16.4
Crown Ethers
Crown Ethers

structure
  cyclic polyethers derived from repeating
  —OCH$_2$CH$_2$— units

properties
  form stable complexes with metal ions

applications
  synthetic reactions involving anions
negative charge concentrated in cavity inside the molecule
negative charge concentrated in cavity inside the molecule
forms stable Lewis acid/Lewis base complex with $K^+$
forms stable Lewis acid/Lewis base complex with $K^+$
Ion-Complexing and Solubility

K$^+$F$^-$

not soluble in benzene
Ion-Complexing and Solubility

Ion-Complexing and Solubility

add 18-crown-6

K⁺F⁻

benzene
18-crown-6 complex of $\text{K}^+$ dissolves in benzene
Ion-Complexing and Solubility

\[
\begin{align*}
\text{F}^- & \text{ carried into benzene} \\
\text{to preserve electroneutrality}
\end{align*}
\]
Complexation of $K^+$ by 18-crown-6
"solubilizes" salt in benzene
Anion of salt is in a relatively unsolvated state
in benzene (sometimes referred to as a
"naked anion")
Unsolvated anion is very reactive
Only catalytic quantities of 18-crown-6 are needed
Example

\[ \text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Br} \xrightarrow{\text{KF}} \text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{F} \]

18-crown-6

benzene

(92%)
16.5
Preparation of Ethers
Acid-Catalyzed Condensation of Alcohols

\[ 2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \]

\[ \downarrow \text{H}_2\text{SO}_4, \ 130^\circ\text{C} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

(60%)  

*Discussed earlier in Section 15.7*
Addition of Alcohols to Alkenes

$$(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{CH}_3\text{OH} \xrightarrow{\text{H}^+} (\text{CH}_3)_3\text{COCH}_3$$

*tert*-Butyl methyl ether

*tert*-Butyl methyl ether (MTBE) was produced on a scale exceeding 15 billion pounds per year in the U.S. during the 1990s. It is an effective octane booster in gasoline, but contaminates ground water if allowed to leak from storage tanks. Further use of MTBE is unlikely.
16.6
The Williamson Ether Synthesis

Think $S_N2$!

*primary* alkyl halide + alkoxide nucleophile
Example

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{ONa} + \text{CH}_3\text{CH}_2\text{I} \]

\[ \rightarrow \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{NaI} \]

(71%)
Another Example

\[
\text{Ph-CH}_2\text{Cl} + \text{CH}_3\text{CHCHCH}_3 \xrightarrow{\text{ONa}} \text{Ph-CH}_2\text{OCHCHCH}_3 \quad (84\%)
\]
Another Example

Alkyl halide must be primary

$\text{Ph-CH}_2\text{Cl} + \text{CH}_3\text{CHCHCH}_3$ $\rightarrow$ $\text{Ph-CH}_2\text{OCHCHCH}_3$ $\quad (84\%)$

Alkoxide ion can be derived from primary, secondary, or tertiary alcohol
Origin of Reactants

\[
\text{Origin of Reactants}
\]

\[
\text{CH}_2\text{OH} \quad \text{CH}_3\text{CHCH}_3
\]

\[
\text{CH}_2\text{Cl} + \text{CH}_3\text{CHCH}_3
\]

\[
\text{CH}_2\text{OCHCHCH}_3 \quad (84\%)
\]
What happens if the alkyl halide is not primary?

\[
\text{CH}_2\text{ONa} + \text{CH}_3\text{CHCH}_3 \rightarrow \text{Br}
\]
What happens if the alkyl halide is not primary?

Elimination by the E2 mechanism becomes the major reaction pathway.

$$\text{CH}_2\text{ONa} + \text{CH}_3\text{CHCHCH}_3 \rightarrow \text{Br}$$

$$\text{CH}_2\text{OH} + \text{H}_2\text{C} \equiv \text{CHCH}_3$$
16.7
Reactions of Ethers:
A Review and a Preview
No reactions of ethers encountered to this point.

Ethers are relatively unreactive.

Their low level of reactivity is one reason why ethers are often used as solvents in chemical reactions.

Ethers oxidize in air to form explosive hydroperoxides and peroxides.
16.8
Acid-Catalyzed Cleavage of Ethers
Example

\[
\text{CH}_3\text{CHCH}_2\text{CH}_3 \quad \text{HBr} \quad \text{heat} \quad \rightarrow \quad \text{CH}_3\text{CHCHCH}_2\text{CH}_3 + \text{CH}_3\text{Br}
\]

\( (81\%) \)
Mechanism

CH₃CHCH₂CH₃

CH₃

O

CH₃

H–Br

CH₃CHCH₂CH₃

CH₃

O⁺

CH₃
Mechanism

\[ \text{CH}_3\text{CHCH}_2\text{CH}_3 \]

\[ \text{CH}_3\text{O} \]

\[ \text{H}\text{Br} \]

\[ \text{CH}_3\text{CHCH}_2\text{CH}_3 \]

\[ \text{CH}_3\text{O}^+ \]

\[ \text{Br}\text{H} \]

\[ \text{CH}_3\text{CHCH}_2\text{CH}_3 \]

\[ \text{O} \]

\[ \text{H} \]

\[ \text{Br} \text{CH}_3 \]
Cleavage of Cyclic Ethers

\[
\text{Cyclic Ether} \xrightarrow{\text{HI} \atop 150^\circ\text{C}} \text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I} \\
(65\%)
\]
Mechanism

\[
\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}
\]

\[
\xrightarrow{\text{HI}}
\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\xrightarrow{\text{O}^+}
\]

\[
\text{O} \\
\text{H}
\]
Mechanism

\[ \text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I} \]

\[ \text{O} \]

\[ \text{H} \]

\[ \text{O}^+ \]

\[ \text{H} \]

\[ \text{O} \]

\[ \text{H} \]

\[ \text{O} \]

\[ \text{H} \]