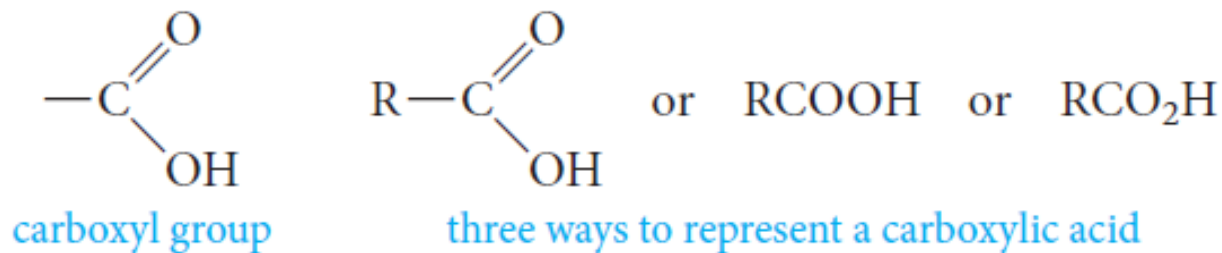


# Carboxylic Acids

The functional group common to all carboxylic acids is the carboxyl group. The name is a contraction of the parts: the *carbonyl* and *hydroxyl* groups. The general formula for a carboxylic acid can be written in expanded or abbreviated forms.

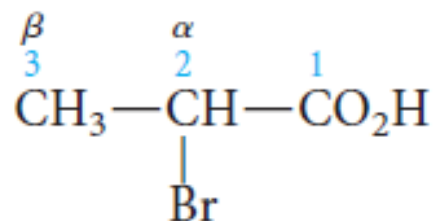


# Nomenclature of Acids

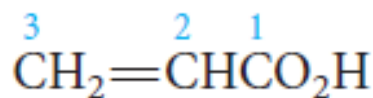
Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, <i>formica</i> )	formic acid	methanoic acid
2	CH <sub>3</sub> COOH	vinegar (Latin, <i>acetum</i> )	acetic acid	ethanoic acid
3	CH <sub>3</sub> CH <sub>2</sub> COOH	milk (Greek, <i>protos pion</i> , first fat)	propionic acid	propanoic acid
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	butter (Latin, <i>butyrum</i> )	butyric acid	butanoic acid
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	valerian root (Latin, <i>valere</i> , to be strong)	valeric acid	pentanoic acid
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	goats (Latin, <i>caper</i> )	caproic acid	hexanoic acid

Many of carboxylic acid have common names. These names usually come from some Latin or Greek word that indicates the original source of the acid.

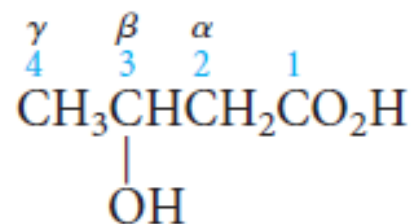
To obtain the IUPAC name of a carboxylic acid, we replace the final *e* in the name of the corresponding alkane with the suffix *-oic* and add the word *acid*. Substituted acids are named in two ways. In the IUPAC system, the chain is numbered beginning with the carboxyl carbon atom, and substituents are located in the usual way. If the common name of the acid is used, substituents are located with Greek letters, beginning with the  $\alpha$ -carbon atom



2-bromopropanoic acid  
( $\alpha$ -bromopropionic acid)

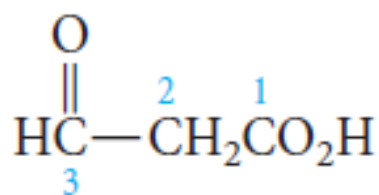


propenoic acid  
(acrylic acid)

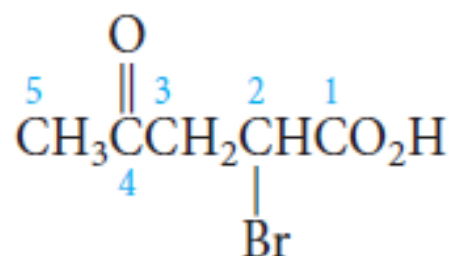


3-hydroxybutanoic acid  
( $\beta$ -hydroxybutyric acid)

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:

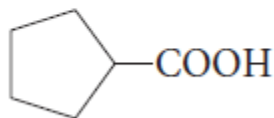


3-oxopropanoic acid

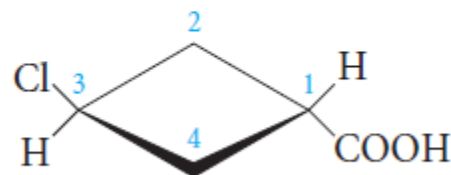


2-bromo-4-oxopentanoic acid

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

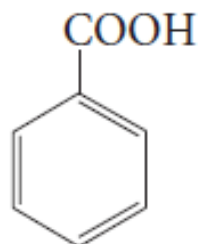


cyclopentanecarboxylic acid

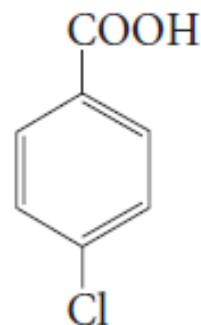


*trans*-3-chlorocyclobutanecarboxylic acid

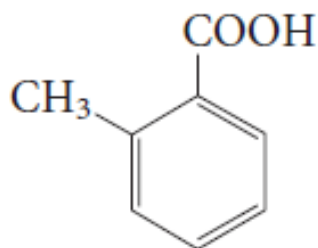
Aromatic acids are named by attaching the suffix *-oic acid* or *-ic acid* to an appropriate prefix derived from the aromatic hydrocarbon.



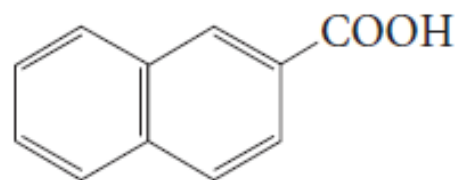
**benzoic acid**  
(benzenecarboxylic acid)



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



***o*-toluic acid**  
(2-methylbenzenecarboxylic acid)



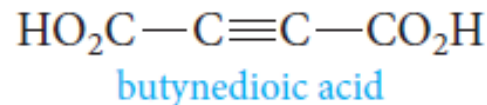
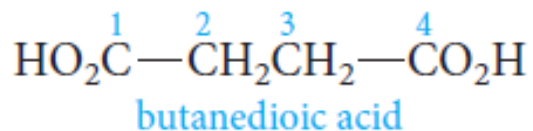
**2-naphthoic acid**  
(2-naphthalenecarboxylic acid)

# Dicarboxylic acids

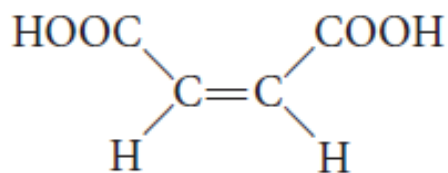
Many dicarboxylic acids occur in nature and go by their common names, which are based on their source

Formula	Common name	Source	IUPAC name
HOOC—COOH	oxalic acid	plants of the <i>oxalic</i> family (for example, sorrel)	ethanedioic acid
HOOC—CH <sub>2</sub> —COOH	malonic acid	apple (Gk. <i>malon</i> )	propanedioic acid
HOOC—(CH <sub>2</sub> ) <sub>2</sub> —COOH	succinic acid	amber (L. <i>succinum</i> )	butanedioic acid
HOOC—(CH <sub>2</sub> ) <sub>3</sub> —COOH	glutaric acid	gluten	pentanedioic acid
HOOC—(CH <sub>2</sub> ) <sub>4</sub> —COOH	adipic acid	fat (L. <i>adeps</i> )	hexanedioic acid

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



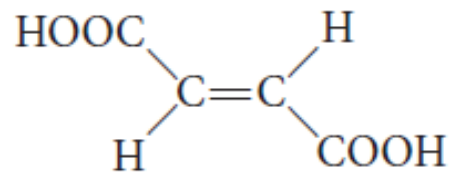
The two butenedioic acids played a historic role in the discovery of *cis-trans* isomerism and are usually known by their common names maleic\*\* and fumaric\*\*\* acid.



maleic acid

(*cis*-2-butenedioic acid)

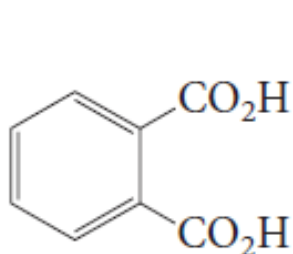
and



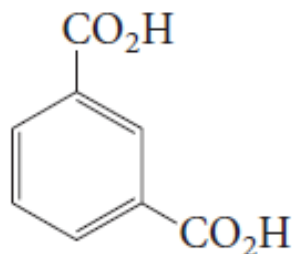
fumaric acid

(*trans*-2-butenedioic acid)

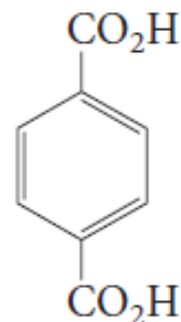
The three benzenedicarboxylic acids are generally known by their common names.



phthalic acid



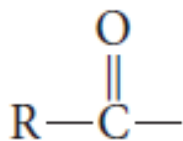
isophthalic acid



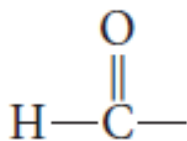
terephthalic acid



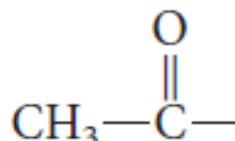
Particular acyl groups are named from the corresponding acid by changing the *-ic* ending to *-yl*.



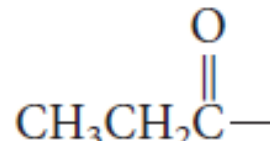
an acyl group



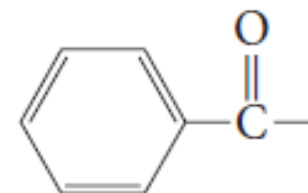
formyl  
(methanoyl)



acetyl  
(ethanoyl)



propanoyl



benzoyl

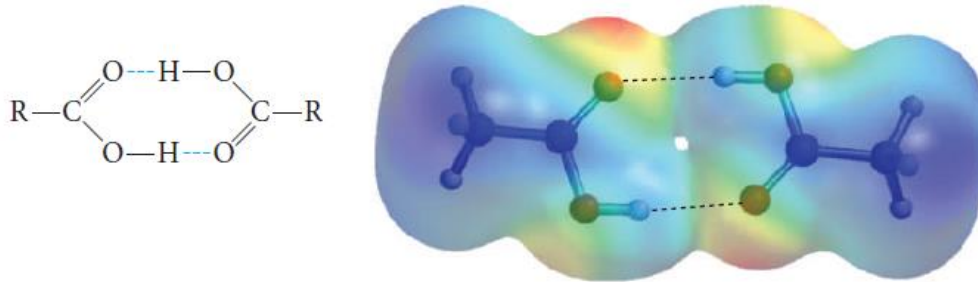


# Physical Properties of Acids

The first members of the carboxylic acid series are colorless liquids with sharp or unpleasant odors.

Carboxylic acids are polar. Like alcohols, they form hydrogen bonds with themselves or with other molecules

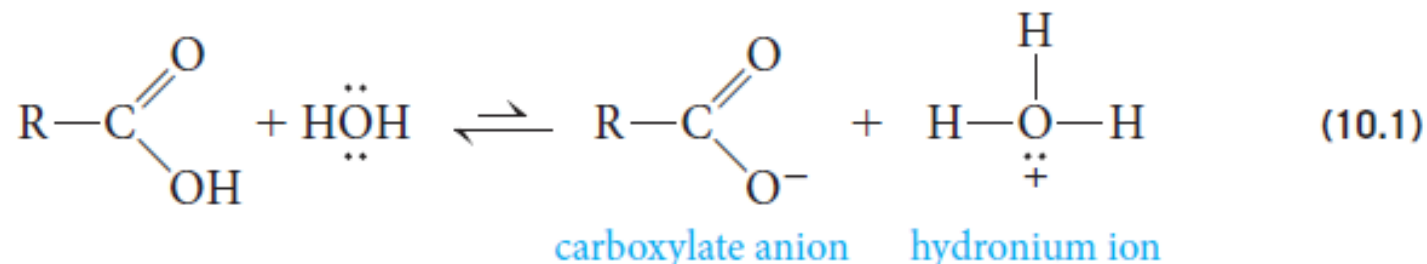
Carboxylic acids form dimers, with the individual units neatly held together by *two* hydrogen bonds between the electronrich oxygens and the electron-poor hydrogens



Hydrogen bonding also explains the water solubility of the lower molecular weight carboxylic acids.

# Acidity and Acidity Constants

Carboxylic acids ( $\text{RCO}_2\text{H}$ ) dissociate in water, yielding a carboxylate anion ( $\text{RCO}_2^-$ ) and a hydronium ion.



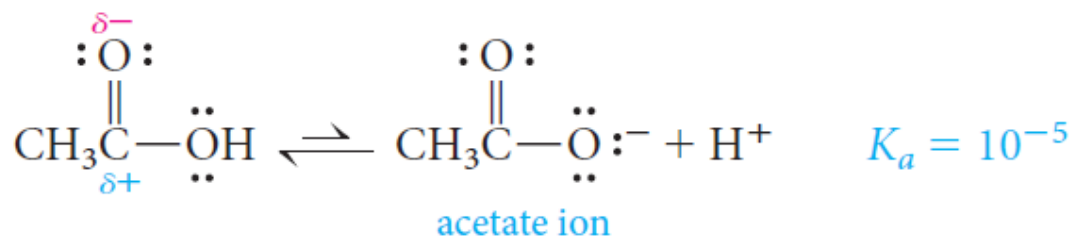
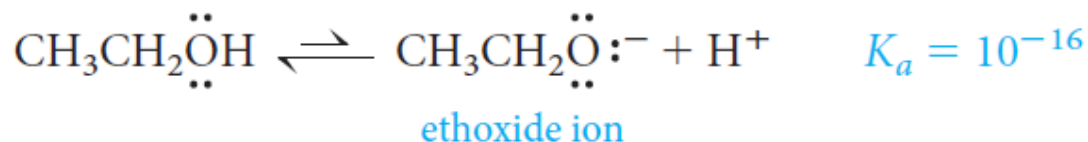
Their acidity constants  $K_a$  in water are given by the expression

$$K_a = \frac{[\text{RCO}_2^-][\text{H}_3\text{O}^+]}{[\text{RCO}_2\text{H}]} \quad (10.2)$$

The larger the value of  $K_a$  or the smaller the value of  $\text{p}K_a$ , the stronger the acid.

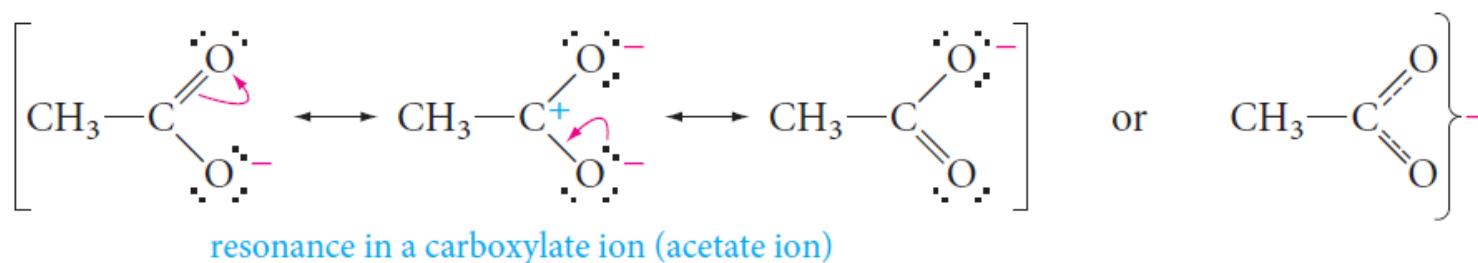
## What Makes Carboxylic Acids Acidic?

Acetic acid is approximately  $10^{11}$ , or 100,000 million, times stronger an acid than ethanol.



# What Makes Carboxylic Acids Acidic?

In ethoxide ion, *the negative charge is localized on a single oxygen atom*. In acetate ion, on the other hand, *the negative charge can be delocalized through resonance*.



The negative charge is spread *equally* over the two oxygens so that each oxygen in the carboxylate ion carries only half the negative charge. The acetate ion is stabilized by resonance compared to the ethoxide ion, and this stabilization helps to drive the equilibrium more to the right. Consequently, more  $H^+$  is formed from acetic acid than from ethanol.

## EXAMPLE

Phenoxide ions are also stabilized by resonance .Why are phenols weaker acids than carboxylic acids?

Draw the resonance contributors  
??????????

### **Solution**

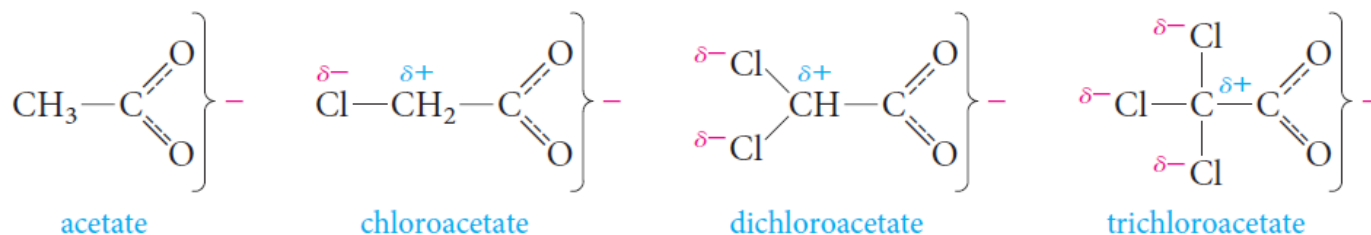
First, the carbon atom to which the hydroxyl group is attached in a phenol is not as positive as a carbonyl carbon. Second, charge delocalization is not as great in phenoxide ions as in carboxylate ions because the contributors to the resonance hybrid are not equivalent. Some of them put the negative charge on carbon instead of on oxygen and disrupt aromaticity.

## PROBLEM

Write two resonance structures for the benzoate ion ( $\text{C}_6\text{H}_5\text{CO}_2^-$ ) that show how the negative charge is delocalized over the two oxygens. Can the negative charge in the benzoate ion be delocalized into the aromatic ring?

# Effect of Structure on Acidity; the Inductive Effect

*Electron-withdrawing groups enhance acidity, and electron-releasing groups reduce acidity*



Because chlorine is more electronegative than carbon, the C-Cl bond is polarized with the chlorine partially negative and the carbon partially positive. Thus, electrons are pulled away from the carboxylate end of the ion toward the chlorine. The effect tends to spread the negative charge over more atoms than in acetate ion itself and thus stabilizes the ion. The more chlorines, the greater the effect and the greater the strength of the acid.



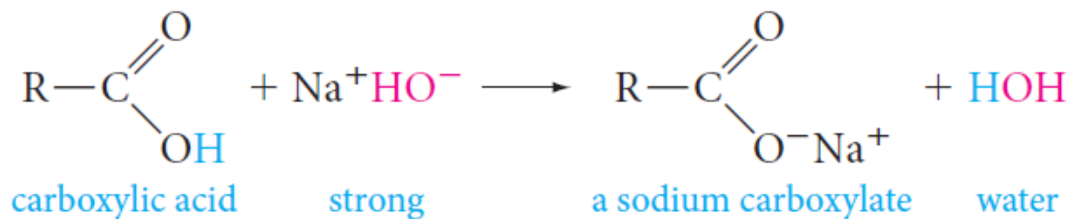
PROBLEM. Account for the relative acidities of benzoic acid and its *ortho*, *meta*, and *para* chloro derivatives

Ka

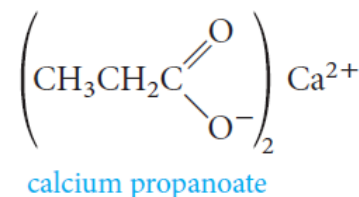
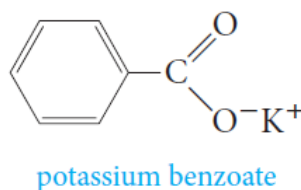
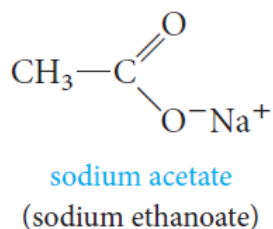
<i>o</i> -chlorobenzoic acid	<i>o</i> -Cl—C <sub>6</sub> H <sub>4</sub> COOH	$12.5 \times 10^{-4}$
<i>m</i> -chlorobenzoic acid	<i>m</i> -Cl—C <sub>6</sub> H <sub>4</sub> COOH	$1.6 \times 10^{-4}$
<i>p</i> -chlorobenzoic acid	<i>p</i> -Cl—C <sub>6</sub> H <sub>4</sub> COOH	$1.0 \times 10^{-4}$

# Conversion of Acids to Salts

Carboxylic acids, when treated with a strong base, form carboxylate salts.



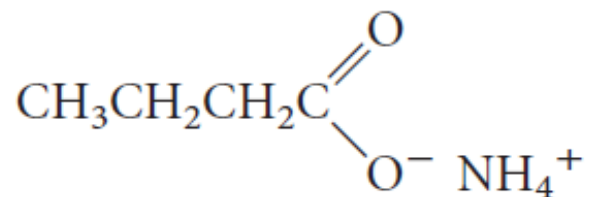
Carboxylate salts are named as shown in the following examples:



The cation is named first, followed by the name of the carboxylate ion, which is obtained by changing the *-ic* ending of the acid to *-ate*.

## EXAMPLE

Name the following carboxylate salt:



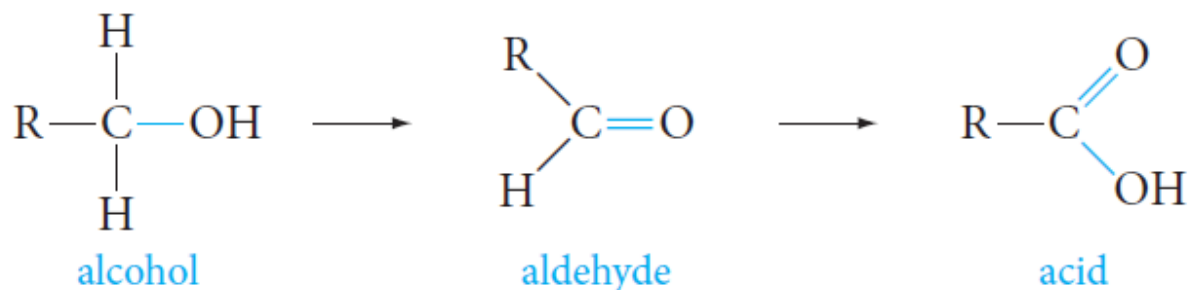
**Solution** The salt is ammonium butanoate (IUPAC) or ammonium butyrate (common).

## PROBLEM

Write an equation for the preparation of potassium 3-bromooctanoate from the corresponding acid.

# Preparation of Acids

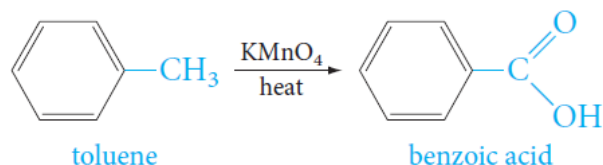
## Oxidation of Primary Alcohols and Aldehydes



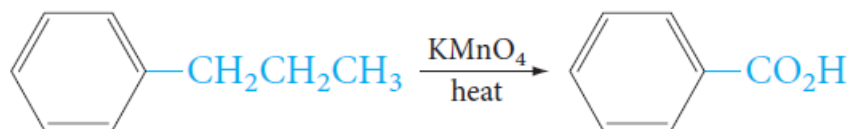
The most commonly used oxidizing agents for these purposes are potassium permanganate ( $\text{KMnO}_4$ ), chromic acid anhydride ( $\text{CrO}_3$ ), nitric acid ( $\text{HNO}_3$ ), and with aldehydes only, silver oxide ( $\text{Ag}_2\text{O}$ ).

# Preparation of Acids

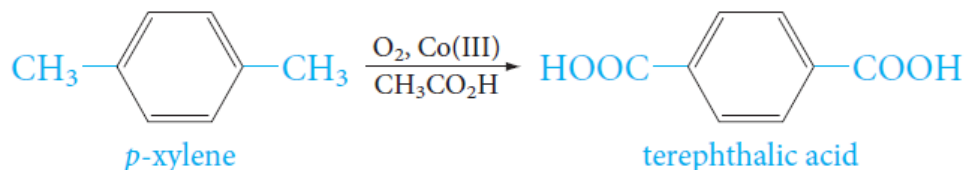
## Oxidation of Aromatic Side Chains



The reaction involves attack of the oxidant at a C-H bond adjacent to the benzene ring. Longer side chains are also oxidized to a carboxyl group.



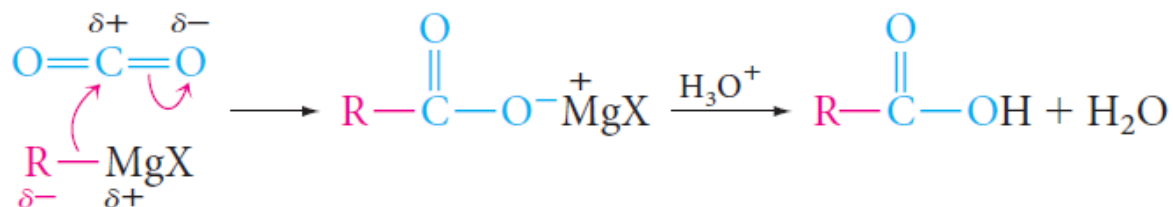
Terephthalic acid, one of the two raw materials needed to manufacture Dacron, is produced in this way, using a cobalt catalyst and air for the oxidation.



# Preparation of Acids

## Reaction of Grignard Reagents with Carbon Dioxide

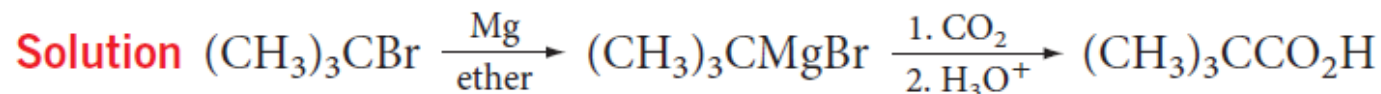
Grignard reagents add to the carbonyl group of carbon dioxide to give acids, after protonation of the intermediate carboxylate salt with a mineral acid like aqueous HCl.



This reaction gives good yields and is an excellent laboratory method for preparing both aliphatic and aromatic acids

# EXAMPLE

Show how  $(\text{CH}_3)_3\text{CBr}$  can be converted to  $(\text{CH}_3)_3\text{CCO}_2\text{H}$ .



**PROBLEM.** Show how 4-methylcyclohexyl chloride can be converted to 4-methylcyclohexanecarboxylic acid.

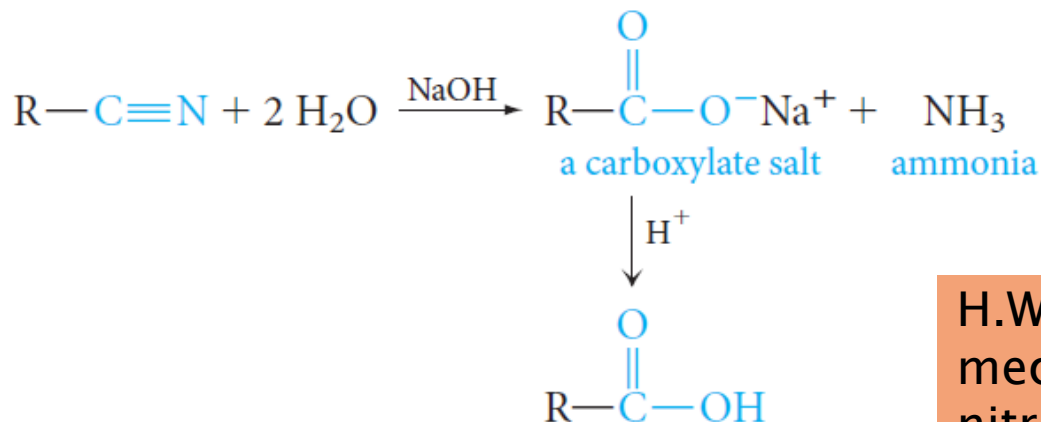
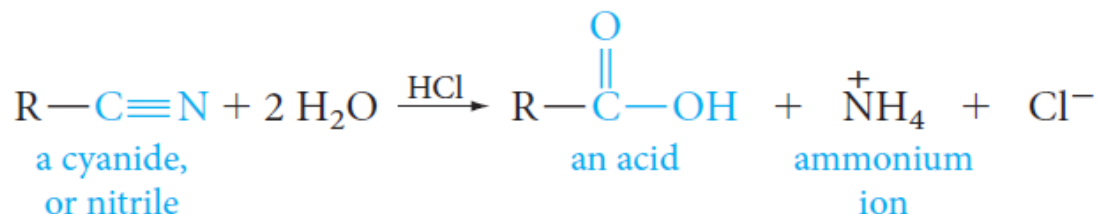
**PROBLEM.** Devise a synthesis of butanoic acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ) from 1-propanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ).



# Preparation of Acids

## Hydrolysis of Cyanides (Nitriles)

The carbon–nitrogen triple bond of organic cyanides can be hydrolyzed to a carboxyl group.



H.W : Write The mechanism of nitrile hydrolysis

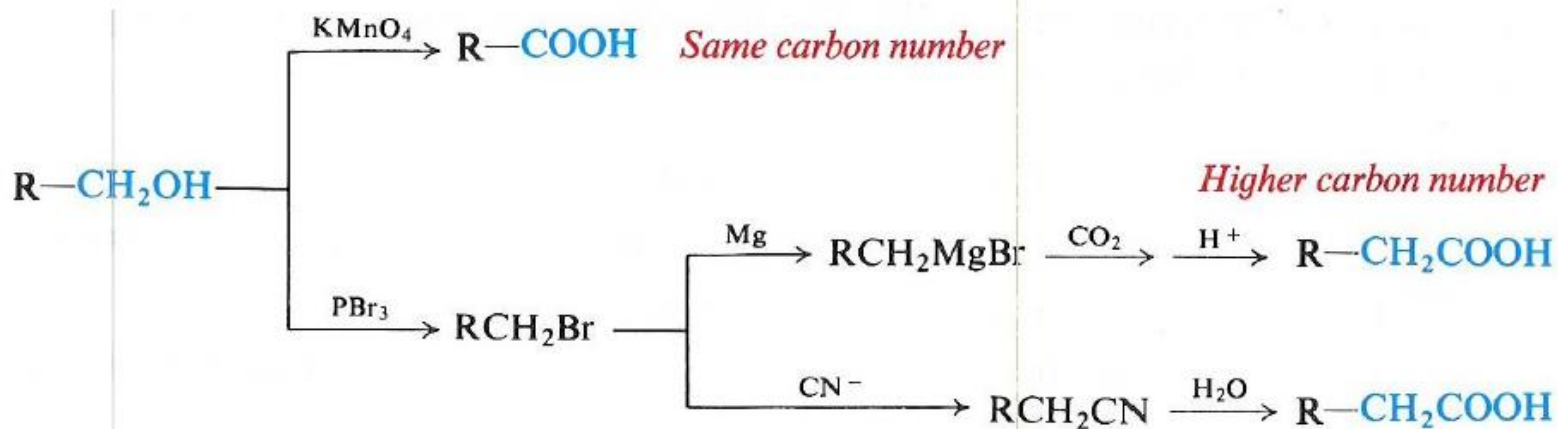
Organic cyanides are commonly named after the corresponding acid, by changing the *-ic* or *-oic* suffix to *-onitrile* (butyronitrile) .

In the IUPAC system, the suffix *-nitrile* is added to the name of the hydrocarbon with the same number of carbon atoms (butanenitrile)

**PROBLEM.** Why is it *not* possible to convert bromobenzene to benzoic acid by the nitrile method? Instead, how could this conversion be accomplished?

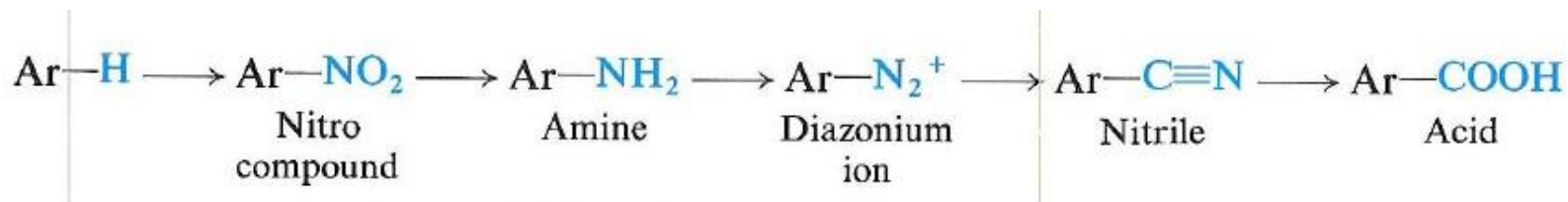
**PROBLEM.** Write equations for synthesizing phenylacetic acid ( $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{H}$ ) from benzyl bromide ( $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ ) by two routes.

# Note



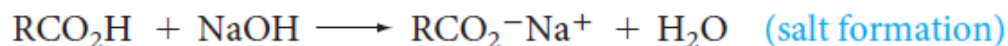
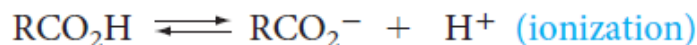
**Problem** Which carboxylic acid can be prepared from *p*-bromotoluene: (a) by direct oxidation? (b) by free-radical chlorination followed by the nitrile synthesis?

# Aromatic Carboxylic can be prepared for Diazonium Salt

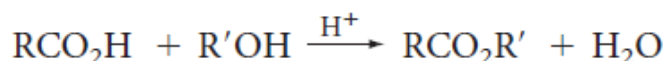


# Reaction of Acids

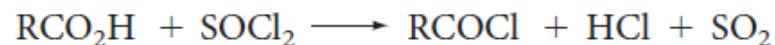
## a. Acid-Base (Secs. 10.4 and 10.6)



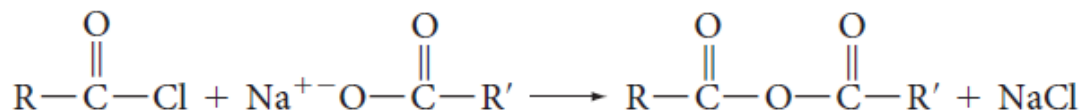
## b. Preparation of Esters (Secs. 10.10 and 10.12)



## c. Preparation of Acid Chlorides (Sec. 10.18)



## d. Preparation of Anhydrides (Sec. 10.19)



## e. Preparation of Amides (Sec. 10.20)

