29

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

29.1 | Carboxylic Acids

Carboxylic acids are weak acids that are widely distributed in nature and are commonly used in consumer products.

One of the most common carboxylic acids is acetic acid, which is the primary ingredient of vinegar. The acetyl group is central to the metabolism of carbohydrates and fats through its role in the enzyme acetyl CoA. Acetic acid is also an important industrial chemical with a global production of approximately 6.5 million metric tons each year. For example, aspirin (acetylsalicylic acid) is formed by the reaction of acetic acid with salicylic acid. Vinyl acetate is just one polymer precursor that is also derived from acetic acid. When vinyl acetate is polymerized, the product is poly(vinyl acetate), which is used in water-based latex paints and in glues for paper and wood.

By the end of this section, you should be able to:

- Recognize the carboxylic acid functional group and name simple molecules containing it
- Understand the connection between acid–base chemistry and solubility

Carboxylic acids contain the *carboxyl* functional group (a combination of *carb*onyl and hydr*oxyl* groups), which is often written as COOH or CO_2H.

Figure 29.1 shows the structural formulas of several carboxylic acids. Notice that oxalic acid and citric acid contain two and three carboxyl groups, respectively. Oxalic acid, which is found in high concentration in rhubarb leaves, is poisonous if ingested. Terephthalic acid is a key component of PET, a durable polymer used in packaging. Lactic acid is generated in muscle cells and tissue during the synthesis of adenosine triphosphate (ATP) from carbohydrates during sustained exercise. Ibuprofen is an analgesic, used to treat pain and inflammation. Benzoic acid is often used as a fungicide.

Structure, Properties, and Nomenclature
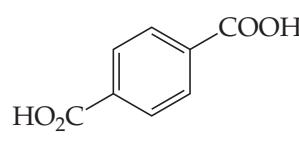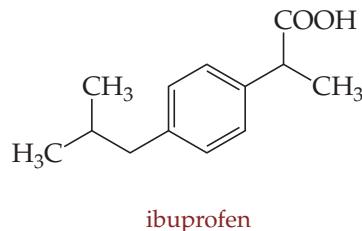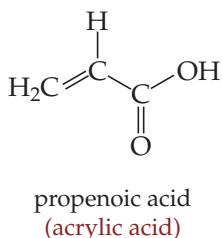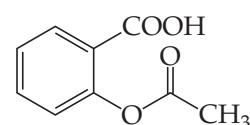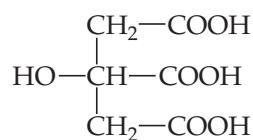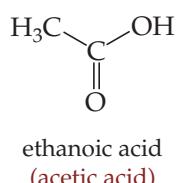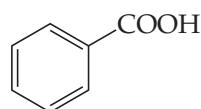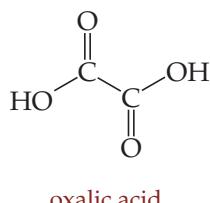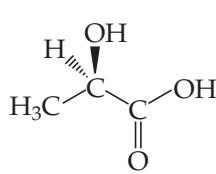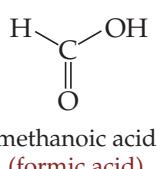
The carboxyl functional group (COOH) that characterizes carboxylic acids is constituted by a sp^2 hybridized carbon atom bonded to two oxygen atoms. One oxygen is sp^2 hybridized, leading to the formation of σ- and π-bonds with carbon (leading to a C—O double bond). The other oxygen is sp^3 hybridized, leading to a C—O single bond.

In Chapter 11, we studied the phenomenon of hydrogen bonding. We have already described the need for two components: a hydrogen bond donor (such as O—H, N—H) and a hydrogen bond acceptor, which is usually an electronegative atom containing a lone

Go Figure Which of these substances have both a carboxylic acid functional group and an alcohol functional group?
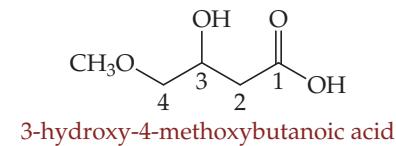
▲ **Figure 29.1 Structural formulas of some common carboxylic acids.** The IUPAC names are given in black type for the monocarboxylic acids, but they are generally referred to by their common names.

pair of electrons such as O, N or F. In the case of carboxylic acids, both hydrogen bond donor and acceptor are present in the same functional group in a favourable geometry. As a result, carboxylic acids are able to dimerize (**Figure 29.2**) in concentrated solutions or as neat (without solvent) liquids. Dimerization is as a result of the intermolecular hydrogen bonding between the carbonyl oxygen and the OH group. Consequently, carboxylic acids have relatively high boiling points (**Table 29.1**).
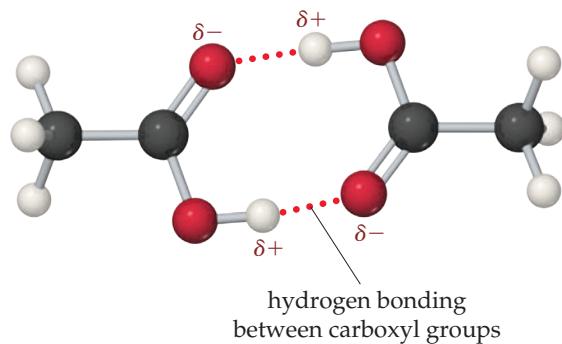
Alkane-derived carboxylic acids have the general formula $C_nH_{2n}O_2$, and are named based on the longest carbon chain (parent alkane) bearing the carboxyl group, although sometimes common names are still employed (**Figure 29.6**). The *e* of the alkane is replaced by *oic acid* to signify the carboxylic acid. Table 29.1 gives the names of the first 10 straight-chain carboxylic acids, their condensed formulas and their melting points.

In terms of the nomenclature hierarchy we have been developing for organic chemistry, the carboxylic acids sit at the pinnacle. All other functional groups we have come across are named as substituents if a carboxylic acid group is present. For example, 3-hydroxy-4-methoxybutanoic acid is *not* named as the alcohol, but rather the carboxylic acid.

3-hydroxy-4-methoxybutanoic acid

Go Figure   Would dimerization be aided by polar or non-polar solvents?


hydrogen bonding between carboxyl groups
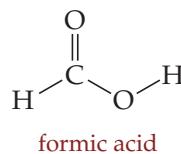
▲ **Figure 29.2 Carboxylic acid dimerization.** In concentrated solution or as neat liquids, carboxylic acids are able to dimerize through intermolecular hydrogen bonding.

TABLE 29.1   First 10 members of the aliphatic carboxylic acid series

| Molecular formula	Condensed structural formula	IUPAC name (common name)	Melting point (°C)*	Boiling point (°C)*
CH_2O_2	HCOOH	Methanoic (formic) acid	8	101
$C_2H_4O_2$	CH_3COOH	Ethanoic (acetic) acid	17	118
$C_3H_6O_2$	CH_3CH_2COOH	Propanoic (propionic) acid	−24	141
$C_4H_8O_2$	$CH_3CH_2CH_2COOH$	Butanoic (butyric) acid	−6	163
$C_5H_{10}O_2$	$CH_3CH_2CH_2CH_2COOH$	Pentanoic (valeric) acid	−20	186
$C_6H_{12}O_2$	$CH_3CH_2CH_2CH_2CH_2COOH$	Hexanoic (caproic) acid	−4	205
$C_7H_{14}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2COOH$	Heptanoic (enanthylic) acid	−10	223
$C_8H_{16}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$	Octanoic (caprylic) acid	16	239
$C_9H_{18}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$	Nonanoic (pelargonic) acid	9	253
$C_{10}H_{20}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$	Decanoic (capric) acid	29	219

* Rounded to the nearest degree.

Carboxylic acids have higher melting and boiling points than their corresponding alkanes, alcohols, aldehydes or ketones because of their added polarity and ability to hydrogen bond (Table 29.1). Although the boiling points of carboxylic acids increase with molecular size in a regular manner, their melting points do not. Unbranched acids made up of an even number of carbon atoms have melting points higher than their odd-numbered homologues, having one more or one less carbon. This difference reflects subtle changes in intermolecular attractive forces in the solid state. The even-numbered carboxylic acids are able to interact more strongly than their odd-numbered homologues, which increases the amount of energy needed to break the interactions in order to melt, thus increasing the melting point. For example, decanoic acid is a waxy solid at room temperature. Formic acid and acetic acid are special in that their melting points seem appropriate for much higher molecular weight species. The reason is that the properties of formic acid and acetic acid are dominated by the hydrogen bonding interactions of the carboxyl group with other molecules. These interactions occur more often because the COOH group makes up a large proportion of the molecule.

formic acid

The number of carbon atoms in the carboxylic acid chain not only affects its melting point, but also its solubility in water. Typically, a carboxylic acid is more water soluble than its alcohol analogue because of more extensive hydrogen bonding capacity. For example, formic, acetic, propanoic and butanoic acids are all infinitely soluble in water. As the length of the carbon chain increases, however, the polar COOH group becomes an ever decreasing proportion of the molecule, and the molecule behaves more like a hydrocarbon in terms of its solubility. The solubility of the carboxylic acids in water decreases correspondingly. In contrast, the solubility of carboxylic acids in non-polar solvents increases as the non-polar hydrocarbon chain length increases. Hence decanoic acid is more "alkane-like" than acetic acid.

Acidity

We have already mentioned that carboxylic acids are weak acids. **Table 29.2** compares the pK_a values for several organic and inorganic acids. Being a weak acid, carboxylic acids dissociate by the following equation:

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \qquad [29.1]$$
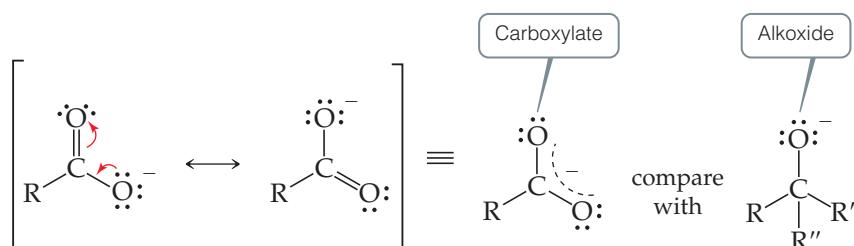
One of the main contributing factors that allows the pK_a of a carboxylic acid to be lower than that of the corresponding alcohol—for example, acetic acid (pK_a 4.8) compared with ethanol (pK_a 16)—is the relative stability of the two conjugate bases, that is, the **carboxylate anion** versus the alkoxide anion. The carboxylate anion is resonance stabilized (**Figure 29.3**), having two contributors to the overall structure, whereas the alkoxide

TABLE 29.2 Relative pK_a values for selected carboxylic acids*

| Compound	Structural formula	pK_a	
Hydrogen chloride	HCl	−7	**Strong acid**
Sulfuric acid	H_2SO_4	−5	
Trichloroacetic acid	Cl_3CCOOH	0.7	
Dichloroacetic acid	$Cl_2CHCOOH$	1.5	
Chloroacetic acid	$ClCH_2COOH$	2.8	
Acetic acid	CH_3COOH	4.8	
Water	H_2O	15.7	**Weak acid**

* Error in measurement ± 0.2.
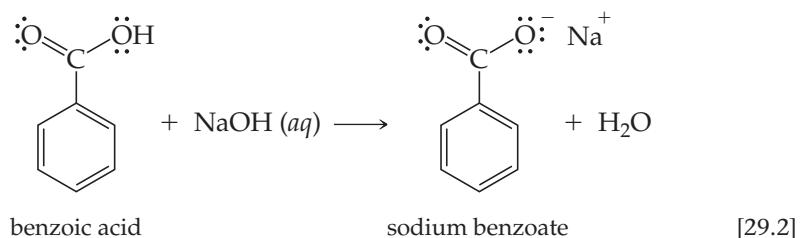
▶ **Figure 29.3** The carboxylate anion is resonance stablilized.
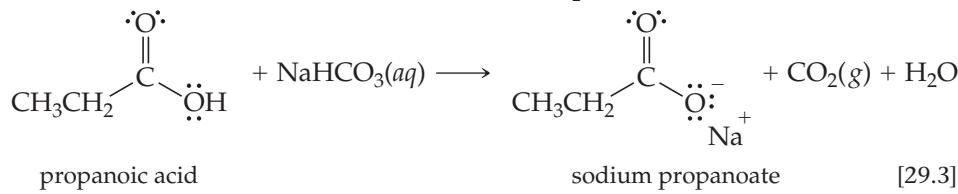
is not resonance stabilized. As a result, the carboxylate anion is not as reactive as the alkoxide.

The pK_a of a carboxylic acid can be influenced inductively by substituents (Table 29.2). The addition of an electron-withdrawing substituent such as a halide adjacent to the COOH group reduces the pK_a by weakening the carboxyl O—H bond (**Figure 29.4**). For example, the pK_a of acetic acid is 4.8 whereas the pK_a of chloroacetic acid is 2.8. The addition of more chlorine atoms reduces the pK_a further (for example, pK_a of trichloroacetic acid is 0.7). The inductive effect is reduced dramatically as the number of intervening bonds between the electron-withdrawing substituent and the COOH group increases. Such an effect is seen in amino acids.

Carboxylic acids react with bases such as NaOH, $NaHCO_3$ or Na_2CO_3 to form the corresponding sodium carboxylate salt. For example, when benzoic acid reacts with an aqueous solution of NaOH, sodium benzoate and water are formed. The conversion of the acid form to the carboxylate salt enhances aqueous solubility. Note that the salts of carboxylic acids are named in the same order as other salts: first cation, then anion. The name of the anion is derived from the carboxylic acid by replacing -*oic acid* with -*oate*.

benzoic acid + NaOH (*aq*) ⟶ sodium benzoate + H_2O [29.2]
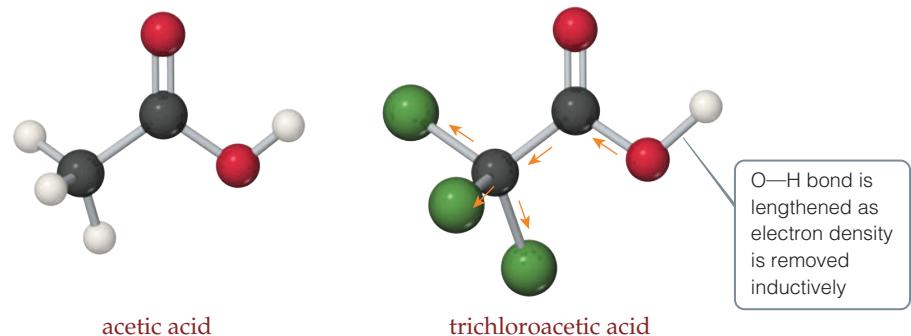
When propanoic acid is reacted with a solution of sodium hydrogen carbonate ($NaHCO_3$), the products are sodium propanoate, carbon dioxide and water. The reaction of carboxylic acids with carbonates such as $NaHCO_3$, Na_2CO_3, K_2CO_3 and $CaCO_3$ has special significance. Oral tablets such as Berocca™ and Aspro Clear™ combine carbonates with vitamin acids or citric acid to dissolve the tablet contents in water. The fizz associated with their dissolution is caused by the release of CO_2.


propanoic acid + $NaHCO_3(aq)$ ⟶ sodium propanoate + $CO_2(g)$ + H_2O [29.3]
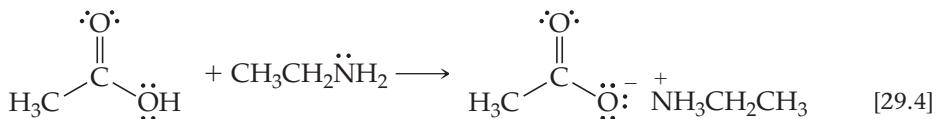
▶ **Figure 29.4** Inductive effect on pK_a. Electron-withdrawing substituents (for example, Cl, NO_2) adjacent to the carboxyl group are able to weaken the carboxyl O—H bond relative to acetic acid, making the compound a stronger acid. Any effect of a substituent that acts "through bonds" rather than by providing an alternative resonance structure, is called an **inductive effect**.

O—H bond is lengthened as electron density is removed inductively

acetic acid   trichloroacetic acid

Carboxylic acids react with amines to form ammonium salts. For example, the reaction of acetic acid with ethanamine yields the ammonium salt, ethyl ammonium acetate:

$$+ \; CH_3CH_2\ddot{N}H_2 \longrightarrow \qquad\qquad [29.4]$$

The reaction types demonstrated in Equations 29.2–29.4 are extremely useful in the preparation of water-soluble compounds, particularly for the pharmaceutical industry. The salt products are highly soluble in aqueous solutions and can be achieved under mild conditions or formed *in situ*, as in the case of soluble aspirin. Water solubility aids in absorption of the therapeutic agent. This reaction is also useful in the *resolution* of chiral carboxylic acids.

Sample Exercise 29.1
Properties of Carboxylic Acids
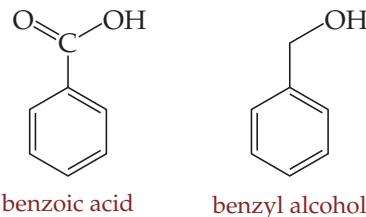
Describe a way of separating benzoic acid from benzyl alcohol.

SOLUTION

Analyze We are asked how to separate an alcohol from a carboxylic acid containing a similar structure.

Plan The carboxylic acid and alcohol functional group have a different reactivity and so can be separated using chemical reactions.
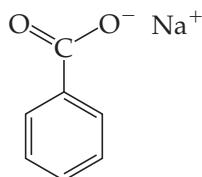
Solve In this case, we can use the differences in acidity between the two compounds and the aqueous solubility of the benzoate anion to separate them.

benzoic acid   benzyl alcohol
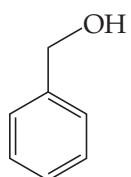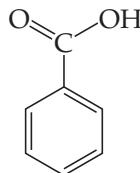
Dissolve in diethyl ether and mix with 0.1 M NaOH

aqueous layer   diethyl ether layer

Acidify with 1 M HCl and filter

Remove diethyl ether by distillation to leave pure product
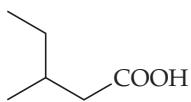
▶ **Practice Exercise**
List the following set of carboxylic acids in order of acidity (lowest first): **(a)** butanoic acid, **(b)** 2-iodobutanoic acid, **(c)** 2-fluorobutanoic acid, **(d)** trifluoroacetic acid, **(e)** 3-iodobutanoic acid.
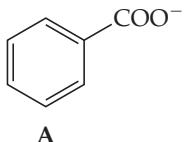
Self-Assessment Exercises

29.1 Name:
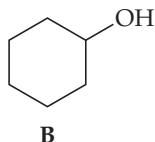
(a) 2-ethylbutanoic acid
(b) 3-ethylbutanoic acid
(c) 3-methylpentanoic acid
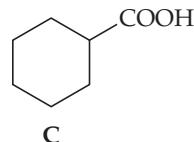
29.2 Order the following species in terms of increasing solubility in water.
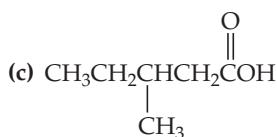
A   **B**   **C**

(a) A < B < C
(b) A < C < B
(c) B < C < A
(d) B < A < C

Exercises

29.3 Give the IUPAC name for each of the following acids:

(a) HCOH

(b) $CH_3CH_2CH_2COH$

(c) $CH_3CH_2CHCH_2COH$
             |
             CH_3
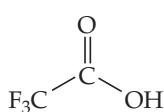
29.4 Draw the structure for 2-bromobutanoic acid and indicate any stereogenic center within the molecule. How many stereoisomers are possible?
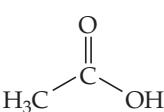
29.5 (a) Would you expect pure acetic acid to be a strongly hydrogen bonded substance? (b) How do the melting and boiling points of the substance support your answer? (See Table 29.1.)

29.6 Describe how you would distinguish between a carboxylic acid and its ester, using nothing more than an aqueous solution of sodium hydrogencarbonate ($NaHCO_3$, sodium bicarbonate).
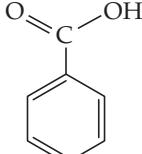
29.7 Which of the following carboxylic acids is the most acidic? Why?
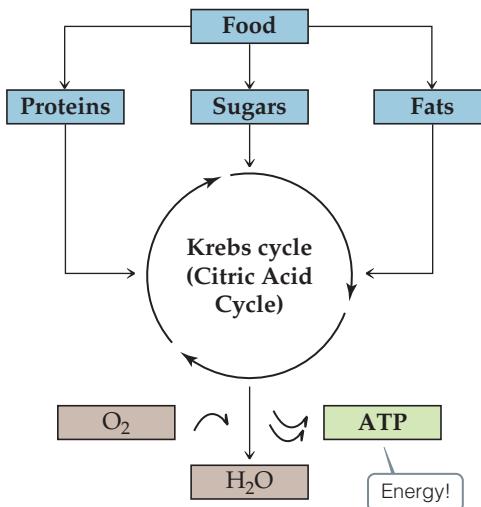

Acid A   Acid B   Acid C

Answers to Self-Assessment Exercises

29.1 (c)   **29.2** (c)

29.2 | Preparation of Carboxylic Acids

Citric acid is a tricarboxylic acid with the structure shown in Figure 29.1. It is used in the food industry as a flavoring agent and acidifier and naturally occurs in fruits, particularly citrus fruits, where it may by up to 8% of the dry weight of lemons and limes. It plays a central role in the metabolism of all animals, plants, and bacteria as part of the Citric Acid Cycle, which is also called the Tricarboxylic Acid Cycle (TCA cycle) or Krebs Cycle. While the cycle has a number of important functions, it is responsible for converting the fats and carbohydrates we eat, together with oxygen, into a usable source of energy. Not surprisingly, it is one of the most studied biochemical pathways. The 1953 Nobel prize in Physiology and Medicine was awarded to Hans Adolf Krebs for his pioneering work on the cycle.
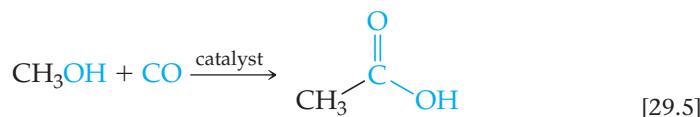
By the end of this section, you should be able to:

- Identify a number of preparation routes to simple carboxylic acids

Carboxylic acids can be synthesized through the oxidation of 1° alcohols, such as ethanol or propan-1-ol. Under appropriate conditions, the corresponding aldehyde may also be isolated as the first product of oxidation.
The oxidation of ethanol to acetic acid in air (with help from enzymes within wine) is responsible for causing wines to turn sour, producing vinegar.
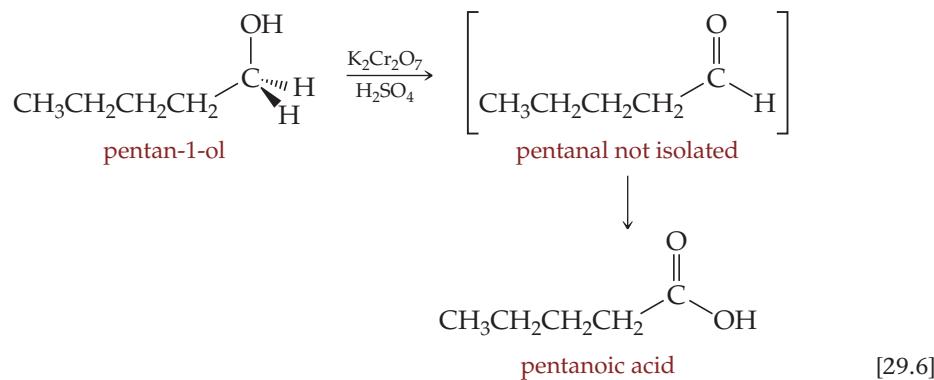
Acetic acid is produced industrially by the reaction of methanol with carbon monoxide in the presence of a rhodium catalyst:

$$CH_3OH + CO \xrightarrow{\text{catalyst}} \underset{CH_3}{\overset{\overset{\displaystyle O}{\|}}{C}}{-}OH \qquad [29.5]$$
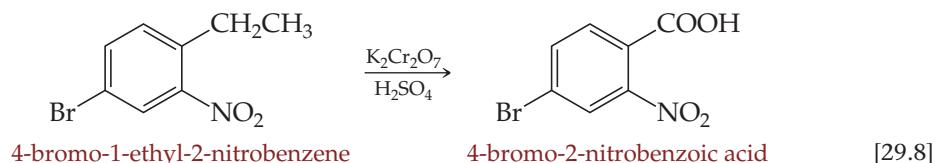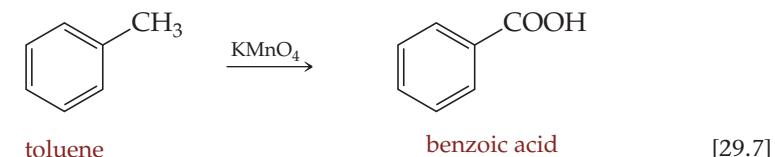
This reaction involves, in effect, the insertion of a carbon monoxide molecule between the CH_3 and OH groups. A reaction of this kind is called *carbonylation*.
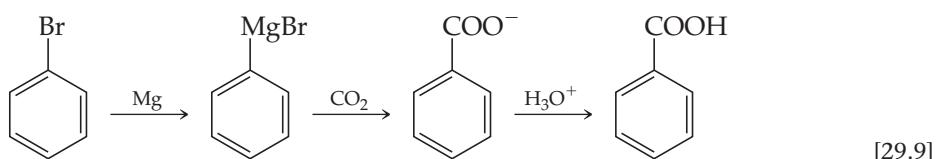
When primary alcohols are oxidized using strong oxidising agents such as potassium dichromate ($K_2Cr_2O_7$) in H_2SO_4 or chromic acid ($CrO_3/H_2O/H_2SO_4$), they are converted to the corresponding carboxylic acid via the intermediary aldehyde. Aldehydes are more prone to oxidation than alcohols. In fact, left to stand, aldehydes are oxidized readily by the oxygen within air, also forming carboxylic acids. Hence, when the oxidation reaction of a primary alcohol proceeds, any aldehyde formed within the reaction is quickly converted to the carboxylic acid. For example, the oxidation of pentan-1-ol in the presence of acidic $K_2Cr_2O_7$ gives pentanoic acid as the major product:

$$\underset{\text{pentan-1-ol}}{CH_3CH_2CH_2CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}{\sim}H} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \left[\underset{\text{pentanal not isolated}}{CH_3CH_2CH_2CH_2{-}\underset{}{\overset{\overset{\displaystyle O}{\|}}{C}}{-}H} \right]$$

$$\underset{\text{pentanoic acid}}{CH_3CH_2CH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} \qquad [29.6]$$
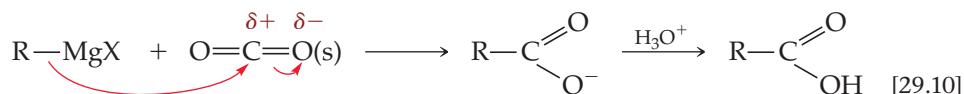
Toluene and other aromatics containing a benzylic CH group are easily oxidized to the corresponding benzoic acid on boiling with solutions of potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$). This occurs even if the benzylic carbon contains one, two or three C—C bonds.

toluene → benzoic acid   [29.7]

4-bromo-1-ethyl-2-nitrobenzene → 4-bromo-2-nitrobenzoic acid   [29.8]

Benzoic acids can also be prepared by the reaction of phenylmagnesium bromide with carbon dioxide (in the form of dry ice), followed by protonation.

[29.9]
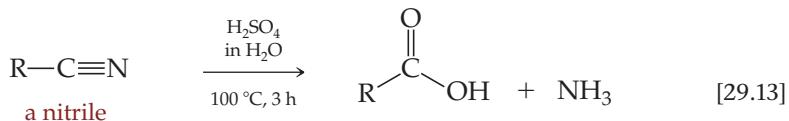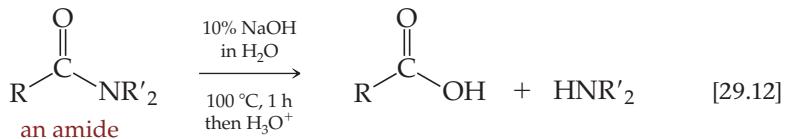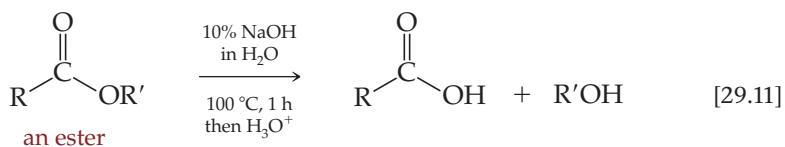
Recall from Chapter 28 that Grignard reagents make excellent nucleophiles, capable of reacting with carbonyl-containing compounds such as aldehydes and ketones. Generally speaking, the action of Grignard reagents (RMgX) on solid carbon dioxide to form carboxylic acids occurs by the following mechanism:

$$R-MgX \ + \ O{=}C{=}O(s) \longrightarrow R-C \overset{O}{\underset{O^-}{\diagdown}} \xrightarrow{H_3O^+} R-C \overset{O}{\underset{OH}{\diagdown}} \quad [29.10]$$

Carboxylic acids are also formed by the hydrolysis of certain functional groups. In the next section we discuss the reaction of carboxylic acids with alcohols to give an ester and with amines to give amides. We will also discuss the hydrolysis of esters to give carboxylic acids, using both acidic and basic conditions.

Carboxylic acids can be prepared by the hydrolysis of amides. It is fair to say that secondary and tertiary amides hydrolyse more slowly than primary amides under the conditions shown here. Finally, carboxylic acids can be formed readily by the hydrolysis of nitriles (RCN) under acidic conditions.

an ester $\xrightarrow[\substack{100\,°C,\,1\,h \\ then\ H_3O^+}]{\substack{10\%\ NaOH \\ in\ H_2O}}$ → + R'OH   [29.11]

an amide $\xrightarrow[\substack{100\,°C,\,1\,h \\ then\ H_3O^+}]{\substack{10\%\ NaOH \\ in\ H_2O}}$ → + HNR'$_2$ [29.12]

$R-C{\equiv}N$ a nitrile $\xrightarrow[\substack{100\,°C,\,3\,h}]{\substack{H_2SO_4 \\ in\ H_2O}}$ → + NH$_3$ [29.13]

Sample Exercise 29.2
### Preparation of Carboxylic Acids
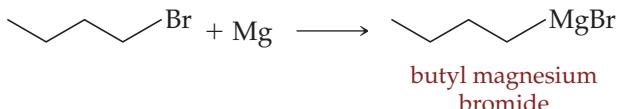
Describe a way of preparing pentanoic acid from 1-bromobutane.

SOLUTION
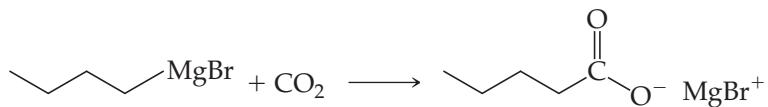
Analyze We are asked to propose a synthesis of a carboxylic acid from a specific starting material and note that the target compound contains one more carbon atom than the reactant.

Plan There are two common methods of extending the number of carbon atoms in a chain: either a nucleophilic substitution by the cyanide ion or the addition of a Grignard reagent to a compound containing a C=O bond. Both could be extended to form a carboxylic acid. In the first case, hydrolysis of a nitrile under acid conditions will yield a carboxylic acid. In the second case, reaction of a Grignard reagent with carbon dioxide followed by dilute acid will furnish a carboxylic acid. We will choose the second route.
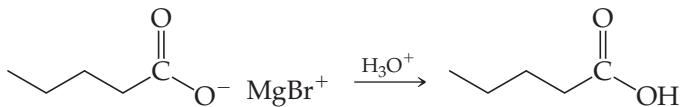
Solve Grignard reagents are very sensitive to moisture so are usually formed at the time they will be used in a "one pot" reaction. First, 1-bromobutane is treated with magnesium in diethyl ether solvent.

butyl magnesium
bromide

Next, carbon dioxide in the form of dry ice is added to the reaction vessel.
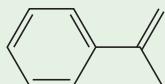

Finally, dilute acid is added to give the desired carboxylic acid.
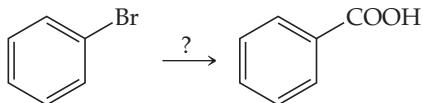
▶ **Practice Exercise**
Write the structural formula of the carboxylic acid formed by treatment of chlorobenzene with magnesium, followed by carbon dioxide and finally aqueous acid.


Self-Assessment Exercise

29.8 What reagents are used to synthesize benzoic acid from bromobenzene?
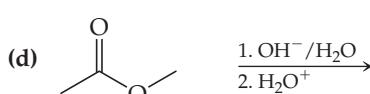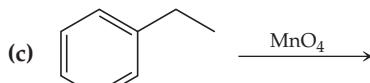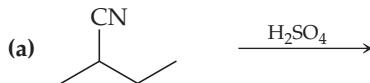

(a) 1) Mg   2) CO_2 3) H_3O^+
(b) 1) OH^- 2) K_2CrO_7/H_2SO_4
(c) 1) O_3 2) $(CH_3)_2S$
(d) $KMnO_4$
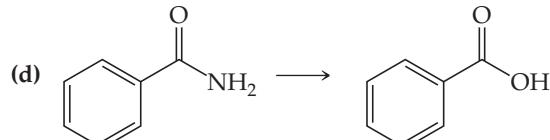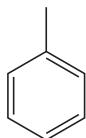
Exercises
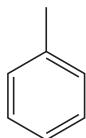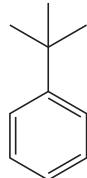
29.9 What is the major organic product in the following reactions?

(a)

$\xrightarrow{H_2SO_4}$

(b)

$\xrightarrow{PCC}$

(c)

$\xrightarrow{MnO_4}$

(d)

$\xrightarrow[\text{2. } H_2O^+]{\text{1. } OH^-/H_2O}$
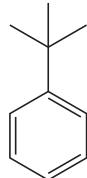
29.10 What reagent(s) are used in the following transformations?

(a)

(b)

(c)

(d)

29.11 Toluene, is converted to benzoic acid by $KMnO_4$ but *tert*-butylbenzene, is not. Explain.
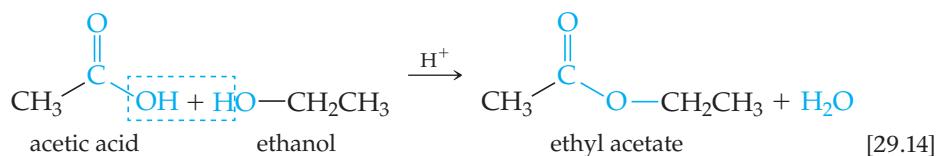
29.3 | Esters and Esterification

The smell of ripe fruit results from a mixture of volatile compounds. Many of these are esters and, quite often, a single ester dominates the aroma of a particular fruit. In general, esters are sweet smelling and have a lower boiling point than carboxylic acids of similar molecular mass. By the end of this section, you should be able to:

- Understand the synthesis and hydrolysis of the ester functional group.

Carboxylic acids can undergo acid-catalyzed condensation reactions with alcohols to form **esters**:

$$CH_3-C(=O)-OH + HO-CH_2CH_3 \xrightarrow{H^+} CH_3-C(=O)-O-CH_2CH_3 + H_2O$$

acetic acid   ethanol   ethyl acetate   [29.14]
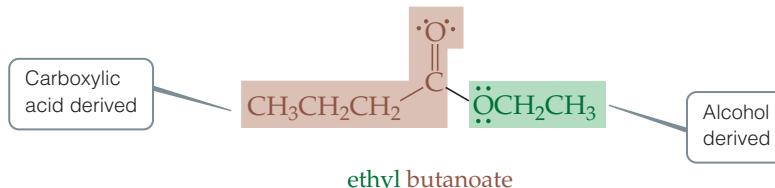
The reaction is termed a *condensation reaction* due to the loss of one mole of water per mole of acid and alcohol. This reaction is commonly known as the **Fischer esterification**, named after the German chemist Emil Fischer (1852–1919), who was awarded the Nobel Prize for Chemistry in 1902.

Esters are compounds in which the OH group of a carboxylic acid is replaced by an OR group:

$$-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-O-R, \quad -COOR, \quad or \quad -CO_2R$$
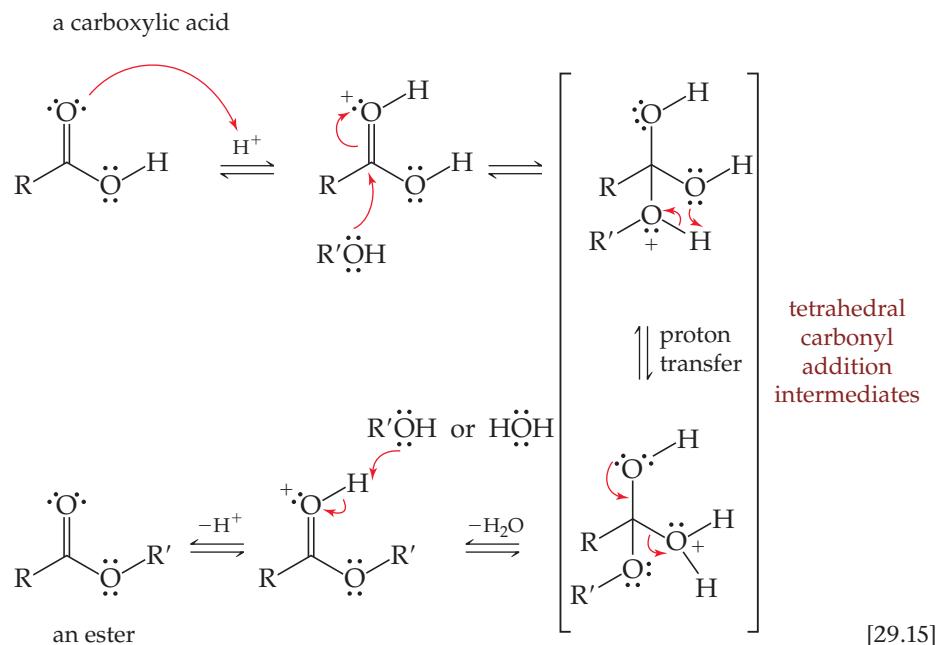
Figure 29.5 shows some common esters, which are named by using first the group from which the alcohol is derived and then the group from which the acid is derived. For example, ethyl butanoate is derived from ethanol and butanoic acid:

Carboxylic acid derived — CH₃CH₂CH₂ — ÖCH₂CH₃ — Alcohol derived

ethyl butanoate

▲ **Figure 29.5 Everyday carboxylic acids and esters.** Many sunburn lotions contain the ester benzocaine; some nail polish remover is ethyl acetate; vegetable oils are also esters.

Esters generally have pleasant odours and are largely responsible for the pleasant aromas of fruit. Table 29.4 lists some common esters and the structures, fragrances and flavors associated with them.
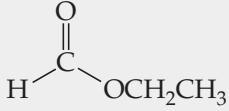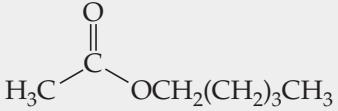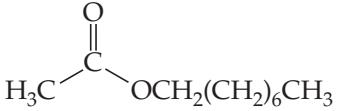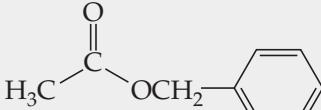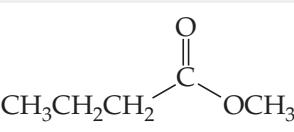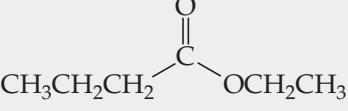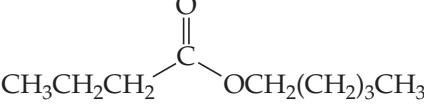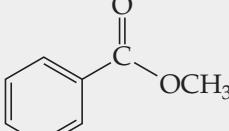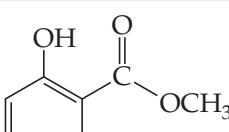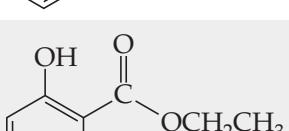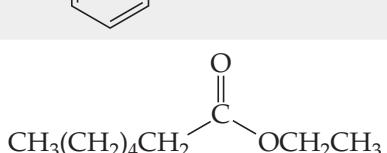
The mechanism of formation of an ester by the acid-catalyzed condensation of an alcohol and a carboxylic acid can be shown as follows:

a carboxylic acid

tetrahedral carbonyl addition intermediates

proton transfer

an ester

[29.15]
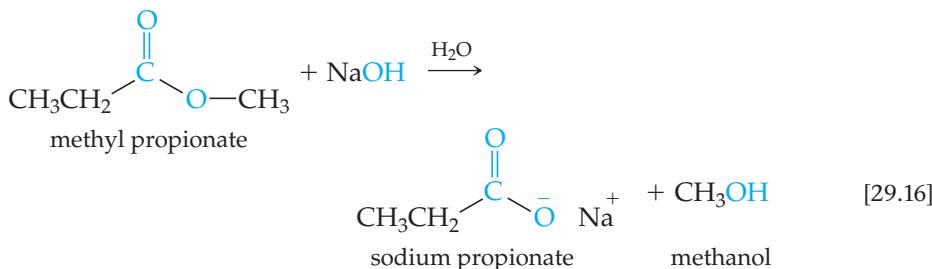
As with aldehydes and ketones, the basis of reactivity of the carboxylic acid occurs at the carbonyl group. The electronegativity of two oxygen atoms on the carbonyl carbon makes this carbon more electropositive than the corresponding carbon of either an aldehyde or ketone. Note from Equation 29.15 that the esterification reaction is fully reversible at each step and that formation of the ester from the carboxylic acid requires an excess of alcohol to drive the reaction in the direction that favors ester formation.

From the mechanism shown in Equation 29.15, it should become apparent that carboxylic acids can be formed from esters by the addition of excess water in the presence of an acid catalyst. This reaction, called hydrolysis, is the reverse of that described and is an important reaction in organic synthesis, as esters are often prepared to protect carboxylic acids.

TABLE 29.4 Simple esters as flavors and fragrances

Ester	Formula	Flavor/fragrance
Ethyl methanoate		rum
Butyl acetate		raspberry
Pentyl acetate		banana
Octyl acetate		orange
Benzyl acetate		jasmine
Methyl butanoate		apple
Ethyl butanoate		pineapple
Pentyl butanoate		pear or apricot
Methyl benzoate		almond
Methyl salicylate		oil of wintergreen
Ethyl salicylate		mint
Ethyl heptanoate		grape

The hydrolysis of esters is also possible in a basic aqueous medium, such as sodium hydroxide solution:

$+ \text{NaOH} \xrightarrow{\text{H}_2\text{O}}$

methyl propionate

$+ \text{CH}_3\text{OH}$ [29.16]

sodium propionate   methanol
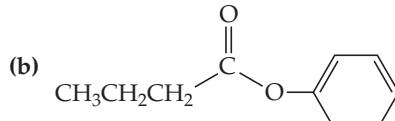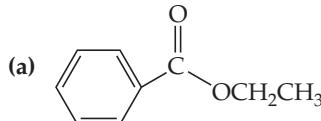
The products of the reaction are the sodium salt of the carboxylic acid and the alcohol. Distillation of the methanol and acidification of the aqueous solution of the sodium carboxylate yields the carboxylic acid. The hydrolysis of an ester in the presence of a base is called **saponification**, a term that comes from the Latin word for soap (*sapon*). The traditional synthesis of soap from animal fat is an example of this reaction.

Sample Exercise 29.3

Naming Esters and Predicting Hydrolysis Products

Name each of the following esters and indicate the products of their reaction with aqueous base.

(a)

(b)
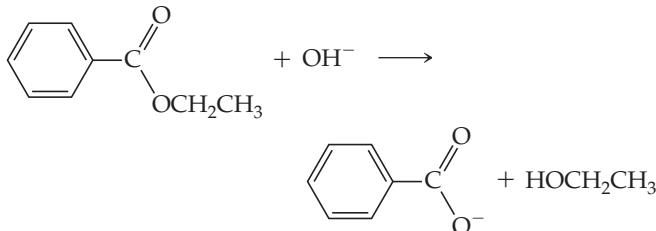
SOLUTION

Analyze We are asked to name each ester and to determine their saponification products.

Plan To name an ester, we must analyze its structure and determine the identities of the alcohol and acid from which it is formed. Identifying these two components will also allow us to determine the products of the saponification.
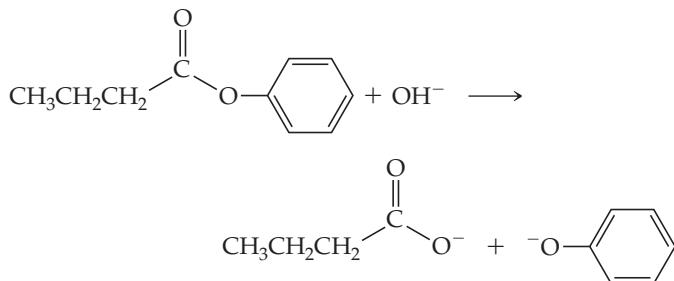
Solve Esters are formed by the condensation reaction between an alcohol and a carboxylic acid. We can identify the alcohol by adding an OH to the alkyl group attached to the O atom of the carboxyl (COO) group. We can identify the acid by adding an H group to the O atom of the carboxyl group. We've learned that the first part of an ester name indicates the alcohol portion and the second part indicates the acid portion. The name conforms to how the ester undergoes hydrolysis, reacting with base to form an alcohol and a carboxylate anion.

(a) This ester is derived from ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$). Its name is therefore ethyl benzoate. The net ionic equation for reaction of ethyl benzoate with hydroxide ion is:

$+ \text{OH}^- \longrightarrow$

$+ \text{HOCH}_2\text{CH}_3$

The products are benzoate ion and ethanol.

(b) This ester is derived from phenol ($\text{C}_6\text{H}_5\text{OH}$) and butanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$). The residue from the phenol is called the phenyl group. The ester is therefore named phenyl butanoate. The net ionic equation for the reaction of phenyl butanoate with hydroxide ion is

$+ \text{OH}^- \longrightarrow$

The products are butanoate ion and phenoxide ion.

▶ **Practice Exercise**
Write the structural formula for the ester formed from propanol and propionic acid.
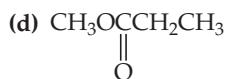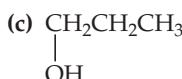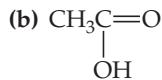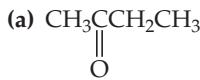
Self-Assessment Exercise

29.12 What are the products of base hydrolysis of ethyl propanoate?
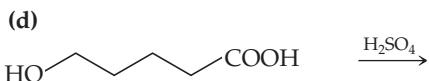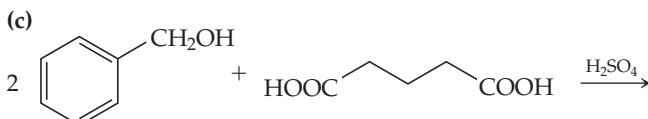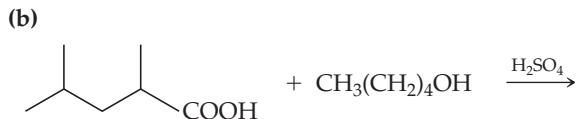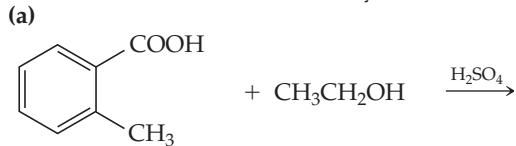
(a) CH_3COOH and $CH_3CH_2CH_2OH$

(b) CH_3CH_2COOH and CH_3CH_2OH

(c) $CH_3CH_2COO^-$ and CH_3CH_2OH

(d) CH_3CH_2COOOH and $CH_3CH_2O^-$

Exercises
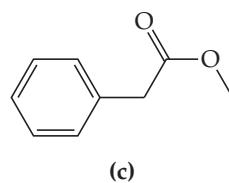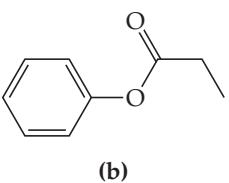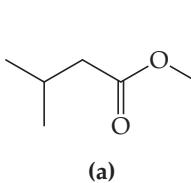
29.13 Identify the functional groups in each of the following compounds:

(a) $CH_3\overset{\underset{\|}{O}}{C}CH_2CH_3$

(b) $CH_3\overset{\underset{|}{OH}}{\overset{\|}{C}}{=}O$

(c) $\overset{\underset{|}{OH}}{C}H_2CH_2CH_3$

(d) $CH_3O\overset{\underset{\|}{O}}{C}CH_2CH_3$
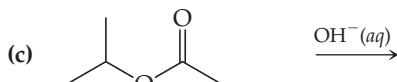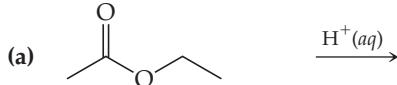
29.14 Draw the products of the following reactions. In each case, the sulfuric acid acts as a catalyst.

(a)

COOH

CH₃

$+ CH_3CH_2OH \xrightarrow{H_2SO_4}$

(b)

COOH

$+ CH_3(CH_2)_4OH \xrightarrow{H_2SO_4}$

(c)

2 CH₂OH

$+$ HOOC⌁⌁COOH $\xrightarrow{H_2SO_4}$

(d)

HO⌁⌁COOH $\xrightarrow{H_2SO_4}$

29.15 Give the condensed formulas for the carboxylic acid and alcohol from which each of the following esters may be formed.

(a)   (b)   (c)

29.16 Draw the products of the following reactions.

(a) $\xrightarrow{H^+(aq)}$

(b) —OCOCH₃ $\xrightarrow{H^+(aq)}$

(c) $\xrightarrow{OH^-(aq)}$

(d) $\xrightarrow{OH^-(aq)}$

29.4 | Fats, Oils, and Waxes

Obesity is an increasing issue in modern society and is considered the main preventable cause of death in the western world. It significantly increases the risk of cardiovascular disease and type 2 diabetes as well as a range of other conditions. Typically, obesity results from a combination of eating too many sweet or fatty foods, which are high in energy-rich carbohydrates or lipids, respectively, while not getting enough exercise but other factors such as depression and genetic susceptibility may contribute. A change of diet and increase in physical activity is used to combat obesity but may require considerable willpower to implement. Obesity is defined by a body mass index (BMI) greater than 30 kg/m^2. BMI is calculated by dividing a person's weight in kg by the square of their height in m.

"Lipid" is a term that covers a range of molecules, all of which are hydrophobic. Fats, oils, and waxes are examples of lipids that we will now examine. By the end of this section, you should be able to:

- Recognize the common structural unit of a lipid
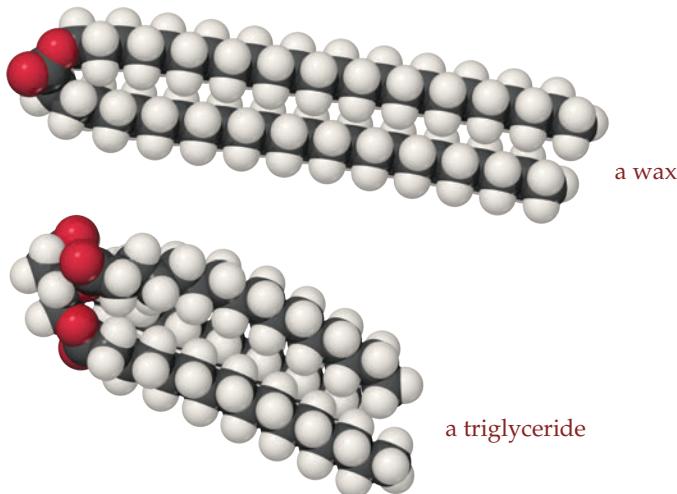
Lipids are naturally occurring substances that can be extracted from cells and tissues by non-polar organic solvents. Common examples of lipids include cholesterol (a steroid), turpentine (a terpene), beeswax and olive oil. Even from this very limited group of compounds, it is quite clear that although lipids can contain a variety of functional groups, their overriding feature is the large proportion of hydrocarbon within the structure. The name "lipid" is derived from a property rather than from any functional group class (the Greek *lipos* means fat). **Complex lipids** are those that can be broken down into smaller constituents, usually by hydrolysis. **Simple lipids** are those that are not easily hydrolysed.

In this section we discuss a group of complex lipids that are esters of long-chain carboxylic acids called **fatty acids**. Two major groups of esters are derived from fatty acids: the waxes and triglycerides. **Waxes**, such as beeswax, are single esters made from fatty acids and long-chain alcohols. **Triglycerides** (more correctly known as triacyl glycerols) are triesters of glycerol and include common fats and oils. **Figure 29.6** shows two general examples of complex lipids. As you can see, even without investigating the type of functional group, both these molecules have alkyl chains of significant length. Their properties are derived from this feature. Waxes are typically greasy solids or semi-solids, while triglycerides can be solid or liquid at room temperature.

The most common triglycerides are those in which each fatty acid component is unbranched and has an alkyl chain more than 12 carbon atoms long. **Table 29.5** shows some of the more common saturated and unsaturated fatty acids found naturally.
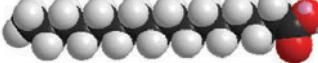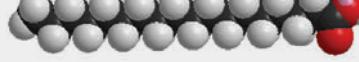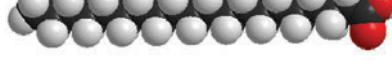
Go Figure What structural features of a triglyceride molecule cause it to be insoluble in water?

a wax

a triglyceride

▲ **Figure 29.6 Complex lipids.** A general example of the structure of a wax ($C_{25}H_{51}COOC_{24}H_{49}$) and a triglyceride using the C_{16} fatty acid, palmitic acid.

TABLE 29.5   Structure and names of some common fatty acids

Name	Chain length	Structure	Melting point (°C)
		Saturated acids	
Lauric acid	C12		45
Myristic acid	C14		53
Palmitic acid	C16		62
Stearic acid	C18		70
Arachidic acid	C20		75
		Unsaturated acids	
Oleic acid	C18 (1 × *cis* double bond)		13
Linoleic acid	C18 (2 × *cis* double bonds)		−5
Arachidonic acid	C20 (4 × *cis* double bonds)		−50

Note the difference in overall shape between saturated and unsaturated fatty acids. This shape difference is responsible for the different physical properties exhibited by the fatty acids and their corresponding triglycerides and waxes. For example, the melting point of stearic acid (mp = 70 °C), a saturated fatty acid, is 57 °C higher than oleic acid (mp = 13 °C) and 75 °C higher than linoleic acid (mp = −5 °C), despite the fact they all contain 18 carbon atoms. The reason is that "kinked" fatty acids—that is, fatty acids that contain one or more double bonds—cannot pack as closely or efficiently as the saturated fatty acids.
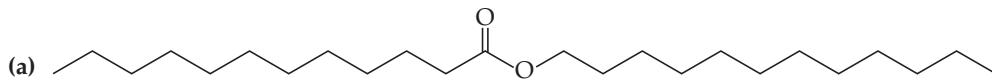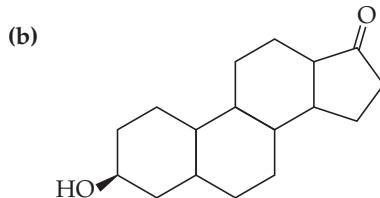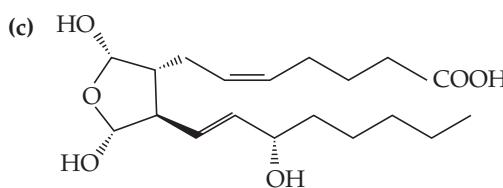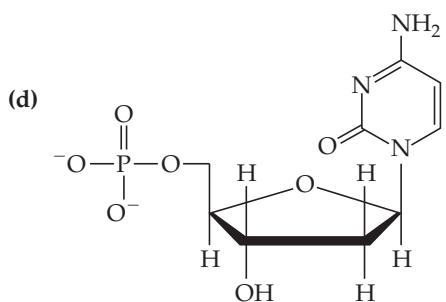
Most saturated triglycerides are **fats** because they are solid at room temperature. Most triglycerides containing double bonds do not pack as well as their saturated analogues and so are classed as **oils**. Oils are triglycerides that are liquid at room temperature. The term *polyunsaturated* simply means there is more than one double bond contained within the triglyceride.

Consumers have come to realise that polyunsaturated vegetable oils are more easily digested than saturated ones. However, this has not always been the case. For many decades, the use of *lard*—a soft, white solid obtained by rendering pig fat—for cooking and baking meant that consumers wanted solid fats instead of liquid oils. Vegetable oils, cheaper to produce and polyunsaturated, are still converted to fats through a process called **hardening**. As chemists, we know this process as catalytic hydrogenation. The basic principle is not to reduce all the double bonds within an unsaturated triglyceride, but to reduce enough of them to yield the required properties and consistency. Needless to say, the process is carefully controlled. Margarine obtained from canola oil is a classic example.

Sample Exercise 29.4
Lipids

Which of the following compounds is *not* classified as a lipid?

(a)

(b)

(c)

(d)

SOLUTION

Analyze We are asked to differentiate between compounds based on their functionality and to class them accordingly.

Plan By definition, *lipids* are naturally occurring substances that can be extracted from cells and tissue by non-polar organic solvents such as hexane. So we will use this definition as a means of classification.

Solve Structure **(a)** is a wax, similar to beeswax. It is soluble in hexane and so is classed as a lipid. Structure **(b)** is a member of the steroid hormones. Its large carbon framework suggests this compound will be soluble in non-polar solvents. Hence this

compound can be generally classed as a lipid. Structure **(c)** is a prostaglandin. Despite the presence of three OH and a carboxylic acid group, the two large alkyl chains would suggest this molecule is hexane soluble. This compound is also a lipid. Structure **(d)** is a nucleotide. Its collection of nitrogen- and oxygen-containing heterocycles and polar phosphate group would mean this compound is more aqueous than hexane soluble. Therefore, this class of compound is not a lipid.

▶ **Practice Exercise**
Draw the structure of a triglyceride containing lauric acid.
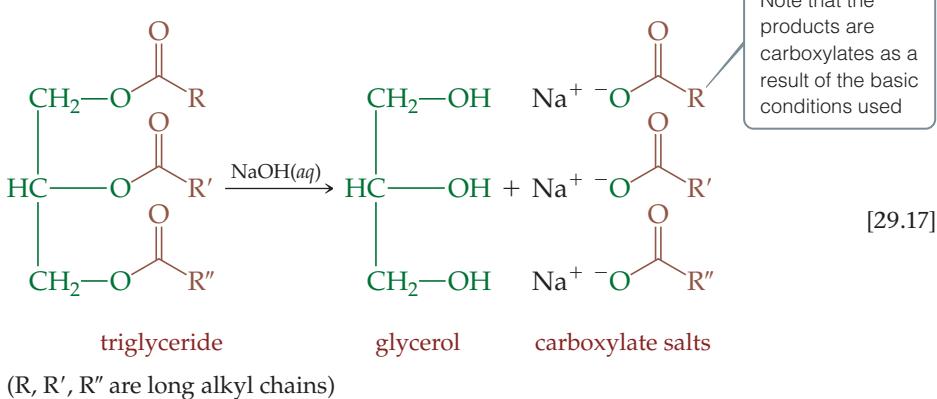
Soaps and Detergents

Historically, in the soap-making process a triglyceride (animal fat or a vegetable oil) was boiled with a strong base, usually NaOH. The resultant soap consisted of a mixture of sodium salts of long-chain carboxylic acids, the fatty acids, which formed during the saponification process (**Figure 29.7**).

▲ **Figure 29.7 Saponification.** Saponification of fats and oils has long been used to make soap. This etching shows a step in the soap-making process during the nineteenth century.

Note that the products are carboxylates as a result of the basic conditions used

[29.17]

triglyceride   glycerol   carboxylate salts

(R, R′, R″ are long alkyl chains)

The cleansing power of a soap is due to its ability to act as an emulsifying agent. That is, it is a substance that can sit at the interface between a hydrophobic liquid and a hydrophilic liquid, allowing the hydrophobic liquid to be dispersed in microscopic droplets. Many common forms of dirt (for example, grease, oil, fat) are hydrophobic and soaps allow them to be dispersed in waste water.

In water, soap forms a cloudy solution of **micelles**, as shown in **Figure 29.8**. Micelles form as a result of the hydrophobicity of the alkyl chains and the hydrophilicity of the polar carboxylate group. Micelles are stabilized by dispersion forces between alkyl groups and by hydrogen bonding between carboxylate anions and water molecules.

A common disadvantage of soap is the presence of *soap scum*, an insoluble precipitate or film that is difficult to remove from household areas such as bathrooms. This scum can be produced in two common ways. Foremost is the reaction of a fatty acid with Ca^{2+}, Mg^{2+} or Fe^{2+} ions found in *hard water*. This reaction, called a *counterion exchange* reaction, converts the sodium salt to the calcium salt, which is insoluble in water.

$$2\ CH_3(CH_2)_{16}COO^-\ Na^+\ +\ Ca^{2+}\ \longrightarrow\ Ca[CH_3(CH_2)_{16}COO]_2 + 2\ Na^+$$
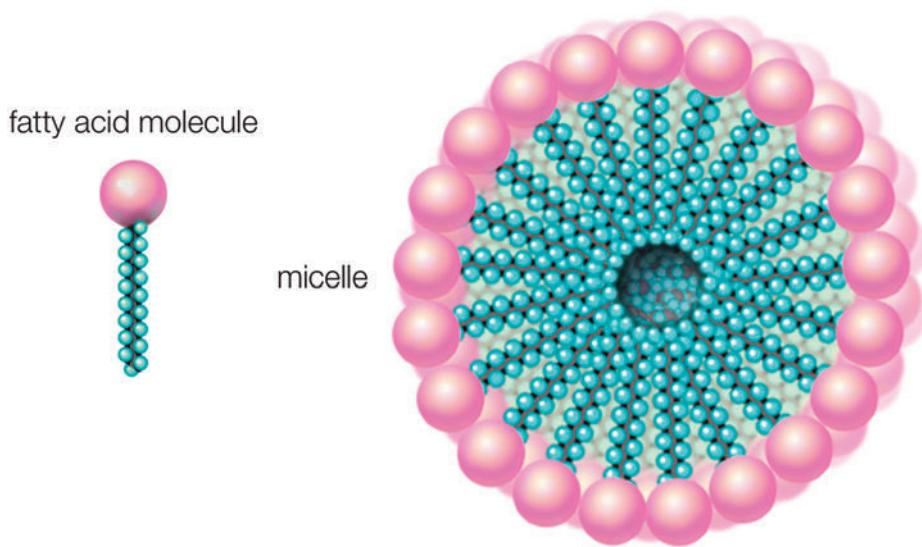
sodium salt of a fatty acid
(soluble in water as micelles)

calcium salt of a fatty acid
hard-water scum
(insoluble in water)   [29.18]
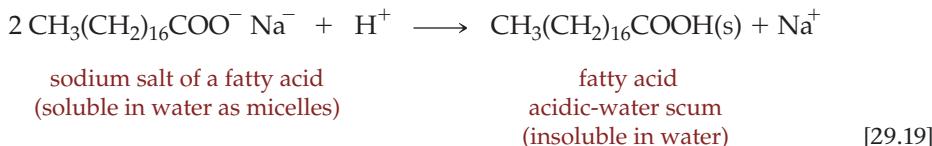
The other common way of building up soap scum is through the precipitation of fatty acids in hard water that has been acidified by some means—for example, acid rain.
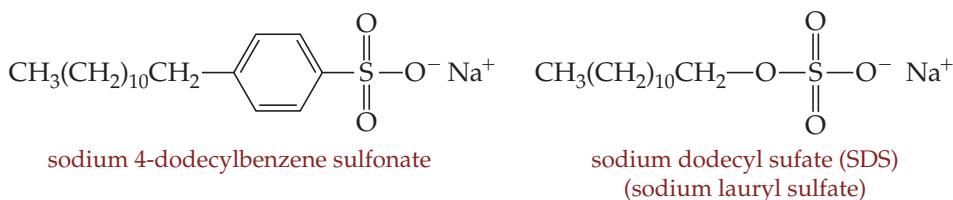
◀ **Figure 29.8 Soap micelle.** In water, soap forms a cloudy solution of micelles. The hydrophobic hydrocarbon chains cluster in the middle of the micelle and the polar (hydrophilic) carboxylate groups are on the surface. The Na^+ counterions are dissolved in the water around the micelle. Note: Micelles are not circular as drawn, but spherical (this is just a slice through a micelle).

Without the ionisable carboxylate group, the fatty acid floats to the top of a water-based solution as a scum.

$$2\ CH_3(CH_2)_{16}COO^-\ Na^-\ +\ H^+\ \longrightarrow\ CH_3(CH_2)_{16}COOH(s) + Na^+$$

<div align="center">

sodium salt of a fatty acid   fatty acid
(soluble in water as micelles)   acidic-water scum
(insoluble in water)   [29.19]

</div>
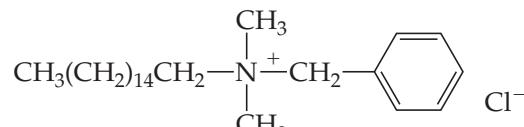
Synthetic detergents have been designed with the problem of soap scum in mind. Essentially, the same desirable characteristics of a fatty-acid soap must be maintained; that is, the detergent should contain a long hydrocarbon chain and a polar head group. It is desirable that this polar head group should not form insoluble salts with Ca^{2+}, Mg^{2+} or Fe^{2+} ions, in particular. Sodium salts of sulfonic acids, called sulfonates or sulfates, provide useful analogues to the carboxylate group. Being stronger acids than carboxylic acids means that sulfonic acids are not as easily protonated, even under the lowest pH conditions found domestically. Of even greater significance is the fact that calcium, magnesium and iron salts of sulfonic acids are soluble in water.

Not all detergents need to contain an anion. Benzalkonium chloride is one used in a variety of domestic liquid cleaning and disinfectant products. **Figure 29.9** illustrates some common examples of synthetic detergents.

◀ **Figure 29.9 Synthetic detergents.** Detergents can be anionic or cationic, but still retain the features of a soap derived from a fatty acid.

<div align="center">

sodium 4-dodecylbenzene sulfonate   sodium dodecyl sufate (SDS)
(sodium lauryl sulfate)

benzylcetyldimethylammonium chloride
(benzalkonium chloride)

</div>

Sample Exercise 29.5
Soap Structure
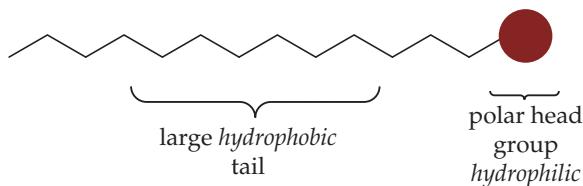
Draw the general structure of the main constituent of a soap micelle and indicate the hydrophilic and hydrophobic regions.

SOLUTION

Analyze We are asked to draw a schematic of the sodium or potassium salt of a fatty acid and indicate polar and non-polar regions.

Plan Since soaps are prepared from the carboxylate salt of a fatty acid, this question requires you to draw a long alkyl chain and a polar carboxylate head group.

Solve Using a simple circle for a head group and the line drawing of a long alkane, we get:

large *hydrophobic* tail

polar head group *hydrophilic*
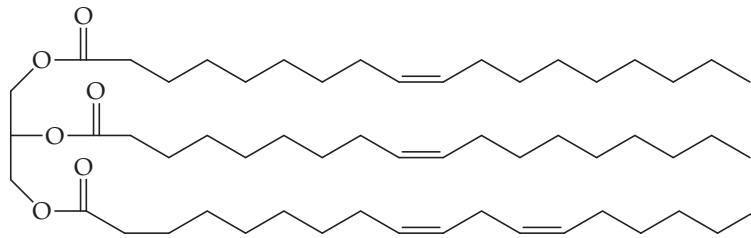
▶ **Practice Exercise**
Detail the common features of a soap and a detergent.

Self-Assessment Exercise

29.17 Olive oil is composed of a number of fatty acids, but a typical molecule has the structure:

Name the fatty acids present in this structure.
(a) Stearic acid + 2 × oleic acid
(b) 2 × Oleic acid + linoleic acid
(c) 2 × Oleic acid + arachidonic acid
(d) Oleic acid + 2 × linoleic acid

Exercises

29.18 **(a)** What is the difference between a fat and an oil? **(b)** What is the difference between an fat and a wax? Draw an example of each to illustrate your point.

29.19 Write a balanced chemical equation using condensed structural formulas for **(a)** the formation of butyl propanoate from the appropriate acid and alcohol, **(b)** the saponification (base hydrolysis) of methyl benzoate.
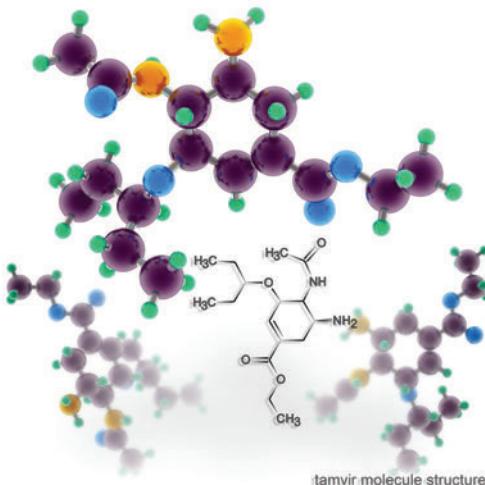
29.20 Triglycerides are formed from fatty acids and glycerol (1,2,3-propanetriol). **(a)** Draw a general formula for the structure of a triglyceride. **(b)** Describe the difference between a saturated and an unsaturated fatty acid. **(c)** Indicate the difference in melting point between a saturated triglyceride and a comparable polyunsaturated triglyceride.
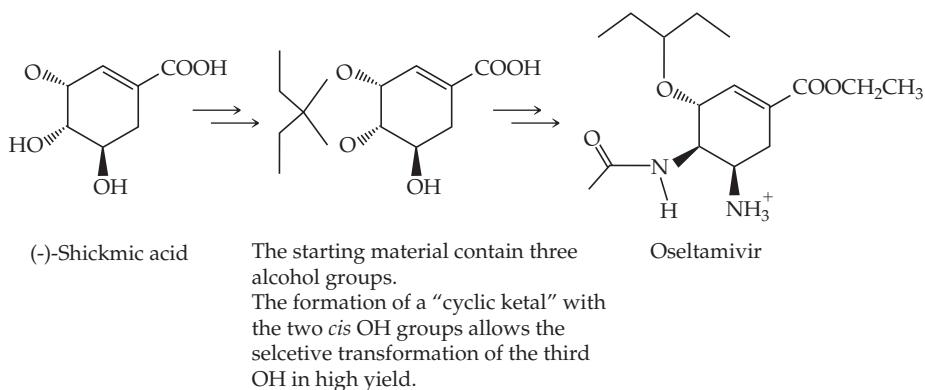
29.5 | Acid Chlorides, Anhydrides, and Nucleophilic Acyl Substitution

tamvir molecule structure

Most molecules around us contain more than one functional group. In our efforts to produce effective pharmaceuticals, we arrive at a substance that may have three, four, or more different functional groups in one molecule. This presents a difficulty in synthesis. How do we react one part of a molecule without affecting another functional group present? For example, treating a compound that contains both an aldehyde and a carboxylic acid group with an alcohol under acidic conditions will result in both an acetal and an ester being formed. As molecules become more complex and the number of functional groups they contain increases, the ability to do a reaction on one part of the molecule without interference from another functional group becomes increasingly difficult.

Sometimes the order in which we conduct a multi-stage synthesis allows us the selectivity we seek. In other cases, we may use "protecting groups". These are transformations that render one part of the molecule inactive while retaining the reactivity of another part. For example, a molecule that contains an alkene and a ketone will react with bromine by an electrophilic addition to the alkene and α-substitution to the carbonyl. If, however, we "protect" the ketone by forming an acetal first, bromination will only occur at the alkene, after which we can "deprotect" the acetal to re-form the original ketone. For this strategy to be efficient, the protecting group chemistry needs to be high-yielding and reversible. The formation of carboxylic acid derivatives, such as esters, is one example of the use of an effective protecting group. While protecting group chemistry is used extensively in a synthesis research laboratory, it is also employed in the manufacture of some pharmaceuticals such as oseltamivir—synthesized by Hoffmann-La Roche as an antiviral medication and marketed under the trade name of Tamiflu®.

(-)-Shickmic acid

The starting material contain three alcohol groups.
The formation of a "cyclic ketal" with the two *cis* OH groups allows the selcetive transformation of the third OH in high yield.

Oseltamivir

At the end of this section, you should be able to:

- Recognize the different functional groups that contain an acyl group
- Know the reagents necessary to convert between the different functional groups

Several functional group classes are derived from the carboxyl group. We have already introduced carboxylic acids and esters. Two others of note are the **acid anhydrides** and
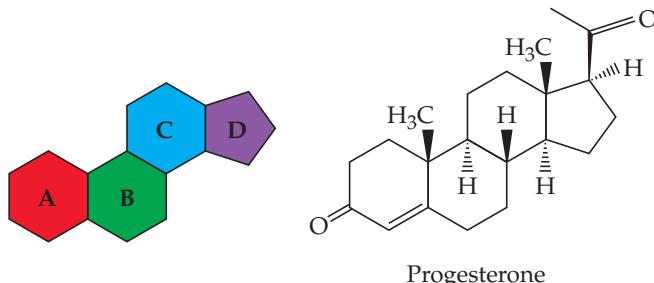
CHEMISTRY AND LIFE | Steroids

Hormones are chemical messengers capable of stimulating or inhibiting particular biochemical processes. One major class of hormones is the steroids. Because steroids are non-polar compounds, they are considered lipids. Their non-polar character allows them to cross cell membranes so they can leave the cells in which they were synthesized and enter their target cells. There have been five Nobel prizes in the area of steroid chemistry giving it a rich and important history across chemistry and medicine.
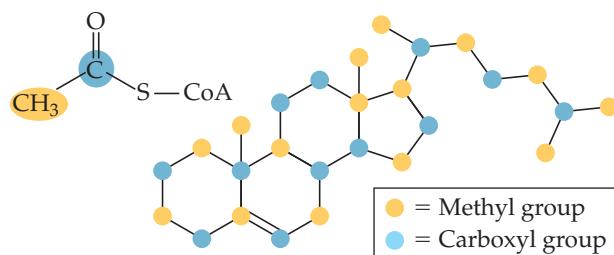
Bile salts are steroids with detergent properties able to emulsify lipids in foodstuff passing through the intestine to enable fat digestion and absorption through the intestinal wall. *Cholesterol* is a steroid found in animal tissues and various foods that is normally synthesized by the liver and is important as a constituent of cell membranes and influences membrane fluidity; it's actually a precursor to all steroid hormones. *Mineralcorticoids* such as aldosterone are secreted by the adrenal cortex and regulate the balance of water and electrolytes or salts (Na^+, Cl^-, HCO_3^-) in the body. The addition of aldosterone causes increased Na^+ readsorption, for example. *Glucocorticoids* such as cortisol (also called hydrocortisone) is also produced by the adrenal cortex and are involved in carbohydrate, protein and fat metabolism. They also have excellent anti-inflammatory properties. The most noted of the steroids are the sex hormones such as the estrogens (for example, progesterone and estrone) and the androgens (for example, testosterone). The estrogens and androgens affect the growth and function of the reproductive organs, the development of secondary sex characteristics and the behavioural patterns of animals. The structure of progesterone is shown in **Figure 29.10**. Anabolic steroids such as stanolozol aid in the development of muscles and are man made.

All steroids contain the characteristic rigid tetracyclic backbone based on the androstane ring system: the four rings are designated A, B, C and D as shown in Figure 29.10. The A, B and C rings are six-membered rings; D is a five-membered ring. In steroids, the rings are all fused with trans stereochemistry.

Steroids are made available from terpenes, which are readily made in nature from acetic acid.

▲ **Figure 29.11** **The tetracyclic backbone of all steroids can be traced back to acetic acid.** The methyl carbons in acetic acid are indicated as yellow dots, and the carbonyl carbons are represented in blue.
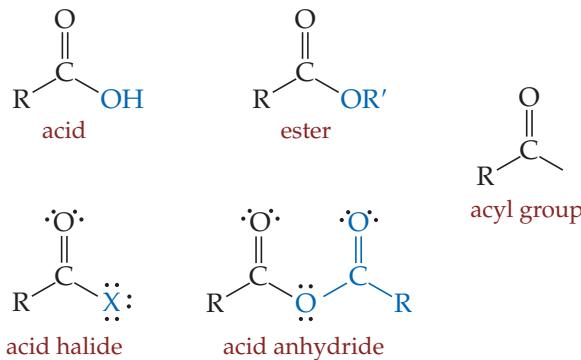
Figure 29.11 shows the origin of the acetic acid carbon atoms in a typical steroid structure. There are about 40 enzyme-catalyzed steps to prepare cholesterol from acetic acid through biosynthesis.

Poison dart frogs are fascinating creatures in that they secrete four steroid toxins from glands located on the back and behind the ears—one of them being among the most toxic substances known to man, batrachotoxin (**Figure 29.12**). Batrachotoxin contains the tetracyclic ring structure of the steroids. As a neurotoxin it affects the nervous system by increasing Na^+ permeability of cellular ion channels. It becomes lethal by permanently blocking nerve signal transmission to muscles, leading to cardiac arrest. The estimated lethal dose for this steroid poison in humans is somewhere between 2 and 200 µg.

▲ **Figure 29.10** **The central tetracyclic structure to all steroids.** Progesterone is an estrone that plays a role in maintaining pregnancy.
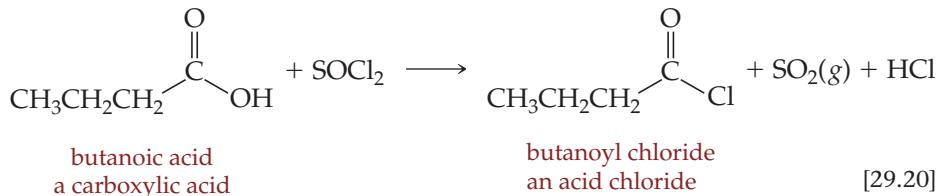
Batrachotoxin

▲ **Figure 29.12** **Poison dart frogs excrete batrachotoxin, a steroid-based structure and one of the most toxic compounds known.**
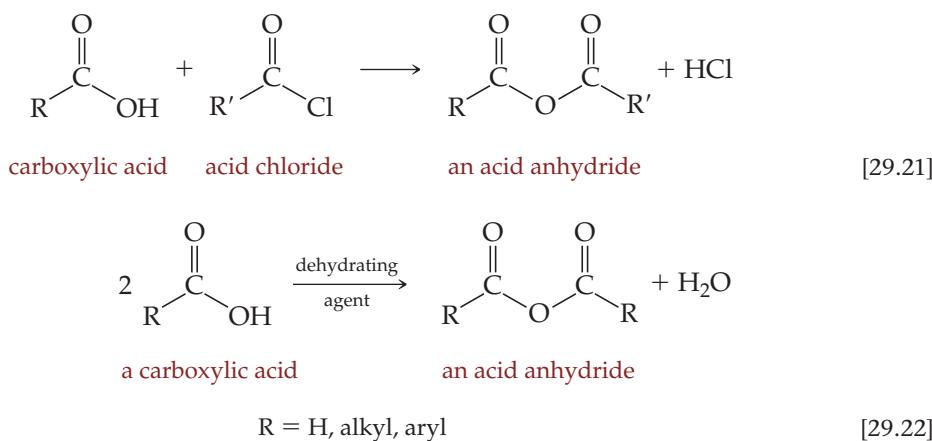
acid halides. The functional group known as an acid anhydride has two **acyl groups** (RCO–) linked by an oxygen atom. An acid halide has a single acyl group bonded to a halogen atom:

acid

ester

acyl group

acid halide

acid anhydride
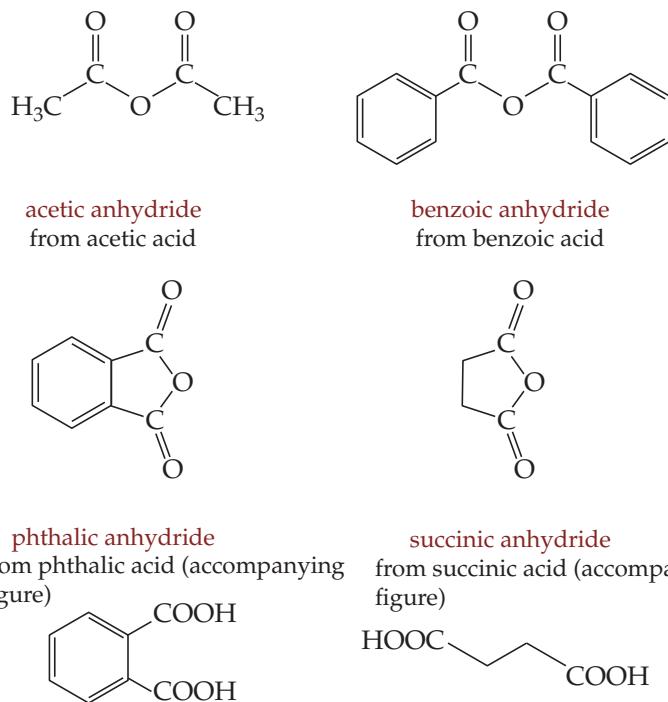
Acid chlorides, which are the most common and practical acid halides, are usually prepared by treatment of a carboxylic acid with thionyl chloride ($SOCl_2$). You may recall this reagent as a useful way of converting alcohols to chloroalkanes (Section 26.5). Acid chlorides are named by replacing the suffix *-oic acid* with *-oyl halide*. For example, $CH_3CH_2CH_2COCl$ is named butanoyl chloride and is derived from butanoic acid.

butanoic acid
a carboxylic acid

butanoyl chloride
an acid chloride

[29.20]

Acid anhydrides such as acetic anhydride, $(CH_3CO)_2O$, are usually prepared by reaction of a carboxylate anion with an acid chloride. In this way, both symmetrical anhydrides (same acyl group) and unsymmetrical anhydrides (different acyl groups) can be produced. Another general method is to dehydrate the carboxylic acid using a suitable dehydrating reagent, such as a more reactive anhydride. In some cases, especially 1,2-dicarboxylic acids such as phthalic acid or succinic acid, anhydrides can be formed by heating.

carboxylic acid   acid chloride

an acid anhydride

[29.21]

a carboxylic acid

an acid anhydride

R = H, alkyl, aryl

[29.22]
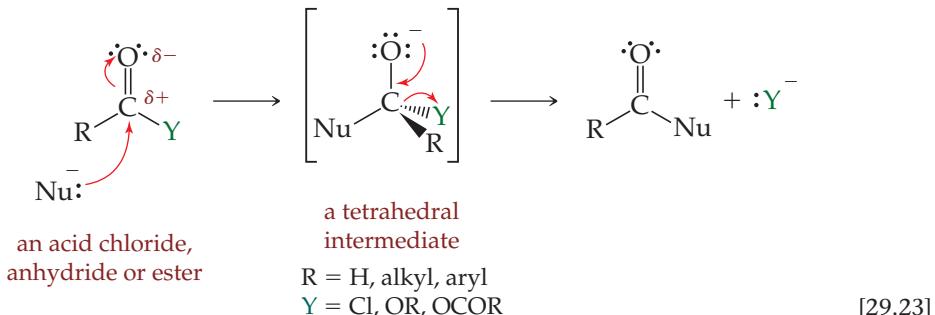
Anhydrides from simple carboxylic acids and cyclic anhydrides from dicarboxylic acids are named by replacing the word *acid* with *anhydride*.

acetic anhydride
from acetic acid

benzoic anhydride
from benzoic acid

phthalic anhydride
from phthalic acid (accompanying figure)

succinic anhydride
from succinic acid (accompanying figure)
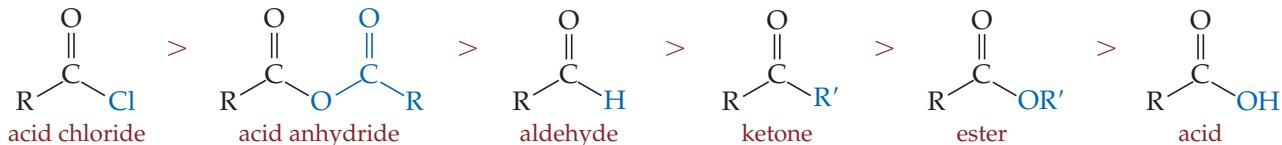
Nucleophilic Acyl Substitution

Esters, acid chlorides and acid anhydrides all undergo nucleophilic substitution reactions at the acyl carbonyl group by the following general mechanism:

an acid chloride, anhydride or ester

a tetrahedral intermediate

$R = H$, alkyl, aryl
$Y = Cl$, OR, OCOR

[29.23]

Such a reaction is called a **nucleophilic acyl substitution** and differs from nucleophilic reactions of aldehydes and ketones by the fate of the tetrahedral intermediate formed (compare the middle structure in equations 28.5 and 29.23). In this case, this intermediate collapses to regenerate the carboxyl group, thereby eliminating the group (Y)—which is typically a *good leaving group*—as a stable anion.

The reactivity of carbonyl compounds towards nucleophilic attack can be summarized as:

| acid chloride | > | acid anhydride | > | aldehyde | > | ketone | > | ester | > | acid |
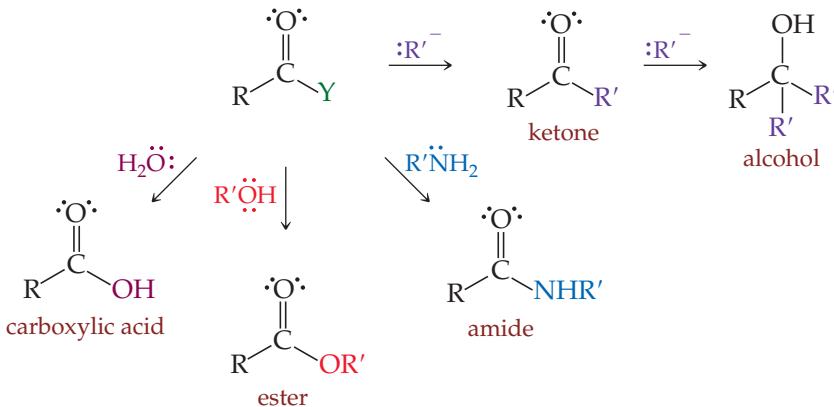
This relative reactivity is governed by two factors: the electropositive nature of the carbonyl carbon atom by substituent inductive effects, and the stability of the leaving group (Y⁻) displaced by substitution. Some useful interconversions using this reaction type are shown in **Figure 29.13** including the reaction of amines with acid chlorides, anhydrides and esters to form **amides**. Amides have an acyl group bonded to a trivalent nitrogen atom, usually of the form RCONHR'. Amide bonds are the key structural features that join amino acids together to form polypeptides and proteins. Amides are named by replacing the suffix *-oic acid* with *amide*. The N in the names shown here refers to functionalization on nitrogen. So, for N-methylbutanamide, the methyl group is bonded to nitrogen.
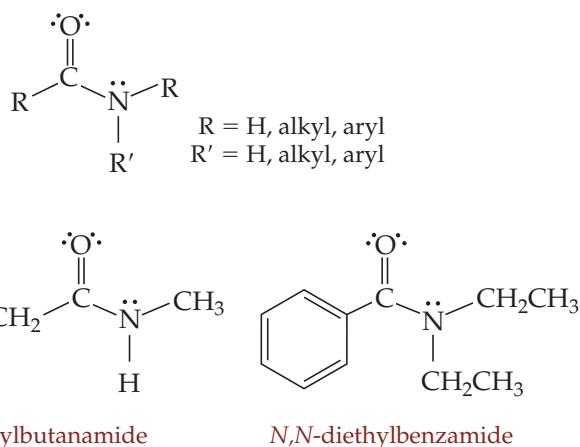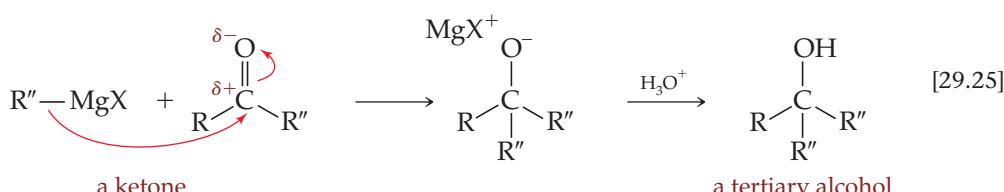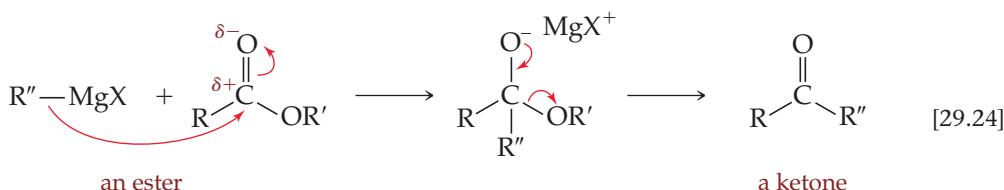
Go Figure   What role do water, alcohol and amine play in these interconversions?
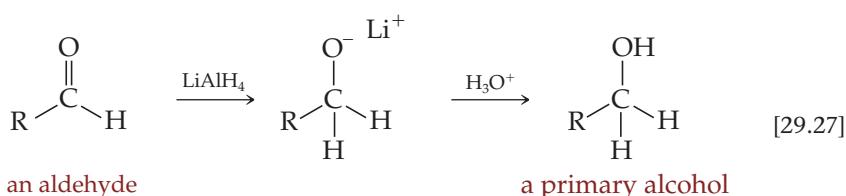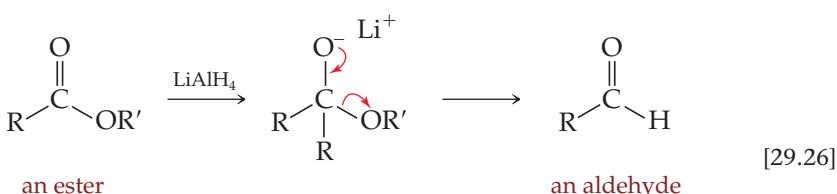
▲ **Figure 29.13 Functional group interconversions.** Acid halides, anhydrides and esters are versatile starting materials, leading to a range of different functional groups. Y = Cl, OR or OCOR.

R = H, alkyl, aryl
R' = H, alkyl, aryl

acetamide   *N*-methylbutanamide   *N,N*-diethylbenzamide

A second interconversion from Figure 29.13 to highlight involves the reaction of acid chlorides, anhydrides and esters with carbanions, such as those generated through Grignard reagents, to form alcohols via a ketone intermediate. The addition of a strong nucleophile such as a Grignard reagent to an ester (or acid chloride or anhydride) usually yields the corresponding 3° alcohol as the final product instead of the expected ketone (based on a stoichiometric addition). For this reason, usually two equivalents of the Grignard reagent are added to the reaction mixture to drive the reaction to completion. Mechanistically, collapse of the tetrahedral intermediate from the ester, after attack of the first equivalent of RMgX, yields a ketone. The ketone is more electrophilic than the ester (and so more reactive towards a second equivalent of RMgX), so it undergoes further reaction to yield the stable alkoxide in preference. Upon the addition of acid, the tertiary alcohol is formed.

an ester   a ketone   [29.24]

a ketone   a tertiary alcohol   [29.25]

We can extrapolate this result to other nucleophiles such as hydride (H^-), which comes in the form of lithium aluminum hydride ($LiAlH_4$), a powerful reducing agent. As shown in Equation 29.26, collapse of the tetrahedral intermediate from the ester yields an aldehyde, which again is more reactive than the ester, and which undergoes a second addition of hydride to form the alkoxide. The addition of mild acid protonates the alkoxide, forming a primary alcohol.

an ester   an aldehyde
[29.26]

an aldehyde   a primary alcohol   [29.27]
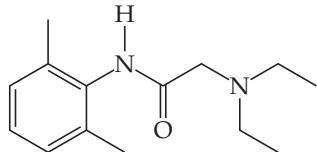
Hence, by appropriate choice of nucleophile, esters can be easily converted into both primary and tertiary alcohols.

- Recognize the different functional groups that contain an acyl group
- Know the reagents necessary to convert between the different functional groups
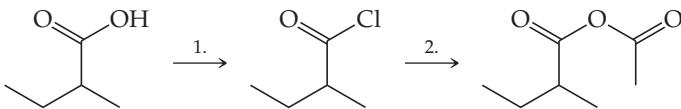
Self-Assessment Exercises

29.21 Lidocaine is used as a local anesthetic. What functional groups does it contains?

(a) amine and amide
(b) amine and ester
(c) carboxylic acid and amide
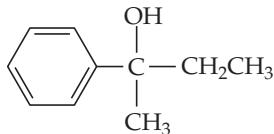
29.22 What reagents would carry out the following transformation?

(a) 1. Cl_2 2. CH_3COOH
(b) 1. $SOCl_2$ 2. CH_3COCH_3
(c) 1. $SOCl_2$ 2. CH_3COOH
(d) 1. HCl 2. CH_3COCl

Exercises
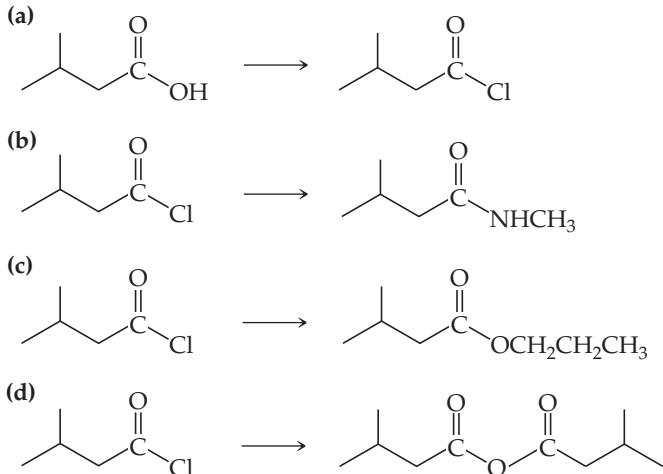
29.23 2-Phenyl-2-butanol can be synthesized by a combination of a Grignard reagent and an ester. Show the combination.
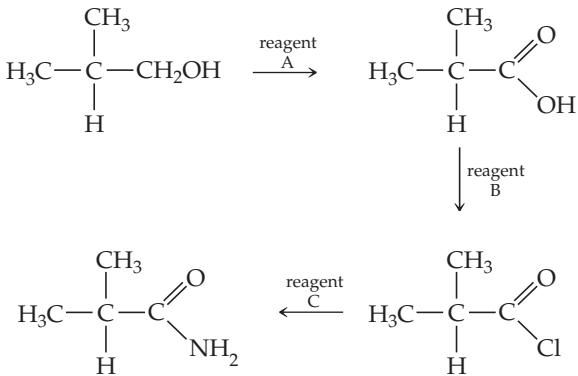
29.24 Draw the condensed structures of the products formed from (a) butanoic acid and methanol, (b) benzoic acid and 2-propanol, (c) the reaction of propanoic acid with $SOCl_2$ and then dimethylamine. Name the compound in each case.

29.25 Acetic anhydride is formed from acetic acid in a condensation reaction that involves the removal of a mole of water from between two acetic acid molecules. Write the chemical equation for this process, and show the structure of acetic anhydride.

29.26 Suggest plausible reagents for the following transformations.

(a)

(b)

(c)

(d)

29.27 List the reagents necessary to undertake the following transformations:

29.6 | Condensation Polymerization
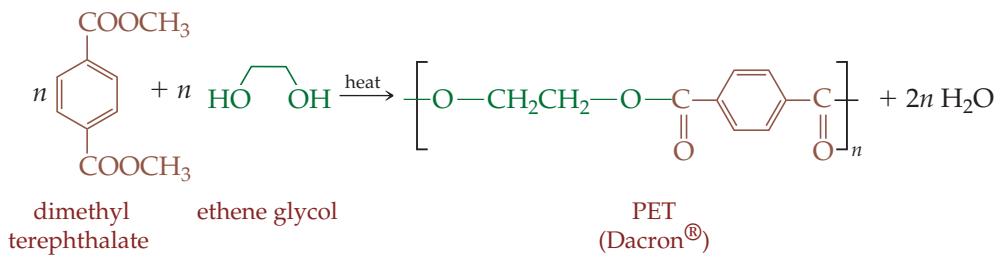
Polymers are an integral part of modern life. They are very large molecules constructed of just a few small molecules that are repeated many times. Their use in our lives is incredibly diverse and ranges from soft-drink bottles to components of life-saving heart valve replacements. A St Jude valve uses the polyester Dacron® to attach it to the surrounding heart tissue. Dacron® is Du Pont's trade name for the fiber formed from polyethene terephthalate (a polyester). About 250,000 valve-replacement procedures are performed annually worldwide, most using a St Jude valve. The valve is secured to the surrounding tissue via a biocompatible polyester sewing ring. The polar, oxygen-containing functional groups along the biocompatible polyester chain afford attractive interactions to facilitate tissue growth.

By the end of this section, you should be able to:
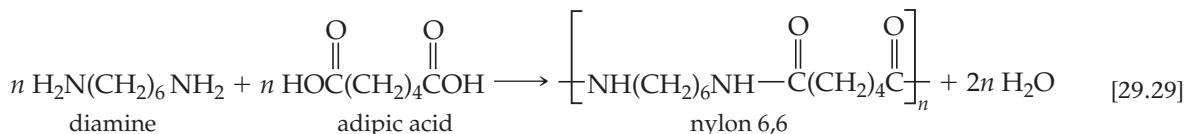
• Recognize the components of a condensation polymer.

In Chapter 26, we discussed one of the major classes of commercially important polymers and their formation by addition polymerization. A second general reaction used to synthesize commercially important polymers is **condensation polymerization** or *step-growth polymerization*. This type of polymerization usually employs difunctional molecules as the monomers, with each new bond being created in a separate step. We discuss two types of condensation polymers in this section: **polyesters** and **polyamides**.
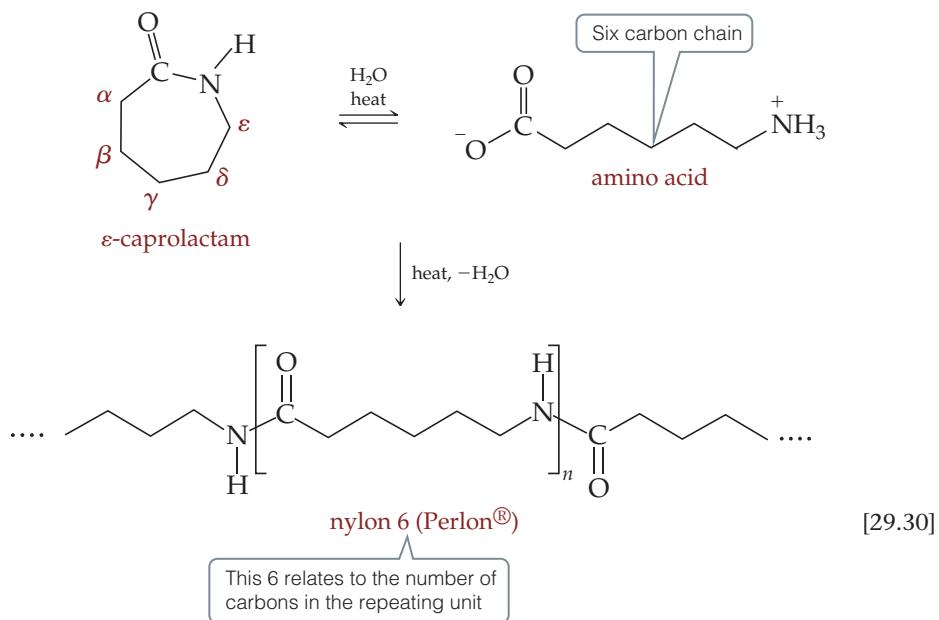
Polyesters are formed by the reaction of a diacid, diacid chloride or diester with a diol. Polymers formed from two different monomers are called **copolymers**. PET (polyethene terephthalate), or *Dacron*®, is the most common polyester copolymer used today.

dimethyl terephthalate   ethene glycol   PET
                                                                 (Dacron®)   [29.28]

Polyamides are formed by the polycondensation of a diamine with a diacid, diacid chloride or diester. The best known of the polyamides is nylon 6,6, discovered by Wallace Carothers (1896–1937) and his associates at Du Pont in 1934. It is named with the notation 6,6 because it is made by the reaction of adipic acid (a diacid within a six-carbon chain) and 1,6-hexanediamine (a six-carbon chain diamine). Nylons are used in home furnishings, apparel, carpet, fishing line and toothbrush bristles, to name but a few.

$$n \text{ H}_2\text{N(CH}_2)_6\,\text{NH}_2 + n \text{ HO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{(CH}_2)_4\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OH} \longrightarrow \left[\!\!-\text{NH(CH}_2)_6\text{NH}-\overset{\text{O}}{\overset{\|}{\text{C}}}\text{(CH}_2)_4\overset{\text{O}}{\overset{\|}{\text{C}}}\!\!-\right]_n + 2n \text{ H}_2\text{O} \qquad [29.29]$$

diamine   adipic acid   nylon 6,6

Nylon 6, also called *Perlon*®, is made from ε-caprolactam, a cyclic amide. Its uses include ropes and ties. When ε-caprolactam is heated with a small amount of water, some of it is hydrolysed to the amino acid. Continued heating gives condensation and polymerization to yield molten nylon 6. Note that a single-digit notation is used because nylon 6 is a polymer made up of one monomer containing six carbons. The monomer can be symbolized as A, which in polymer form creates the same simple repeating unit -A-A-A-A-. Nylon 6,6 is a polymer comprising two different monomers, symbolized as A and B, which forms copolymers of the form -A-B-A-B-.

ε-caprolactam

amino acid

Six carbon chain

heat, −H₂O

nylon 6 (Perlon®)   [29.30]

This 6 relates to the number of carbons in the repeating unit
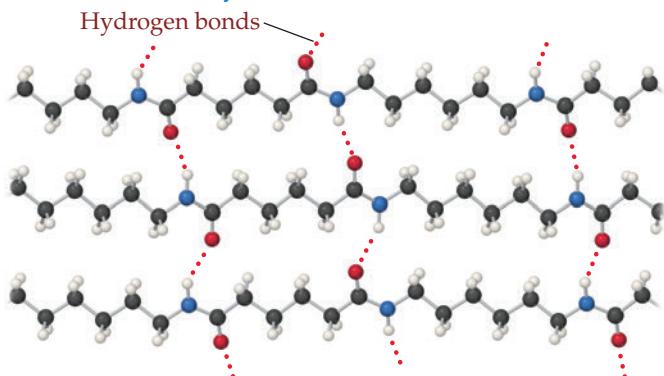
Polymers such as nylon and polyesters can also be formed into *fibres* that, like hair, are very long relative to their cross-sectional area and are not elastic. These fibres can be woven into fabrics or cords and fashioned into clothing and other useful objects.

Fibres of nylon 6,6 are cold-drawn, meaning they are drawn out at room temperature. As the fibres are drawn, hydrogen bonds form between individual polymer strands, such that the carbonyl of one amide bond hydrogen bonds to an amide hydrogen atom on another strand (**Figure 29.14**). The tensile strength and stiffness of nylon 6,6 are attributable to the hydrogen bonding that occurs in these fibres.

Various substances may also be added to polymers to provide protection against the effects of sunlight or against degradation by oxidation. For example, manganese(II) salts and copper(I) salts, in concentrations as low as $5-10^{-4}$ % (w/w), are added to nylons to provide protection from light and oxidation and to help maintain whiteness.

Go Figure

What role do the hydrogen bonds play in a polymeric material such as nylon?

Hydrogen bonds

▲ **Figure 29.14 Hydrogen bonding in nylon 6,6.** The unusual and desirable physical properties of nylon 6,6 are a result of intermolecular hydrogen bonding.
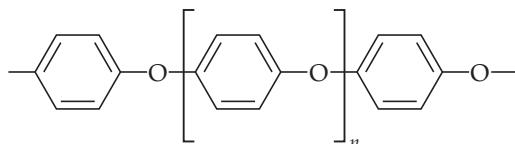
CHEMISTRY AND LIFE | Towards the Plastic Car

Many polymers can be formulated and processed to have sufficient structural strength, rigidity and heat stability to replace metals, glass and other materials in a variety of applications. The housings of electric motors and kitchen appliances such as coffee makers and can openers, for example, are now commonly made from specially formulated polymers. Engineering polymers are tailored to particular applications through choice of polymers, blending of polymers and modifications of processing steps. They generally have lower costs or superior performance over the materials they replace. In addition, shaping and colouring of the individual parts and their assembly to form the final product are often much easier.

The modern car provides many examples of the inroads engineering polymers have made in car design and construction. Car interiors have long been formed mainly of plastics. Through development of high-performance materials, significant progress has been made in introducing engineering polymers as engine components. **Figure 29.15**, for example, shows the manifold in a series of Ford V-8 utility and van engines. The manifold, which is made of nylon, must be stable at high temperatures. The use of an engineering polymer in this application eliminates machining and several assembly steps.

Car body parts can also be formed from engineering polymers. Components formed from engineering polymers usually weigh less than the components they replace, thus improving fuel economy. The bumper bars of Volkswagen's New Beetle (**Figure 29.16**), for example, are made of nylon reinforced with a second polymer, poly(phenylene ether) (PPE), which has the following structure:

Because the poly(phenylene ether) polymer is linear and rather rigid, it confers rigidity and ensures shape retention.

A big advantage of most engineering polymers over metals is that they eliminate the need for costly corrosion protection steps in manufacture. In addition, some engineering polymer formulations permit manufacturing with the colour built in, thus eliminating painting steps.

▲ **Figure 29.15 Plastic engines**. The intake manifold of some Ford V-8 engines is formed from nylon.
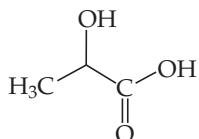

▲ **Figure 29.16 Plastic fenders**. The bumper bars of this Volkswagen Beetle are made of General Electric Noryl GTX, a composite of nylon and poly(phenylene ether).

Sample Exercise 29.6
Condensation Polymers

What is the structure of the polymer formed from lactic acid, a naturally occurring compound obtained from carbohydrates?
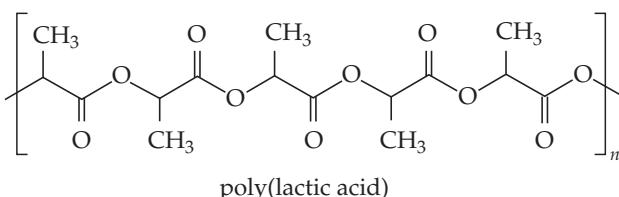

SOLUTION

Analyze We are given the structure of lactic acid and asked to derive the structure of the polymer made through self-condensation.
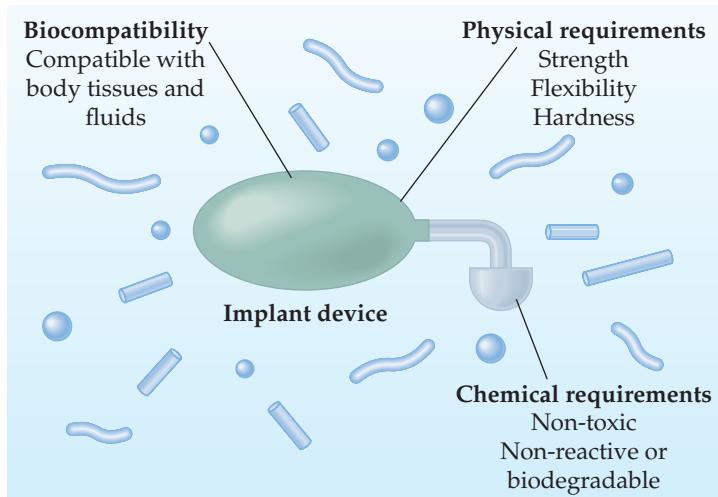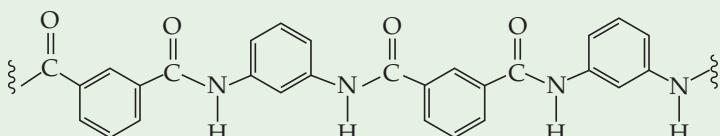
Plan Identify functional groups capable of forming a condensation polymer, then draw the polymer linking these functional groups up.

Solve Identification of the alcohol and carboxylic acid functional groups is important to determine the place of condensation. Condensation occurs by the formation of ester groups.

poly(lactic acid)

▶ **Practice Exercise**
Indicate whether the following polymer is a step (condensation) or chain (addition) growth polymer. Draw the structure of the monomer/s used in the preparation of this polymer.
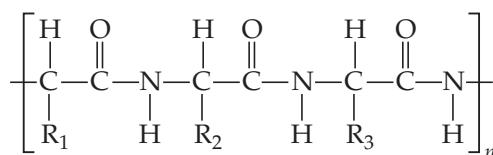

▲ **Figure 29.17 Schematic illustration of a human-made device implanted in a biological system**. To function successfully, the device must be biocompatible with its surroundings and meet the necessary physical and chemical requirements, some of which are listed for illustrative purposes.

Polymers for Medicine

Increasingly, modern synthetic materials such as polymers are being used in medical and biological applications. For our discussion here, a **biomaterial** is any material that has a biomedical application. The material might have a therapeutic use in a treatment, injury or disease or it might have a diagnostic use as part of a system for identifying a disease or for monitoring a quantity such as the glucose level in blood. Whether the use is therapeutic or diagnostic, the biomaterial is in contact with biological fluids, so it must have properties that meet the demands of that application. For example, a polymer used to make a disposable contact lens must be soft and have an easily wetted surface, whereas the polymer used to fill a dental cavity must be hard and wear resistant. The most important characteristics that influence the choice of a biomaterial are biocompatibility, physical requirements and chemical requirements, as illustrated in **Figure 29.17**.

Specialized polymers have been developed for a variety of biomedical applications. The degree to which the body accepts or rejects the foreign polymer is determined by the nature of the groups along the chain and the possibilities for interactions with the body's own molecules. Our bodies are composed largely of biopolymers such as proteins, polysaccharides (sugars) and polynucleotides (RNA, DNA). We will learn more about these molecules in Chapter 31. For now, we can simply note that the body's biopolymers have complex structures, with polar groups along the polymer chain. Proteins, for example,

are long strings of amino acids (the monomers) that have formed a condensation polymer. The protein chain has the following structure:
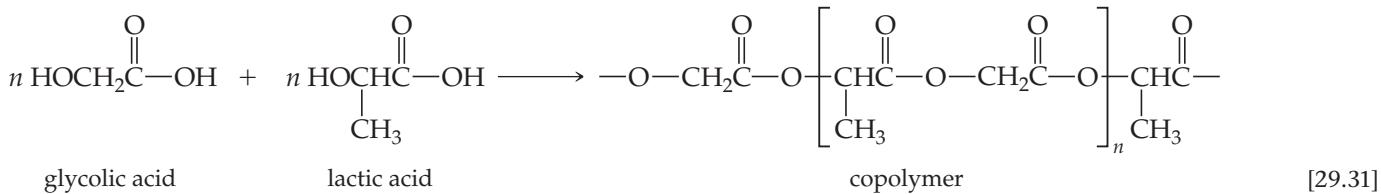

where the R groups vary along the chain (–CH_3, –$CH(CH_3)_2$, and so on). Twenty different amino acids are used in different combinations to make up proteins in humans. By contrast, synthetic polymers are simpler, formed from a single repeating unit or perhaps two different repeating units. This difference in complexity is one of the reasons why synthetic polymers are identified by the body as foreign objects. Another reason is that there may be few or no polar groups along the chain that can interact with the body's aqueous medium.

Polymers can be characterized by their physical properties. Elastomers are used as biomaterials in flexible tubing, over leads for implanted heart pacemakers and as catheters (tubes implanted into the body to administer a drug or to drain fluids). Thermoplastics, such as polyethene or polyesters, are employed as membranes in blood dialysis machines and as replacements for blood vessels. Thermoset plastics find limited, but important, uses. Because they are hard, inflexible and somewhat brittle, they are most often used in dental devices or in orthopedic applications, such as joint replacements. To fill a cavity, for example, the dentist may pack some material into the cavity, then shine an ultraviolet lamp on it. The light initiates a photochemical reaction that forms a hard, highly cross-linked thermoset polymer.

CHEMISTRY AND LIFE   Biodegradable Sutures
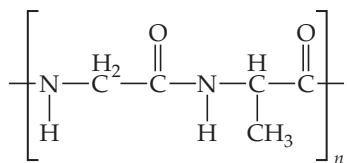
Until the 1980s, if you had to have stitches in a wound, you had to go back later to get the stitches removed. Stitches that are used to hold living tissue together are called *sutures*. Since the 1980s, biodegradable sutures have been available. After the sutures have been applied to the tissue, they slowly dissolve away and do not release any harmful by-products. Today biodegradable sutures are made out of lactic acid—glycolic acid copolymers that slowly hydrolyze over time.

$$n \ HOCH_2\overset{O}{\underset{}{\overset{\|}{C}}}-OH \ + \ n \ HOCH\overset{O}{\underset{CH_3}{\overset{\|}{C}}}-OH \longrightarrow -O-CH_2\overset{O}{\overset{\|}{C}}-O\left[CH\overset{O}{\overset{\|}{C}}-O-CH_2\overset{O}{\overset{\|}{C}}-O\right]_n CH\overset{O}{\overset{\|}{C}}-$$

| glycolic acid | lactic acid | copolymer | [29.31] |
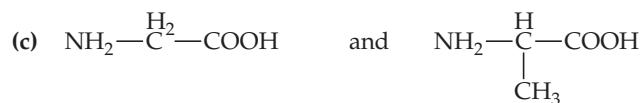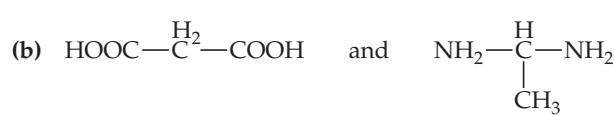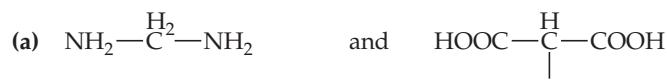
Self-Assessment Exercise

29.28 The material that makes up much of a spider's web is a polymer with the structure:
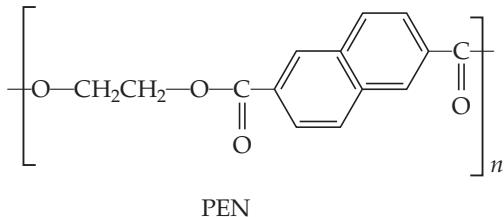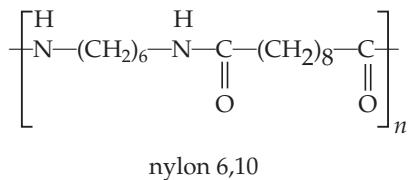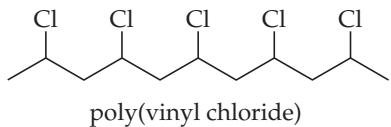
Identify the monomer units a spider uses to make its web.

(a) $NH_2-\overset{H_2}{C}-NH_2$ and $HOOC-\overset{H}{\underset{CH_3}{C}}-COOH$

(b) $HOOC-\overset{H_2}{C}-COOH$ and $NH_2-\overset{H}{\underset{CH_3}{C}}-NH_2$

(c) $NH_2-\overset{H_2}{C}-COOH$ and $NH_2-\overset{H}{\underset{CH_3}{C}}-COOH$

Exercises

29.29 Write a chemical equation for the formation of a polymer via a condensation reaction from the monomers succinic acid ($HOOCCH_2CH_2COOH$) and ethenediamine ($H_2NCH_2CH_2NH_2$).
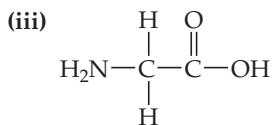
**29.30** Draw the structure of the monomer/s employed to form each of the following polymers: **(a)** poly(vinyl chloride), **(b)** nylon 6,10 and **(c)** poly(ethene naphthalate).

poly(vinyl chloride)

nylon 6,10

PEN
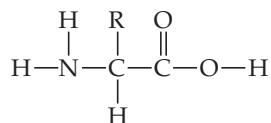
29.31 Consider the molecules shown here. **(a)** Which of these would be most likely to form an addition polymer? **(b)** Which would be most likely to form a condensation polymer?

(i)

(ii)

(iii)
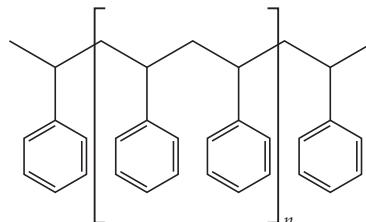
29.32 Proteins are polymers formed by condensation reactions of amino acids, which have the general structure
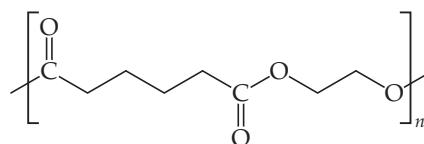
In this structure, R represents —H, —CH_3 or another group of atoms. Draw the general structure for a poly(amino acid) polymer formed by condensation polymerization of the molecule shown here.

29.33 On the basis of the structure of polystyrene and poly(ethene adipate) shown here, which class of polymer would you expect to form the most effective interface with biological systems? Explain.
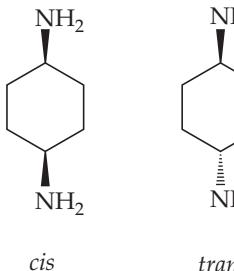
polystyrene

poly(ethene adipate)

29.34 If you were going to attempt to grow skin cells in a medium that affords an appropriate scaffolding for the cells and you had only two fabrics available, one made from polystyrene and the other from PET, which would you choose for your experiments? Explain.

29.35 **(a)** Draw the structure of Qiana®, a polyamide synthesized by the reaction of hexanedioic acid with *trans*-1,4-cyclohexanediamine. **(b)** What effect, if any, would there be in using *cis*-1,4-cyclohexanediamine instead of *trans*-1,4-cyclohexanediamine?

cis   *trans*
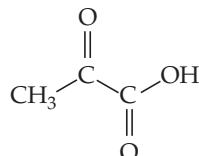
1,4-cyclohexane diamine

Sample Integrative Problem
Putting Concepts Together

Pyruvic acid has the following structure:
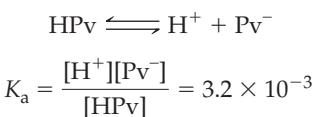
It is formed in the body from carbohydrate metabolism. In the muscle it is reduced to lactic acid in the course of exertion. The acid-dissociation constant for pyruvic acid is 3.2×10^{-3}. **(a)** Why does pyruvic acid have a higher acid-dissociation constant than acetic acid? **(b)** Would you expect pyruvic acid to exist primarily as the neutral acid or as dissociated ions in muscle tissue, assuming a pH of about 7.4 and an acid concentration of 2×10^{-4} M? **(c)** What would you predict for the solubility properties of pyruvic acid? Explain. **(d)** What is the hybridization of each carbon atom in pyruvic acid? **(e)** Assuming H atoms as the reducing agent, write a balanced chemical equation for the reduction of pyruvic acid to lactic acid. (Although H atoms don't exist as such in biochemical systems, biochemical reducing agents deliver hydrogen for such reductions.)

SOLUTION

(a) The acid ionization constant for pyruvic acid should be somewhat greater than that of acetic acid because the carbonyl function on the α-carbon atom exerts an electron-withdrawing effect on the carboxylic acid group. In the C—O—H bond system, the electrons are shifted from hydrogen, facilitating loss of the hydrogen as a proton.

(b) To determine the extent of ionization, we first set up the ionization equilibrium and equilibrium constant expression. Using HPv as the symbol for the acid, we have

$$HPv \rightleftharpoons H^+ + Pv^-$$

$$K_a = \frac{[H^+][Pv^-]}{[HPv]} = 3.2 \times 10^{-3}$$

Let $[Pv^-] = x$. Then the concentration of undissociated acid is $2 \times 10^{-4} - x$. The concentration of $[H^+]$ is fixed at 4.0×10^{-8} (the antilog of the pH value). Substituting, we obtain

$$3.2 \times 10^{-3} = \frac{[4.0 \times 10^{-8}][x]}{[2 \times 10^{-4} - x]}$$
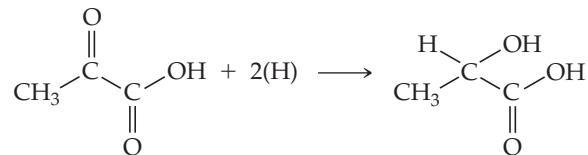
Solving for x, we obtain $x[3.2 \times 10^{-3} + 4.0 \times 10^{-8}] = 6.4 \times 10^{-7}$

The second term in the brackets is negligible compared with the first, so $x = [Pv^-] = 6.4 \times 10^{-7}/3.2 \times 10^{-3} = 2 \times 10^{-4}$ M. This is the initial concentration of acid, which means that essentially all the acid has dissociated. We might have expected this result because the acid is quite dilute and the acid-dissociation constant is fairly high.

(c) Pyruvic acid should be quite soluble in water because it has polar functional groups and a small hydrocarbon component. It is miscible with water, ethanol and diethyl ether.

(d) The methyl group carbon has sp^2 hybridization. The carbon carrying the carbonyl group has sp^2 hybridization because of the double bond to oxygen. Similarly, the carboxylic acid carbon is sp^2 hybridized.

(e) The balanced chemical equation for this reaction is

Essentially, the ketonic functional group has been reduced to an alcohol.

Chapter Summary and Key Terms

SECTION 29.1 **Carboxylic acids** are weak acids. They react with bases to form **carboxylate anions**, which are very stable due to resonance. Carboxylic acids readily form hydrogen bonded dimers in concentrated solution or neat.

SECTION 29.2 Carboxylic acids are commonly prepared by oxidation of primary alcohols or aldehydes or by the oxidation of benzylic carbon atoms, yielding benzoic acid derivatives. They can also be prepared by hydrolysis of nitriles, amides and esters.

SECTION 29.3 **Esters** are formed by the condensation reaction of carboxylic acids and alcohols. This reaction is called the **Fischer esterification**. Esters can form amides by a condensation reaction with amines. Esters undergo hydrolysis, called **saponification**, in the presence of strong bases.

SECTION 29.4 Esters such as **fats**, **oils**, **waxes** and **triglycerides** are abundant in biological systems. They form part of a general class called **lipids**. Lipids come in two forms; **complex** and **simple**, depending on

the chemical properties of the lipid. Polyunsaturated triglycerides can be hardened by catalytic hydrogenation, which changes the texture of the triglyceride from a liquid form to a solid/semi-solid form. This process is called **hardening**. The saponification of a triglyceride leads to a **soap**. In water, soaps form a **micelle**, encapsulating dirt particles. Hard waters that contain Ca^{2+} often leave an insoluble scum. **Synthetic detergents** are designer soaps that eliminate the unwanted properties associated with the formation of calcium salts.

SECTION 29.5 **Acid anhydrides** and **acid halides** also contain an **acyl group** and are more reactive than their ester or carboxylic acid

analogues. Both the anhydrides and acid halides are useful starting materials with which to make esters and **amides** through **nucleophilic acyl substitution** reactions.

SECTION 29.6 A **condensation polymerization** occurs when a small molecule is lost upon reaction. The two main types of condensation polymers are **polyesters** and **polyamides**. A polymer formed from two different monomers is called a **copolymer**. A **biomaterial** is any bio-compatible material that has a biomedical application. Biomaterials are commonly polymers with special properties matched to the application.
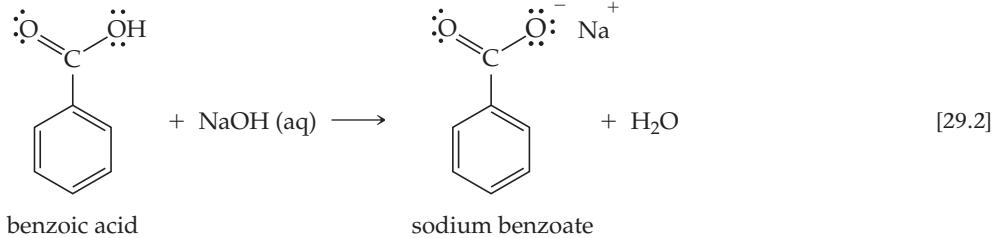
Key Skills

- Be able to prepare carboxylic acids from a range of starting materials. (Section 29.2)

- Know how to name carboxylic acids, esters, amides and acid chlorides and to discern these functional groups. (Sections 29.3–29.5)

- Be able to define terms such as lipid, oil and fat and reference these terms to classes of compounds. (Section 29.4)

- Understand the differences and similarities between a soap and a detergent. (Section 29.4)
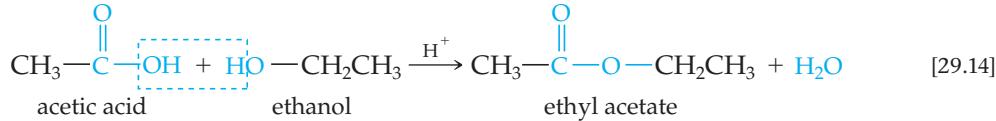
- Be able to determine the products of acyl nucleophilic substitution of esters, acid chlorides and anhydrides with a range of nucleophiles. (Section 29.5)

- Be familiar with the chemistry of carboxylic acids—including their acidity, the stability of carboxylate salts, their reaction with alcohols to form esters and their reaction with amines to form amides. (Sections 29.2–29.5)

- Be able to draw and name polyesters from monomers and identify monomers within polyesters. (Section 29.6)

Key Equations

- Acid–base reaction

benzoic acid + NaOH (aq) ⟶ sodium benzoate + H_2O [29.2]

- Esterification

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-CH_2CH_3 \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + H_2O \quad [29.14]$$

acetic acid + ethanol ⟶ ethyl acetate

- Nucleophilic acyl substitution

[29.23]

an acid chloride, anhydride or ester ⟶ a tetrahedral intermediate ⟶

R = H, alkyl, aryl
Y = Cl, OR, OCOR
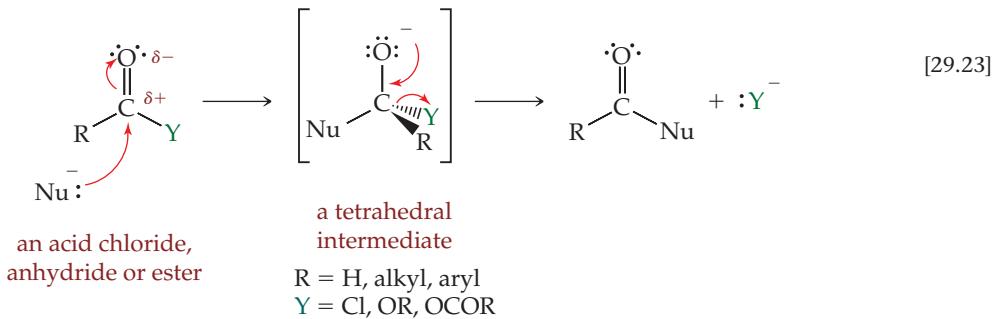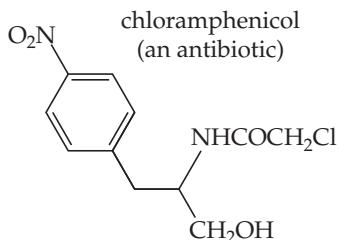
Exercises
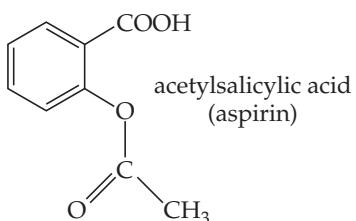
Visualizing Concepts

**29.36** Identify each of the functional groups in the following molecules. [Sections 29.1 and 29.2]

(a)

O₂N

chloramphenicol
(an antibiotic)

NHCOCH₂Cl

CH₂OH

(b)

COOH

acetylsalicylic acid
(aspirin)

O

C

O   CH₃

(c)

H

N   CH₃

C

O

HO

paracetamol

**(d)**   H₃C

N

H

heroin

H₃CCOO

O

H   OH
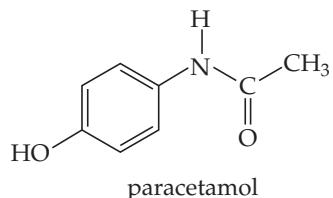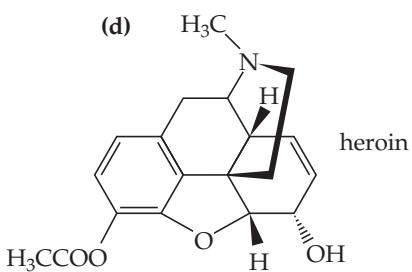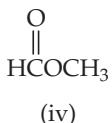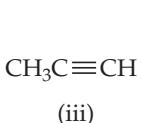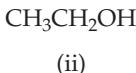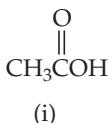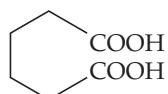
29.37 What features must a molecule have to participate in hydrogen bonding with other molecules of the same kind? Which of the following compounds would you expect to **(a)** have the highest melting point, **(b)** be most soluble in mild aqueous base? Explain. [Section 29.1]

O
||
CH₃COH   CH₃CH₂OH   CH₃C≡CH

(i)   (ii)   (iii)

O
||
HCOCH₃

(iv)

29.38 Draw the structure of the alcohol precursor, its systematic name and the reaction conditions you might use to obtain the following compounds by oxidation. [Section 29.1]

(a)

COOH
COOH

(b)

CH₃CH₂CH₂CH₂CH₂COOH

(c)

O

OH

(d)

COOH
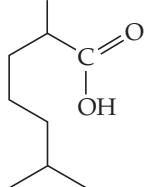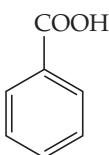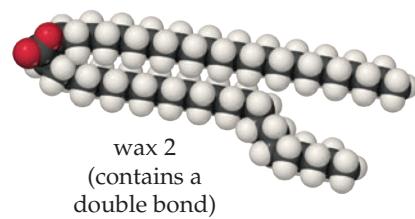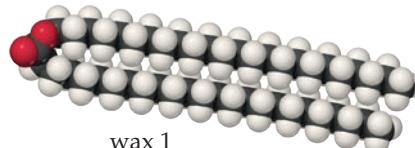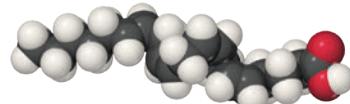
29.39 Which of the following waxes will have the lower melting point? [Section 29.4]

wax 1

wax 2
(contains a
double bond)

29.40 Which of the following fatty acids, when reacted with potassium hydroxide, would form better micelles and hence make the best soap? Explain. [Section 29.4]
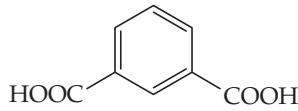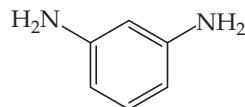
arachidic acid

arachidonic acid

29.41 The polyamide Nomex is prepared from the condensation polymerization of 1,3-benzenediamine with 1,3-benzenedicarboxylic acid. **(a)** Draw a structural formula representation of the polymer, being sure to indicate the repeat unit. **(b)** Would you expect such a polymer to have applications requiring high strength and high temperature, or to be more useful as a *glad-wrap* alternative? Explain your answer. [Section 29.6]

H₂N   NH₂

HOOC   COOH
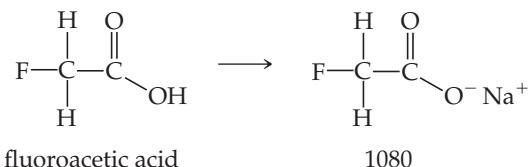
1,3-benzenediamine   1,3-benzenedicarboxylic acid

Carboxylic Acids (Section 29.1)

29.42 Although carboxylic acids and alcohols both contain an −OH group, one is acidic in water and the other is not. Explain the difference.

29.43 "Bath bombs" contain calcium carbonate and citric acid. When placed into water, they fizz and dissolve rapidly. What are the products of this reaction?

29.44 **(a)** Sodium monofluoroacetate, known as "1080", is a commonly used rabbit and fox poison. What reagent could be used to convert fluoroacetic acid into 1080? **(b)** Explain why the pK_a for fluoroacetic acid ($pK_a = 2.59$) is lower than the pK_a of acetic acid (CH_3COOH, $pK_a = 4.76$).


fluoroacetic acid   1080
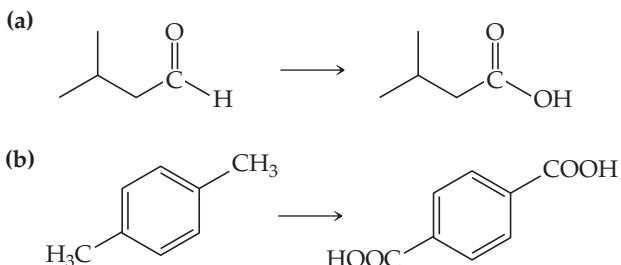
29.45 **(a)** The structural formula for acetic acid is shown in this table. Replacing hydrogen atoms on the carbon with chlorine atoms causes an increase in acidity, as follows:

Acid	Formula	K_a (25 °C)
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	$CH_2ClCOOH$	1.4×10^{-3}
Dichloroacetic	$CHCl_2COOH$	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

Using Lewis structures as the basis of your discussion, explain the observed trend in acidities in the series. Calculate the pH of a 0.010 M solution of each acid.

## Preparation of Carboxylic Acids (Section 29.2)

**29.46** Suggest plausible reagents for the transformations shown here.

(a)

(b)
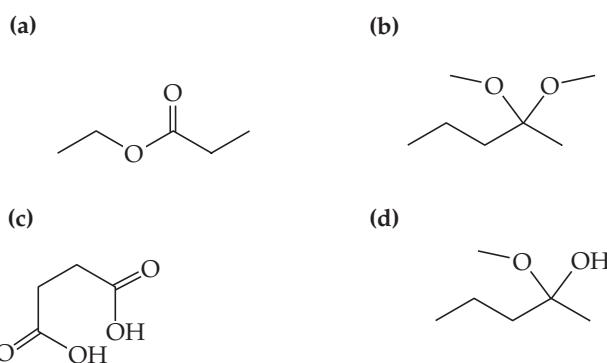
29.47 Describe methods for preparing butanoic acid from each of the following:
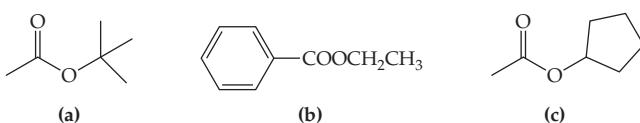
(a) butan-1-ol

(b) butanal

(c) methyl butanoate

(d) butanoyl chloride

## Esters and Esterification (Section 29.3)
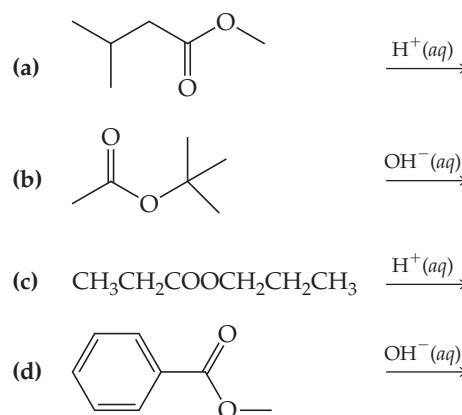
29.48 Classify the following compounds as acetals, alcohols, hemiacetals, carboxylic acids, esters or ethers:

(a)   **(b)**

(c)   **(d)**

**29.49** Name the following esters and draw the starting materials needed to synthesize them.

(a)   **(b)**   **(c)**

29.50 Draw the products of the following hydrolysis reactions.

(a)

$\xrightarrow{H^+(aq)}$

(b)

$\xrightarrow{OH^-(aq)}$

(c) $CH_3CH_2COOCH_2CH_2CH_3$ $\xrightarrow{H^+(aq)}$

(d)

$\xrightarrow{OH^-(aq)}$
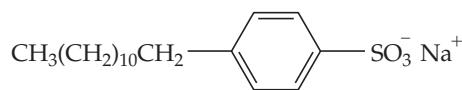
Fats, Oils, and Waxes (Section 29.4)

29.51 Write a balanced chemical equation using condensed structural formulas for the saponification (base hydrolysis) of **(a)** methyl propionate, **(b)** phenyl acetate.

29.52 Locate the stereogenic center/s in a triglyceride bearing one palmitic acid, one stearic acid and one arachidic side chain (see Table 29.5).

29.53 The structure of a synthetic detergent is shown here. **(a)** What features make this compound act like a natural soap? **(b)** Draw a simple micelle using this molecule to demonstrate the detergent's application. Label the hydrophobic and hydrophilic regions of the micelle.

$$CH_3(CH_2)_{10}CH_2 \text{—} \bigcirc \text{—} SO_3^- Na^+$$
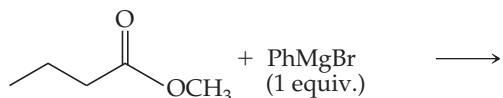
sodium 4-dodecylbenzene sulfonate (SDS)
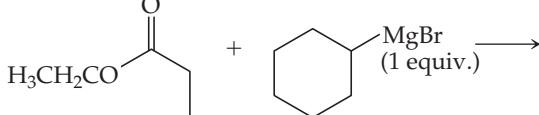
Nucleophilic Acyl Substitution (Section 29.5)

29.54 Draw the major product expected under the following conditions (Ph = C_6H_5):

(a)

+ PhMgBr
(1 equiv.)

(b)

+ MgBr (1 equiv.)
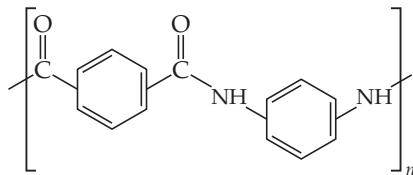
29.55 Draw the condensed structure of the compounds formed by reactions between **(a)** benzoic acid and ethanol, **(b)** ethanoyl chloride and methylamine, **(c)** acetic acid and phenol. Name the compound in each case.

29.56 γ-Hydroxybutanoic acid (GHB) can be prepared enzymatically from 1,4-butanediol. **(a)** Devise a method of preparing GHB in the laboratory from 1,4-butanediol. What compromise did you have to make? **(b)** GHB can form a cyclic ester under acidic conditions. Draw the structure of this ester.
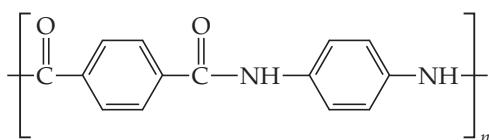
Condensation Polymerization (Section 29.6)

**29.57** The nylon Nomex®, a condensation polymer, has the following structure:

Draw the structures of the two monomers that yield Nomex®.

29.58 Kevlar®, a high-performance polymer, has the following structure:

Write the structural formulas for the two compounds that are condensed to form this polymer.

29.59 In addition to the condensation of dicarboxylic acids with diamines, nylons can also be formed by the condensation reactions of aminocarboxylic acids with themselves. Nylon 4, for example, is formed by the polycondensation of 4-aminobutyric acid ($NH_2CH_2CH_2CH_2COOH$). Write a chemical equation to show the formation of nylon 4 from this monomer.

29.60 Briefly explain why it is important to achieve correct 1:1 stoichiometry of monomers in a condensation polymerization.

29.61 PET soft drink bottles can be recycled by heating the PET with methanol in the presence of an acid catalyst. The result of this reaction is the isolation of ethene glycol and dimethyl terephthalate (the dimethyl ester of terephthalic acid). These compounds are then reused in the manufacture of new PET-containing products. Write a reaction for the acid-catalyzed degradation of PET with methanol.

29.62 Poly(vinyl alcohol), PVA, is a useful water-soluble polymer. It cannot be prepared directly from vinyl alcohol, because vinyl alcohol tautomerizes spontaneously to acetaldehyde. It can, however, be prepared from poly(vinyl acetate). Design an experiment for the conversion of poly(vinyl acetate) to poly(vinyl alcohol).


poly(vinyl alcohol)

poly(vinyl acetate)

29.63 Glyptal® resin makes a strong thermoset polymer with applications in the electronics and car industries. It is prepared by the condensation of terephthalic acid and glycerol. Draw the structure of Glyptal® and explain its remarkable strength and rigidity.

Integrative Exercises

29.64 Bromobenzene is reacted first with magnesium, then carbon dioxide followed by dilute acid in a Grignard reaction. **(a)** Draw the structure of the product of this reaction. A 0.0050 M solution of the product has a pH of 3.25. **(b)** What is the K_a of the product? **(c)** The conjugate base of the product is a resonance-stabilized anion. Draw all the major resonance structures of this anion.

29.65 Many esters are volatile compounds with distinct fragrances. The boiling point of an ester is often lower than you might expect from the boiling points of the carboxylic acid and alcohol from which it is derived. For example, ethyl methanoate has a boiling point of 54 °C and the boiling points of ethanol and methanoic acid are 78 °C and 100 °C, respectively. **(a)** Draw the structure of ethyl methanoate and indicate the approximate bond angle associated with the carbonyl carbon and ether oxygen atom.

(b) What intermolecular force is responsible for an increase in boiling point as molecular mass increases in a series of similar compounds? **(c)** What additional intermolecular forces are present in carboxylic acids and alcohols that are not present in the related ester?

29.66 Ethene is an important product from the petrochemical industry. Devise a synthesis of *N*-ethyl acetamide using ethene as the only carbon source. [*Hint*: NH_2^- is a powerful nucleophile.]

N-ethyl acetamide

Design an Experiment

Imagine you are a materials chemist working on a new polyester based on cyclohexane. You want to investigate the difference between a copolymer formed from a dicarboxylic acid with a diol and the polymer formed from a single monomer unit containing both carboxylic acid and alcohol functional groups. For economy of manufacture, you start with 1,4-dibromocyclohexane to make both types of monomer.

How do you synthesize the starting monomers? Do you need to pay attention to the relative quantities of reagents that you use? When making 4-hydroxycyclohexanecarboxylic acid is it important which order you use to install the two different functional groups? How might you carry out the polymerization reaction? What sort of properties do you anticipate for your polymer?