

15.13

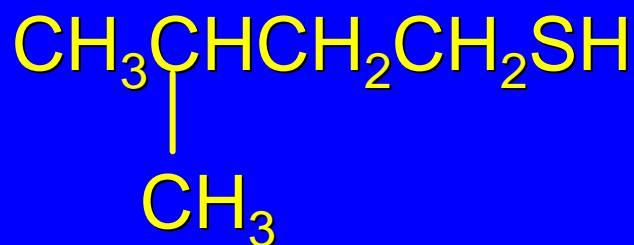
Preparation of Thiols

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

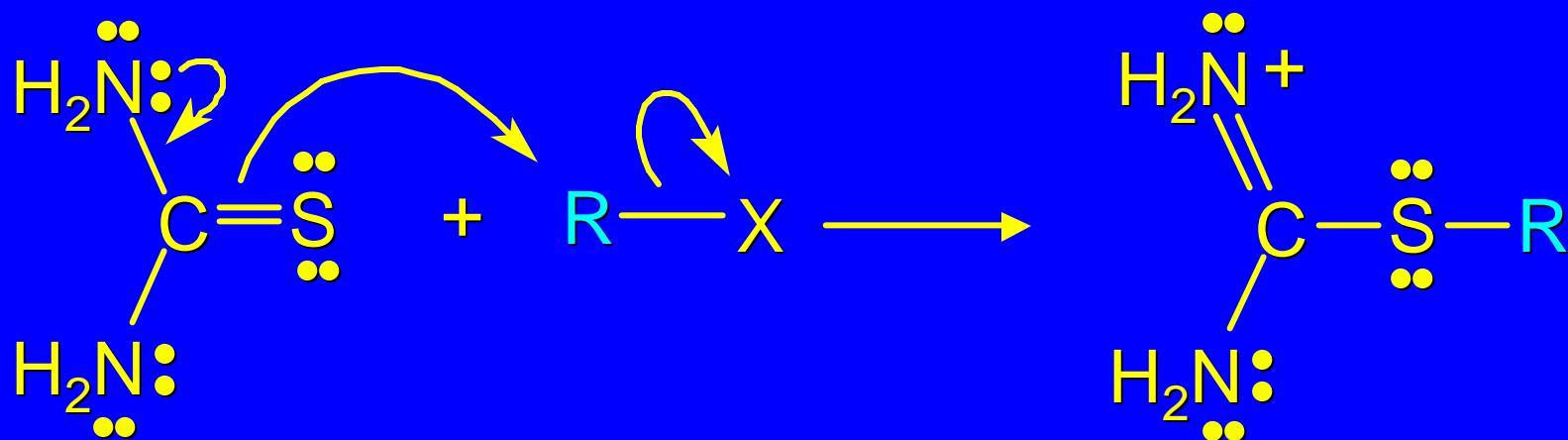
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3-Methyl-1-butanethiol

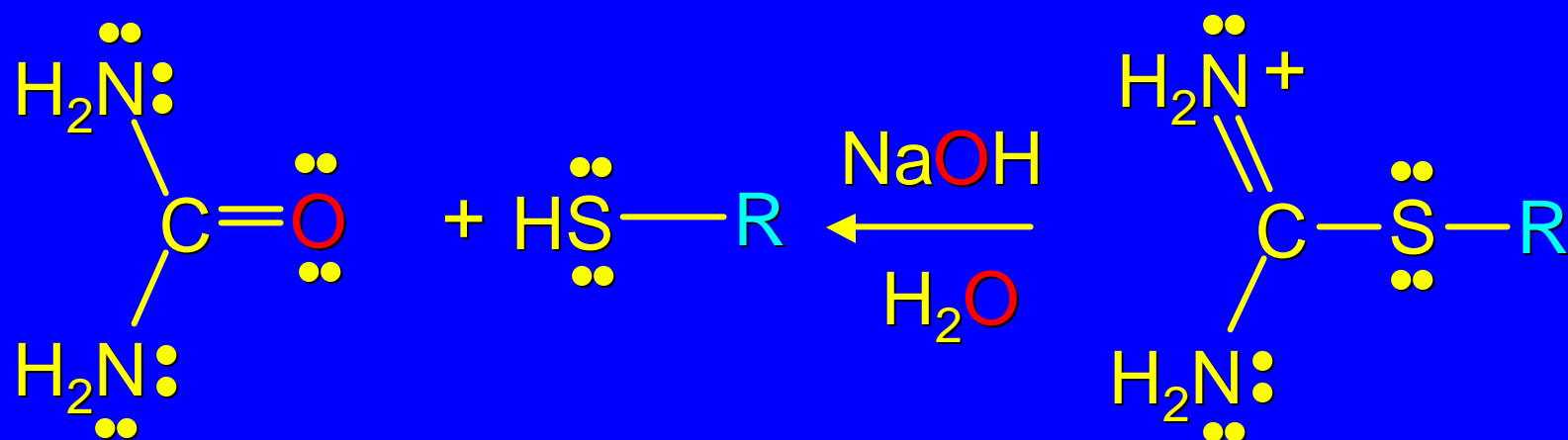
Thiols are prepared from alkyl halides



S_N2 using thiourea as source of nucleophilic sulfur

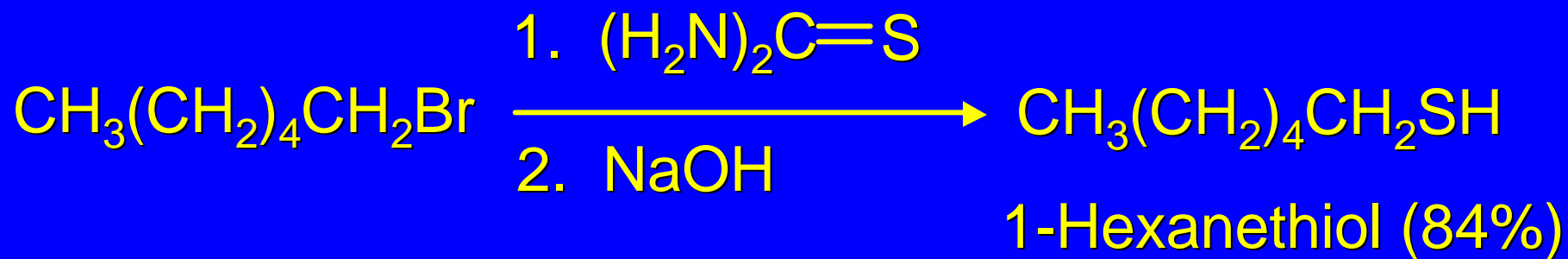
the product is an isothiuronium salt

Thiols are prepared from alkyl halides



hydrolysis in base converts the isothiuronium salt to the desired thiol

Example



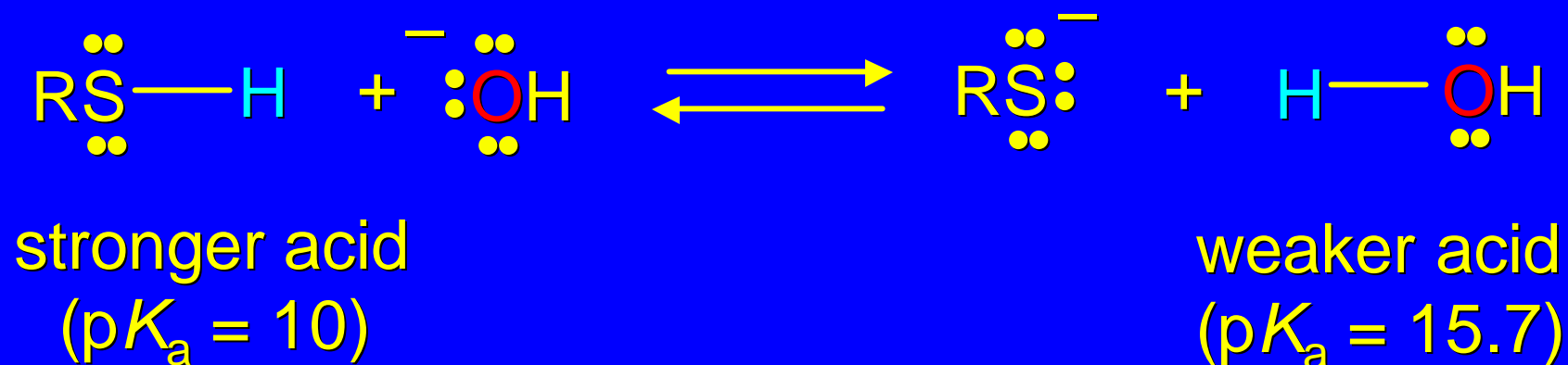
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Properties of Thiols

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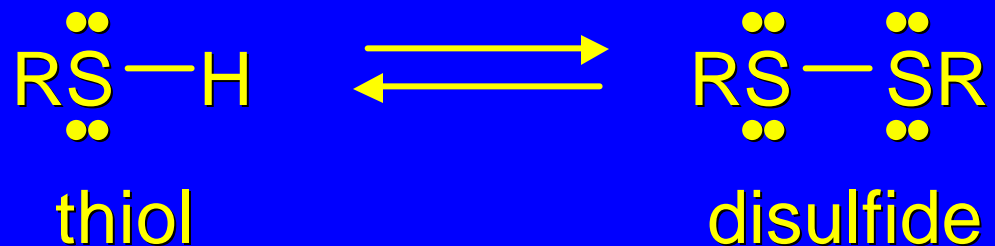
1. low molecular weight thiols have foul odors
2. hydrogen bonding is much weaker in thiols than in alcohols
3. thiols are stronger acids than alcohols
4. thiols are more easily oxidized than alcohols; oxidation takes place at sulfur

Thiols are stronger acids than alcohols

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



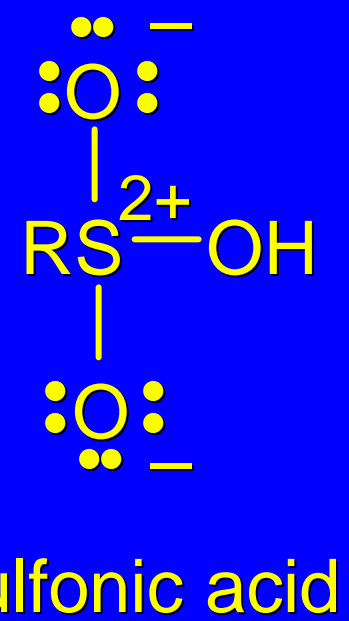
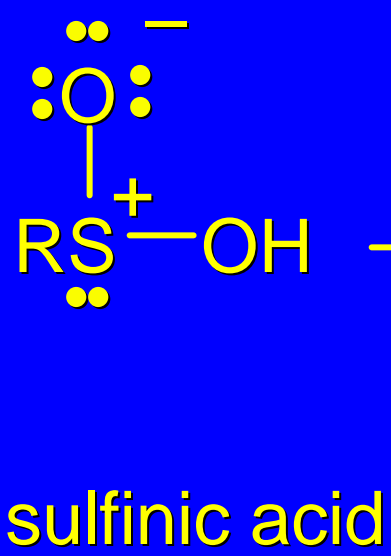
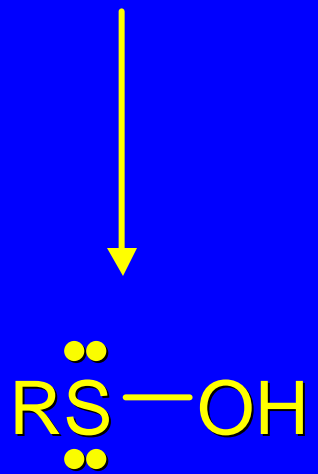
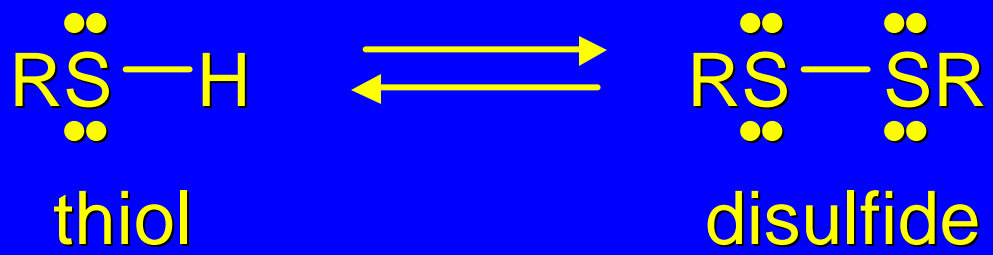
Oxidation of thiols take place at sulfur



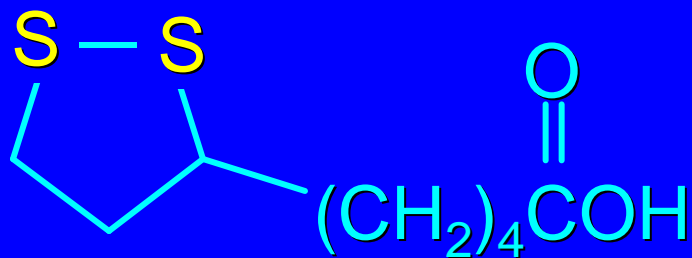
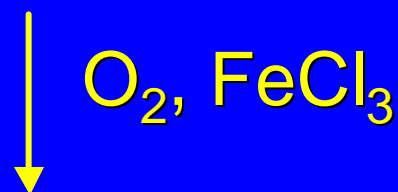
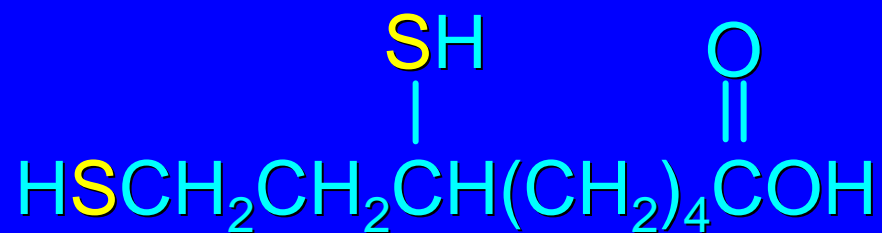
thiol-disulfide redox pair is important in biochemistry

other oxidative processes place 1,2, or 3 oxygen atoms on sulfur

Oxidation of thiols take place at sulfur



Example: sulfide-disulfide redox pair



α -Lipoic acid (78%)

15.15

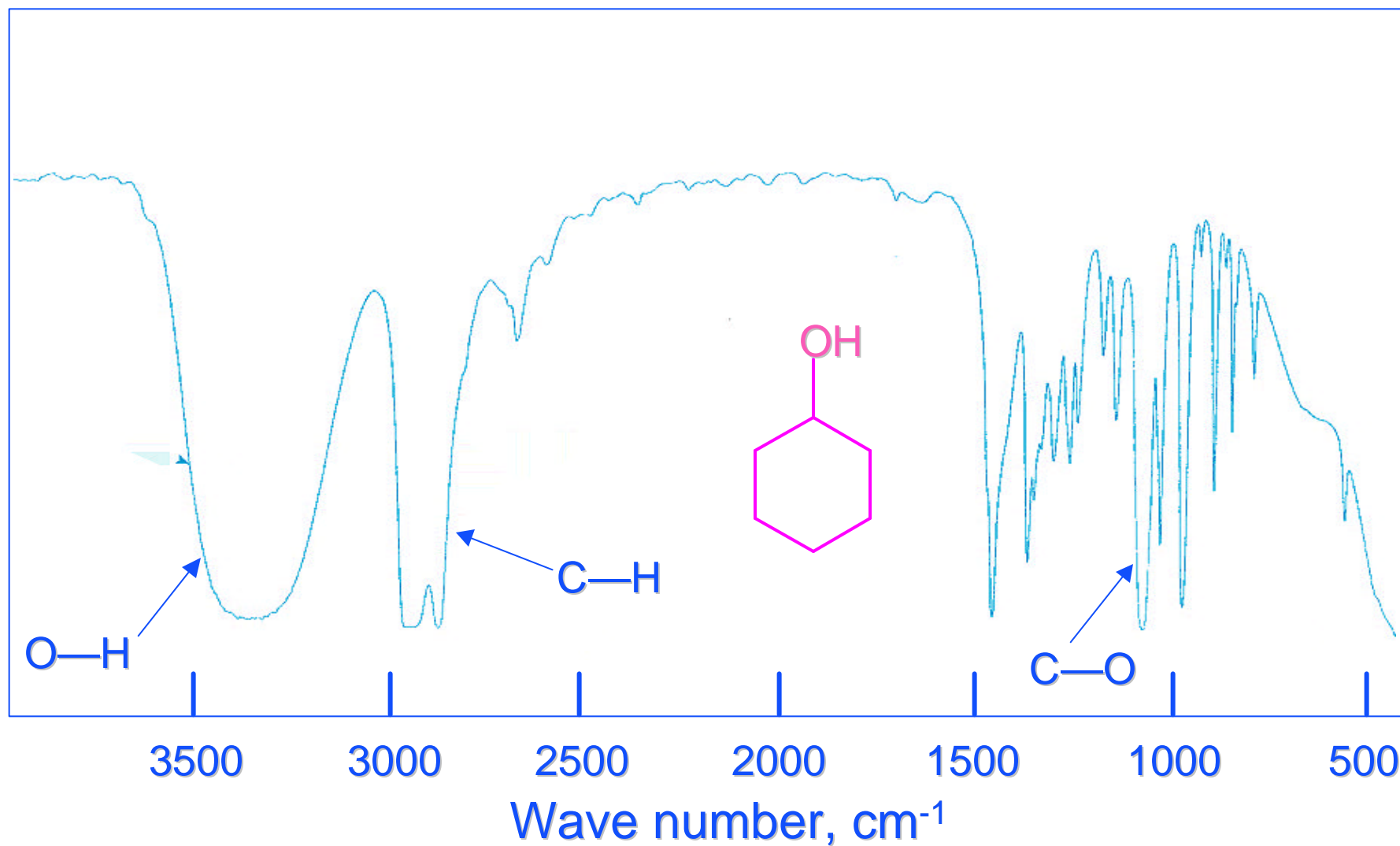
Spectroscopic Analysis of Alcohols

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



^1H NMR

chemical shift of O—H proton is variable; depends on temperature and concentration

O—H proton can be identified by adding D_2O ; signal for O—H disappears (converted to O—D)

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

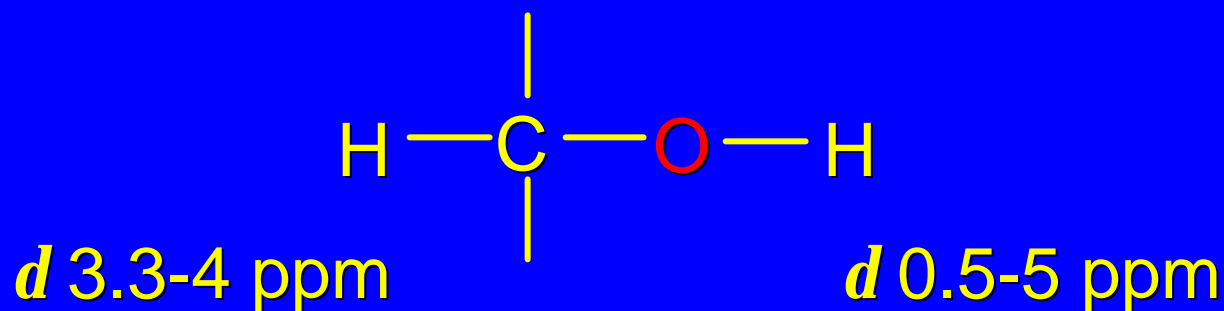
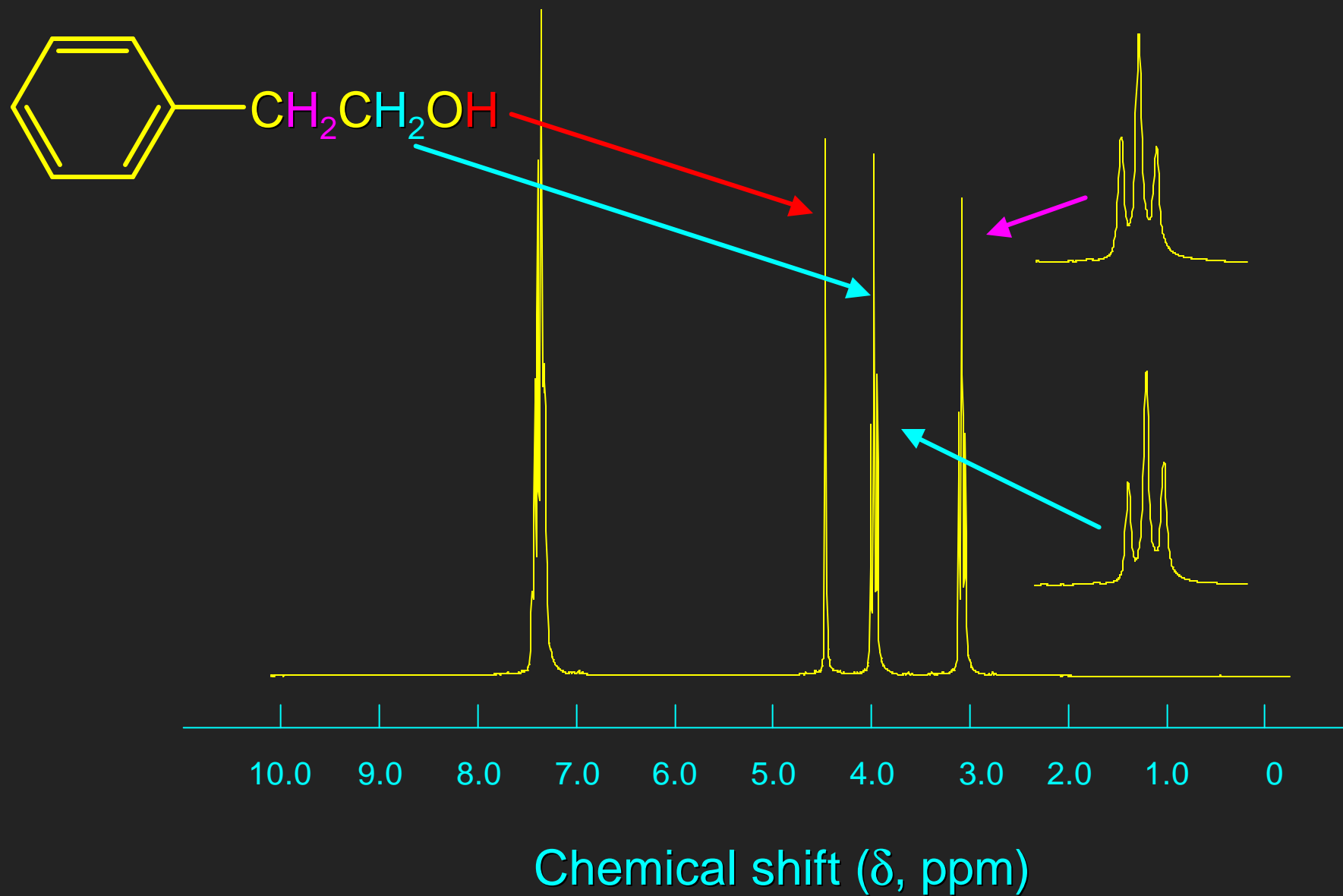


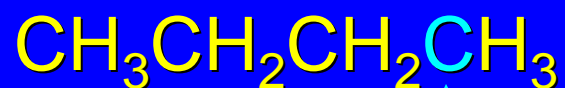
Figure 15.5 (page 607)



^{13}C NMR

chemical shift of C—OH is δ 60-75 ppm

C—O is about 35-50 ppm less shielded than C—H



δ 13 ppm



δ 61.4 ppm

UV-VIS

Unless there are other chromophores in the molecule, alcohols are transparent above about 200 nm; λ_{max} for methanol, for example, is 177 nm.

Mass Spectrometry of Alcohols

molecular ion peak is usually small

a peak corresponding to loss of H_2O 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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