Chapter 14: Ethers and Epoxides

I. Introduction:
• Formula of ethers is R-O-R where R is alkyl
  • Symmetrical or unsymmetrical

II. Physical Properties
A. H-Bonding
• Ethers cannot H-bond to each other.
• Lower BP than alcohols…
• Can H-bond with –OH or –NH molecules.
• Do not react readily with bases (like alcohols do)

B. Boiling points

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>BP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH</td>
<td>78</td>
</tr>
<tr>
<td>Dimethyl Ether</td>
<td>CH₃OCH₃</td>
<td>-25</td>
</tr>
<tr>
<td>Butane</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>0.5</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>CH₃CH₂OCH₂CH₃</td>
<td>34.6</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>CH₃CH₂CH₂CH₂OH</td>
<td>116</td>
</tr>
</tbody>
</table>

C. Solubility
• Nonpolar solutes dissolve better in ether than in alcohol.
• Ether has large dipole moment, so polar solutes also dissolve.
• Ethers solvate cations.

D. Uses
• Solvents for organic reactions. (Diethyl ether and THF, the Grignard reaction).
  • Ethers will often form complexes with molecules that have vacant orbitals, enabling ‘unstable’ molecules to be used as reagents.

E.g. Hydroboration uses BH₃·THF
• Grignard reagents
III. Nomenclature of Ethers and Epoxides

A. IUPAC Nomenclature of Ethers

- In the IUPAC system, ethers are named as “alkoxy-” substituents on a parent chain.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Name as Main Group</th>
<th>Name as Substituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>-ol</td>
<td>Hydroxy</td>
</tr>
<tr>
<td>Alkenes</td>
<td>-ene</td>
<td>Alkenyl</td>
</tr>
<tr>
<td>Alkynes</td>
<td>-yne</td>
<td>Alkynyl</td>
</tr>
<tr>
<td>Alkanes</td>
<td>-ane</td>
<td>Alkyl</td>
</tr>
<tr>
<td>Ethers</td>
<td>-ether</td>
<td>Alkoxy</td>
</tr>
<tr>
<td>Halides</td>
<td>--------</td>
<td>Halo</td>
</tr>
</tbody>
</table>

B. Common Names of Ethers

- Alkyl alkyl ether
- Current rule is to list the alkyl groups in alphabetical order
- Old rule: calls for one to list the alkyl groups in order of increasing complexity (still seen occasionally)
- If the ether is symmetrical then we use dialkyl, or just alkyl.

C. Common Names of Cyclic Ethers

- Epoxides are often prepared from alkenes. In the common naming system, the word “oxide” is added after the name of the alkene that would have formed the epoxide.
IV Synthesis of Ethers
A. Williamson Ether Synthesis (review form chapter 11)

B. Alkoxymercuration-Demercuration (Chapter 8)

V. New Reaction of Ethers
A. Acid-Promoted Cleavage of Ethers

- Ethers are unreactive toward base, but protonated ethers can undergo substitution reactions with strong acids.

- Exception: Phenols are not converted into aryl halides because they can’t undergo substitutions without a catalyst.

B. Autoxidation of Ethers

- In the presence of atmospheric oxygen, ethers slowly oxidize to hydroperoxides and dialkyl peroxides.

- Both are highly explosive.

- Precautions:
  - Do not distill to dryness.
  - Store in full bottles with tight caps.
VI Synthesis of Epoxides

A. Epoxidation of Alkenes (Review)
   - Epoxides are very reactive compared to straight chain ethers because of ring strain in the three membered ring.
   - Acid Promotion: Epoxide formation using peroxyacids

   - Base-Promoted Cyclization of Halohydrins
     - Mechanism: Intramolecular $S_{N}2_{i}$ reaction (Intramolecular: within the same molecule)

B. Ring-Opening (Acid Conditions)

1. Using water or alcohols as a nucleophile:
   - Epoxides react to release their considerable (25kcal/mol) ring strain energy.
   - Regioselectivity Nucleophile attack more substituted carbon
   - Mechanism:
2. Using halides from H-X as a nucleophile:

C. Ring Opening (Base Conditions)
Epoxide’s high ring strain makes it susceptible to nucleophilic attack.

- If we use OH⁻ / H₂O then we form a trans 1,2-diol.
- If we use RO⁻ / ROH then we form a trans 1,2-alkoxy alcohol.
- Regioselectivity:
  - Organometallics (Grignards and organolithiums) can open epoxides