CHEM 222 section 01

LECTURE #02

Thurs., Sept.06, 2007

Lecture topics & readings

Today's class

- review preparation & properties of alcohols
- start reactions of alcohols

Before next class

- remember labs next week...
- review Chem 221 concepts & reactions
- read ROH material: 10.1 10.4 (+ other references in notes)

Next class

finish ROH rxns: 10.5, 19.2start ethers, etc: rest of Ch.10

(1)

Ch.10: Rxns of alcohols, amines, ethers, epoxides, sulfur-containing compounds & organometallics

Chapter Goals & hints

Understand rxns involving common heteroatomic functional groups.

- Use mechanisms to help remember reactions & outcomes.
- Identify similarities and reasons for differences.

Topics Outline:

10.1-2	Nu S _N rxns of ROH & other ways to form alkyl halides
10.3	Converting alcohols into sulfonate esters
10.4	Elimination rxns of alcohols: dehydration
10.5, 19.2	Oxidation of alcohols
10.6	Amines: don't undergo S_N or E rxnsbut common bases
10.7-8	Nu substitution rxns of ethers & epoxides (prep'n - 4.9)
[10.9]	Arene oxides (read for interest - not in detail)
10.10	Crown ethers
10.11	Thiols, sulfides, and sulfonium salts
10.12	Organometallic compounds: RLi, RMgBr, R2CuLi
10.13	Cover only: Gilman reagents, R ₂ CuLi (organocuprates)
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Review: Preparation and properties of alcohols

Alcohols:

• OH group bonded to sp3 C

OH

SUBCLASS: Enols

- OH group bonded to sp²-hyb .C
- Undergo different reactions
 cannot do Nu substitution



Preparation of alcohols (except enols):

1) Nucleophilic substitution (Bruice Ch.8)

$$CH_3-CH_2-Br + OH^- \longrightarrow CH_3-CH_2-OH + Br^-$$
Halide
= good leaving group

Mechanism?

- S_N2: 1°, 2°
- 5_N1: 3°

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Review: Preparation of alcohols (continued)

2) Hydration of alkenes (Bruice 4.5)

$$\begin{array}{ccc} CH_3CH = CH_2 & \xrightarrow{\text{H_2SO}_4$} & CH_3CHCH_3 \\ & \text{propene} & & OH \\ & & \text{2-propanol} \end{array}$$

Markovnikov addition:

H goes where more H's are

- · via carbocation
- · rearrangement possible
- 3) Industrial "hydration": Oxymercuration (4.8)

$$CH_{3}CH = CH_{2} \xrightarrow{\text{1.) Hg(OAc)}_{2}, H_{2}O/THF} CH_{3}CHCH_{3}$$
propene
$$OH$$
2-propanol

Markovnikov addition

- · concerted add'n step
- · no rearrangements
- · 2nd step removes Hg...
- 4) Hydroboration of alkenes (4.10)

$$\begin{array}{ccc} \text{CH}_3\text{CH} \!=\! \text{CH}_2 & \frac{\textbf{1. BH}_3 \, / \, \text{THF}}{\textbf{2. HO}^-, \, \textbf{H}_2\textbf{O}_2, \, \textbf{H}_2\textbf{O}} & \text{CH}_3\text{C}\frac{\textbf{H}}_2\text{CH}_2\text{OH} \\ & \text{propene} & \text{1-propanol} \end{array}$$

Anti-Markovnikov addition

- · concerted add'n step
- no rearrangements
- 2nd step removes B...

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Review: Properties of alcohols

Alcohols:

• Can participate in hydrogen-bonding:

Relatively easy to deprotonate (in dry organic solvent):

$$R \stackrel{\text{H}}{-} \stackrel{\text{H}}{\stackrel{\text{C}}{-}} \stackrel{\text{H}}{\stackrel{\text{O}}{\cdot}} \stackrel{\text{Base}}{\stackrel{\text{(conj.acid's})}{\stackrel{\text{(conj.acid's})}{\stackrel{\text{D}}{\rightarrow}}}} R \stackrel{\text{H}}{-} \stackrel{\overset{\text{O}}{\stackrel{\text{O}}{\rightarrow}}} \stackrel{\text{C}}{\stackrel{\text{O}}{\rightarrow}} \stackrel{\text{olkoxide}}{\stackrel{\text{good Nu}}{\stackrel{\text{O}}{\rightarrow}}} \stackrel{\text{good Nu}}{\stackrel{\text{Strong B:}}{\stackrel{\text{O}}{\rightarrow}}}$$

Relatively weak nucleophiles (...except when deprotonated...)

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New: Reactions of alcohols

Reactivity trend:

- Centered around the OH group
- Electrophilic carbon
- OH- is NOT a good leaving group!
 - stronger base ⇒ poorer L.G.

$R - C - O \cdot \delta - H$

Reactions coming up: (on board - take notes) Bruice:

- 1) Nucleophilic substitutions (with activated alcohols) 10.1
- 2) Ways to replace OH with a good L.G.:

a. Using SOCl₂
b. Using PBr₃
c. Sulfonate esters
10.3
3) Elimination: Dehydration

4) Oxidation 10.5, 19.2

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