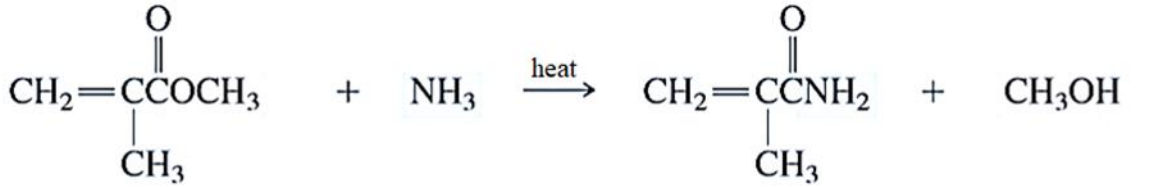
Benzoic acid **Methanol** **Methyl benzoate**

c) Conversion to acid anhydrides:



d) Conversion to amides:

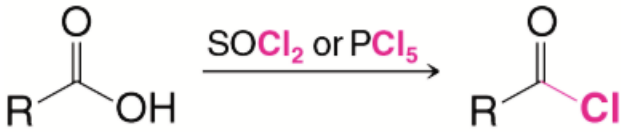


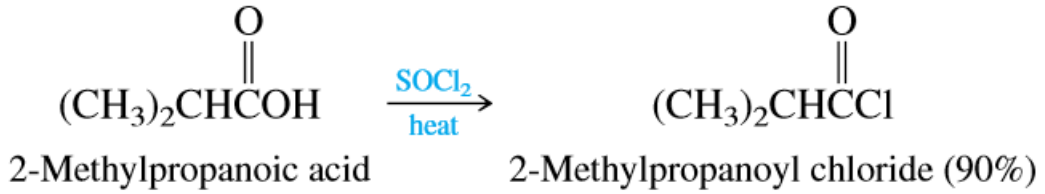


Methyl 2-methylpropenoate — Ammonia — 2-Methylpropenamide (75%) — Methyl alcohol

Preparation and Reaction of Acid derivatives

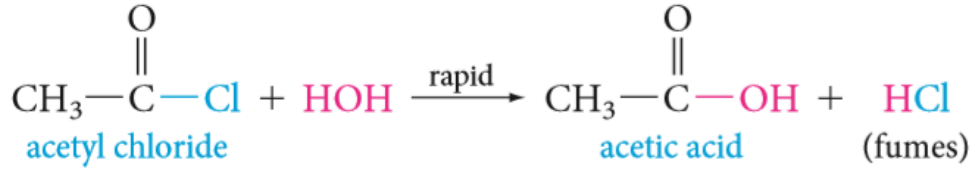
Preparation of Acyl Chlorides



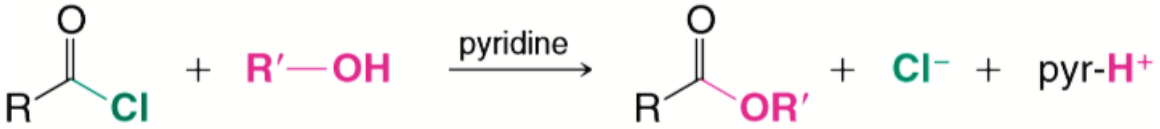


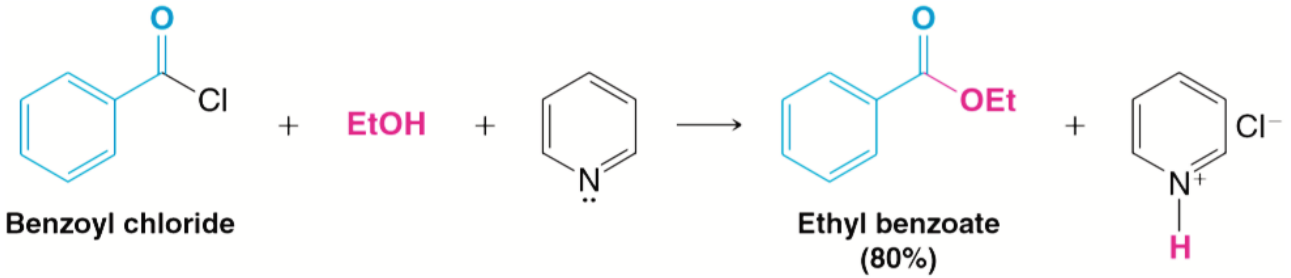
Reaction of Acyl Chlorides

1- Conversion to Acids (hydrolysis):



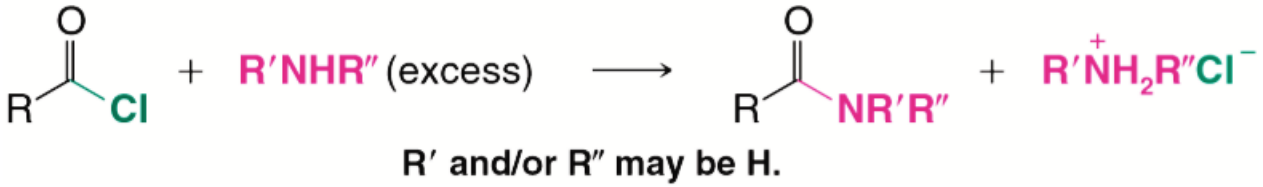
2- Conversion to Esters:

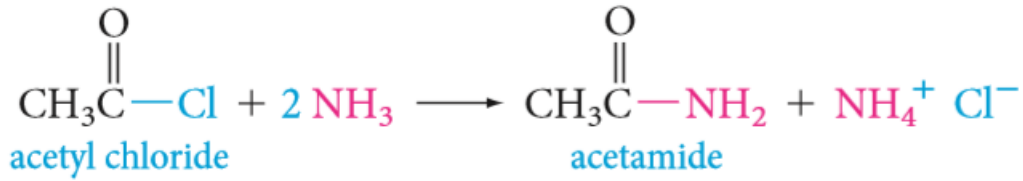




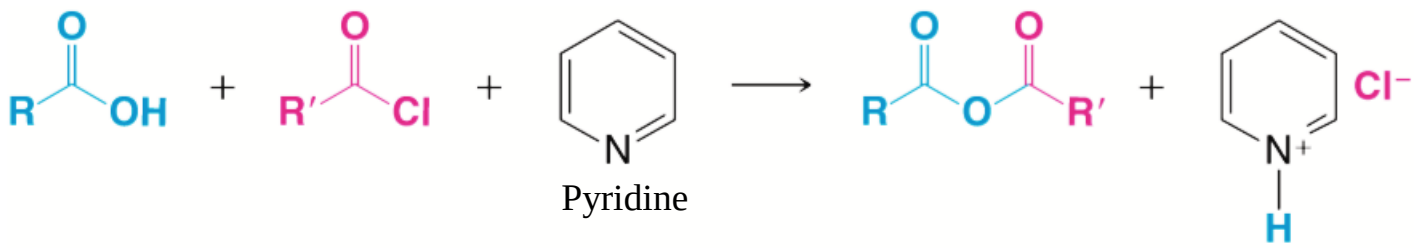
Reaction of Acyl Chlorides

3- Conversion to Amides:

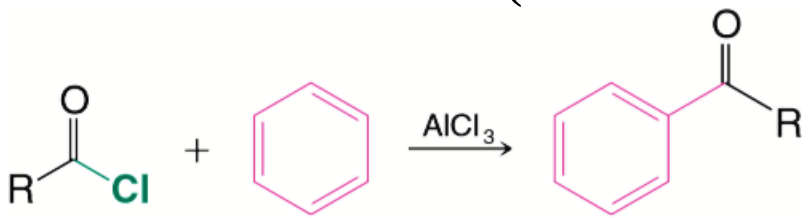


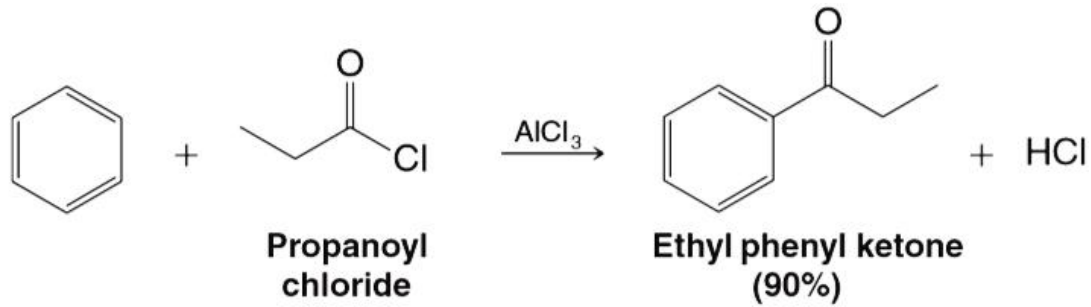


4- Conversion to Acid Anhydrides:



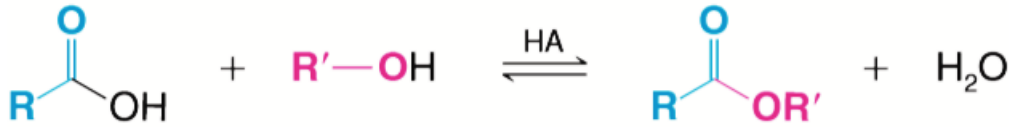
5- Conversion to Ketones (Friedel–Crafts acylation):

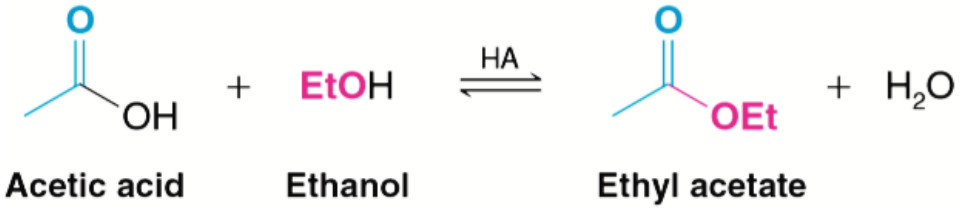




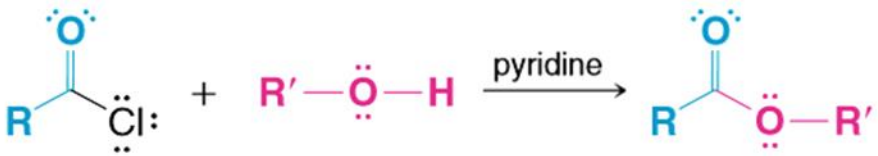
Preparation and Reaction of Acid derivatives

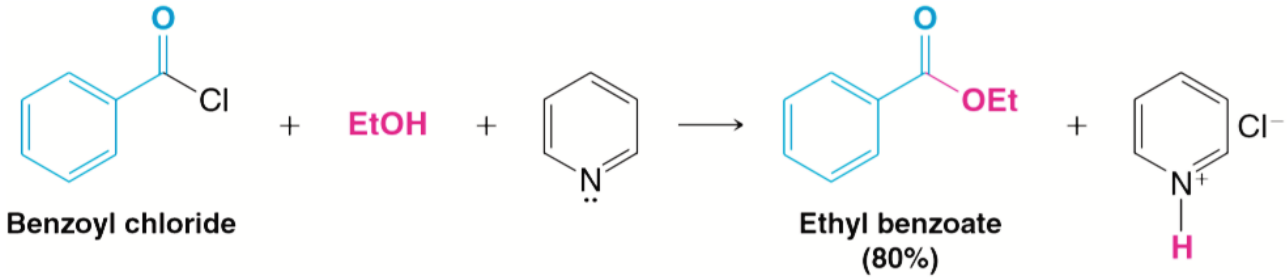
Preparation of Esters: Esterification



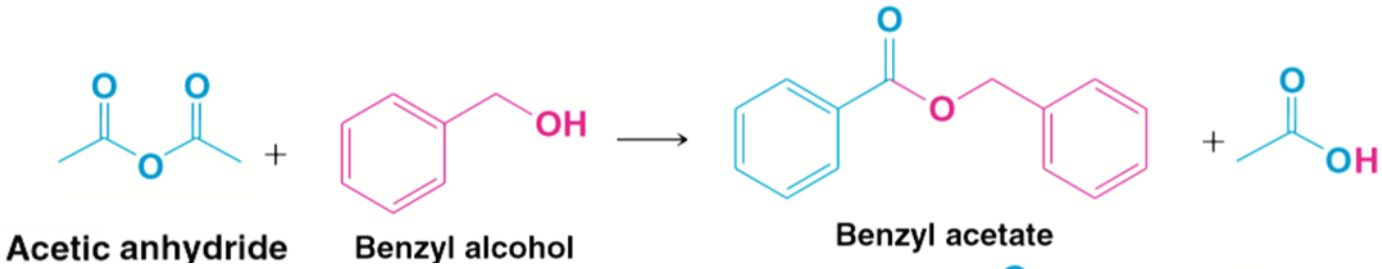


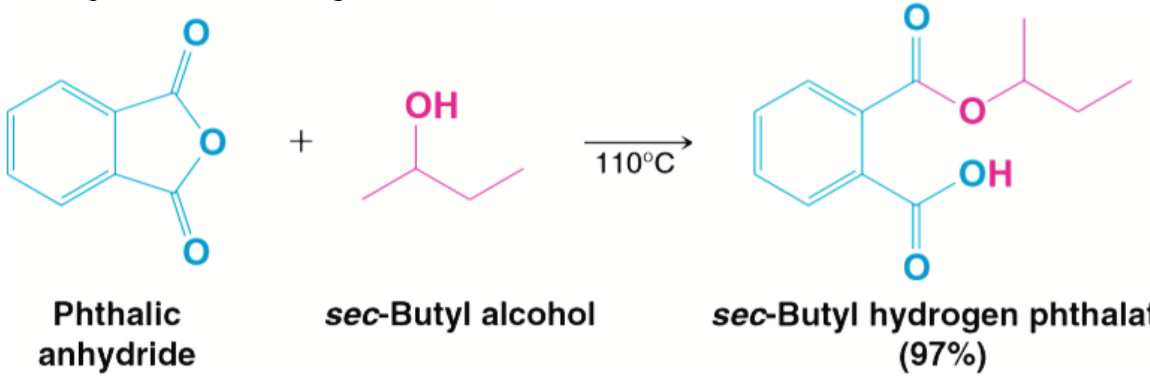
2- Esters from Acyl Chlorides:





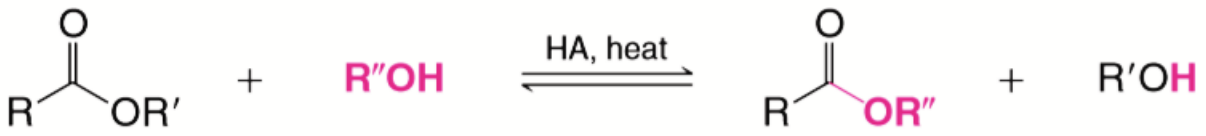
3- Esters from Carboxylic Acid Anhydrides:

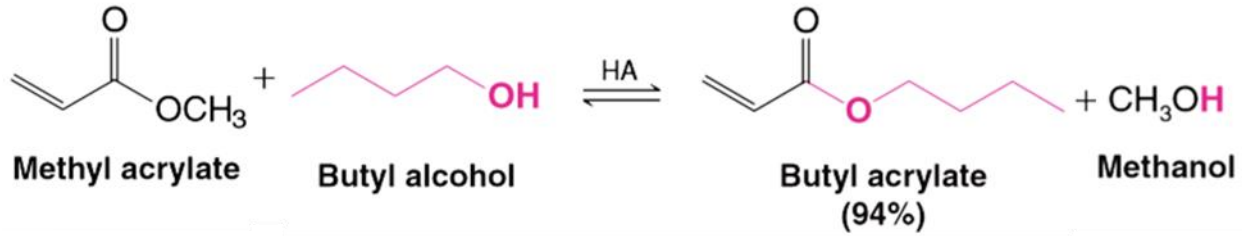




Preparation of Esters: Esterification

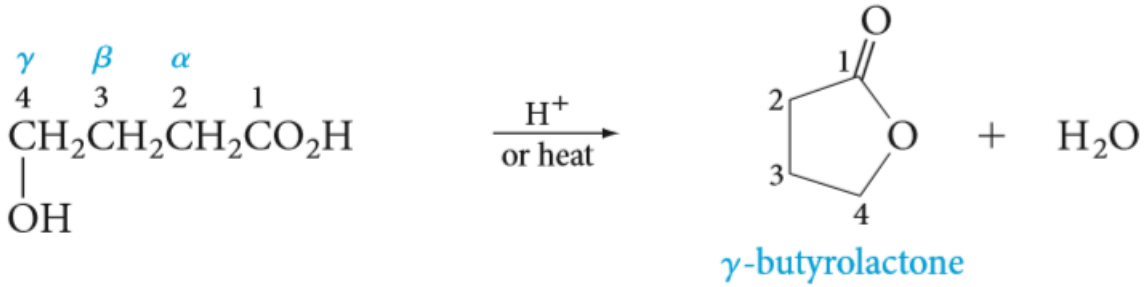
4- Esters can synthesized by Transesterification:



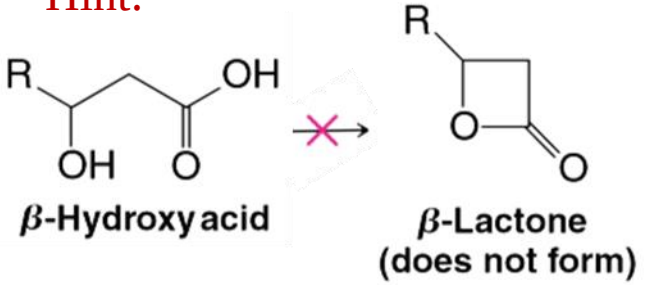


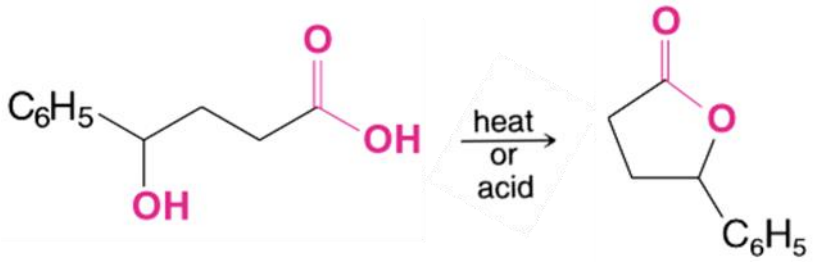
Cyclic Esters: Lactones

Carboxylic acids whose molecules have a hydroxyl group on a γ or δ carbon undergo an intramolecular esterification to give cyclic esters known as *γ - or δ -lactones*.



Hint:

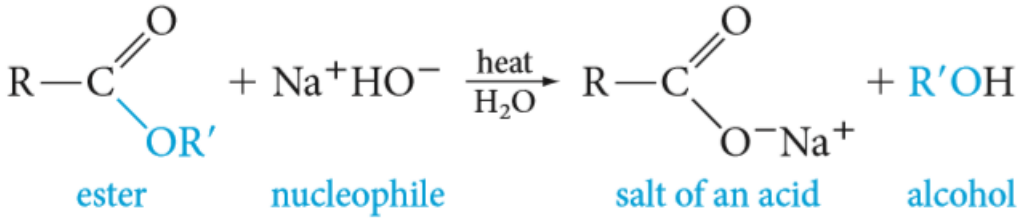




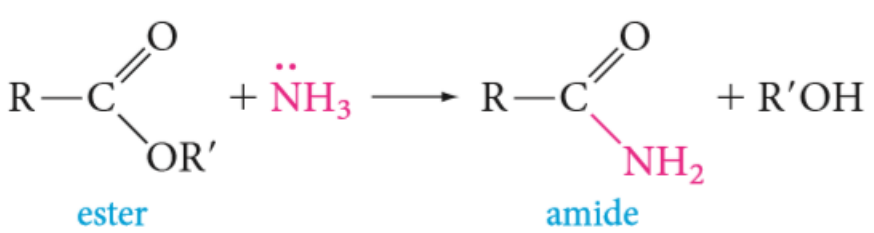
Preparation and Reaction of Acid derivatives

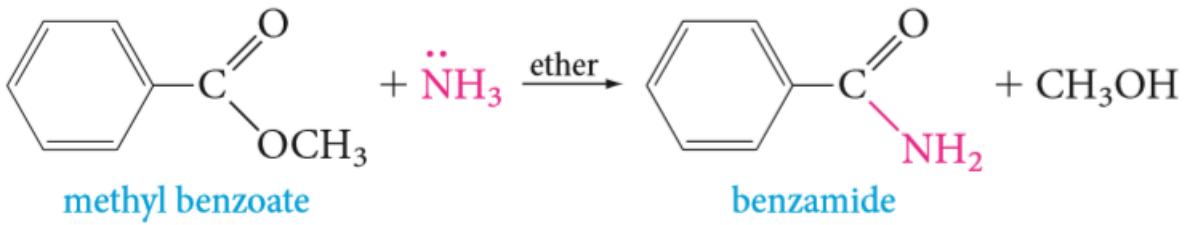
Reaction of Esters

1- Saponification of Esters:

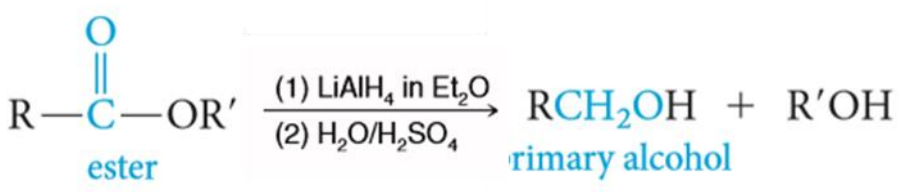


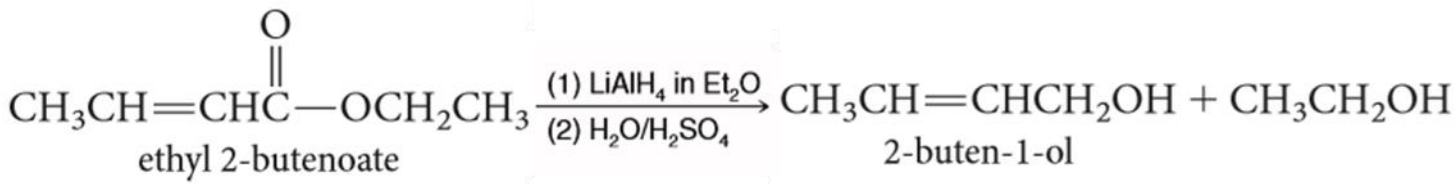
2- Ammonolysis of Esters:





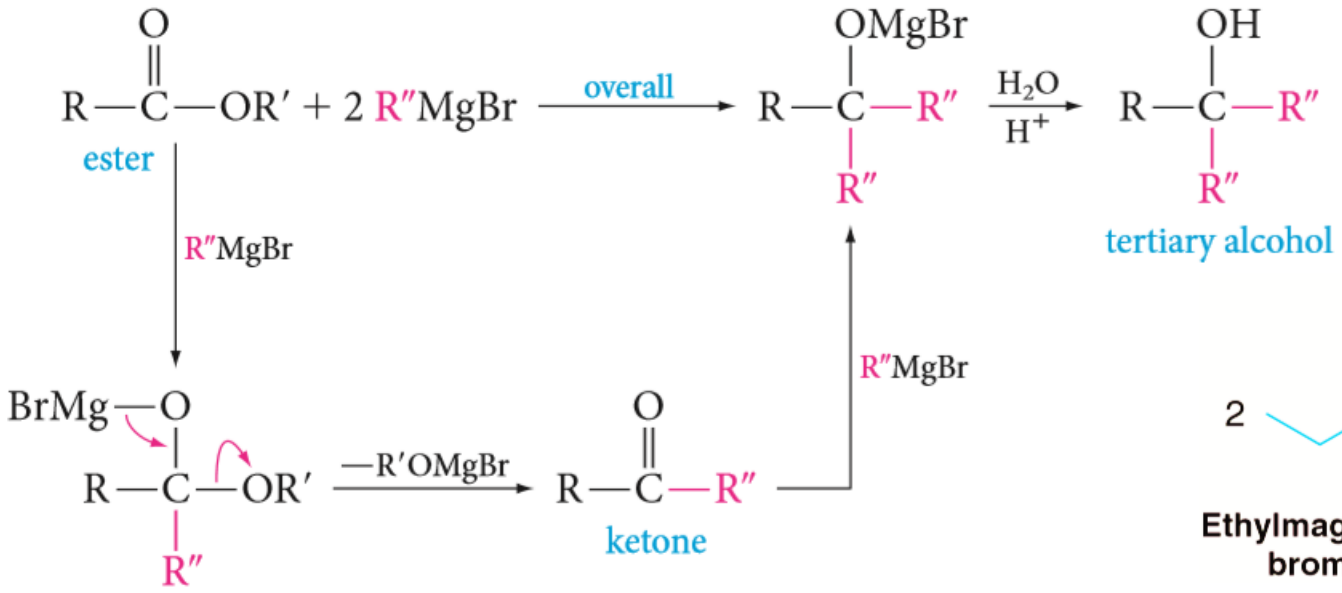
3- Reduction of Esters:

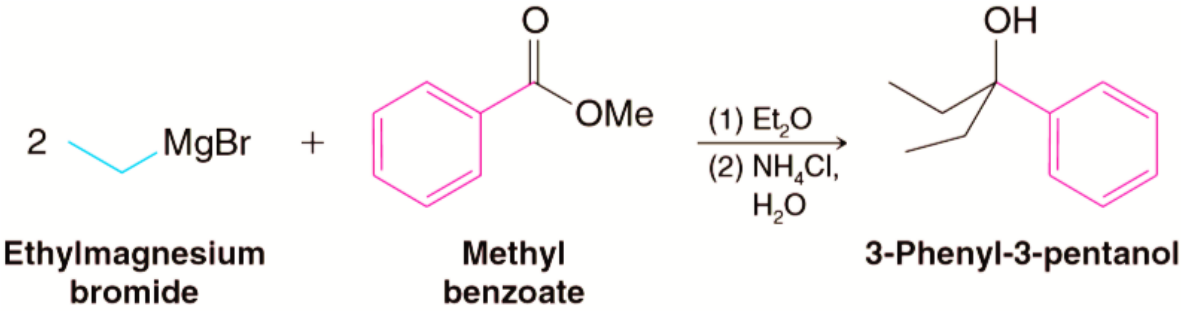




Reaction of Esters

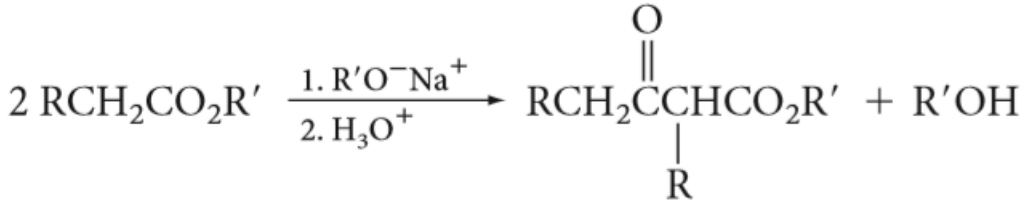
4- Reaction of Esters with Grignard Reagents:

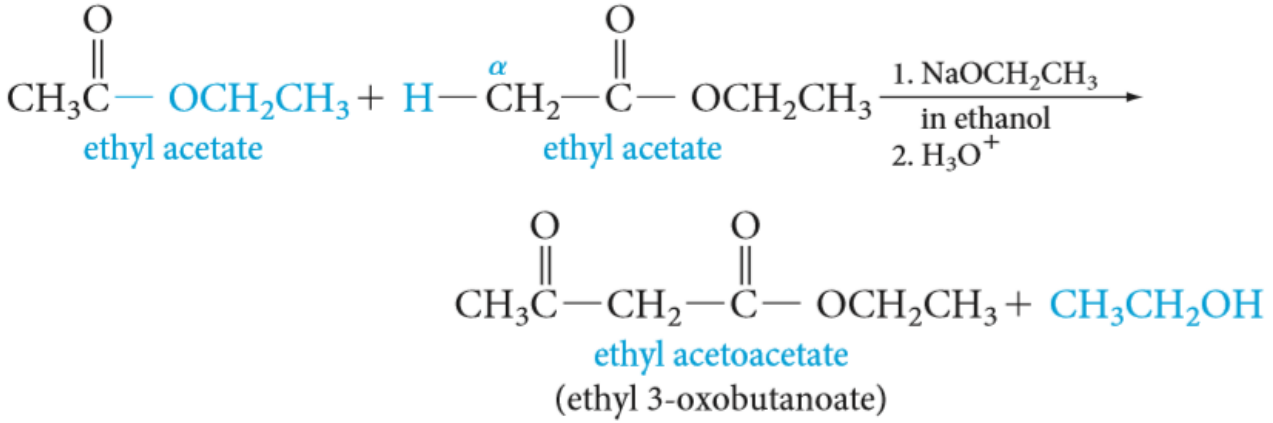




5- The α-Hydrogen of Esters: The **Claisen Condensation**:

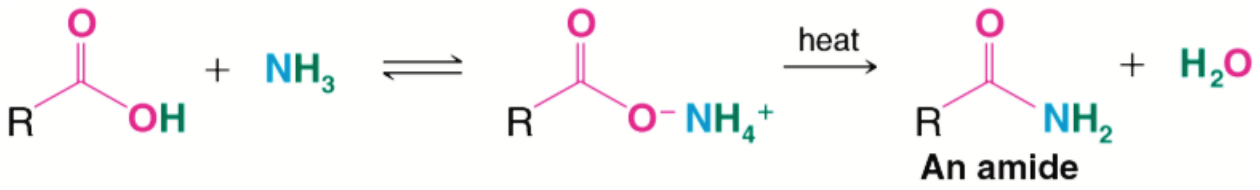
Being adjacent to a carbonyl group, the *α-hydrogens* of an ester are weakly acidic and can be removed by a strong base.





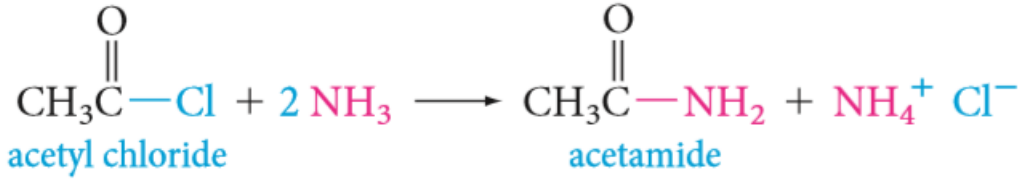
Preparation and Reaction of Acid derivatives

Preparation of Amides

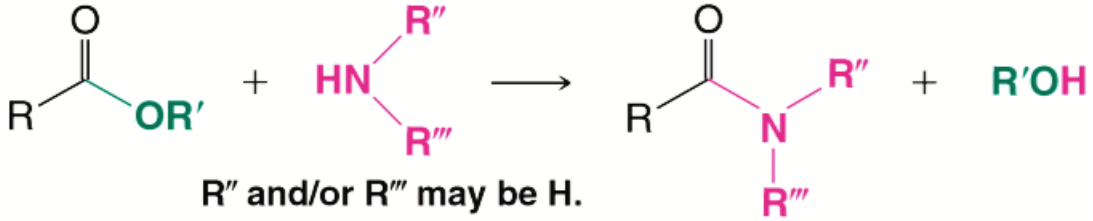


An amide

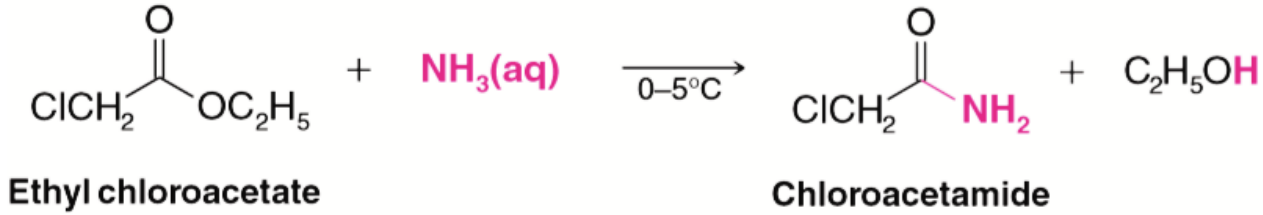
R′ and/or R″ may be H.



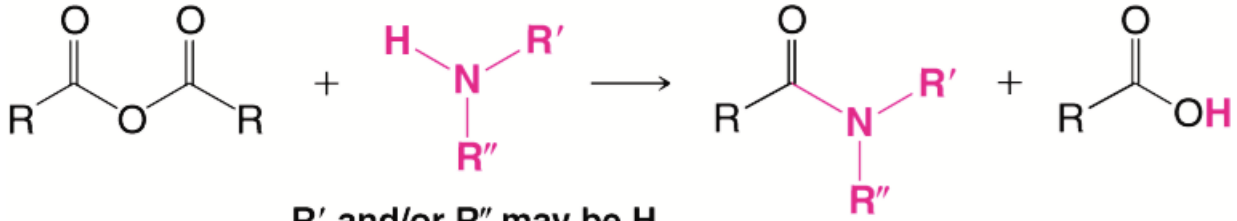
acetyl chloride — acetamide



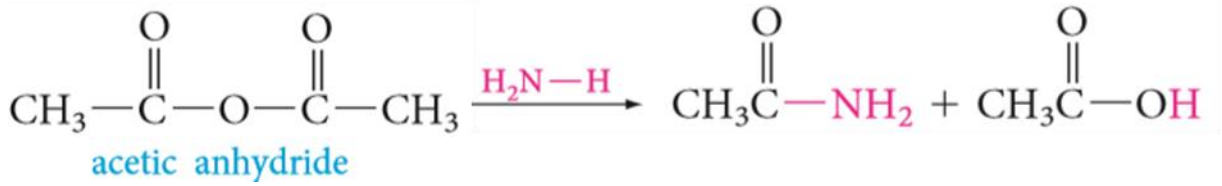
R″ and/or R‴ may be H.



Ethyl chloroacetate — Chloroacetamide (62–87%)



R′ and/or R″ may be H.

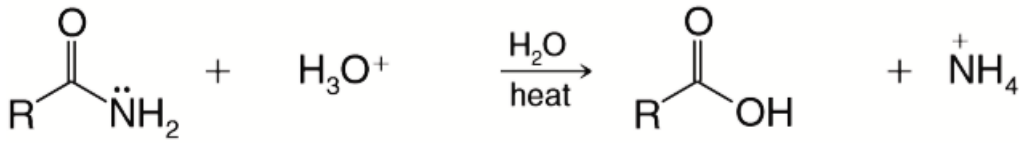


acetic anhydride

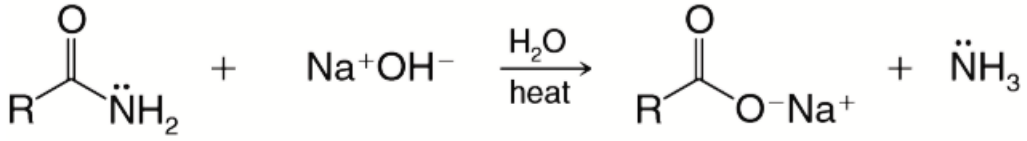
Reaction of Amides

1- Conversion to acids (hydrolysis):

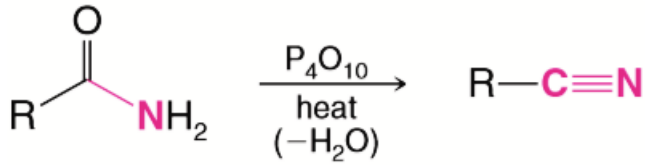
Acidic Hydrolysis:

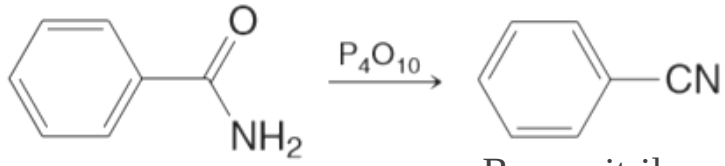


Basic Hydrolysis:



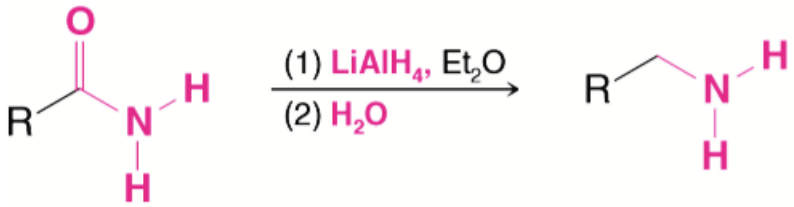
2- Nitriles from the Dehydration of Amides:

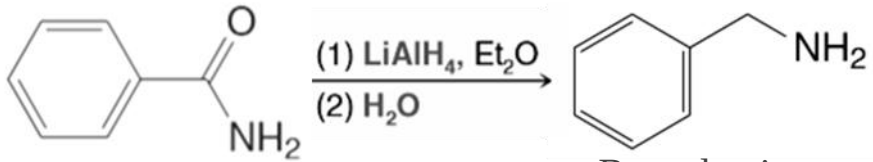




Benzonitrile

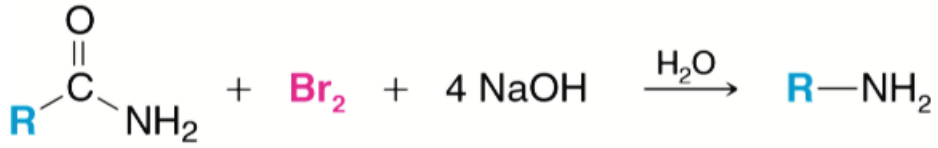
3- Reduction of Amides:

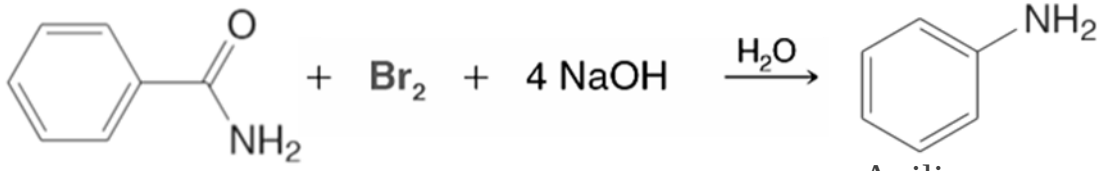




Benzylamine

4- Hofmann degradation:

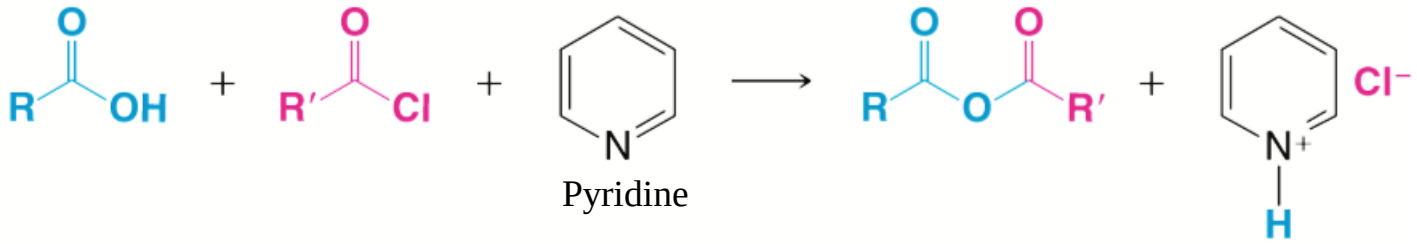




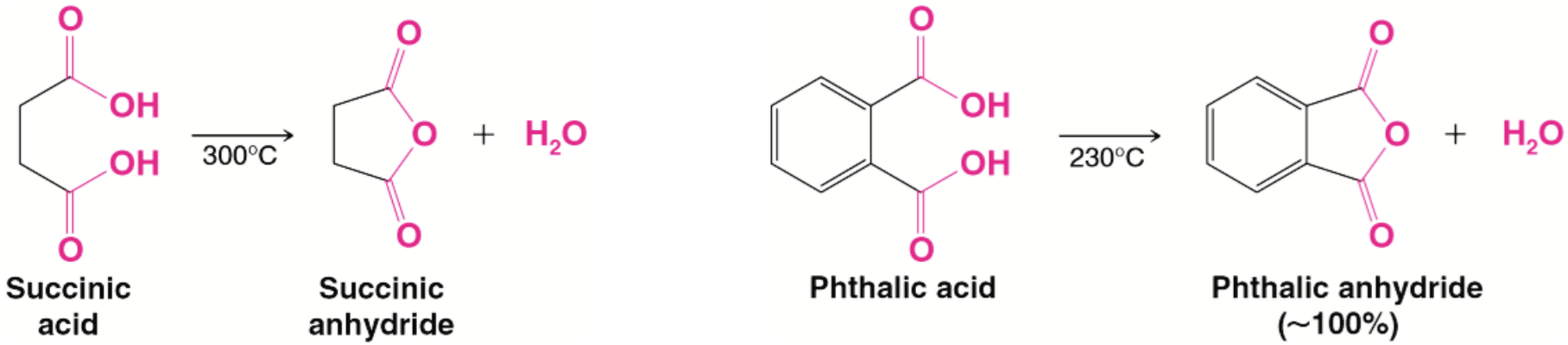
Aniline

Preparation and Reaction of Acid derivatives

Preparation of Acid Anhydride

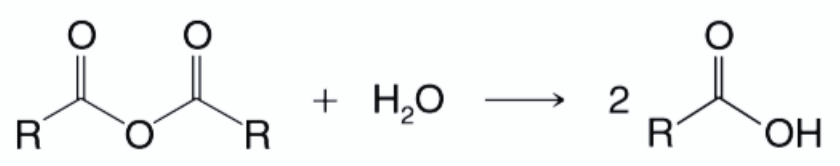


Cyclic anhydrides can sometimes be prepared simply by heating the appropriate dicarboxylic acid.



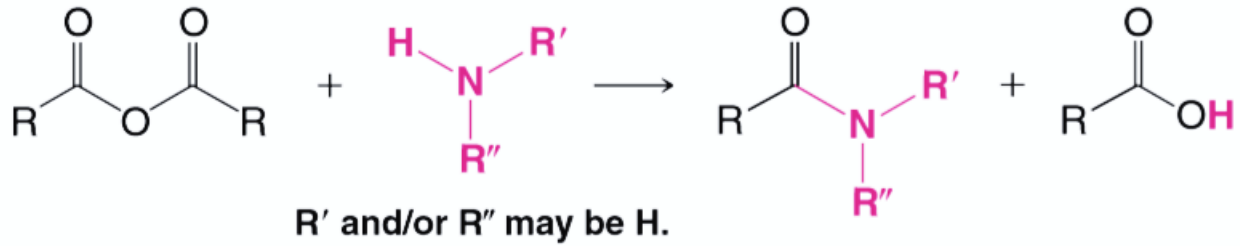
Reaction of Acid Anhydride

1- Conversion to Acids (hydrolysis):



2- Conversion to Esters:

3- Conversion to Amides:



4- Conversion to Aryl ketones (Friedel–Crafts acylation):