16.14
Epoxides in Biological Processes
Naturally Occurring Epoxides

are common

are involved in numerous biological processes
Biosynthesis of Epoxides

\[
\begin{align*}
\text{C} &= \text{C} + \text{O}_2 + \text{H}^+ + \text{NADH} \\
\rightarrow \text{enzyme} \\
\text{C} &= \text{C} + \text{H}_2\text{O} + \text{NAD}^+
\end{align*}
\]

enzyme-catalyzed oxygen transfer from \( \text{O}_2 \) to alkene

enzymes are referred to as monooxygenases
Example: biological epoxidation of squalene

\[ \text{O}_2, \text{NADH, NADH monoxygenase} \]

this reaction is an important step in the biosynthesis of cholesterol
16.15
Preparation of Sulfides
Preparation of RSR′

prepared by nucleophilic substitution (S_N2)

\[ R - \overset{\cdot}{S} - + R' - X \rightarrow R - \overset{\cdot}{S} - R' \]

CH₃CHCH=CH₂ \xrightarrow{\text{NaSCH₃ methanol}} CH₃CHCH=CH₂

\( \text{Cl} \) \hspace{4cm} \text{SCH₃}
16.16
Oxidation of Sulfides:
Sulfoxides and Sulfones
either the sulfoxide or the sulfone can be isolated depending on the oxidizing agent and reaction conditions
Example

Sodium metaperiodate oxidizes sulfides to sulfoxides and no further.

\[
\text{SCH}_3 \quad \overset{\text{NaIO}_4, \text{water}}{\longrightarrow} \quad \text{SCH}_3 \quad (91\%)
\]
Example

1 equiv of H$_2$O$_2$ or a peroxy acid gives a sulfoxide, 2 equiv give a sulfone

(74-78%)
16.17
Alkylation of Sulfides:
Sulfonium Salts
Sulfides can act as nucleophiles

Product is a sulfonium salt
Example

\[
\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SCH}_3 \xrightarrow{\text{CH}_3\text{I}} \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SCH}_3^+ \text{CH}_3^- \]

Section 16.18
Spectroscopic Analysis of Ethers
**Infrared Spectroscopy**

C—O stretching: 1070 and 1150 cm$^{-1}$ (strong)
Figure 16.8  Infrared Spectrum of Dipropyl Ether

CH$_3$CH$_2$CH$_2$OCH$_2$CH$_2$CH$_3$

Wave number, cm$^{-1}$
H—C—O proton is deshielded by O; range is ca. δ 3.3-4.0 ppm.

δ 0.8 ppm  δ 1.4 ppm  δ 0.8 ppm

CH₃CH₂CH₂OCH₂CH₂CH₃

δ 3.2 ppm
$^{13}C$ NMR

Carbons of C—O—C appear in the range $\delta$ 57-87 ppm.

- 26.0 ppm
- 68.0 ppm
Simple ethers have their absorption maximum at about 185 nm and are transparent to ultraviolet radiation above about 220 nm.
Molecular ion fragments to give oxygen-stabilized carbocation.

Mass Spectrometry

\[
\text{CH}_3\text{CH}_2\text{O} = \text{CH} \quad \text{CH}_3\text{CH}_2\text{O} = \text{CHCH}_2\text{CH}_3
\]

\[
\text{m/z 73} \quad \text{m/z 87} \quad \text{m/z 102}
\]