• Ring-opening reactions of epoxides - nucleophiles
• Acid-catalyzed ring opening
• Epoxides in biological processes
• Thiols, sulfides, sulfoxides and sulfones
Ring-opening reactions of epoxides with nucleophiles

Reaction controlled by steric environment of electrophile (like $S_{N2}$)

Other nucleophiles useful – NaN₃, NaCN, etc.
Examples

Ph\(\stackrel{\text{O}}{\text{O}}\) \xrightarrow{\text{NaN}_{3}} \text{DMF} \quad \text{Ph} \quad \text{N}_3 \quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{Ph} \quad \text{N}_3

Ph\(\stackrel{\text{O}}{\text{O}}\) \xrightarrow{\text{NaOCH}_3} \text{DMF} \quad \text{Ph} \quad \text{OCH}_3 \quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{Ph} \quad \text{OCH}_3

Ph\(\stackrel{\text{O}}{\text{O}}\) \xrightarrow{\text{KSCH}_3} \text{DMSO} \quad \text{Ph} \quad \text{SCH}_3 \quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{Ph} \quad \text{SCH}_3
Ring-opening reactions of epoxides in acidic media

- Protonation first, development of cation on more substituted C
- Attack at more hindered carbon is therefore prevalent
Stereochemistry

Inversion observed in most cases
Epoxide opening in Biological systems

Squalene epoxide

Oxido squalene cyclase

Lanosterol
Sulfur derivatives – Thiols, Sulfides, Sulfoxides, Sulfones

- **Thiol**: \( \text{SH} \)
  - Reaction 1: \( \text{NaOH} \)
  - Reaction 2: \( \text{CH}_3\text{Br} \)
  - **Sulfide**: \( \text{SCH}_3 \)

- **Sulfide**
  - Reaction: \( \text{CH}_3\text{I} \)
  - **Sulfonium salt**: \( \text{S}-\text{CH}_3 \)

- **Sulfide**
  - Reaction: \( \text{xs ROOH} \)
  - **Sulfone**: \( \text{SO}-\text{CH}_3 \)
Nucleophilic substitution at the primary carbon of adenosine triphosphate
Figure 16.7
Monday

• Chapter 17 – Nucleophilic addition to aldehydes and ketones
• Lab – Preparation of a phosphonium salt – Exp 73