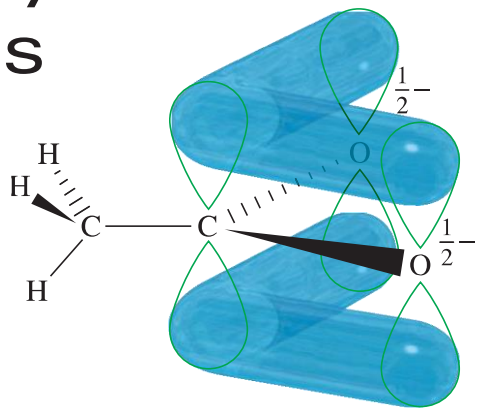
20 Carboxylic Acids



GOALS FOR CHAPTER 20

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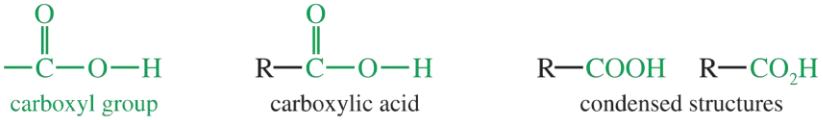
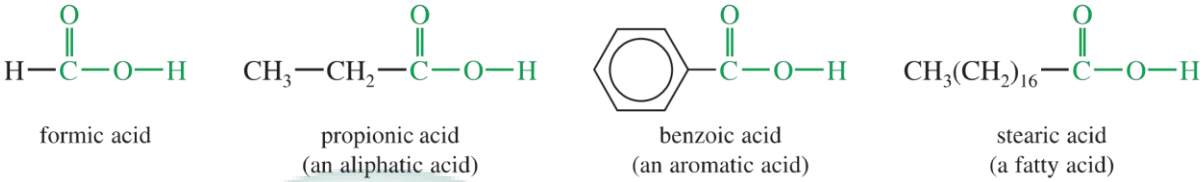
1. Draw and name carboxylic acids and dicarboxylic acids, and use spectral information to determine their structures.
2. Describe the trends in the acidity and physical properties of carboxylic acids, and explain how their acidity varies with their substituents.
3. Propose single-step and multistep syntheses of carboxylic acids from compounds containing other functional groups.
4. Predict the products and propose mechanisms for the reactions of carboxylic acids with reducing agents, alcohols, amines, and organometallic reagents.
5. Propose multistep syntheses using carboxylic acids and acid chlorides as starting materials and intermediates.

20-1 Introduction

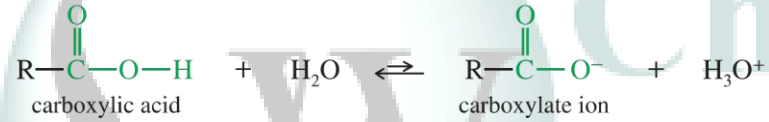
The combination of a **carb**onyl group and a hydr**oxyl** on the same carbon atom is called a **carboxyl group.** Compounds containing the carboxyl group are distinctly acidic and are called **carboxylic acids.**



Carboxylic acids are classified according to the substituent bonded to the carboxyl group. An **aliphatic acid** has an alkyl group bonded to the carboxyl group, and an **aromatic acid** has an aryl group. The simplest acid is *formic acid*, with a hydrogen atom bonded to the carboxyl group. **Fatty acids** are long-chain aliphatic acids derived from the hydrolysis of fats and oils (Section 20-6).



A carboxylic acid donates protons by heterolytic cleavage of the acidic O—H bond to give a proton and a **carboxylate ion.** We consider the ranges of acidity and the factors affecting the acidity of carboxylic acids in Section 20-4.

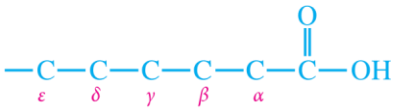


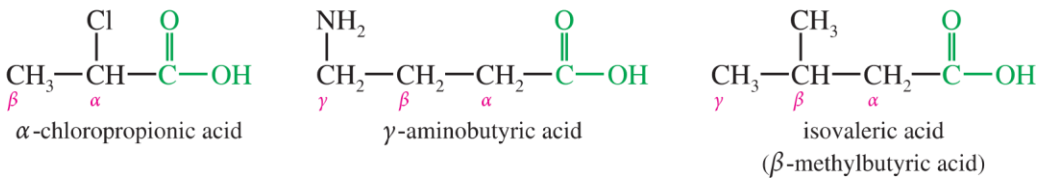
20-2 Nomenclature of Carboxylic Acids

20-2A Common Names

Several aliphatic carboxylic acids have been known for centuries, and their common names reflect their historical sources. *Formic acid* was extracted from ants: *formica* in Latin. Acetic acid was isolated from vinegar, called *acetum* ("sour") in Latin. Propionic acid was considered to be the first fatty acid, and the name is derived from the Greek *protos pion* ("first fat"). Butyric acid results from the oxidation of butyraldehyde, the principal flavor of butter: *butyrum* in Latin. Caproic, caprylic, and capric acids are found in the skin secretions of goats: *caper* in Latin. The names and physical properties of some carboxylic acids are listed in Table 20-1.

In common names, the positions of substituents are named using Greek letters. Notice that the lettering begins with the carbon atom *next* to the carboxyl carbon, the α carbon. With common names, the prefix *iso-* is sometimes used for acids ending in the $-CH(CH_3)_2$ grouping.





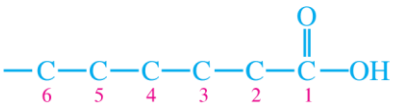
20-2B IUPAC Names

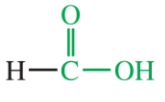
The IUPAC nomenclature for carboxylic acids uses the name of the alkane that corresponds to the longest continuous chain of carbon atoms. The final *-e* in the alkane name is replaced by the suffix *-oic acid*. The chain is numbered, *starting with the carboxyl*

TABLE 20-1 Names and Physical Properties of Carboxylic Acids

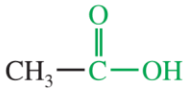
IUPAC Name	Common Name	Formula	mp (°C)	bp (°C)	Solubility (g/100 g H_2O)
methanoic	formic	$HCOOH$	8	101	∞ (miscible)
ethanoic	acetic	CH_3COOH	17	118	∞
propanoic	propionic	CH_3CH_2COOH	−21	141	∞
prop-2-enoic	acrylic	$H_2C{=}CH{-}COOH$	14	141	∞
butanoic	butyric	$CH_3(CH_2)_2COOH$	−6	163	∞
2-methylpropanoic	isobutyric	$(CH_3)_2CHCOOH$	−46	155	23.0
trans-but-2-enoic	crotonic	$CH_3{-}CH{=}CH{-}COOH$	71	185	8.6
pentanoic	valeric	$CH_3(CH_2)_3COOH$	−34	186	3.7
2,2-dimethylpropanoic	pivalic	$(CH_3)_3C{-}COOH$	35	164	2.5
hexanoic	caproic	$CH_3(CH_2)_4COOH$	−4	206	1.0
octanoic	caprylic	$CH_3(CH_2)_6COOH$	16	240	0.7
decanoic	capric	$CH_3(CH_2)_8COOH$	31	269	0.2
dodecanoic	lauric	$CH_3(CH_2)_{10}COOH$	44		i
tetradecanoic	myristic	$CH_3(CH_2)_{12}COOH$	54		i
hexadecanoic	palmitic	$CH_3(CH_2)_{14}COOH$	63		i
octadecanoic	stearic	$CH_3(CH_2)_{16}COOH$	72		i
benzoic	benzoic	C_6H_5COOH	122	249	0.3

carbon atom, to give positions of substituents along the chain. In naming, the carboxyl group takes priority over any of the other functional groups we have discussed.

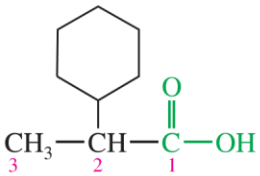




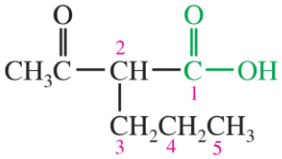
IUPAC name: methanoic acid
common name: formic acid



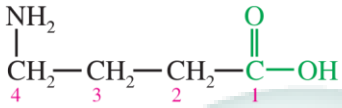
ethanoic acid
acetic acid



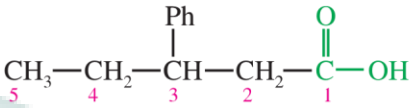
2-cyclohexylpropanoic acid
α-cyclohexylpropionic acid



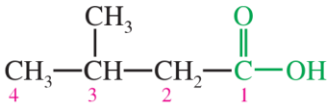
2-acetylpentanoic acid
α-acetylvaleric acid



IUPAC name: 4-aminobutanoic acid
common name: γ-aminobutyric acid

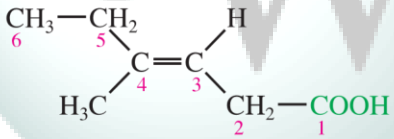


3-phenylpentanoic acid
β-phenylvaleric acid

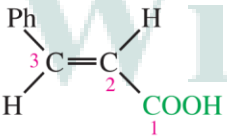


3-methylbutanoic acid
isovaleric acid

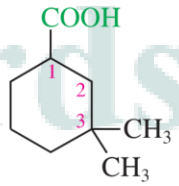
Unsaturated acids are named using the name of the corresponding alkene, with the final *-e* replaced by *-oic acid*. The carbon chain is numbered starting with the carboxyl carbon, and a number gives the location of the double bond. The stereochemical terms *cis* and *trans* (and *Z* and *E*) are used as they are with other alkenes. Cycloalkanes with —COOH substituents are generally named as *cycloalkanecarboxylic acids*.



old IUPAC name: (*E*)-4-methyl-3-hexenoic acid
new IUPAC name: (*E*)-4-methylhex-3-enoic acid

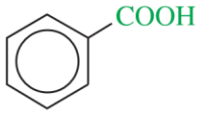


trans-3-phenyl-2-propenoic acid
(*E*)-3-phenylprop-2-enoic acid
(cinnamic acid)

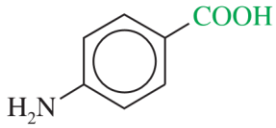


3,3-dimethylcyclohexanecarboxylic acid

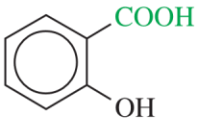
Aromatic acids of the form Ar—COOH are named as derivatives of *benzoic acid*, Ph—COOH. As with other aromatic compounds, the prefixes *ortho-*, *meta-*, and *para-* may be used to give the positions of additional substituents. Numbers are used if there are more than two substituents on the aromatic ring. Many aromatic acids have historical names that are unrelated to their structures.



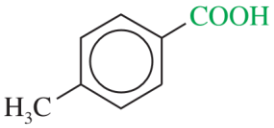
benzoic acid



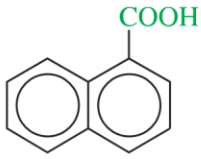
p-aminobenzoic acid



o-hydroxybenzoic acid
(salicylic acid)



p-methylbenzoic acid
(*p*-toluic acid)



α-naphthoic acid

20-2C Nomenclature of Dicarboxylic Acids

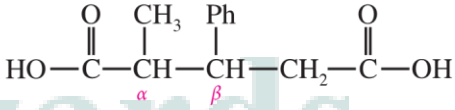
Common Names of Dicarboxylic Acids A **dicarboxylic acid** (also called a *diacid*) is a compound with two carboxyl groups. The common names of simple dicarboxylic acids are used more frequently than their systematic names. A common mnemonic for these names is "***O***h ***m***y, ***s***uch ***g***ood ***a***pple ***p***ie," standing for *o*xalic, *m*alonic, *s*uccinic, *g*lutaric, *a*dipic, and *p*imelic acids. The names and physical properties of some dicarboxylic acids are given in Table 20-2.

TABLE 20-2 Names and Physical Properties of Dicarboxylic Acids

IUPAC Name	Common Name	Formula	mp (°C)	Solubility (g/100 g H_2O)
ethanedioic	oxalic	HOOC—COOH	189	14
propanedioic	malonic	$HOOCCH_2COOH$	136	74
butanedioic	succinic	$HOOC(CH_2)_2COOH$	185	8
pentanedioic	glutaric	$HOOC(CH_2)_3COOH$	98	64
hexanedioic	adipic	$HOOC(CH_2)_4COOH$	151	2
heptanedioic	pimelic	$HOOC(CH_2)_5COOH$	106	5
cis-but-2-enedioic	maleic	*cis*-HOOCCH=CHCOOH	130.5	79
trans-but-2-enedioic	fumaric	*trans*-HOOCCH=CHCOOH	302	0.7
benzene-1,2-dicarboxylic	phthalic	$1,2\text{-}C_6H_4(COOH)_2$	231	0.7
benzene-1,3-dicarboxylic	isophthalic	$1,3\text{-}C_6H_4(COOH)_2$	348	
benzene-1,4-dicarboxylic	terephthalic	$1,4\text{-}C_6H_4(COOH)_2$	300 sublimes	0.002

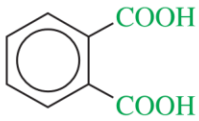
Substituted dicarboxylic acids are given common names using Greek letters, as with the simple carboxylic acids. Greek letters are assigned beginning with the carbon atom next to the carboxyl group that is closer to the substituents.

β-bromoadipic acid

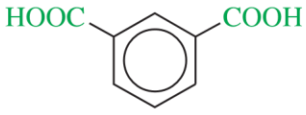


α-methyl-β-phenylglutaric acid

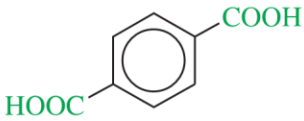
Benzenoid compounds with two carboxyl groups are named **phthalic acids.** *Phthalic acid* itself is the ortho isomer. The meta isomer is called *isophthalic acid*, and the para isomer is called *terephthalic acid*.



o-phthalic acid
phthalic acid

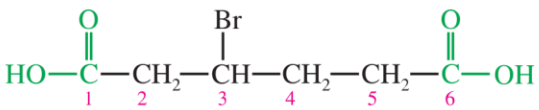


m-phthalic acid
isophthalic acid

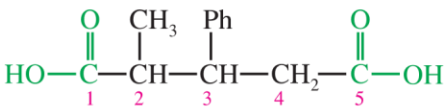


p-phthalic acid
terephthalic acid

IUPAC Names of Dicarboxylic Acids Aliphatic dicarboxylic acids are named simply by adding the suffix *-dioic acid* to the name of the parent alkane. For straight-chain dicarboxylic acids, the parent alkane name is determined by using the longest continuous chain that contains both carboxyl groups. The chain is numbered beginning with the carboxyl carbon atom that is closer to the substituents, and these numbers are used to give the positions of the substituents.

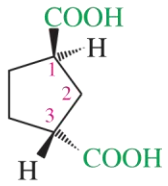


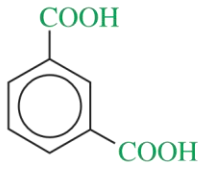
3-bromohexanedioic acid



2-methyl-3-phenylpentanedioic acid

The system for naming cyclic dicarboxylic acids treats the carboxyl groups as substituents on the cyclic structure.





old IUPAC name: *trans*-1,3-cyclopentanedicarboxylic acid 1,3-benzenedicarboxylic acid
new IUPAC name: (1*R*,3*R*)-cyclopentane-1,3-dicarboxylic acid benzene-1,3-dicarboxylic acid

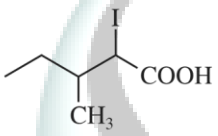
PROBLEM 20-1

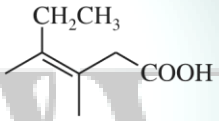
Draw the structures of the following carboxylic acids.

(a) α-methylbutyric acid
(b) 2-bromobutanoic acid
(c) 4-aminopentanoic acid
(d) *cis*-4-phenylbut-2-enoic acid
(e) *trans*-2-methylcyclohexanecarboxylic acid
(f) 2,3-dimethylfumaric acid
(g) *m*-chlorobenzoic acid
(h) 3-methylphthalic acid
(i) β-aminoadipic acid
(j) 3-chloroheptanedioic acid
(k) 4-oxoheptanoic acid
(l) phenylacetic acid

PROBLEM 20-2

Name the following carboxylic acids (when possible, give both a common name and a systematic name).

(a)


(b)


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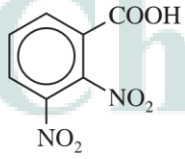

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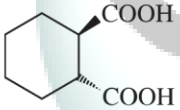

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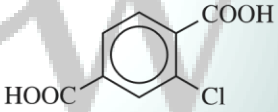

(f)