15.13
Preparation of Thiols
Nomenclature of Thiols

1) analogous to alcohols, but suffix is -thiol rather than -ol
2) final -e of alkane name is retained, not dropped as with alcohols
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\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{SH}
\]

3-Methyl-1-butanimethiol
Thiols are prepared from alkyl halides

$\text{SN}_2$ using thiourea as source of nucleophilic sulfur

the product is an isothiouronium salt
Thiols are prepared from alkyl halides.

Hydrolysis in base converts the isothiouronium salt to the desired thiol.
Example

\[
\text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{Br} \quad \xrightarrow{1. \ (\text{H}_2\text{N})_2\text{C}==\text{S}} \quad \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{SH} \\
\quad \xrightarrow{2. \ \text{NaOH}} \\
\text{1-Hexanethiol (84%)}
\]
15.14 Properties of Thiols
1. low molecular weight thiols have foul odors
2. hydrogen bonding is much weaker in thiols than in alcohols
3. thiols are stronger acids than alcohols
4. thiols are more easily oxidized than alcohols; oxidation takes place at sulfur
Thiols are stronger acids than alcohols

have pKₐ s of about 10; can be deprotonated in aqueous base

\[
\begin{align*}
\text{RS} \quad \text{H} &+ \quad \text{OH}^- \\
\text{RS}^- &\quad + \quad \text{H} \quad \text{OH}
\end{align*}
\]

stronger acid (pKₐ = 10)  weaker acid (pKₐ = 15.7)
Oxidation of thiols take place at sulfur

\[ \text{thiol} \quad \text{RS} - \text{H} \quad \leftrightarrow \quad \text{disulfide} \quad \text{RS} - \text{SR} \]

thiol-disulfide redox pair is important in biochemistry

other oxidative processes place 1, 2, or 3 oxygen atoms on sulfur
Oxidation of thiols take place at sulfur.
Example: sulfide-disulfide redox pair

\[
\text{SH} \quad \text{O} \\
\text{HSCH}_2\text{CH}_2\text{CH}\text{(CH}_2\text{)}_4\text{COH} \downarrow \text{O}_2, \text{FeCl}_3 \\
\text{S} \quad \text{S} \quad \text{O} \\
\text{(CH}_2\text{)}_4\text{COH} \quad \alpha\text{-Lipoic acid (78%)}
\]
15.15
Spectroscopic Analysis of Alcohols
Infrared Spectroscopy

O–H stretching: 3200-3650 cm\(^{-1}\) (broad)
C–O stretching: 1025-1200 cm\(^{-1}\) (broad)
Figure 15.4: Infrared Spectrum of Cyclohexanol
chemical shift of O—H proton is variable; depends on temperature and concentration

O—H proton can be identified by adding D$_2$O; signal for O—H disappears (converted to O—D)

H—C—O signal is less shielded than H—C—H

\[
\begin{array}{c}
H \\
\hline
C \\
\hline
O \\
\hline
H
\end{array}
\]

$\delta$ 3.3-4 ppm $\quad$ $\delta$ 0.5-5 ppm
Figure 15.5 (page 607)

Chemical shift (δ, ppm)
Chemical shift of C—OH is $\delta$ 60-75 ppm. C—O is about 35-50 ppm less shielded than C—H.
Unless there are other chromophores in the molecule, alcohols are transparent above about 200 nm; \( \lambda_{\text{max}} \) for methanol, for example, is 177 nm.
molecular ion peak is usually small

a peak corresponding to loss of H$_2$O from the molecular ion (M - 18) is usually present

peak corresponding to loss of an alkyl group to give an oxygen-stabilized carbocation is usually prominent
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