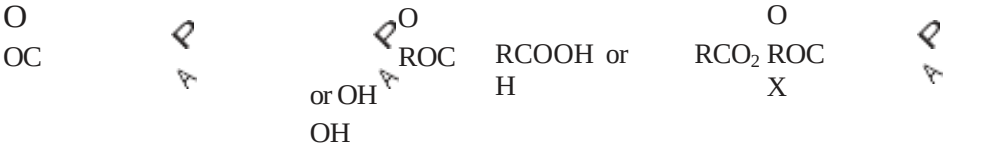
Carboxylic Acids and Their Derivatives

The taste of vinegar, the sting of an ant, the rancid smell of butter, and the relief derived from aspirin or ibuprofen—all of these are due to compounds that belong to the most important family of organic acids, the **carboxylic acids**. The resilience of polyester and nylon fabrics, the re- markable propertiesof Velcro, thesoftnessof silk, theno-calorie sugar substitutes, the strength of bacterial cell walls, and the strength of our own cell membranes— all of these are due to properties of derivatives of carboxylic acids. The functional group common to all carboxylic acids is the **carboxyl group**. The name is a contraction of the parts: the *carb*onyl and hydr*oxyl* groups. The general formula for a carboxylic acid can be written in expanded or abbreviated forms.



carboxyl group three ways to represent a carboxylic acid acid derivatives

In this chapter, we will describe the structures, properties, preparation, and reactions of carboxylic acids and will also discuss some common **carboxylic acid derivatives**, in which the hydroxyl group of an acid is replaced by other func- tional groups.

Nomenclature of Acids

Because of their abundance in nature, carboxylic acids were among the earliest classes of compounds studied by organic chemists. It is not surprising, then, that many of them have common names. These names usually come from some Latin or Greek word that indicates the original source of the acid. Table 10.1 lists the first ten unbranched carboxylic acids, with their common and IUPAC names. To obtain the IUPAC name of a carboxylic acid, we replace the final *e* in the name of the corresponding alkane with the suffix *-oic* and add the word *acid*. Substituted acids are named in two ways. In the IUPAC system, the chain is numbered beginning with the carboxyl carbon atom, and substituents are located in the usual way. If the common name of the acid is used, sub- stituents are located with Greek letters, beginning with the *a*-carbon atom. IUPAC and common naming systems should not bemixed.

2- bromopropanoic acid propenoic acid 3- hydroxybutanoic acid

(*a*-bromopropionic acid) (acrylic acid) (*b*-hydroxybutyric acid)

The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming. In the latter cases, the prefix *oxo-* is used to locate the carbonyl group of the aldehyde or ketone, as in these examples:

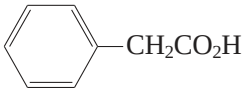
Table 1 Aliphatic Carboxylic Acids

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

PROBLEM Write the structure for

a. 3-hydroxyhexanoic acid
b. 2-iodo-2-methyloctanoic acid
c. 2-butynoic acid
d. 5-ethyl-6-oxoheptanoic acid

PROBLEM Give an IUPAC name for

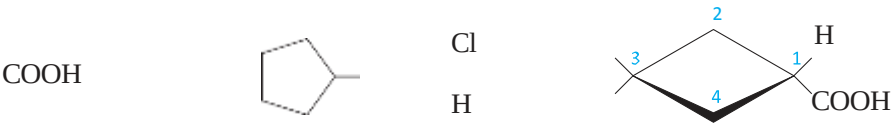
a. 

b. $Br_2CHCH_2CO_2H$

c. $CH_3CH''CHCO_2H$

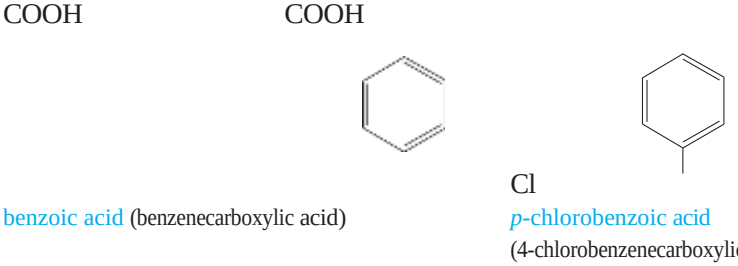
d. $(CH_3)_3CCH_2CH_2CO_2H$

When the carboxyl group is attached to a ring, the ending *-carboxylic acid* is added to the name of the parentcycloalkane.

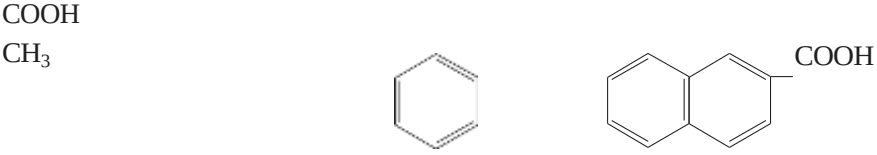


cyclopentanecarboxylic acid *trans*-3-chlorocyclobutanecarboxylic acid

Aromatic acids are named by attaching the suffix *-oic acid* or *-ic acid* to an appro- priate prefix derived from the aromatic hydrocarbon.



benzoic acid (benzenecarboxylic acid) *p*-chlorobenzoic acid (4-chlorobenzenecarboxylic acid)



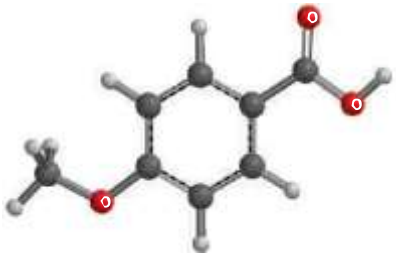
o-toluic acid (2-methylbenzenecarboxylic acid) 2-naphthoic acid (2-naphthalenecarboxylic acid)

PROBLEM Write the structure for

a. *cis*-3-isopropylcyclohexanecarboxylic acid
b. *o*-nitrobenzoic acid

PROBLEM Give the correct name for

a. 

b. 

Aliphatic Dicarboxylic Acids **Table 2**

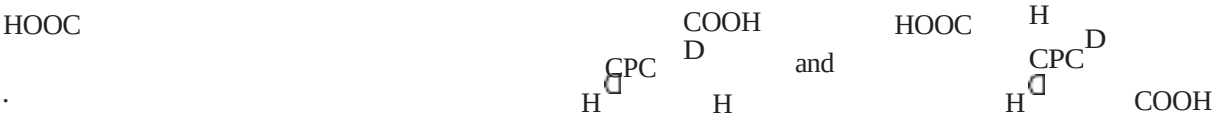
Formula	Common name	Source	IUPAC name
HOOC–COOH	oxalic acid	plants of the *oxalic* family (for example, sorrel)	ethanedioic acid
HOOC–CH_2–COOH	malonic acid	apple (Gk. *malon*)	propanedioic acid
HOOC–$(CH_2)_2$–COOH	succinic acid	amber (L. *succinum*)	butanedioic acid
HOOC–$(CH_2)_3$–COOH	glutaric acid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

Aliphatic dicarboxylic acids are given the suffix *-dioic acid* in the IUPAC system.
For example,

1 2 3 4
HO_2C
butanedioic acid

CH_2CH_2 CO_2H HO_2C C≡C CO_2H
butynedioic acid

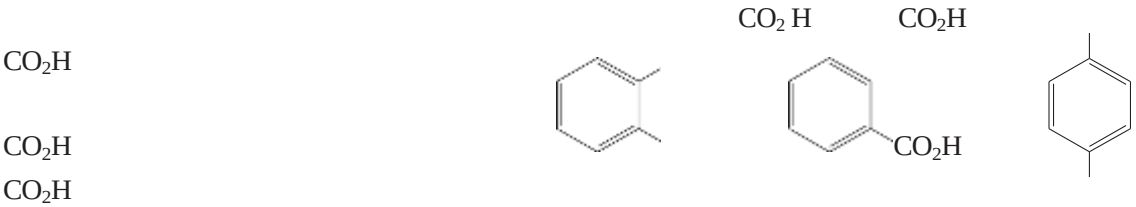
Many dicarboxylic acids occur in nature and go by their common names, which are based on their source. Table 10.2 lists some common aliphatic diacids.* The most important commercial compound in this group is adipic acid, used to manufacture nylon.
The two butenedioic acids played a historic role in the discovery of *cis–trans* isom- erism and are usually known by their common names maleic** and fumaric*** acid.



maleic acid
(*cis*-2-butenedioic acid)

fumaric acid
(*trans*-2-butenedioic acid)

The three benzenedicarboxylic acids are generally known by their common names.



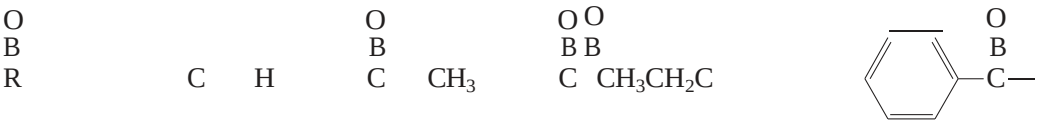
phthalic acid

isophthalic acid

terephthalic acid

All three are important commercial chemicals, used to make polymers and other use- ful materials.

Finally, it is useful to have a name for an **acyl group**. Particular acyl groups are named from the corresponding acid by changing the *-ic* ending to *-yl.*



PROBLEM Write the formula for

a. 4-formylbenzoic acid

b. benzoyl bromide

c. octanoyl bromide

d. acetylcyclopentane