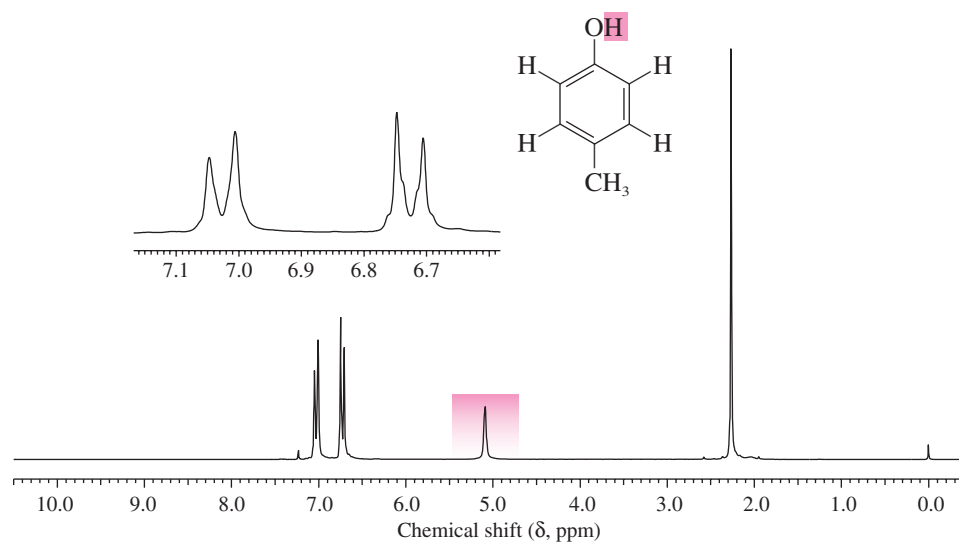


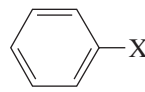
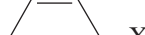

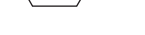
**FIGURE 24.4**

The 200-MHz  $^1\text{H}$  NMR spectrum of *p*-cresol.



Notice, too, that the most shielded carbons of the aromatic ring are the ones that are ortho and para to the hydroxyl group in keeping with our experience that the OH group donates electrons preferentially to these positions.

**UV-VIS:** Just as with arylamines (Section 22.19), it is informative to look at the UV-VIS behavior of phenols in terms of how the OH group affects the benzene chromophore.

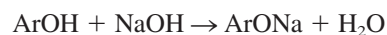
	X	$\lambda_{max}$ (nm)
	H	204, 256
	NH <sub>2</sub>	230, 280
	OH	210, 270
	O <sup>-</sup>	235, 287

An OH group affects the UV-VIS spectrum of benzene in a way similar to that of an NH<sub>2</sub> group, but to a smaller extent. In basic solution, in which OH is converted to O<sup>-</sup>, however, the shift to longer wavelengths exceeds that of an NH<sub>2</sub> group.

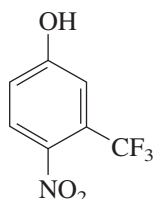
**Mass Spectrometry:** A peak for the molecular ion is usually quite prominent in the mass spectra of phenols. It is, for example, the most intense peak in phenol.

## 24.16 SUMMARY

- Section 24.1 Phenol is both an important industrial chemical and the parent of a large class of compounds widely distributed as natural products. Although *benzenol* is the systematic name for C<sub>6</sub>H<sub>5</sub>OH, the IUPAC rules permit *phenol* to be used instead. Substituted derivatives are named on the basis of phenol as the parent compound.
- Section 24.2 Phenols are polar compounds, but less polar than alcohols. They resemble arylamines in having an electron-rich aromatic ring.
- Section 24.3 The —OH group of phenols makes it possible for them to participate in hydrogen bonding. This contributes to the higher boiling points and greater water-solubility of phenolic compounds compared with arenes and aryl halides.
- Section 24.4 With pK<sub>a</sub>'s of approximately 10, phenols are stronger acids than alcohols, but weaker than carboxylic acids. They are converted quantitatively to phenoxide anions on treatment with aqueous sodium hydroxide.

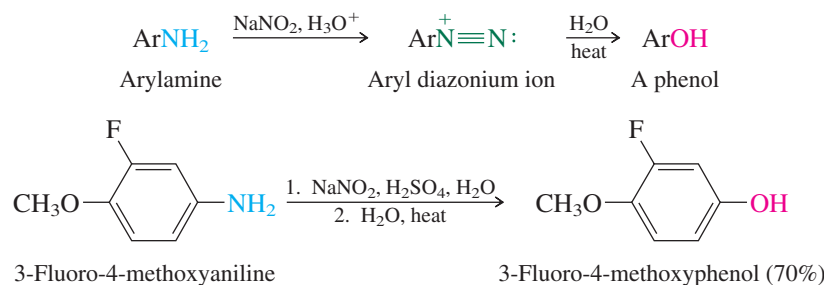


Section 24.5 Electron-releasing substituents attached to the ring have a negligible effect on the acidity of phenols. Strongly electron-withdrawing groups increase the acidity. The compound 4-nitro-3-(trifluoromethyl)phenol, for example, is 10,000 times more acidic than phenol.

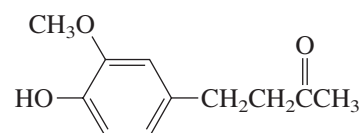


4-Nitro-3-(trifluoromethyl)phenol:  
p*K*<sub>a</sub> = 6.0

Section 24.6 Table 24.3 listed the main industrial methods for the preparation of phenol. Laboratory syntheses of phenols are usually carried out by hydrolysis of aryl diazonium salts.



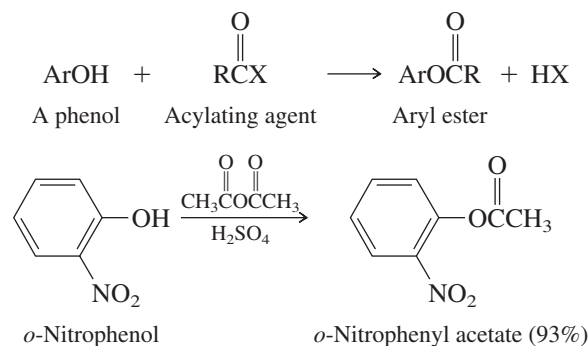
Section 24.7 Many phenols occur naturally.



Zingerone  
(responsible for spicy taste of ginger)

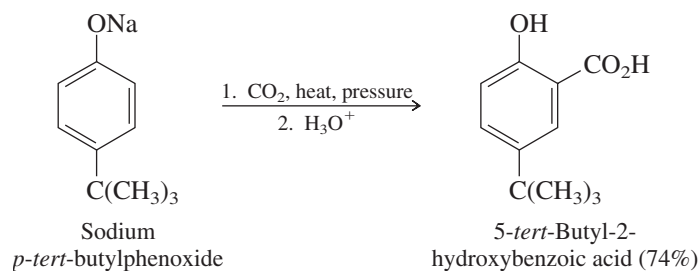
Section 24.8 The hydroxyl group of a phenol is a strongly activating substituent, and electrophilic aromatic substitution occurs readily in phenol and its derivatives. Typical examples were presented in Table 24.4.

Section 24.9 On reaction with acyl chlorides and acid anhydrides, phenols may undergo either acylation of the hydroxyl group (O-acylation) or acylation of the ring (C-acylation). The product of C-acylation is more stable and predominates under conditions of thermodynamic control when aluminum chloride is present (see entry 6 in Table 24.4, Section 24.8). O-acylation is faster than C-acylation, and aryl esters are formed under conditions of kinetic control.

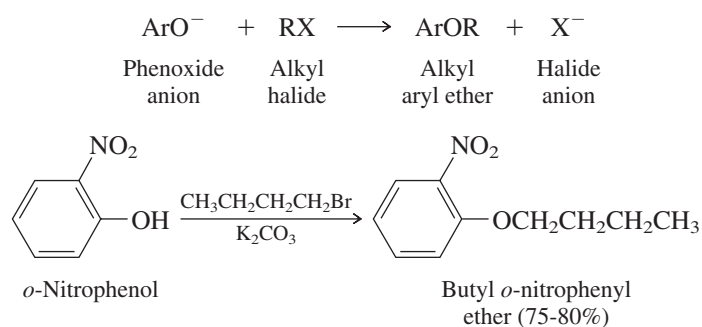


Section 24.10 The Kolbe–Schmitt synthesis of salicylic acid is a vital step in the preparation of aspirin. Phenols, as their sodium salts, undergo highly

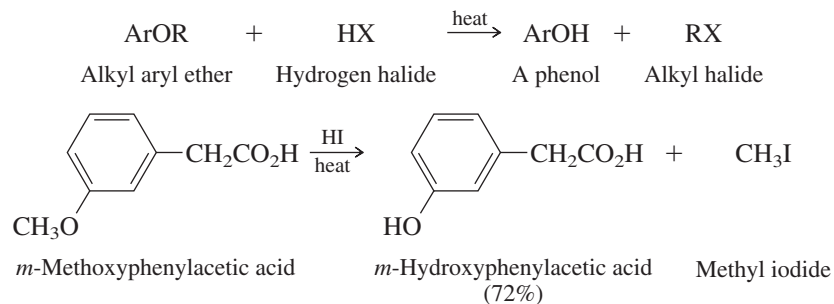
regioselective ortho carboxylation on treatment with carbon dioxide at elevated temperature and pressure.



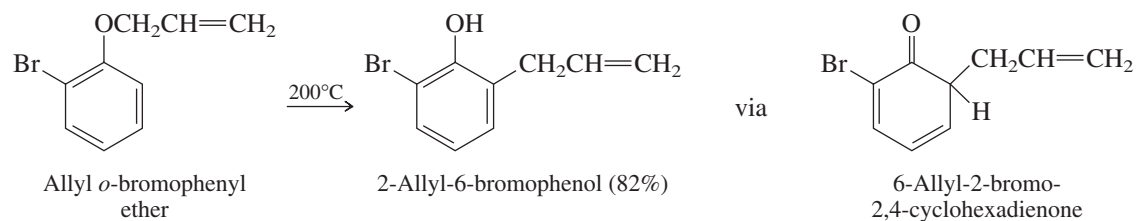
Section 24.11 Phenoxide anions are nucleophilic toward alkyl halides, and the preparation of alkyl aryl ethers is easily achieved under  $\text{S}_{\text{N}}2$  conditions.



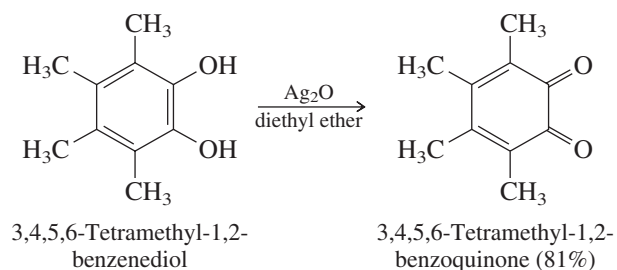
Section 24.12 The cleavage of alkyl aryl ethers by hydrogen halides yields a phenol and an alkyl halide.



Section 24.13 On being heated, allyl aryl ethers undergo a **Claisen rearrangement** to form *o*-allylphenols. A cyclohexadienone, formed by a concerted six- $\pi$ -electron reorganization, is an intermediate.



Section 24.14 Oxidation of 1,2- and 1,4-benzenediols gives colored compounds known as **quinones**.



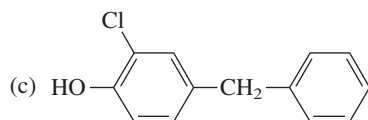
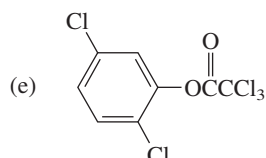
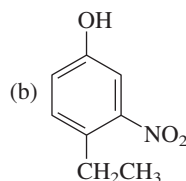
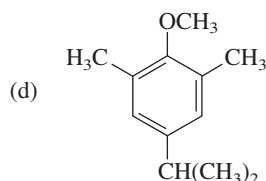
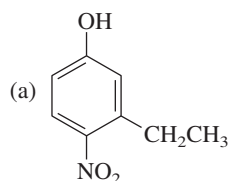
Section 24.15 The IR and  $^1\text{H}$  NMR spectra of phenols are similar to those for alcohols, except that the OH proton is somewhat less shielded in a phenol than in an alcohol. In  $^{13}\text{C}$  NMR, an OH group deshields the carbon of an aromatic ring to which it is attached. An OH group causes a shift in the UV-VIS spectrum of benzene to longer wavelengths. The effect is quite large in basic solution because of conversion of OH to  $\text{O}^-$ .

## PROBLEMS

24.11 The IUPAC rules permit the use of common names for a number of familiar phenols and aryl ethers. These common names are listed here along with their systematic names. Write the structure of each compound.

- Vanillin* (4-hydroxy-3-methoxybenzaldehyde): a component of vanilla bean oil, which contributes to its characteristic flavor
- Thymol* (2-isopropyl-5-methylphenol): obtained from oil of thyme
- Carvacrol* (5-isopropyl-2-methylphenol): present in oil of thyme and marjoram
- Eugenol* (4-allyl-2-methoxyphenol): obtained from oil of cloves
- Gallic acid* (3,4,5-trihydroxybenzoic acid): prepared by hydrolysis of tannins derived from plants
- Salicyl alcohol* (*o*-hydroxybenzyl alcohol): obtained from bark of poplar and willow trees

24.12 Name each of the following compounds:



24.13 Write a balanced chemical equation for each of the following reactions:

- Phenol + sodium hydroxide
- Product of part (a) + ethyl bromide
- Product of part (a) + butyl *p*-toluenesulfonate
- Product of part (a) + acetic anhydride
- o*-Cresol + benzoyl chloride
- m*-Cresol + ethylene oxide
- 2,6-Dichlorophenol + bromine
- p*-Cresol + excess aqueous bromine
- Isopropyl phenyl ether + excess hydrogen bromide + heat

24.14 Which phenol in each of the following pairs is more acidic? Justify your choice.

- 2,4,6-Trimethylphenol or 2,4,6-trinitrophenol
- 2,6-Dichlorophenol or 3,5-dichlorophenol
- 3-Nitrophenol or 4-nitrophenol