



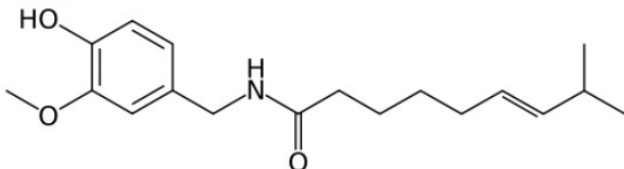
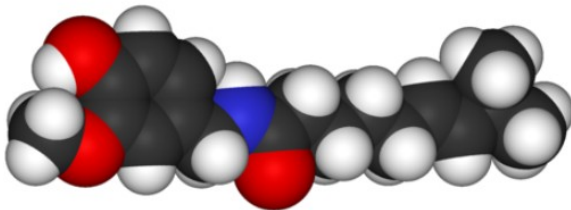
20

羧酸，腈

The burning sensation produced by touching or eating chili peppers is due to capsaicin, a carboxylic acid derivative called an amide. Image copyright Marie C. Fields, 2010. Used under license from Shutterstock.com

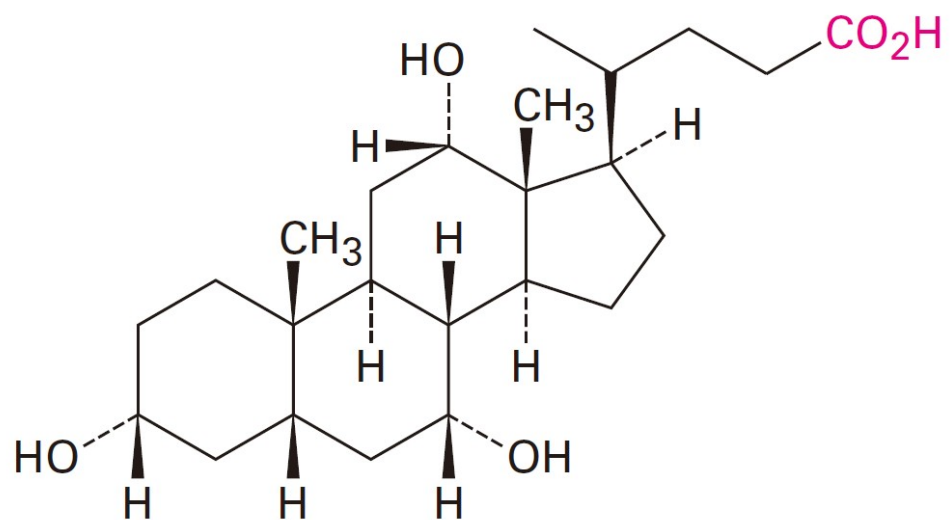
辣椒素 Capsaicin

- 辣椒素又名辣素，辣椒碱，即反式-8-甲基-N-香草基-6-壬烯酰胺，是辣椒属植物红辣椒的活性成分。它对包括人类在内的哺乳动物都有刺激性并可在皮肤中产生灼烧感。

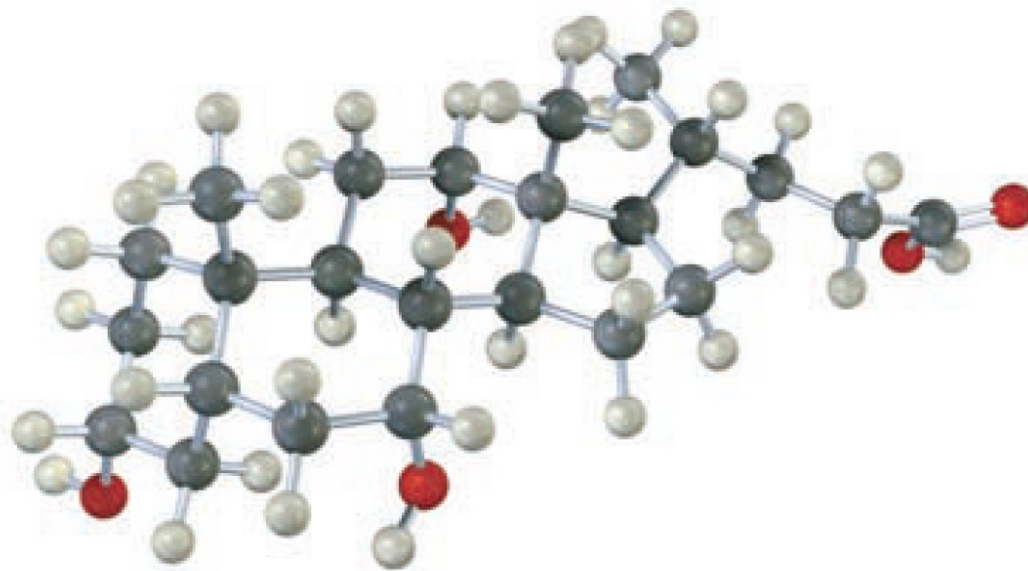
辣椒素	
	
	
IUPAC名	
8-Methyl- <i>N</i> -vanillyl- <i>trans</i> -6-nonenamide	
英文名	Capsaicin
别名	(<i>E</i>)- <i>N</i> -(4-羟基-3-甲氧基苄基)-8-甲基-6-壬烯酰胺

羧酸的重要性

- 在自然界中广泛存在

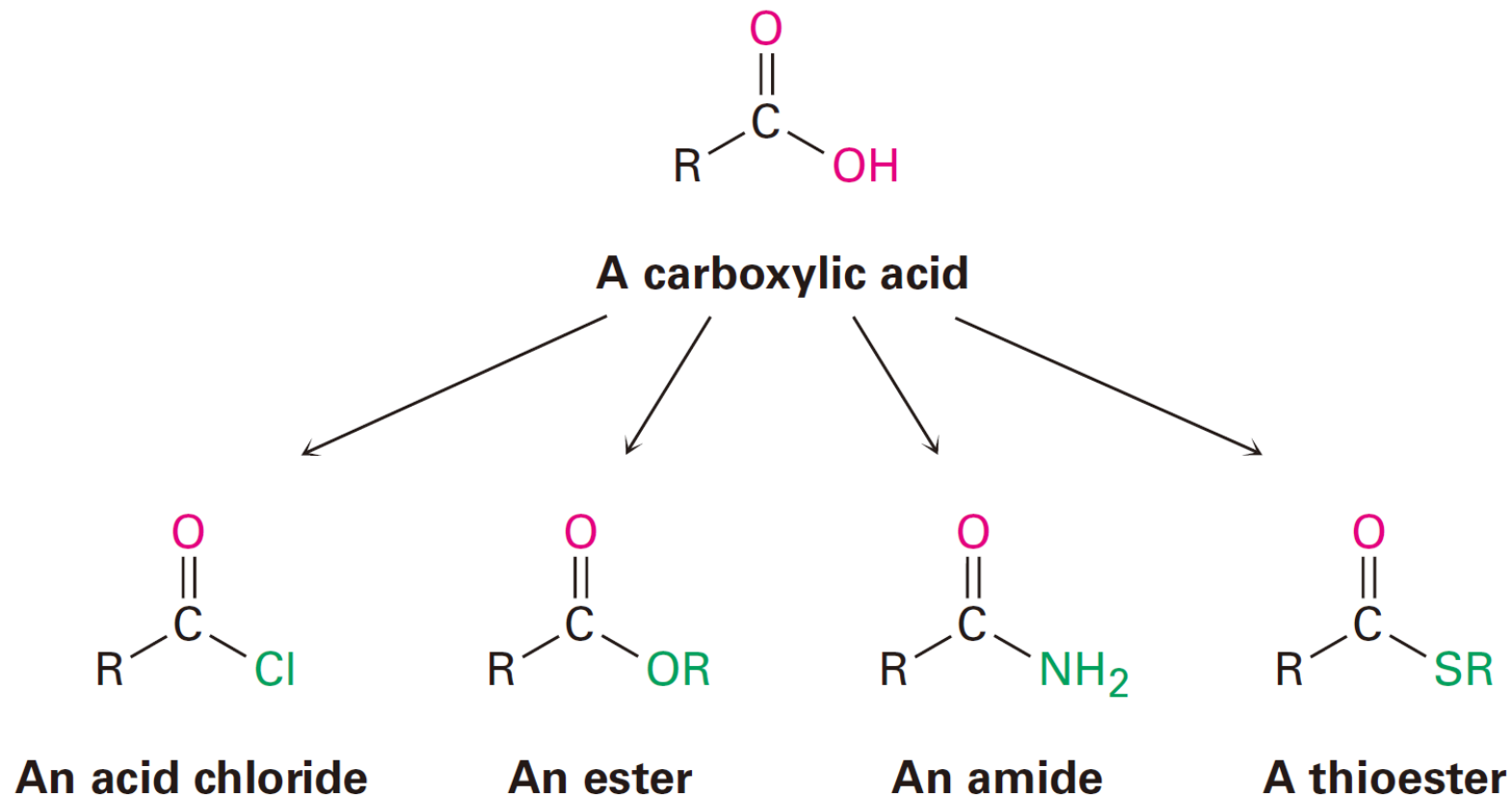


Cholic acid 胆酸



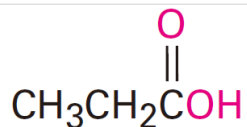
羧酸的重要性

- 制备各种羧酸衍生物的原料

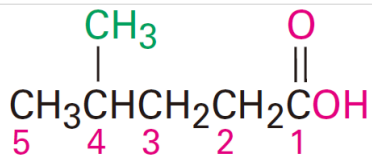


20.1 命名

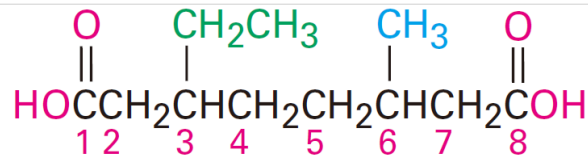
- 羧酸的命名



Propanoic acid

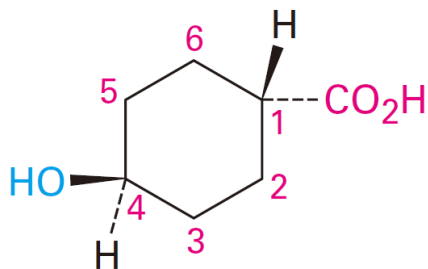


4-Methylpentanoic acid

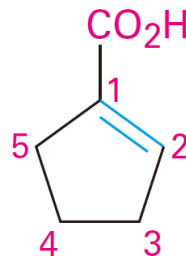


3-Ethyl-6-methyloctanedioic acid

Compounds that have a $-\text{CO}_2\text{H}$ group bonded to a ring are named using the suffix *-carboxylic acid*. The CO_2H carbon is attached to C1 in this system and is not itself numbered. As a substituent, the CO_2H group is called a **carboxyl group**.



trans-4-Hydroxycyclohexanecarboxylic acid



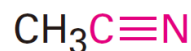
1-Cyclopentenecarboxylic acid

20.1 命名

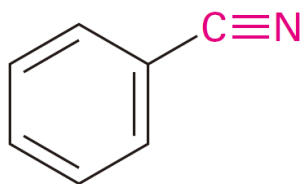
- 腈的命名



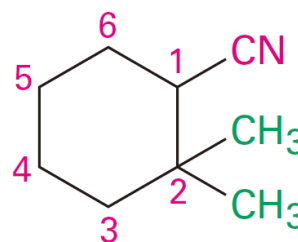
Nitriles can also be named as derivatives of carboxylic acids by replacing the *-ic acid* or *-oic acid* ending with *-onitrile*, or by replacing the *-carboxylic acid* ending with *-carbonitrile*. The nitrile carbon atom is attached to C1 but is not itself numbered.



Acetonitrile
(from acetic acid)



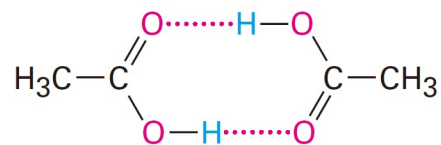
Benzonitrile
(from benzoic acid)



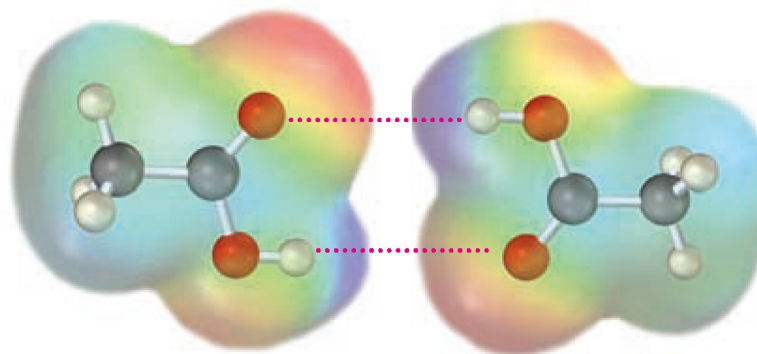
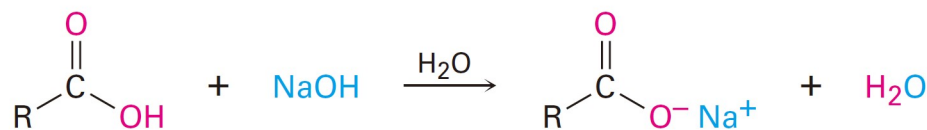
2,2-Dimethylcyclohexanecarbonitrile
(from 2,2-dimethylcyclohexane-
carboxylic acid)

20.2 羧酸的结构和性质

- 分子间氢键：沸点升高
- 酸性

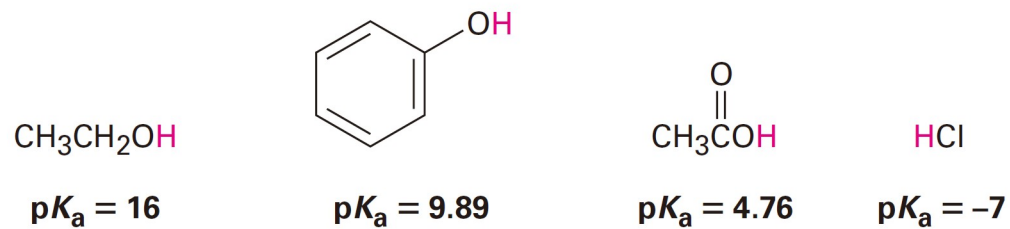


Acetic acid dimer



A carboxylic acid
(water-insoluble)

A carboxylic acid salt
(water-soluble)



20.2 羧酸的结构和性质

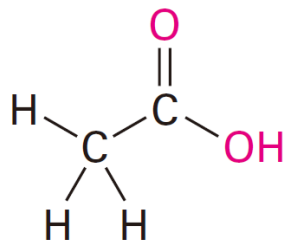
- 课堂练习

Problem 20.3

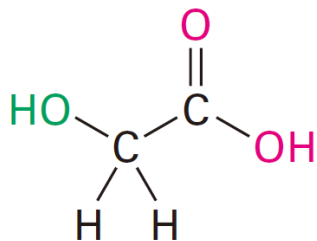
Assume you have a mixture of naphthalene and benzoic acid that you want to separate. How might you take advantage of the acidity of one component in the mixture to effect a separation?



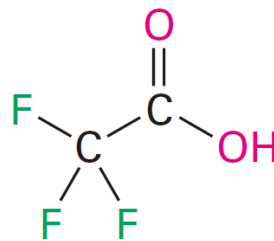
20.4 取代基对酸性的影响



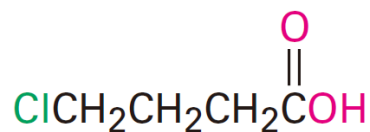
$pK_a = 4.76$



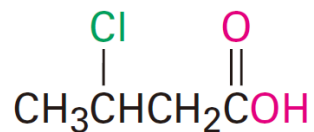
$pK_a = 3.83$



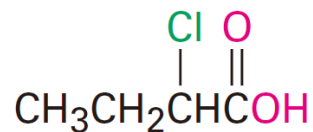
$pK_a = -0.23$



$pK_a = 4.52$



$pK_a = 4.05$

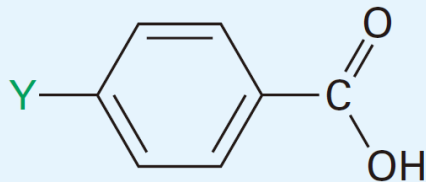


$pK_a = 2.86$



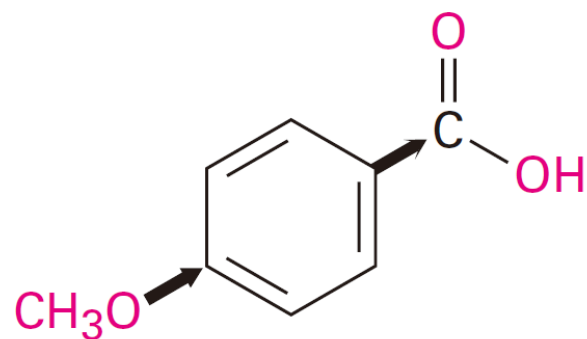
20.4 取代基对酸性的影响

Table 20.4 Substituent Effects on Acidity of *p*-Substituted Benzoic Acids

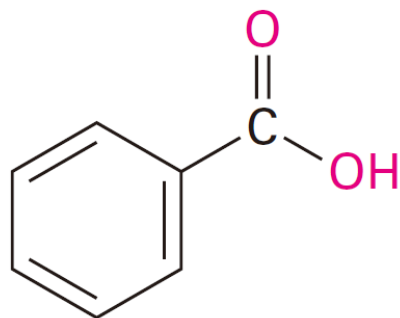


	Y	$K_a \times 10^{-5}$	pK_a	
<div style="display: flex; align-items: center;"> <div style="width: 20px; height: 100px; background: linear-gradient(to top, blue, red); margin-right: 5px;"></div> <div style="text-align: center;"> <p>Stronger acid</p> <p>↑</p> <p>Weaker acid</p> </div> </div>	$-\text{NO}_2$	39	3.41	Deactivating groups
	$-\text{CN}$	28	3.55	
	$-\text{CHO}$	18	3.75	
	$-\text{Br}$	11	3.96	
	$-\text{Cl}$	10	4.0	
	$-\text{H}$	6.46	4.19	
	$-\text{CH}_3$	4.3	4.34	Activating groups
	$-\text{OCH}_3$	3.5	4.46	
	$-\text{OH}$	3.3	4.48	

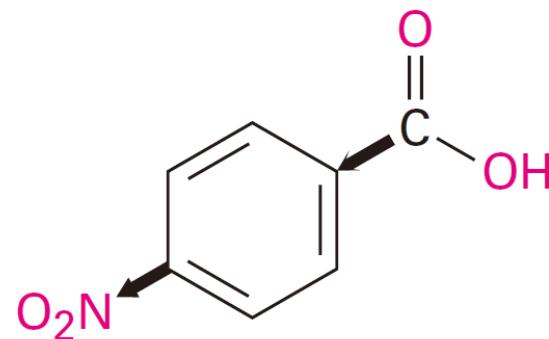
20.4 取代基对酸性的影响



p-Methoxybenzoic acid
($pK_a = 4.46$)



Benzoic acid
($pK_a = 4.19$)

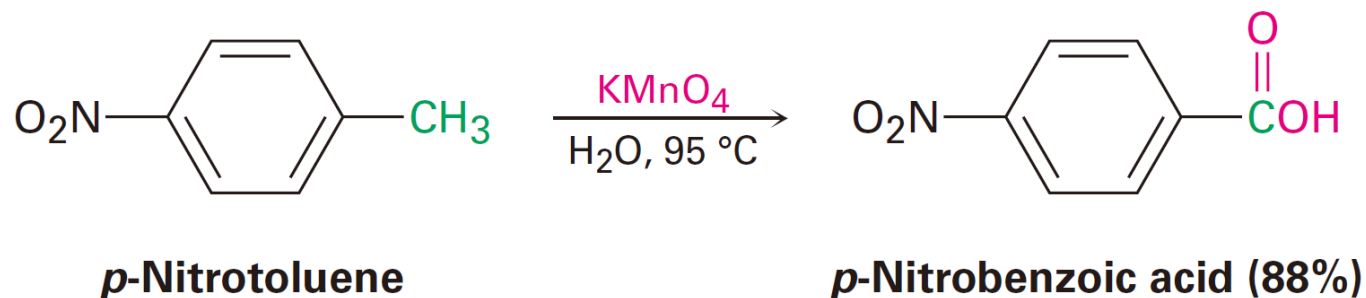


p-Nitrobenzoic acid
($pK_a = 3.41$)

Acidity

20.5 羧酸的制备

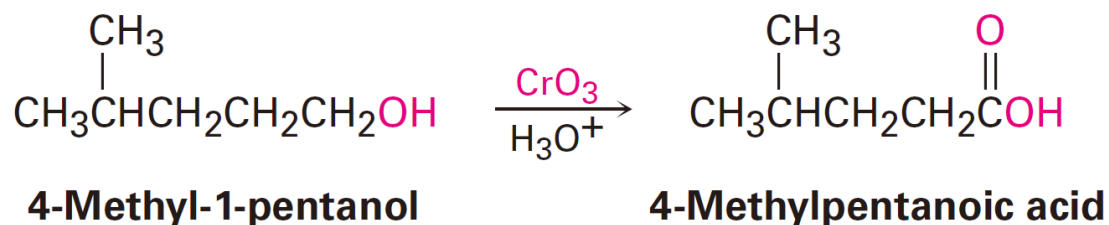
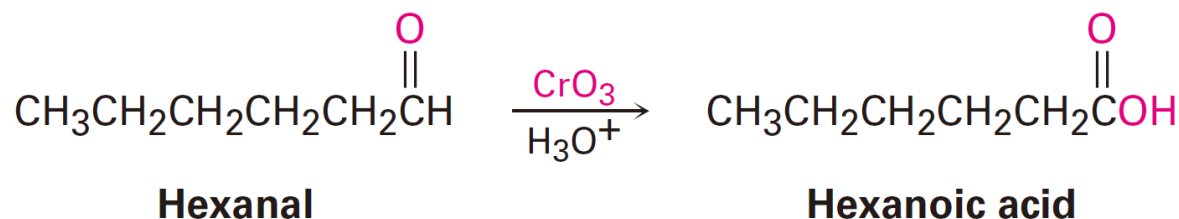
- 氧化苄位 C-H 键
 - Oxidation of a substituted alkylbenzene with KMnO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$ gives a substituted benzoic acid (**Section 16.9**). Both primary and secondary alkyl groups can be oxidized, but tertiary groups are not affected.



20.5 羧酸的制备

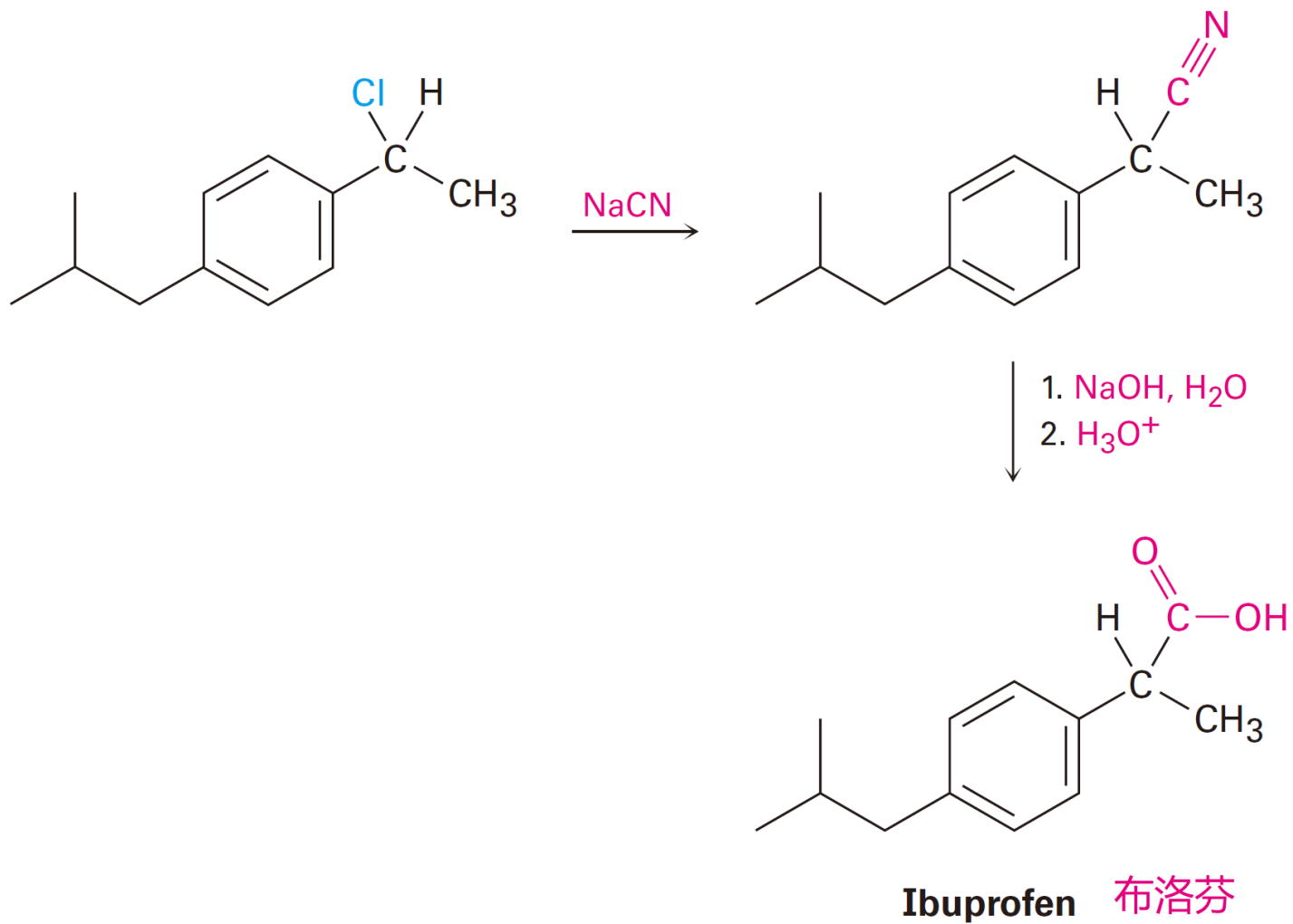
- 氧化醇

- Oxidation of a primary alcohol or an aldehyde yields a carboxylic acid (**Sections 17.7 and 19.3**). Primary alcohols are often oxidized with CrO_3 in aqueous acid, and aldehydes are similarly oxidized.



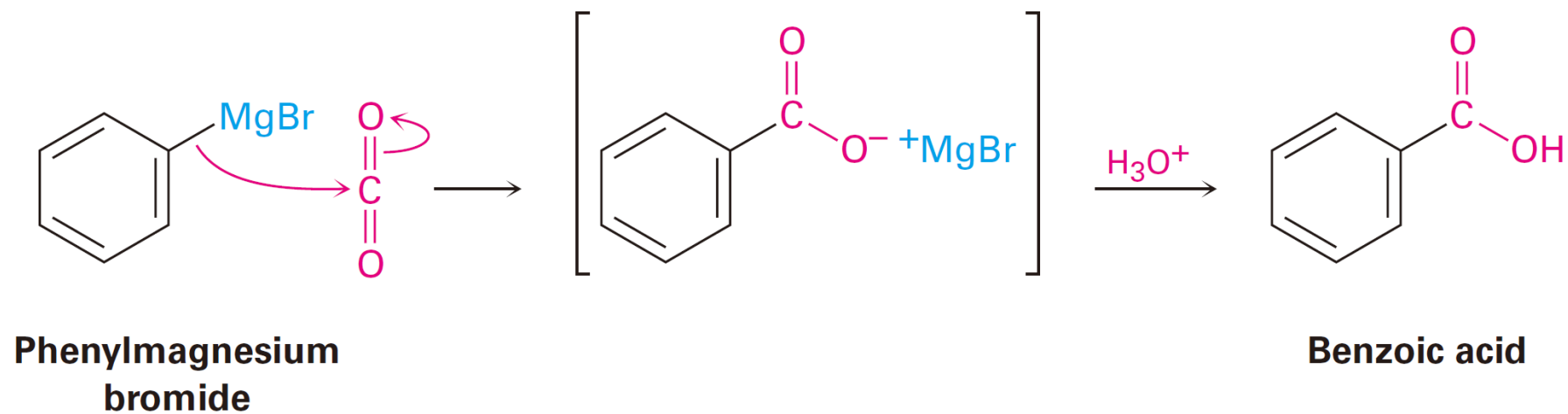
20.5 羧酸的制备

- 腈的水解



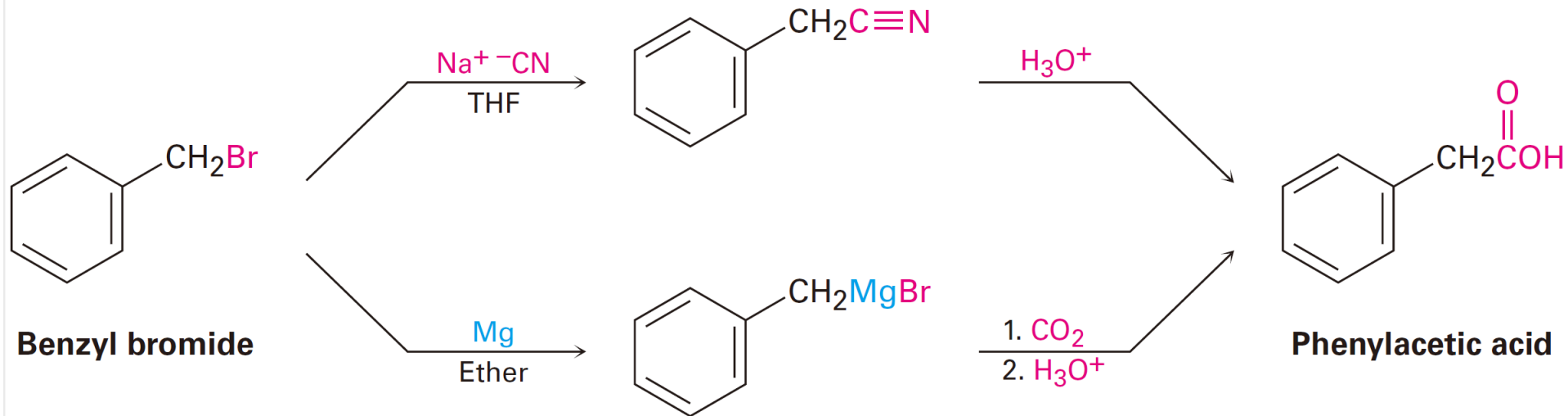
20.5 羧酸的制备

- 格氏试剂对 CO_2 加成



20.5 羧酸的制备

Solution

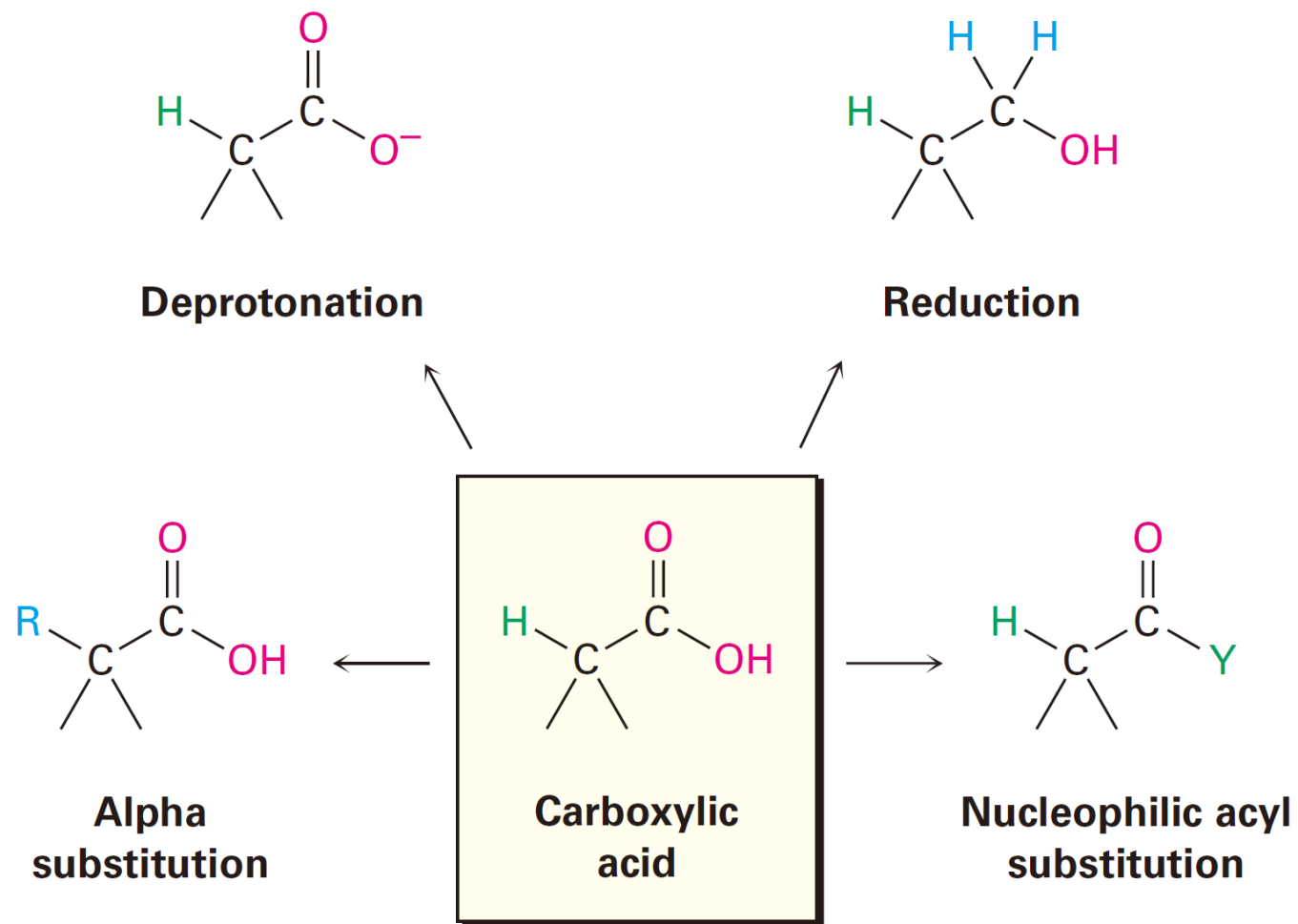


Problem 20.10

How would you prepare the following carboxylic acids?

- (a) $(\text{CH}_3)_3\text{CCO}_2\text{H}$ from $(\text{CH}_3)_3\text{CCl}$
- (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ from $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

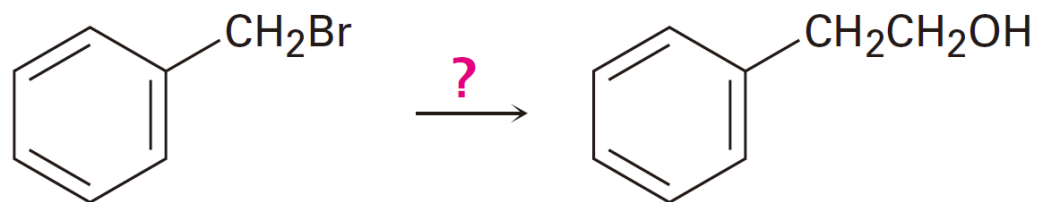
20.6 羧酸的反应



20.6 羧酸的反应

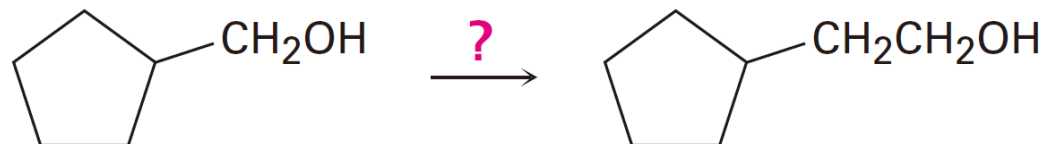
Problem 20.11

How might you prepare 2-phenylethanol from benzyl bromide? More than one step is needed.



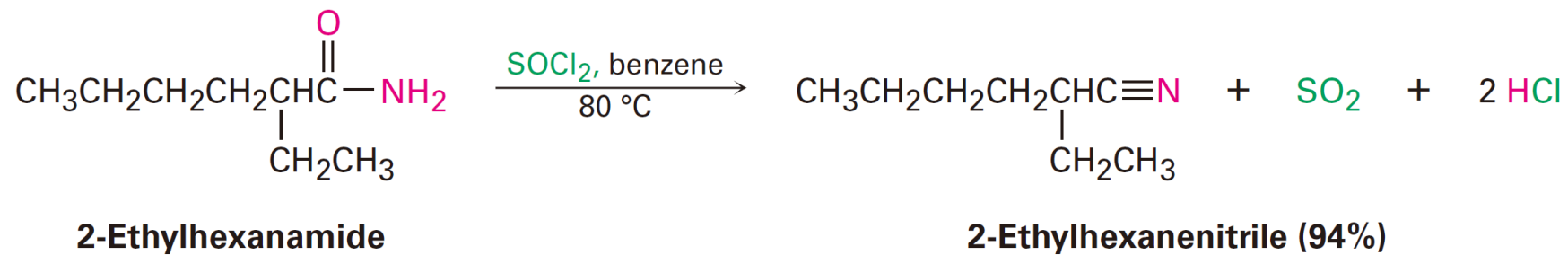
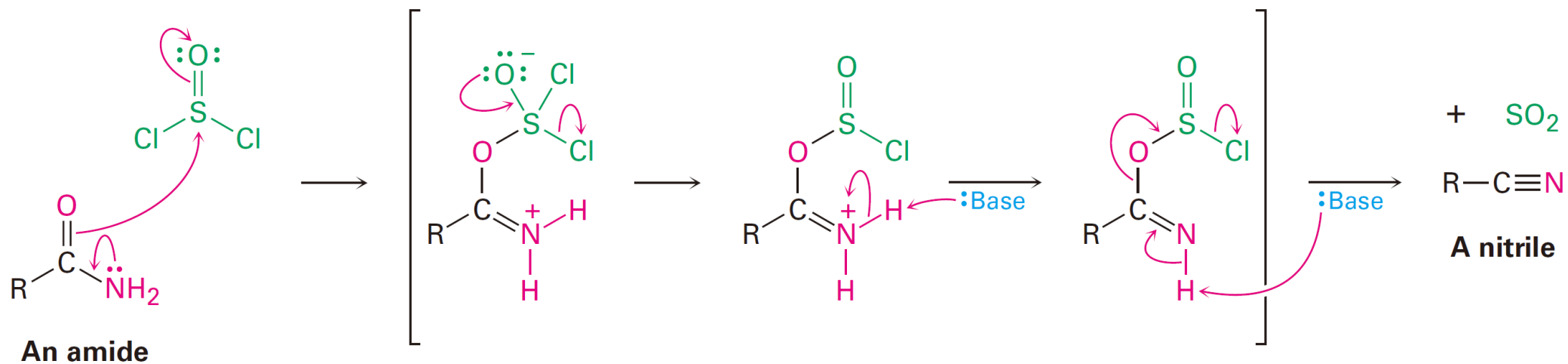
Problem 20.12

How might you carry out the following transformation? More than one step is needed.



20.7 腈的化学

• 腈的制备



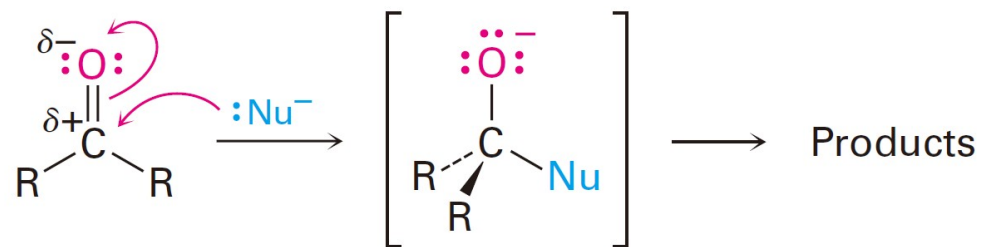
POCl₃也可以作为脱水剂



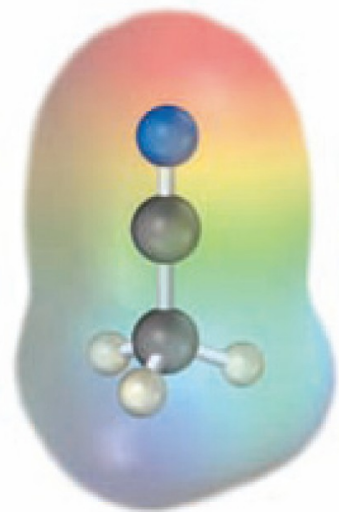
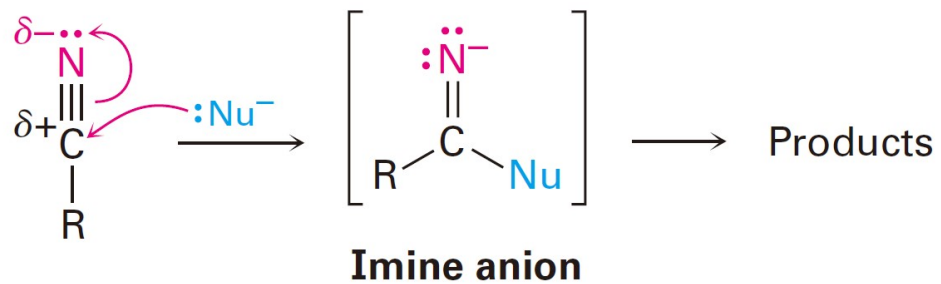
20.7 腈的化学

- 腈的反应

Carbonyl compound

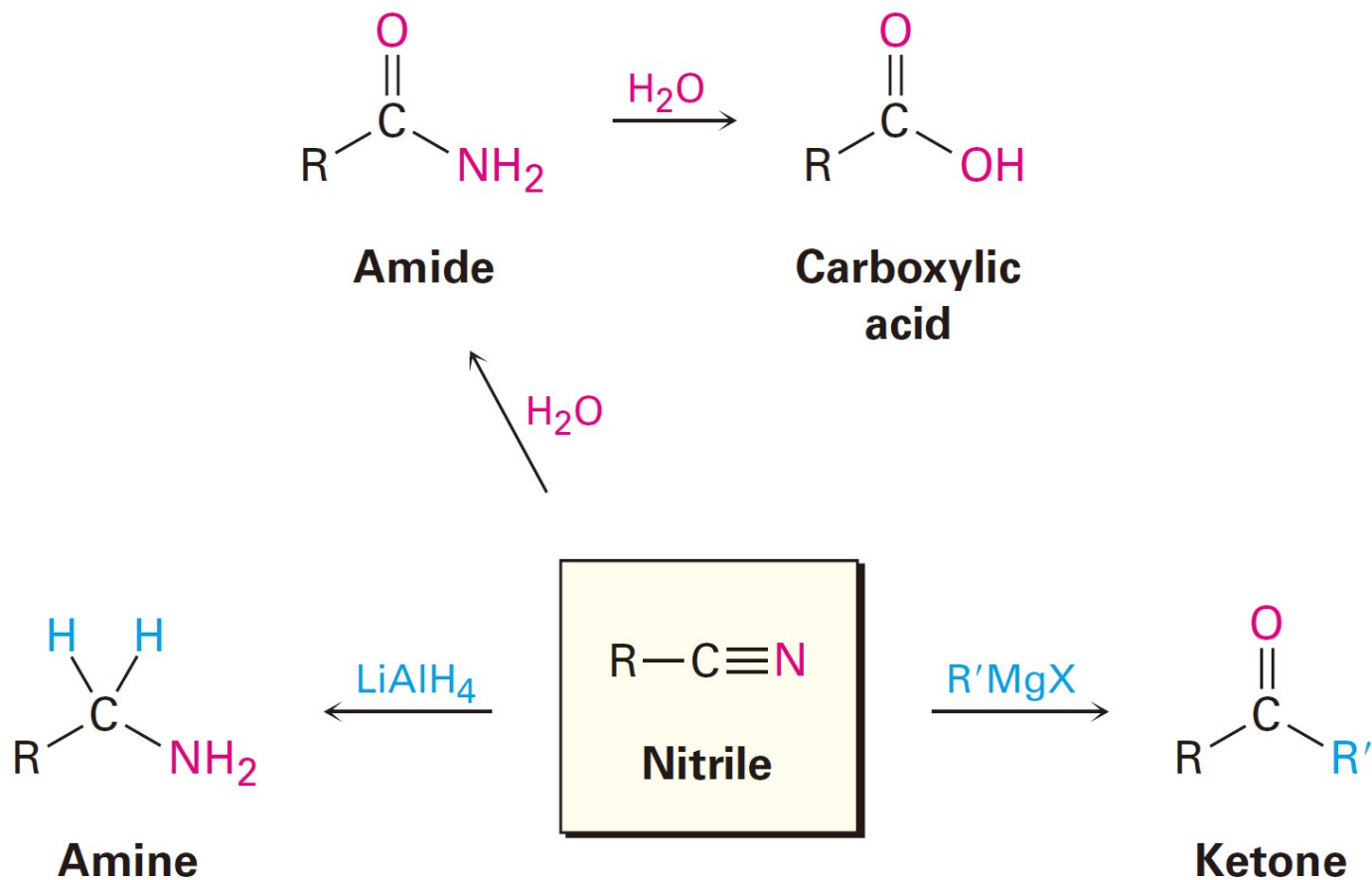


Nitrile



20.7 腈的化学

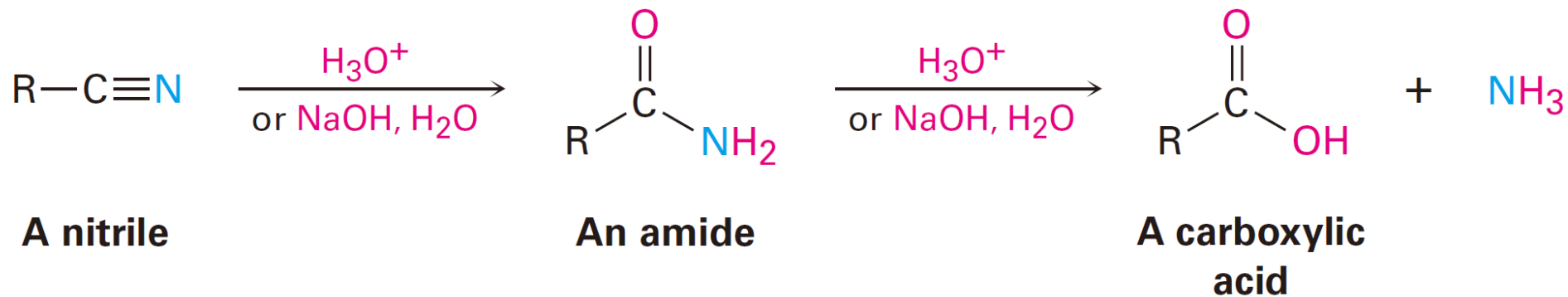
- 腈的反应



20.7 腈的化学

- 腈的水解

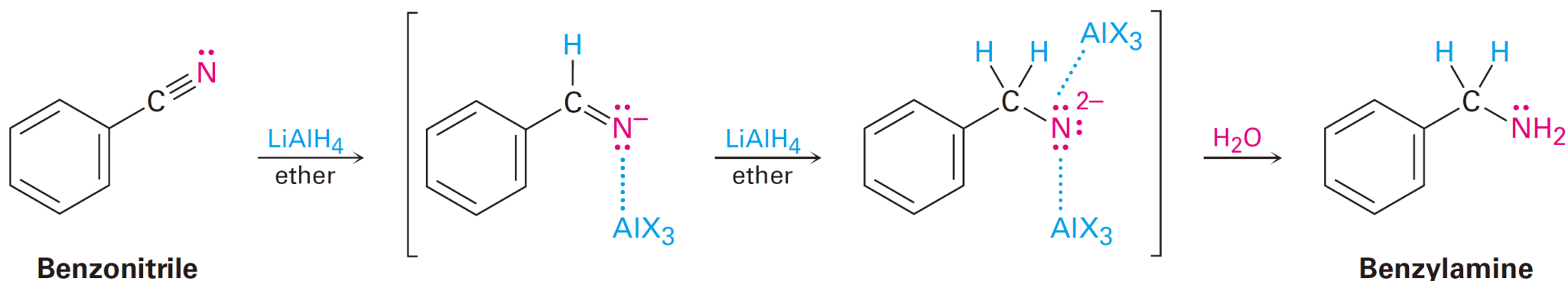
Hydrolysis: Conversion of Nitriles into Carboxylic Acids Among the most useful reactions of nitriles is their hydrolysis to yield first an amide and then a carboxylic acid plus ammonia or an amine. The reaction occurs in either basic or acidic aqueous solution:



20.7 腈的化学

- 腈的还原

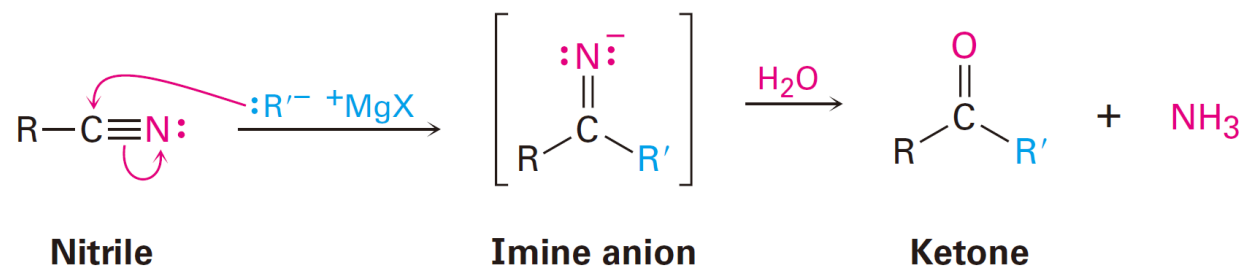
Reduction: Conversion of Nitriles into Amines Reduction of a nitrile with LiAlH_4 gives a primary amine, RNH_2 . The reaction occurs by nucleophilic addition of hydride ion to the polar $\text{C}\equiv\text{N}$ bond, yielding an imine anion, which still contains a $\text{C}=\text{N}$ bond and therefore undergoes a second nucleophilic addition of hydride to give a *dianion*. Both monoanion and dianion intermediates are undoubtedly stabilized by Lewis acid–base complexation to an aluminum species, facilitating the second addition that would otherwise be difficult. Protonation of the dianion by addition of water in a subsequent step gives the amine.



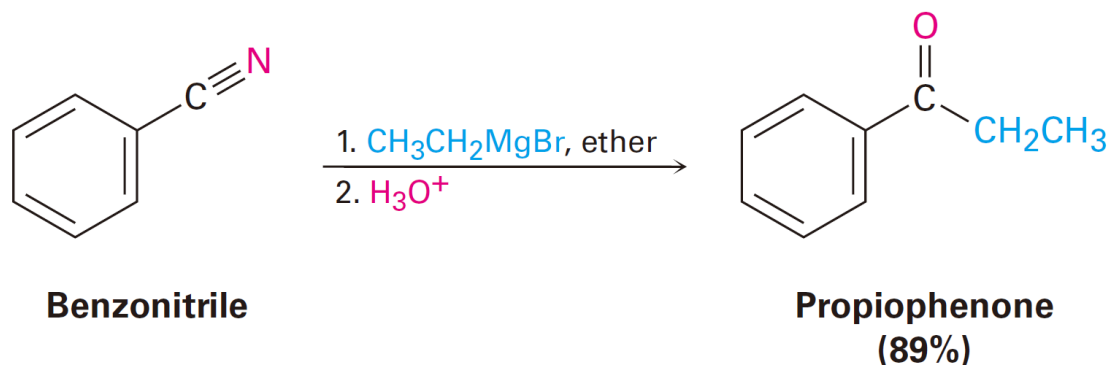
20.7 腈的化学

- 格氏试剂与腈的反应

Reaction of Nitriles with Grignard Reagents Grignard reagents add to a nitrile to give an intermediate imine anion that is hydrolyzed by addition of water to yield a ketone. The mechanism of the hydrolysis is the exact reverse of imine formation (see Figure 19.6 on page 737).

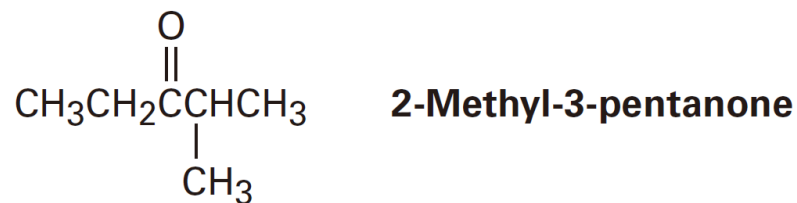


The reaction is similar to the reduction of a nitrile to an amine, except that only one nucleophilic addition occurs rather than two and the attacking nucleophile is a carbanion ($R:^-$) rather than a hydride ion. For example:



20.7 腈的化学

- 例题 How would you prepare 2-methyl-3-pentanone from a nitrile?

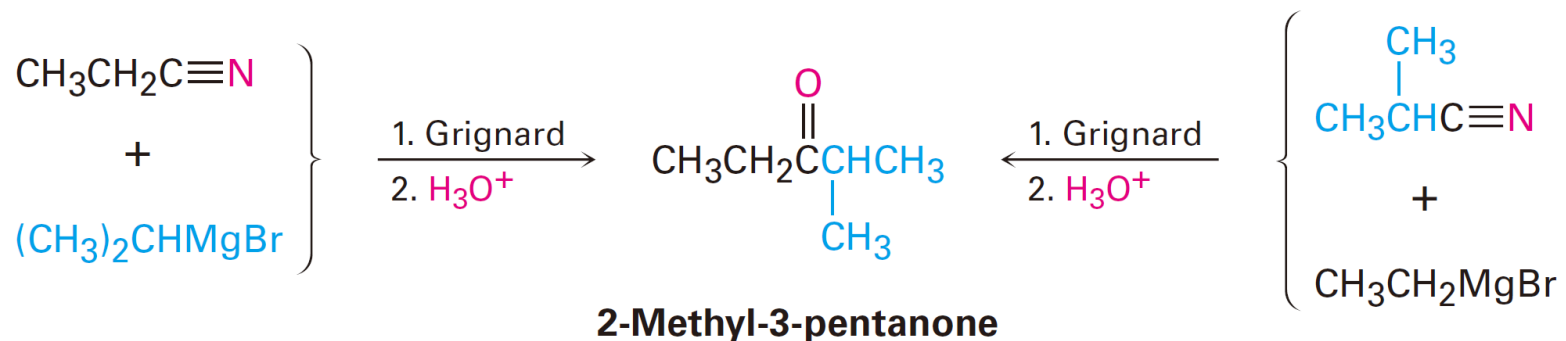


Strategy

A ketone results from the reaction between a Grignard reagent and a nitrile, with the $\text{C} \equiv \text{N}$ carbon of the nitrile becoming the carbonyl carbon. Identify the two groups attached to the carbonyl carbon atom in the product. One will come from the Grignard reagent, and the other will come from the nitrile.

Solution

There are two possibilities.

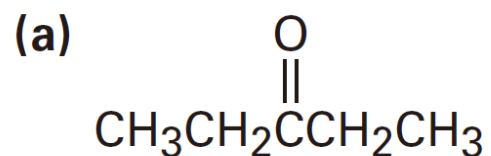
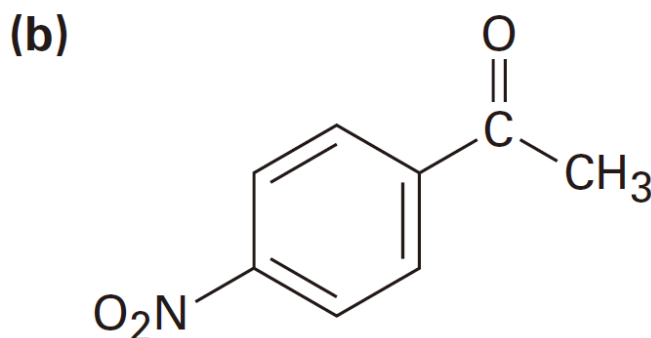


20.7 腈的化学

- 课堂练习

Problem 20.13

How would you prepare the following carbonyl compounds from a nitrile?



Problem 20.14

How would you prepare 1-phenyl-2-butanone, $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_2\text{CH}_3$, from benzyl bromide, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$? More than one step is required.



20.8 羧酸和腈的波普分析

- 红外

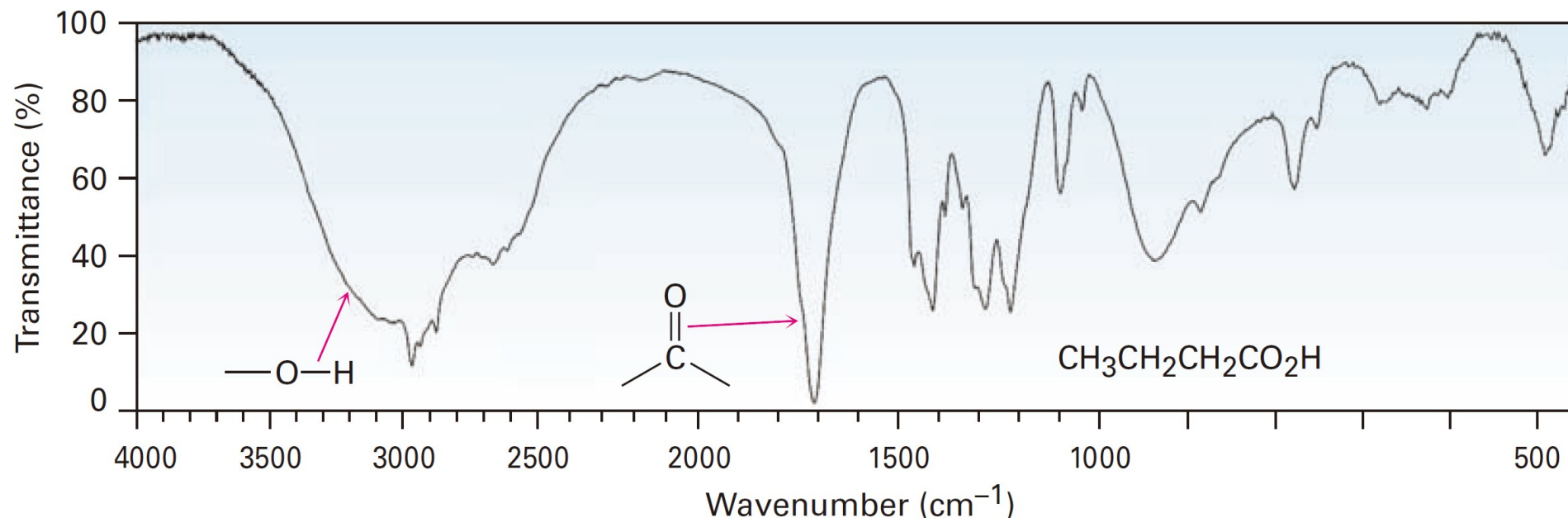
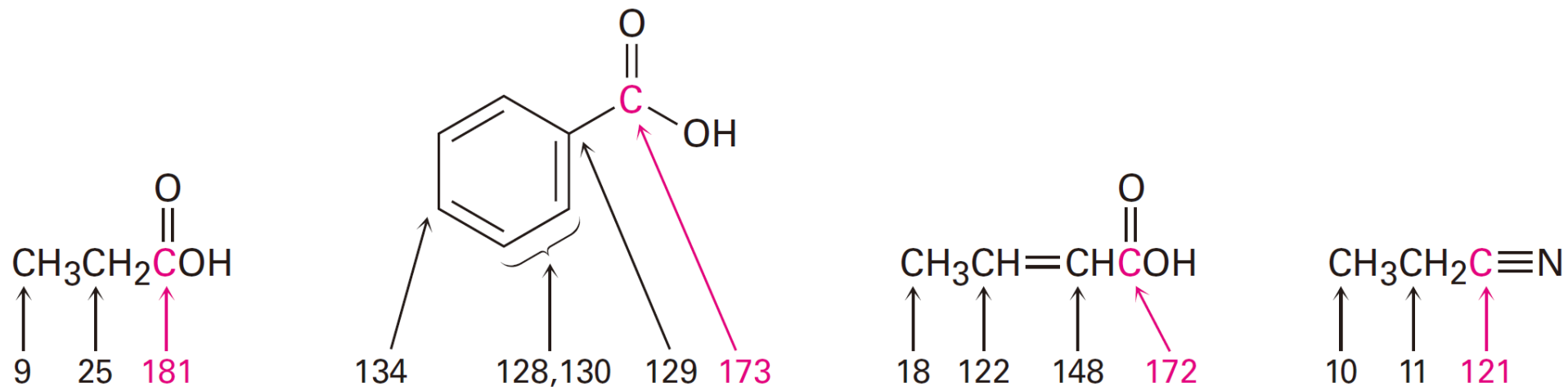


Figure 20.5 IR spectrum of butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$.

Nitriles show an intense and easily recognizable $\text{C}\equiv\text{N}$ bond absorption near 2250 cm^{-1} for saturated compounds and 2230 cm^{-1} for aromatic and conjugated molecules. Few other functional groups absorb in this region, so IR spectroscopy is highly diagnostic for nitriles.

20.8 羧酸和腈的波普分析

- 核磁



20.8 羧酸和腈的波谱分析

- 核磁

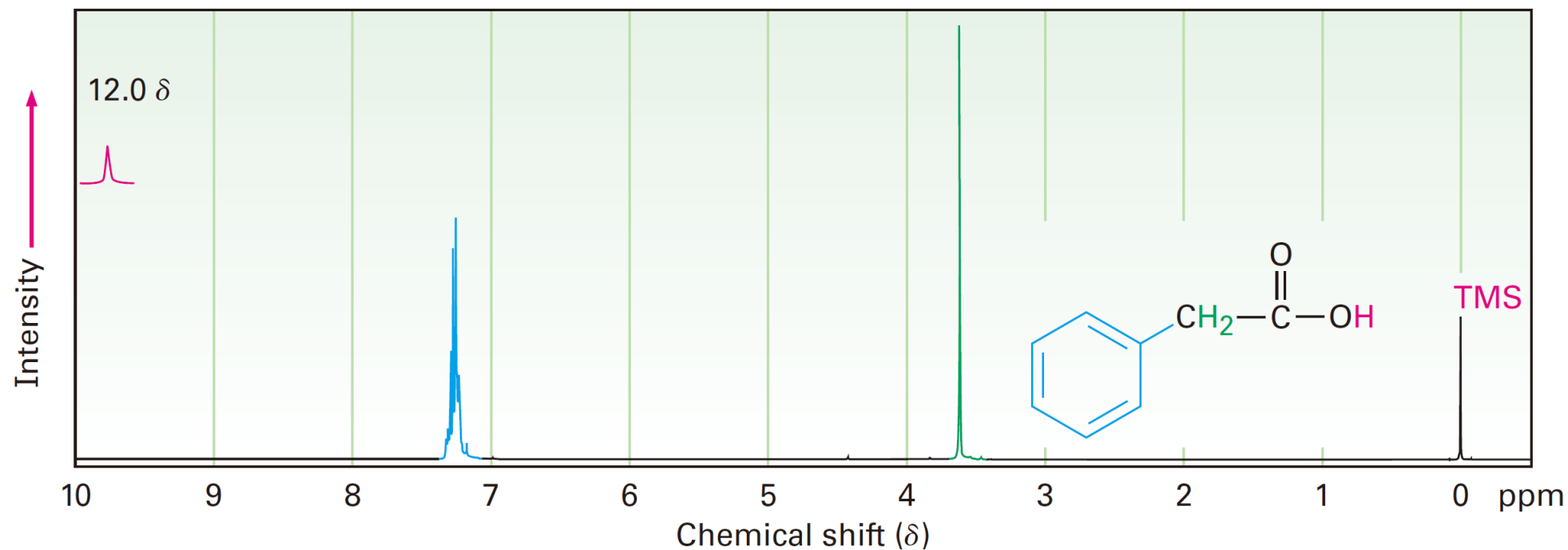


Figure 20.6 Proton NMR spectrum of phenylacetic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{H}$.

Problem 20.16

How could you distinguish between the isomers cyclopentanecarboxylic acid and 4-hydroxycyclohexanone by ^1H and ^{13}C NMR spectroscopy? (See Problem 20.15.)

作业

- 20.48, 20.49, 20.52, 20.53, 20.55, 20.57, 20.61

