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.*

An **ester** is a carboxylic acid derivative in which the O!H group is replaced by an !OR group.

O
B
CH_3COOCH_3
methyl acetate (methyl ethanoate) bp 578C

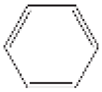
O
B
$CH_3COOCH_2CH_3$
ethyl acetate (ethyl ethanoate) bp 778C

O
B
$CH_3CH_2CH_2COOCH_3$
methyl butanoate bp 102.38C

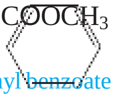
Notice the different names of the following pair of isomeric esters, where the R and R9 groups are interchanged.

O
B
CH_3COOO

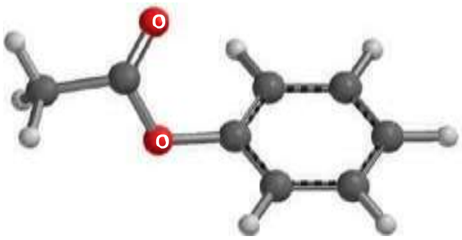
phenyl acetate bp 195.78C

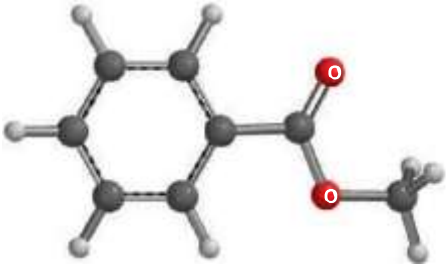


O
B OCOOCH$_3$



methyl benzoate bp 196.68C





Esters are named as two words that are *not* run together.

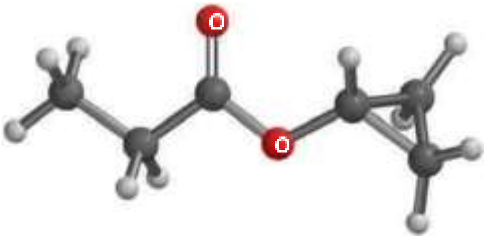
E

Name $CH_3CH_2CO_2CH(CH_3)_2$.

Solution The related acid is $CH_3CH_2CO_2H$, so the last part of the name is *propanoate* (change the *-ic* of propanoic to *-ate*). The alkyl group that replaces the hydrogen is *isopropyl*, or 2-*propyl*, so the correct name is *isopropyl propanoate*, or 2-*propyl propanoate*.

PROBLEM Write the IUPAC name for

a. 

b. 

PROBLEM Write the structure of

a. 3-pentyl butanoate

b. methyl 2-methylhexanoate

Many esters are rather pleasant-smelling substances and are responsible for the flavor and fragrance of many fruits and flowers. Among the more common are pentyl acetate (bananas), octyl acetate (oranges), ethyl butanoate (pineapples), and pentyl butanoate (apricots). Natural flavors can be exceedingly complex. For example, no fewer than 53 esters have been identified among the volatile constituents of Bartlett pears! Mixtures of esters are used as perfumes and artificial flavors. Low-molecular- weight esters are also used by insects and animals to transmit signals. Female elephants release (*Z*)-7-dodecen-1-yl acetate to signal their readiness to mate. Many moths release the same ester to attractmates.

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.

O O
B B H^1
ROCOOH 1 HOOR9 R OCOOR9 1 H_2O

acid alcohol ester

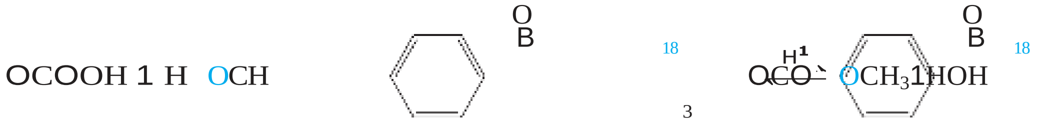
The process is called **Fischer esterification** after Emil Fischer, who devel- oped the method. Although the reaction is an equilibrium, it can be shifted to the right in several ways. If either the alcohol or the acid is inexpensive, a large excess can be used. Alternatively, the ester and/or water may be removed as formed (by distillation, for example), thus driving the reactionforward.

PROBLEM Following eq., write an equation for the preparation of ethyl pentanoate from the correct acid and alcohol.

The Mechanism of Acid-Catalyzed Esterification; Nucleophilic Acyl Substitution

We can ask the following simple mechanistic question about Fischer esterification: Is the water molecule formed from the hydroxyl group of the acid and the hydrogen of the alcohol (as shown in color in eq. 10.17) or from the hydrogen of the acid and the hydroxyl group of the alcohol? This question may seem rather trivial, but the answer provides a key to understanding much of the chemistry of acids, esters, and their derivatives.

This question was resolved using isotopic labeling. For example, Fischer esterifi- cation of benzoic acid with methanol that had been enriched with the ^{18}O isotope of oxygen gave labeled methyl benzoate.*



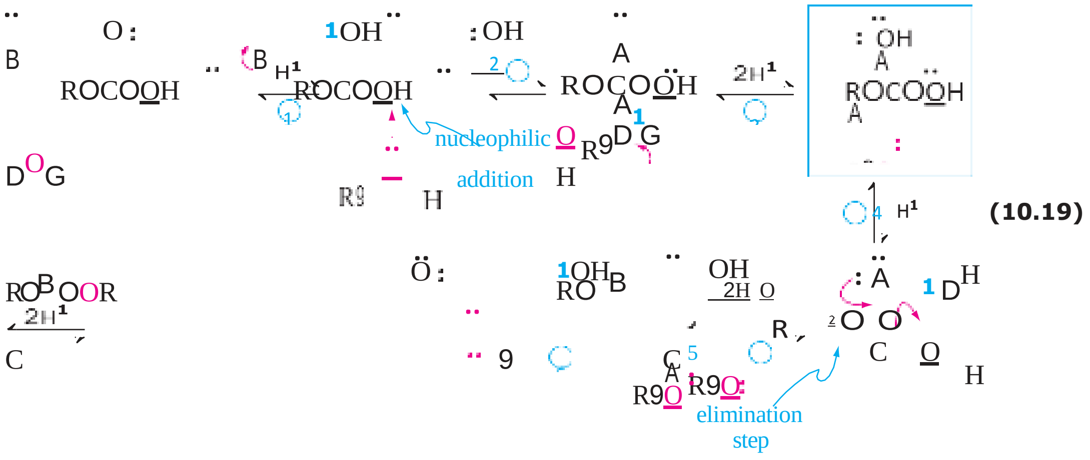
O O
B B
OCOOH 1 H ^{18}OCH$_3$ H^1 OCO ^{18}OCH$_3$1HOH

methyl benzoate

(10.18)

None of the ^{18}O appeared in the water. Thus it is clear that *the water was formed using the hydroxyl group of the acid and the hydrogen of the alcohol.* In other words, in Fischer esterification, the !OR group of the alcohol replaces the !OH group of the acid.

How can we explain this experimental fact? A mechanism consistent with this result is as follows (the oxygen atom of the alcohol is shown in color so that its path can be traced):



(10.19)

Let us go through this mechanism, which looks more complicated than it really is, one step at a time.

Step 1. The carbonyl group of the acid is reversibly protonated. This step explains how the acid catalyst works. Protonation increases the positive charge on the carboxyl carbon and enhances its reactivity toward nucleophiles (recall the similar effect of acid catalysts with aldehydes and ketones, eq. 9.9).

Note that the carbonyl oxygen gets protonated because it is the more basic oxygen.

Step 2. *This is the crucial step.* The alcohol, as a nucleophile, attacks the carbonyl carbon of the protonated acid. This is the step in which the new C!O bond (the ester bond) is formed.

Steps 3and 4. These steps are equilibria in which oxygens lose or gain a proton. Such acid–base equilibria are reversible and rapid and go on constantly in any acidic solution of an oxygen-containing compound. In step 4, it does not matter which !OH group is protonated since these groups are equivalent.

Step 5. This is the step in which water, one product of the overall reaction, is formed. For this step to occur, an !OH group must be protonated to improve its leaving-group capacity. (This step is similar to the reverse of step 2.)

Step 6. This deprotonation step gives the ester and regenerates the acid catalyst. (This step is similar to the reverse of step 1.)

Some other features of the mechanism in eq. 10.19 are worth examining. The reaction begins with a carboxylic acid, in which the carboxyl carbon is trigonal and sp^2-hybridized. The end product is an ester; the ester carbon is also trigonal and sp^2- hybridized. However, the reaction proceeds through a neutral **tetrahedral intermediate** (shown in a box in eq. 10.19 and in color in eq. 10.20), in which the carbon atom has

A **tetrahedral intermediate** has an sp^3-hybridized carbon atom.

four groups attached to it and is thus *sp*^{3}-hybridized. If we omit all of the proton-transfer steps in eq. 10.19, we can focus on this feature of the reaction:

The net result of this process is substitution of the ! OR9 group of the alcohol for the !OH group of the acid. Hence the reaction is referred to as **nucleophilic acyl substitution**. But the reaction is not a direct substitution. Instead, it occurs in two steps: (1) nucleophilic addition, followed by (2) elimination. We will see in the next and subsequent sections of this chapter that this is a general mechanism for nucleophilic substitutions at the carbonyl carbon atoms of carboxylic acid derivatives.

PROBLEM 10.17 Following eq. 10.19, write out the steps in the mechanism for the acid-catalyzed preparation of ethyl acetate from ethanol and acetic acid. In the United States, this method is used commercially to produce more than 100 million pounds of ethyl acetate annually, mainly for use as a solvent in the paint industry, but also as a solvent for nail polish and various glues.