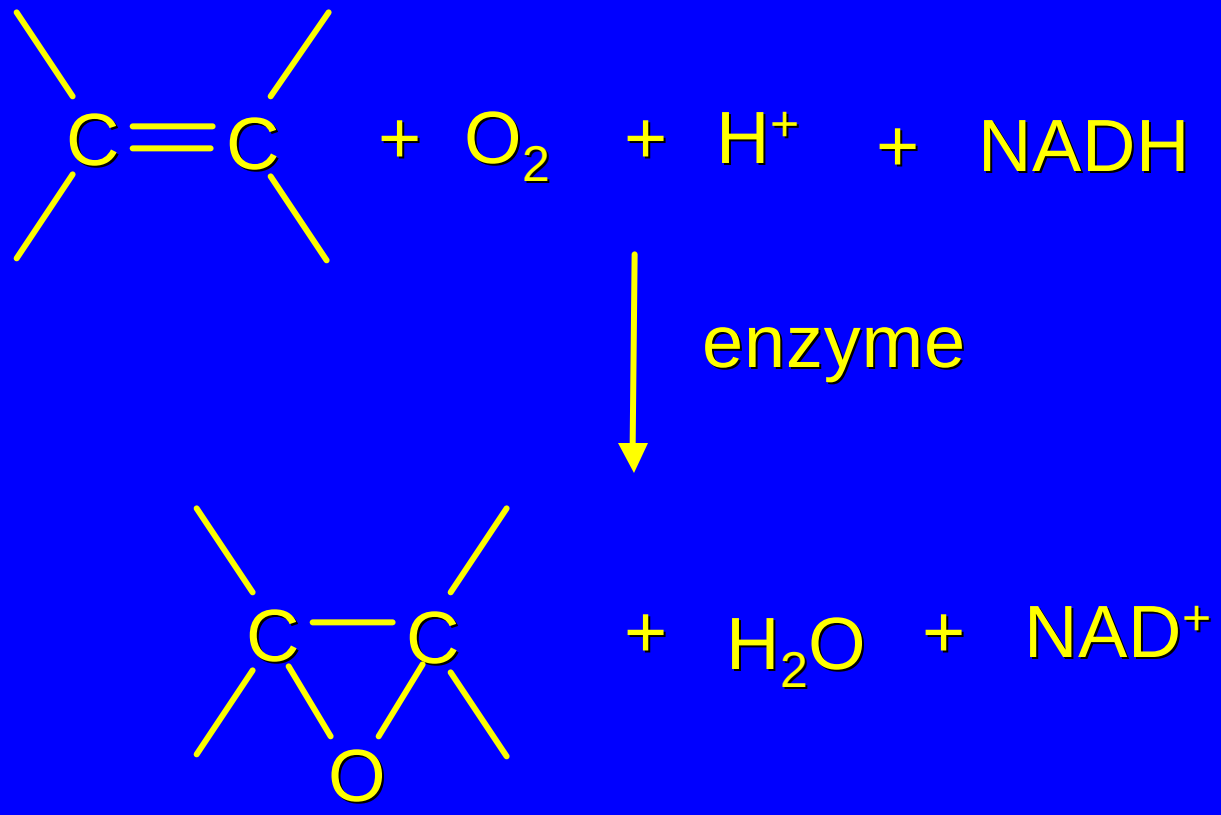
16.14
Epoxides in Biological Processes

Naturally Occurring Epoxides

are common

are involved in numerous biological processes

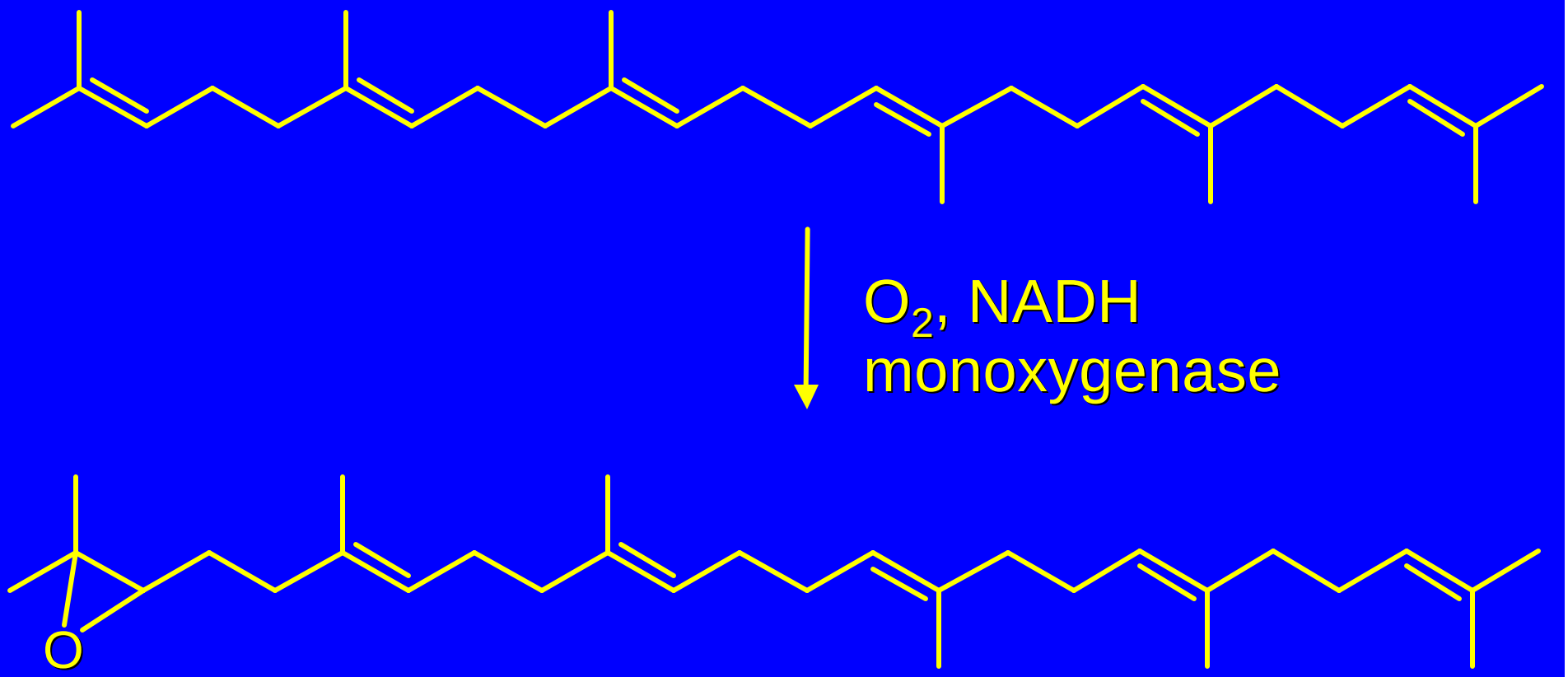
Biosynthesis of Epoxides



enzyme-catalyzed oxygen transfer from O_2 to alkene

enzymes are referred to as monooxygenases

Example: biological epoxidation of squalene

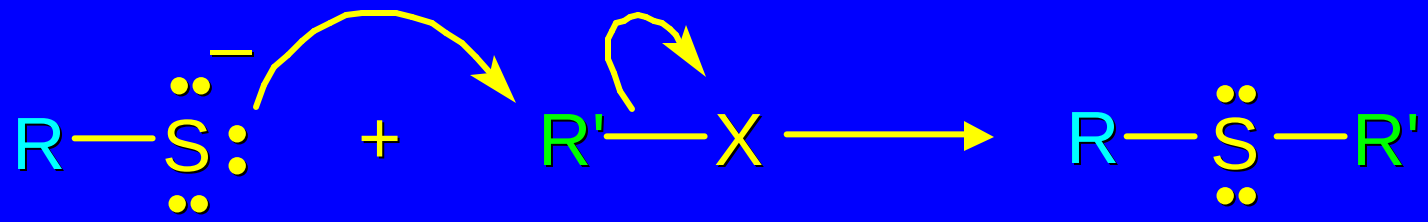


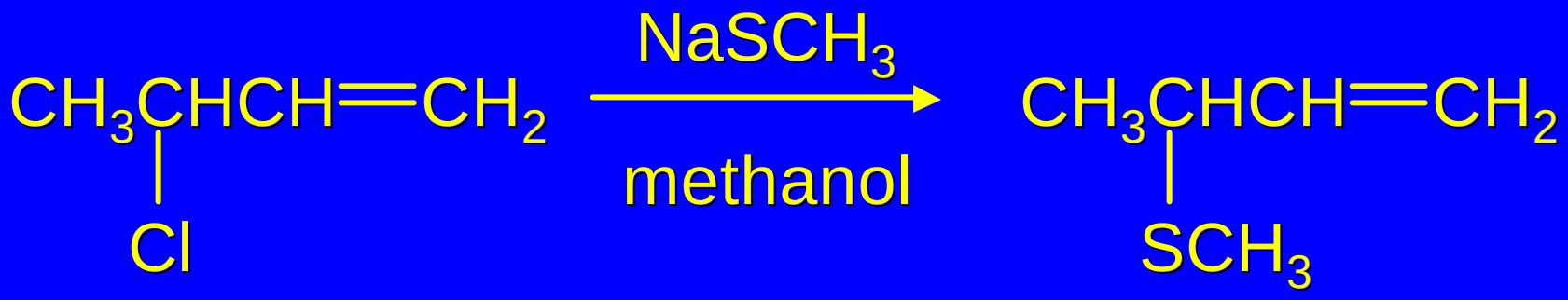
this reaction is an important step in the biosynthesis of cholesterol

16.15
Preparation of Sulfides

Preparation of RSR'

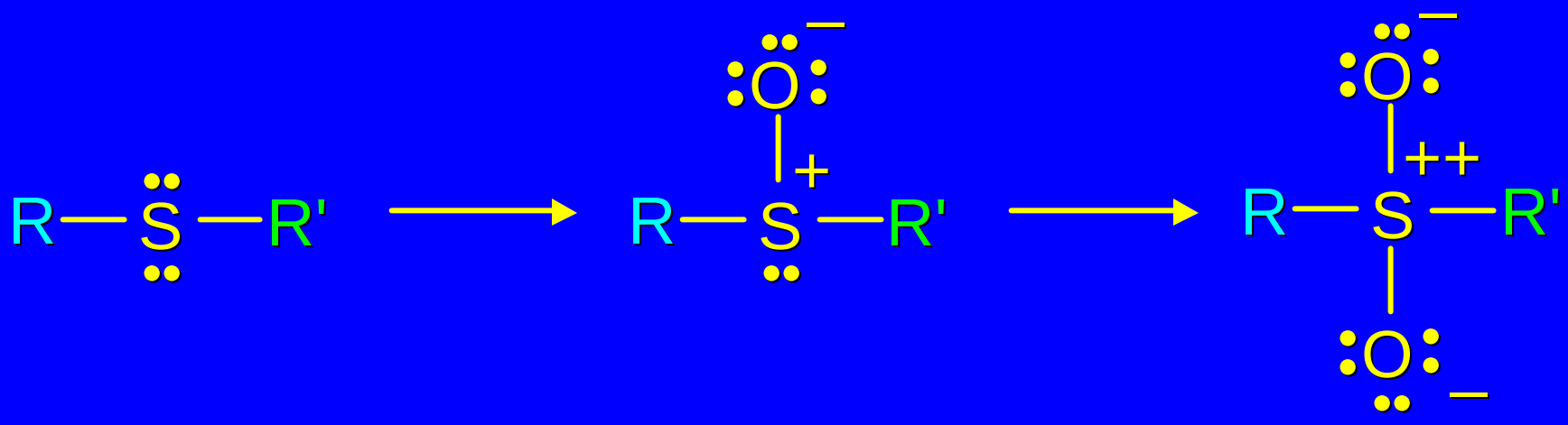
prepared by nucleophilic substitution (S_N2)





16.16
Oxidation of Sulfides: Sulfoxides and Sulfones

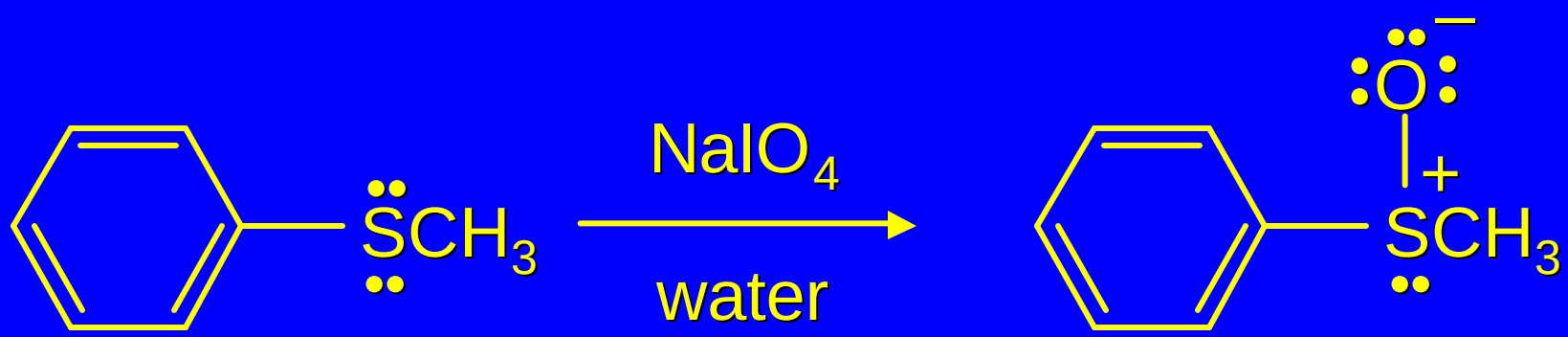
Oxidation of RSR'



sulfide sulfoxide sulfone

either the sulfoxide or the sulfone can be isolated depending on the oxidizing agent and reaction conditions

Example

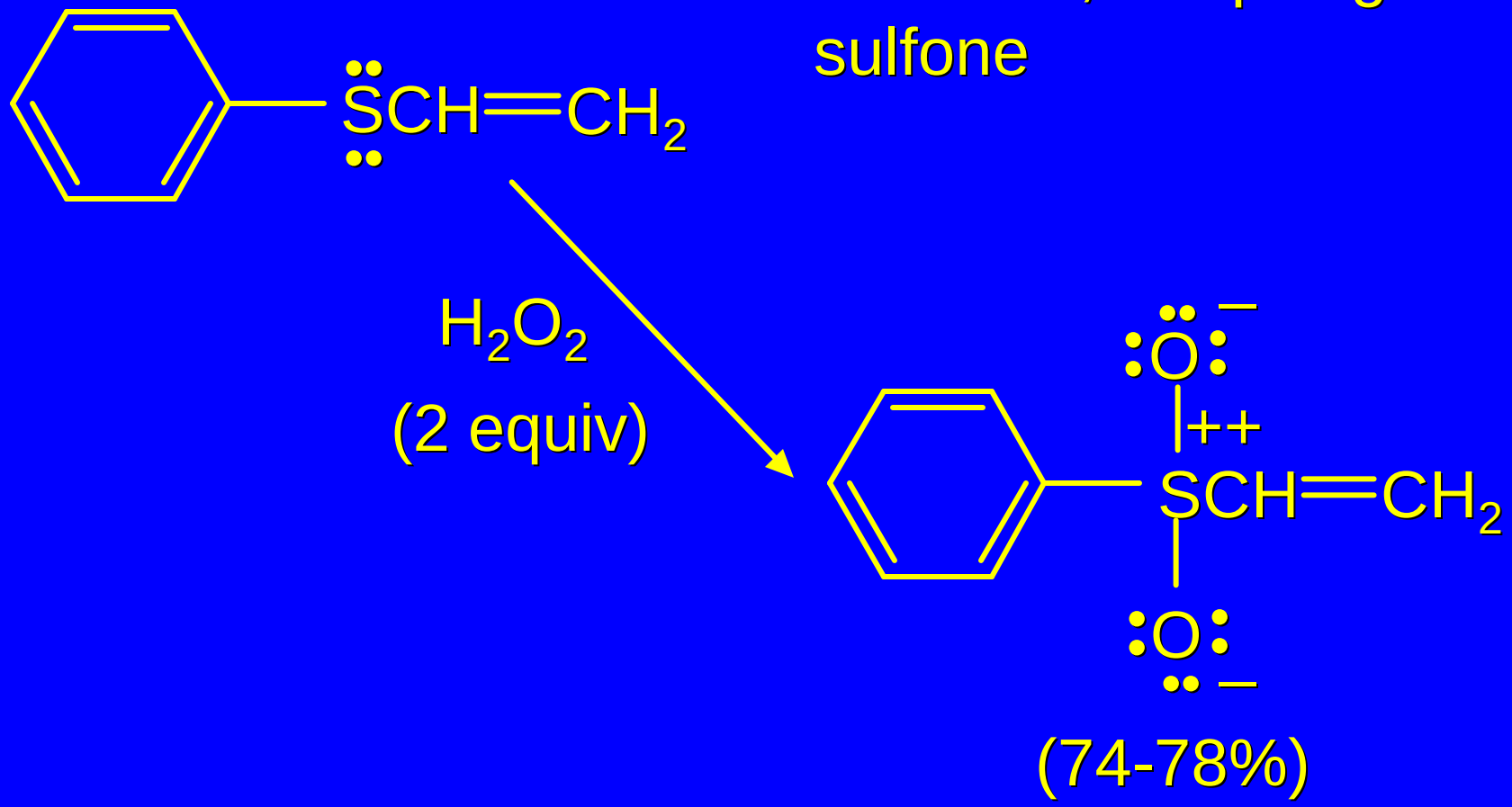


(91%)

Sodium metaperiodate oxidizes sulfides to sulfoxides and no further.

Example

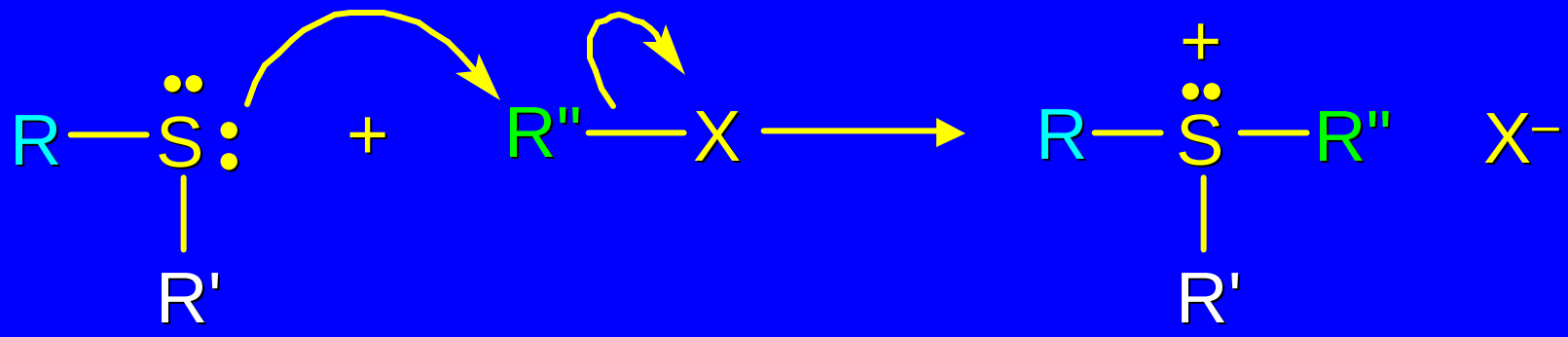
1 equiv of H_2O_2 or a peroxy acid gives a sulfoxide, 2 equiv give a sulfone



(74-78%)

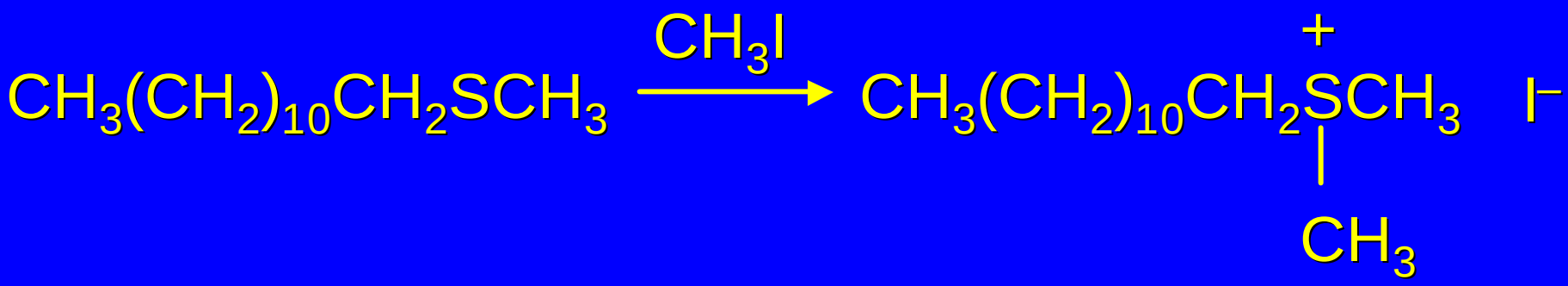
16.17
Alkylation of Sulfides: Sulfonium Salts

Sulfides can act as nucleophiles



product is a sulfonium salt

Example

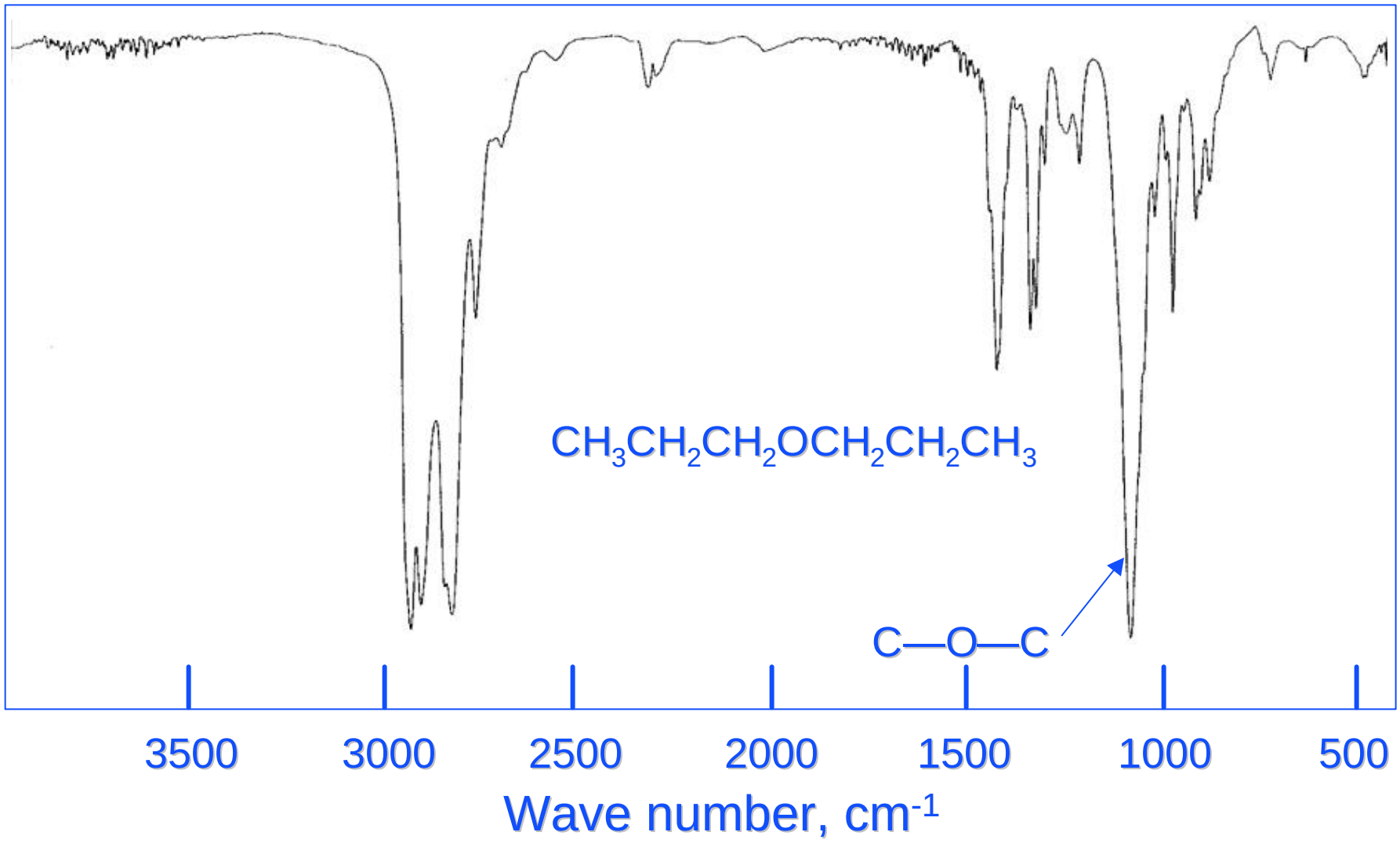


Section 16.18
Spectroscopic Analysis of Ethers

Infrared Spectroscopy

C—O stretching: 1070 and 1150 cm^{-1} (strong)

Figure 16.8 Infrared Spectrum of Dipropyl Ether



^{1}H NMR

H—C—O proton is deshielded by O; range is *ca.* δ 3.3-4.0 ppm.

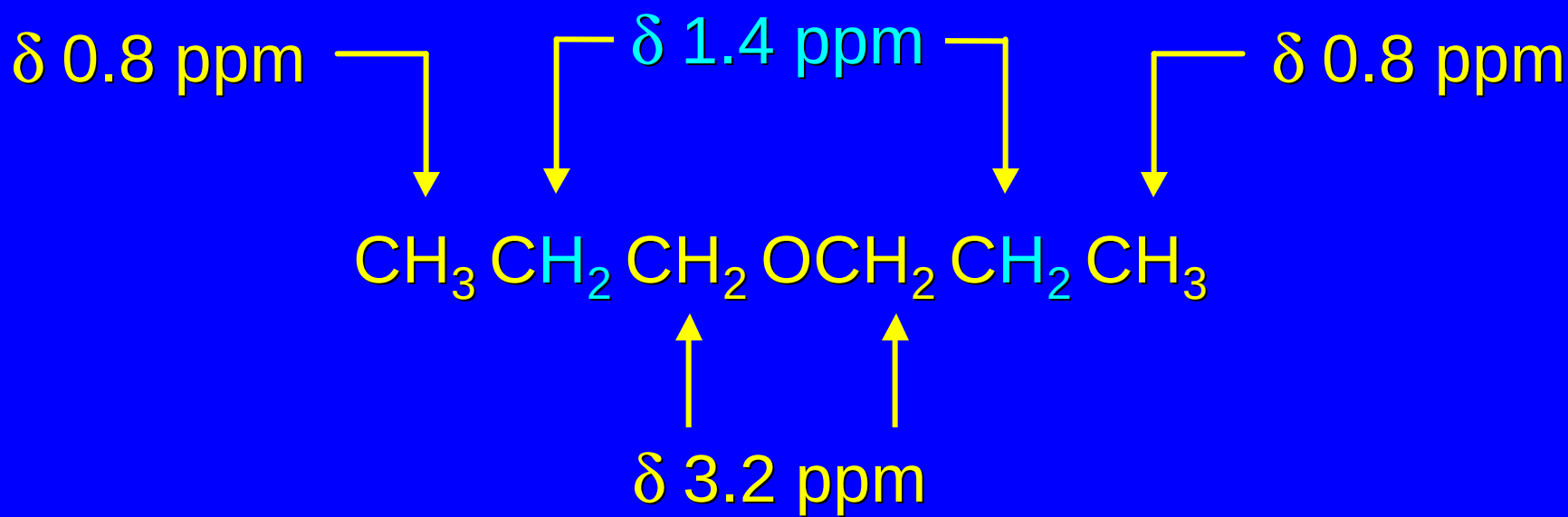
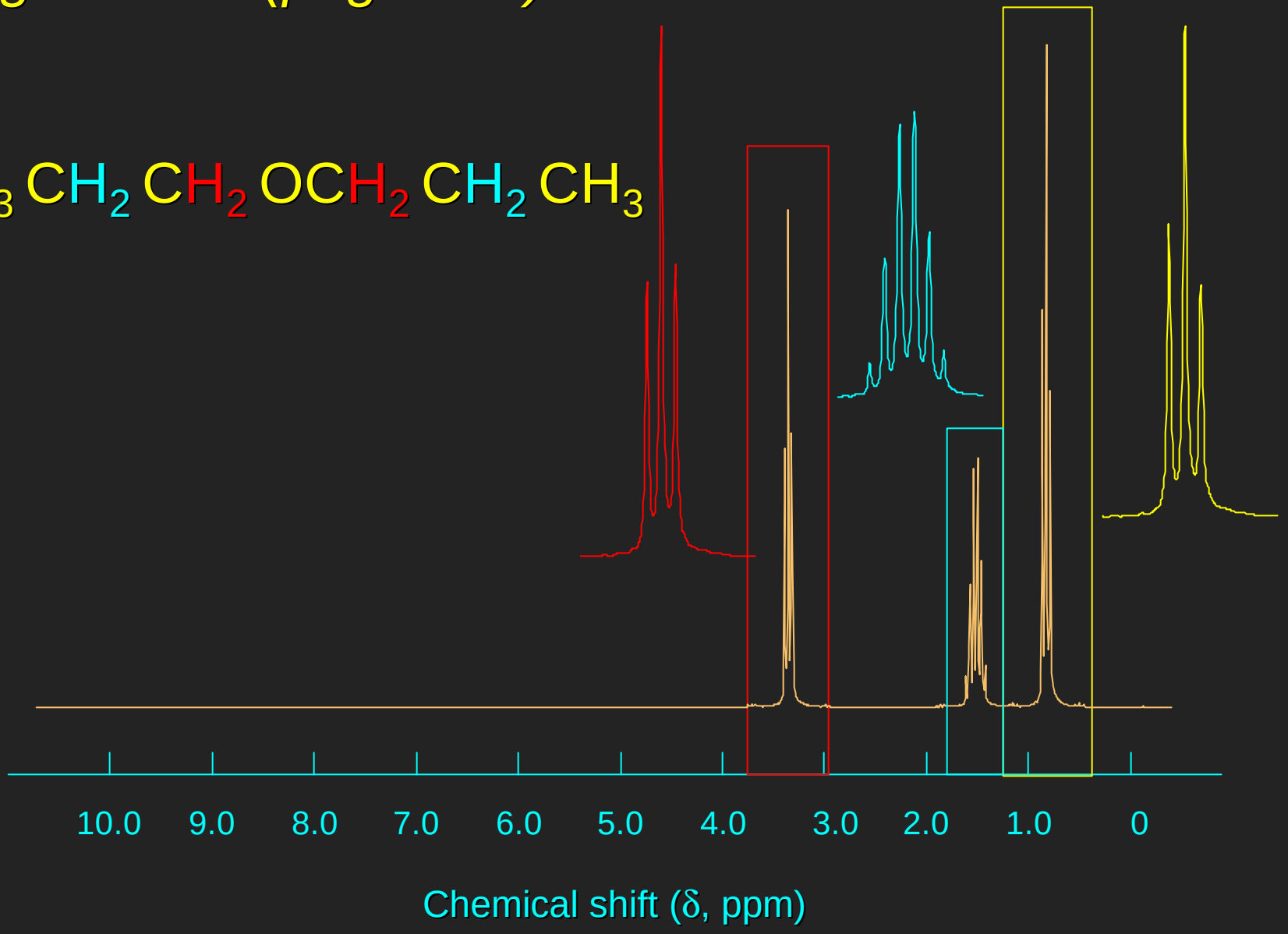


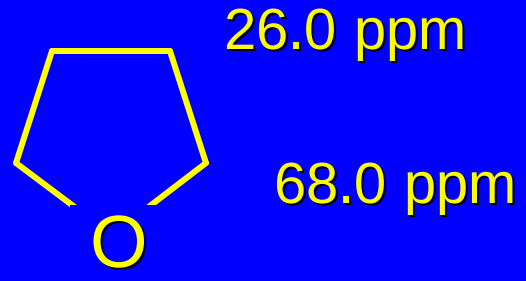
Figure 16.9 (page 642)

$CH_3\,CH_2\,CH_2\,OCH_2\,CH_2\,CH_3$



^{13}C NMR

Carbons of C—O—C appear in the range δ 57-87 ppm.



UV-VIS

Simple ethers have their absorption maximum at about 185 nm and are transparent to ultraviolet radiation above about 220 nm.

Mass Spectrometry

Molecular ion fragments to give oxygen-stabilized carbocation.