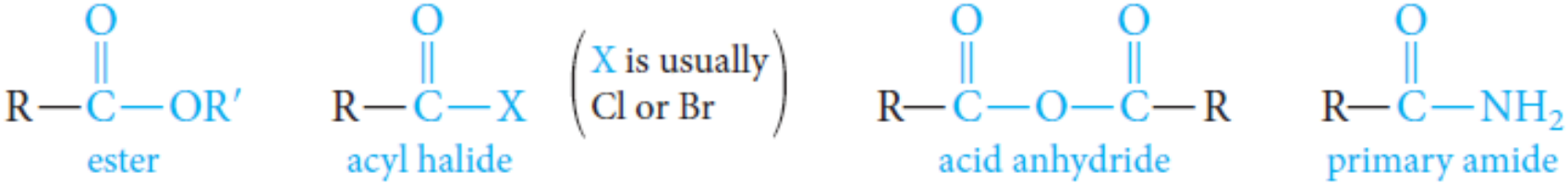
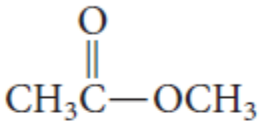
Carboxylic Acid Derivatives

Carboxylic acid derivatives are compounds in which the hydroxyl part of the carboxyl group is replaced by various other groups. All acid derivatives can be hydrolyzed to the corresponding carboxylic acid. In the remainder of this chapter, we will consider the preparation and reactions of the more important of these acid derivatives. Their general formulas are as follows:

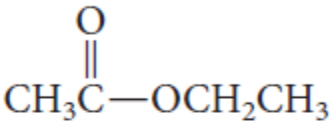


Esters

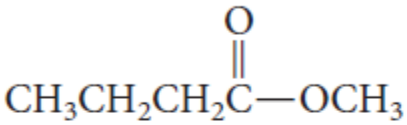
Esters are derived from acids by replacing the —OH group by an —OR group. They are named in a manner analogous to carboxylic acid salts. The R part of the —OR group is named first, followed by the name of the acid, with the *-ic* ending changed to *-ate*.



methyl acetate
(methyl ethanoate)
bp 57°C

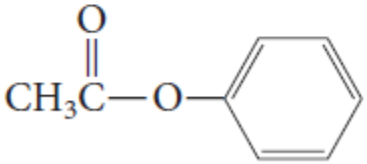


ethyl acetate
(ethyl ethanoate)
bp 77°C

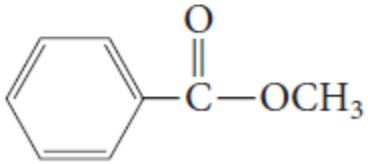


methyl butanoate
bp 102.3°C

Notice the different names of the following pair of isomeric esters, where the R and R′ groups are interchanged.



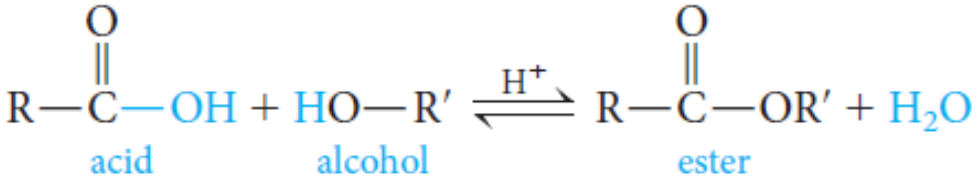
phenyl acetate
bp 195.7°C



methyl benzoate
bp 196.6°C

Preparation of Esters; Fischer Esterification

When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (usually HCl or H_2SO_4), an equilibrium is established with the ester and water.



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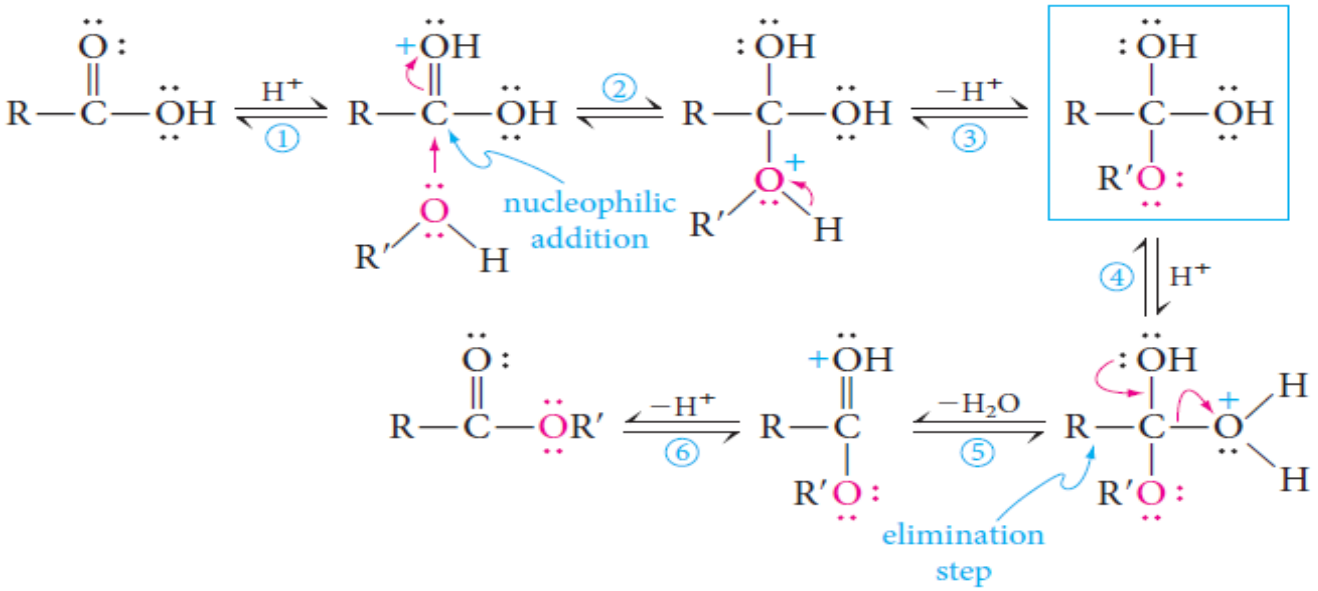
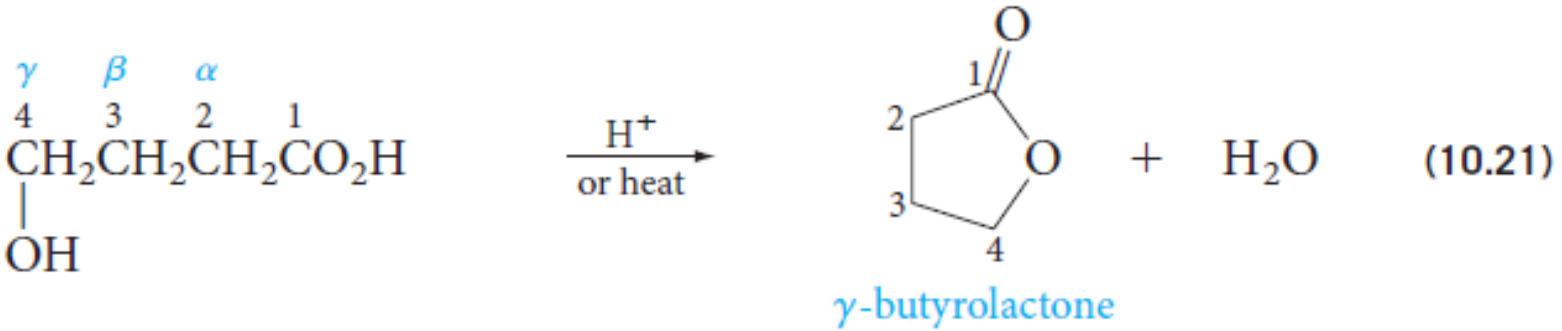
Mechanism



Lactones

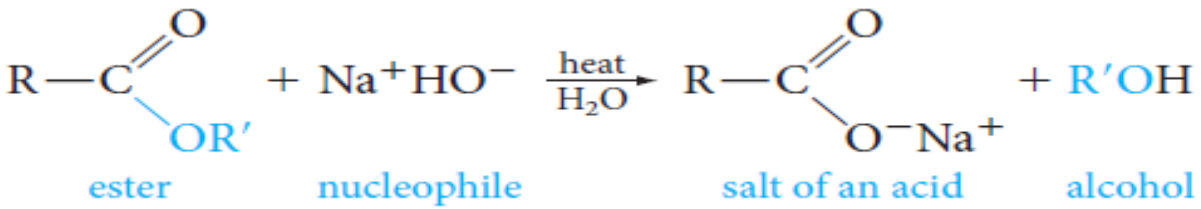
Hydroxy acids contain both functional groups required for ester formation. If these groups can come in contact through bending of the chain, they may react with one another to form **cyclic esters** called **lactones**. For example,



Most common lactones have five- or six-membered rings, although lactones with smaller or larger rings are known.

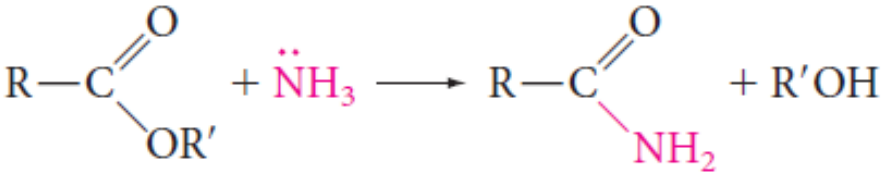
Saponification of Esters

Esters are commonly hydrolyzed with base. The reaction is called saponification (from the Latin *sapon,* soap) because this type of reaction is used to make soaps from fats



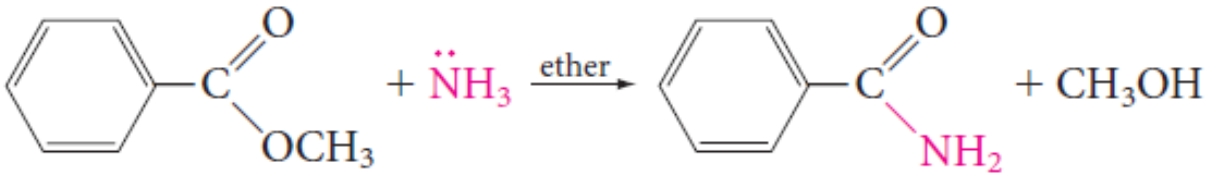
Ammonolysis of Esters

Ammonia converts esters to amides.



ester amide

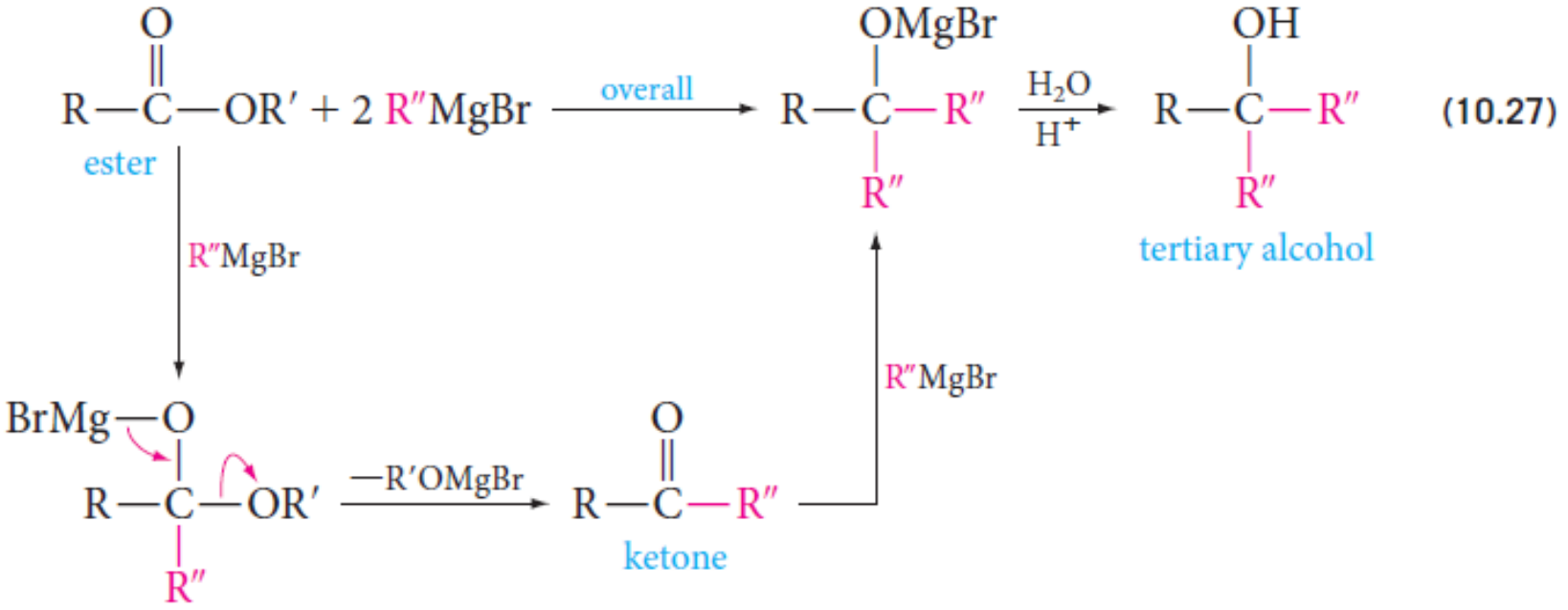
For example,



methyl benzoate benzamide

Reaction of Esters with Grignard Reagents

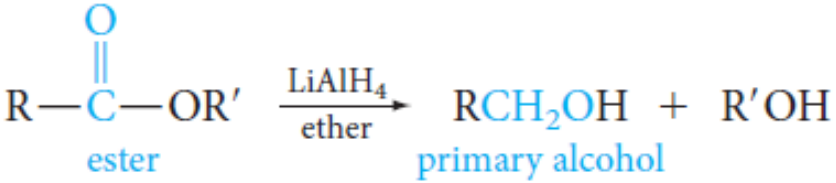
Esters react with two equivalents of a Grignard reagent to give tertiary alcohols. The reaction proceeds by *irreversible* nucleophilic attack of the Grignard reagent on the ester carbonyl group. The initial product, a ketone, reacts further in the usual way to give the tertiary alcohol.



Dr. Ahmed Mutanabbi Abdula

Reduction of Esters

Esters can be reduced to primary alcohols by lithium aluminum hydride ($LiAlH_4$).



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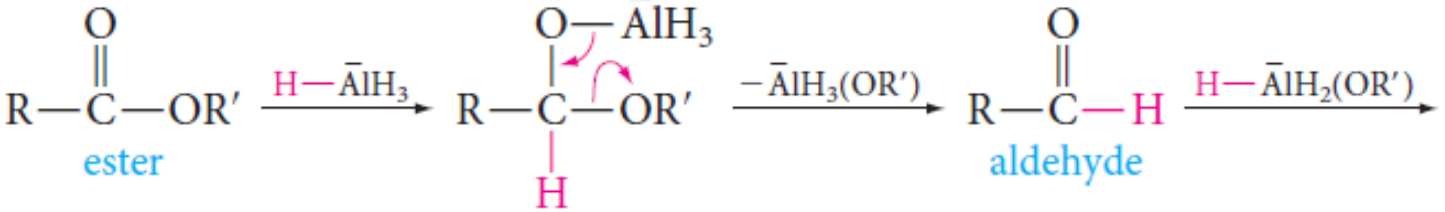
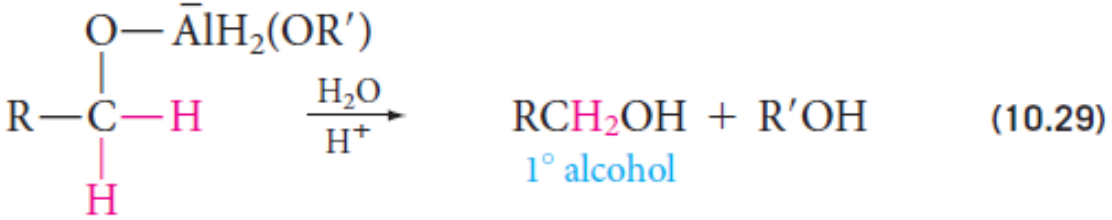
The mechanism is similar to the hydride reduction of aldehydes and ketones (eq. 9.33).





(10.29)