16.4
Crown Ethers

Crown Ethers

structure

cyclic polyethers derived from repeating —OCH_2CH_2— units

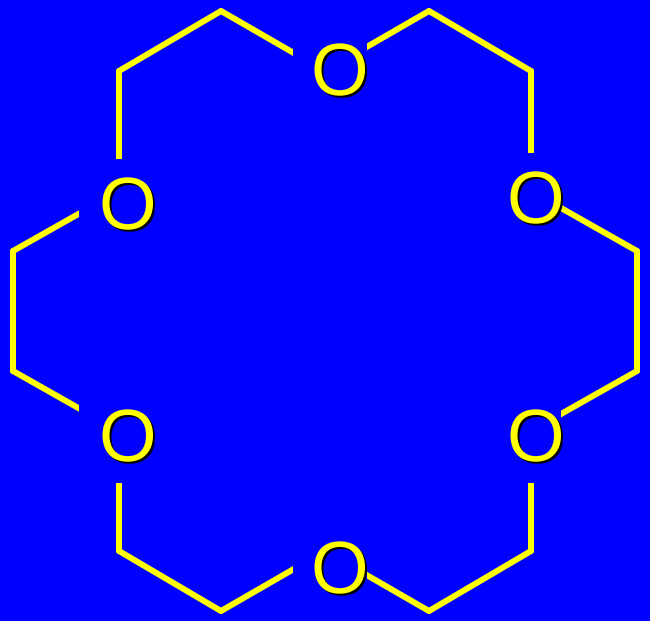
properties

form stable complexes with metal ions

applications

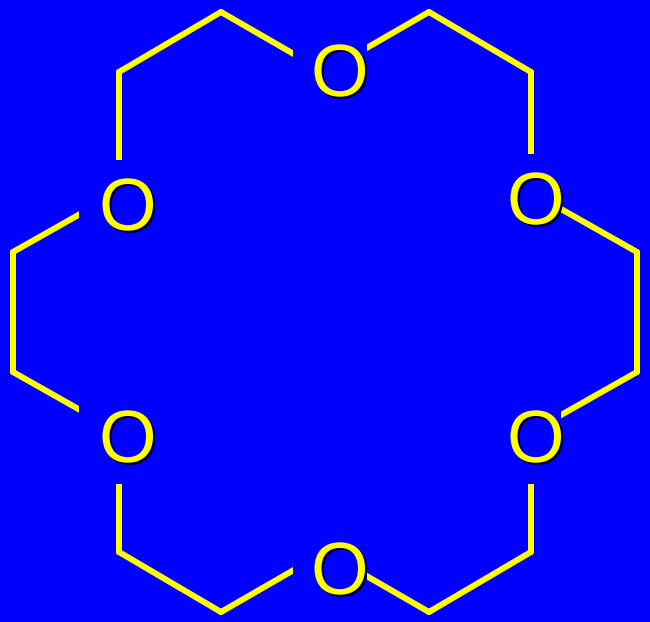
synthetic reactions involving anions

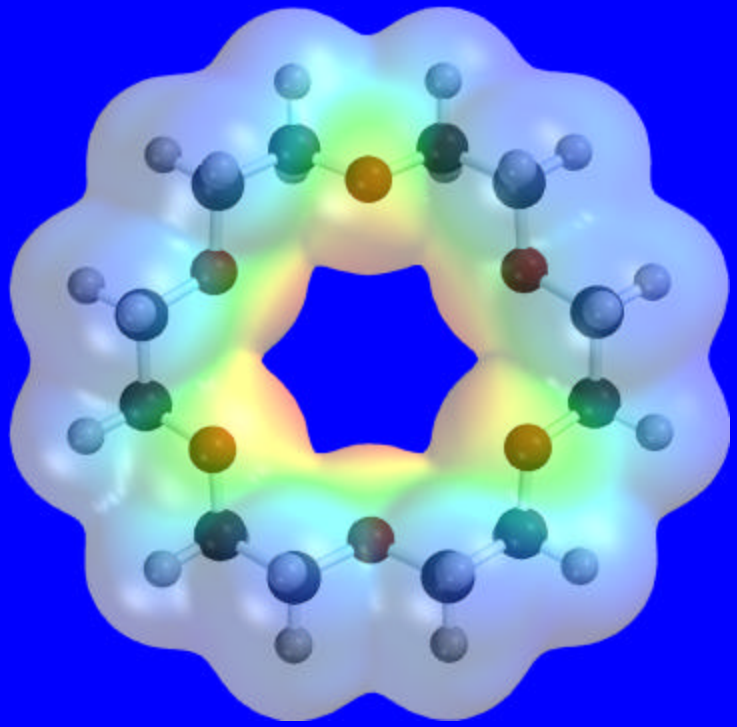
18-Crown-6



negative charge concentrated in cavity inside the molecule

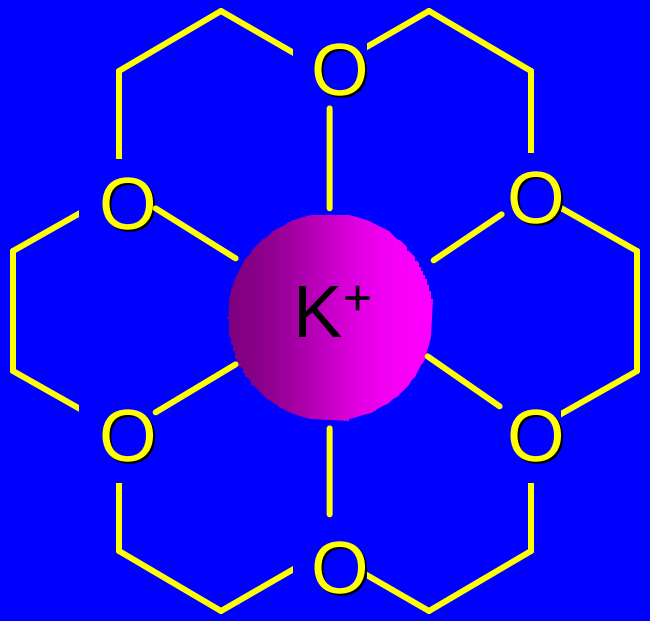
18-Crown-6





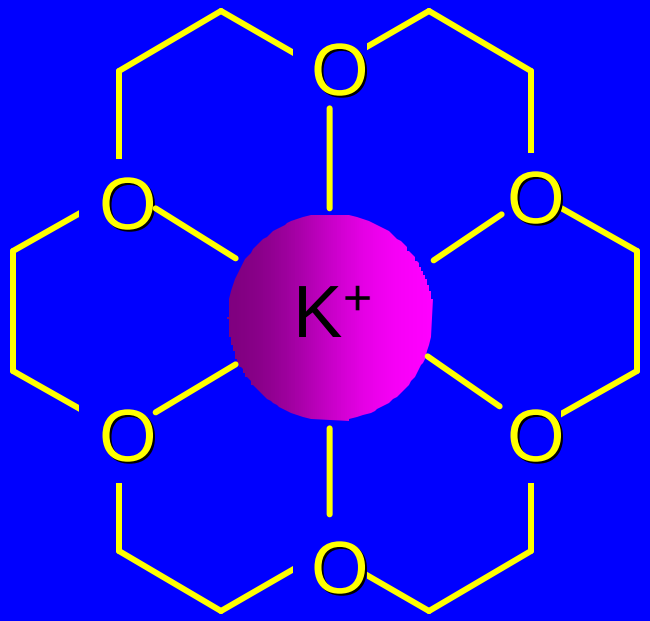
negative charge concentrated in cavity inside the molecule

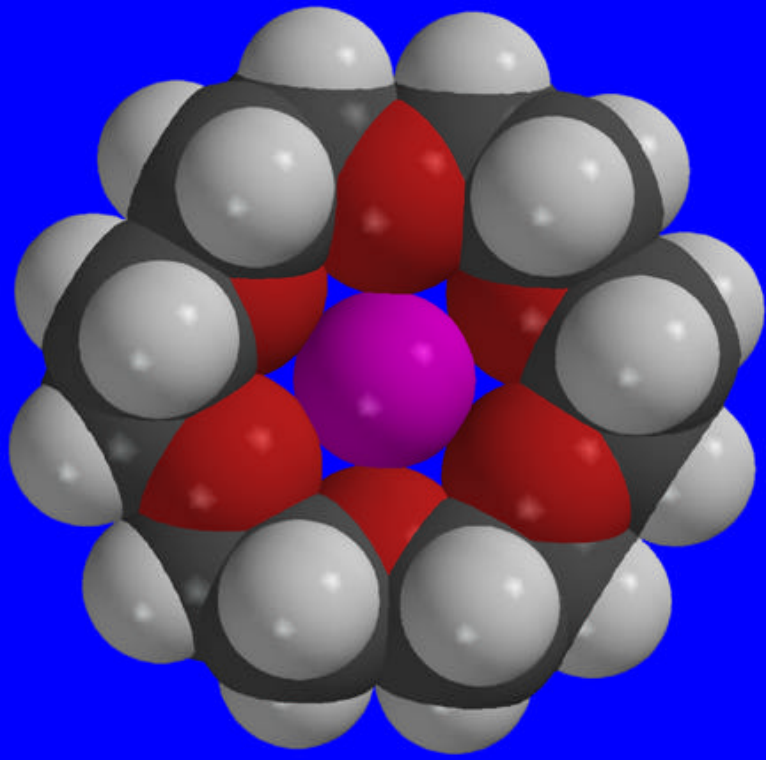
18-Crown-6



forms stable Lewis acid/Lewis base complex with K^+

18-Crown-6





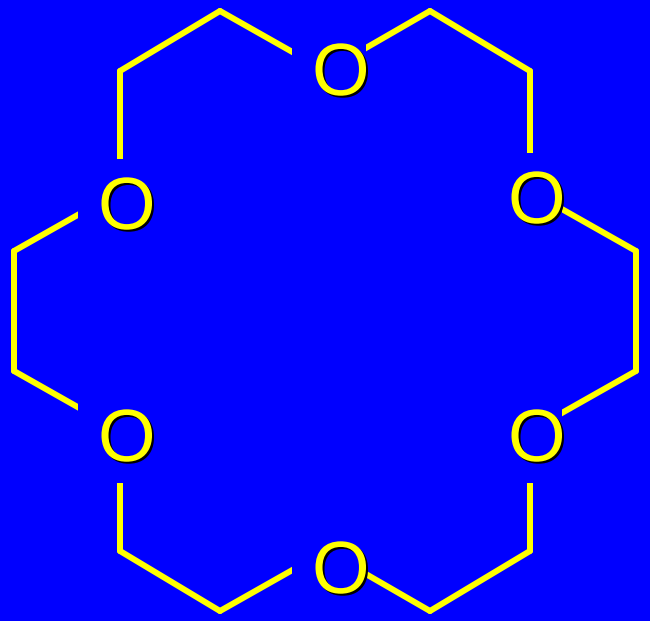
forms stable Lewis acid/Lewis base complex with K^+

Ion-Complexing and Solubility

K^+F^-

not soluble in benzene

Ion-Complexing and Solubility

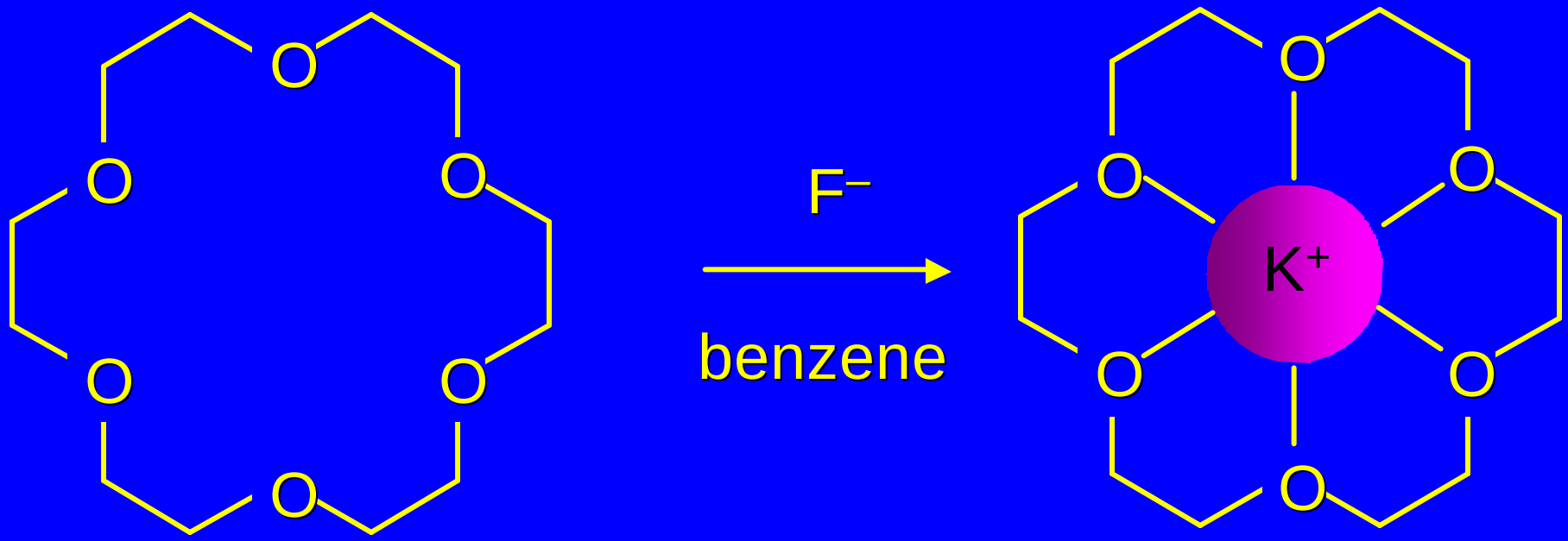


K^+F^-

benzene

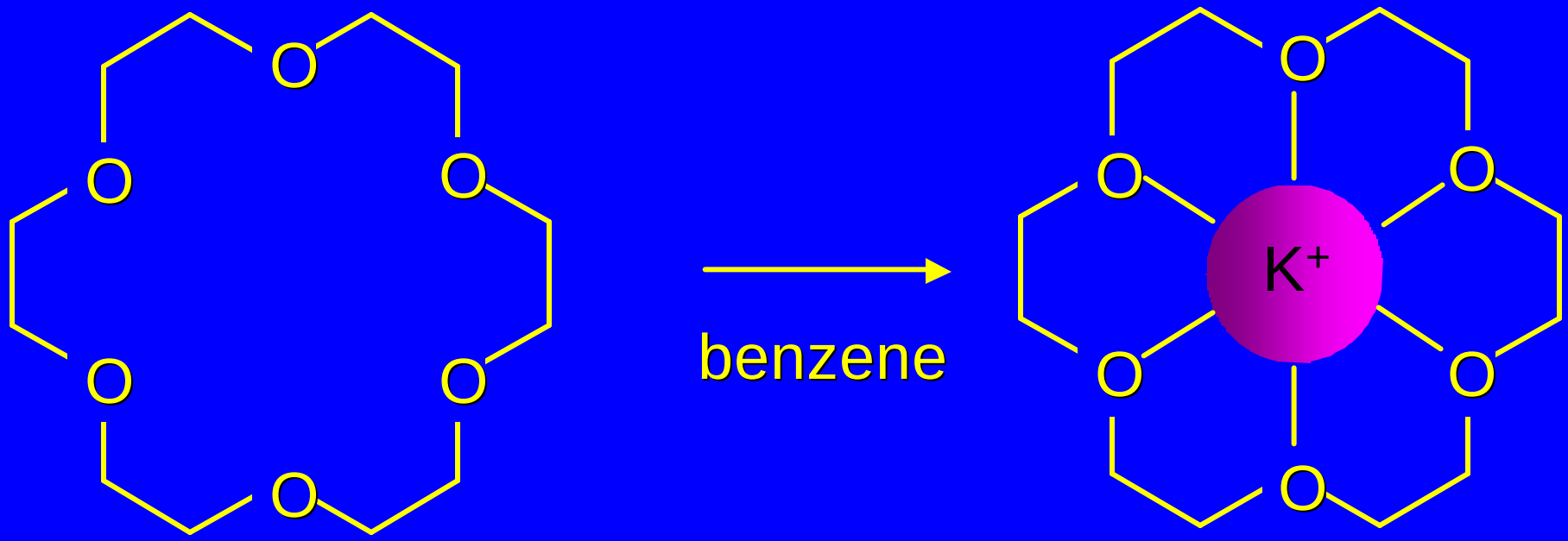
add 18-crown-6

Ion-Complexing and Solubility



18-crown-6 complex of K^+ dissolves in benzene

Ion-Complexing and Solubility



F^- carried into benzene
to preserve electroneutrality

+ F^-

Application to organic synthesis

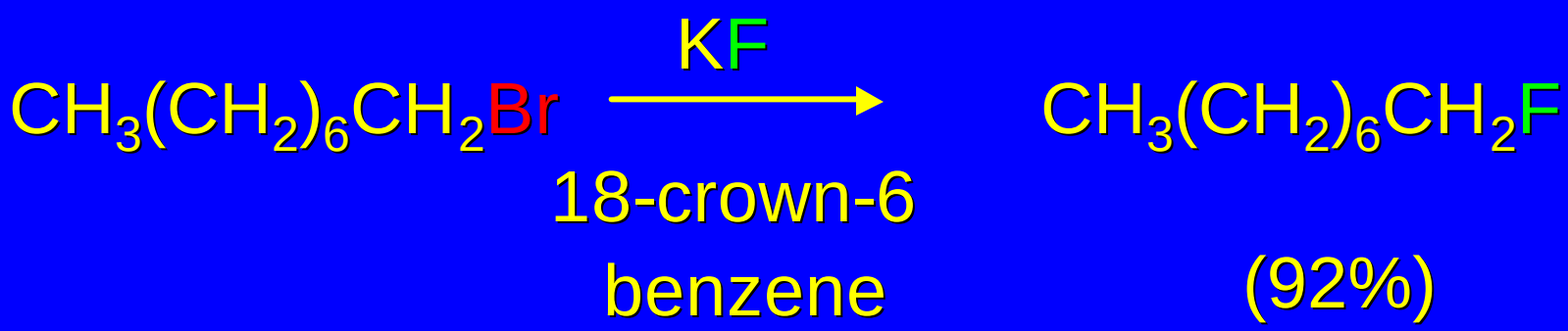
Complexaton of K^+ by 18-crown-6 "solubilizes" salt in benzene

Anion of salt is in a relatively unsolvated state in benzene (sometimes referred to as a "naked anion")

Unsolvated anion is very reactive

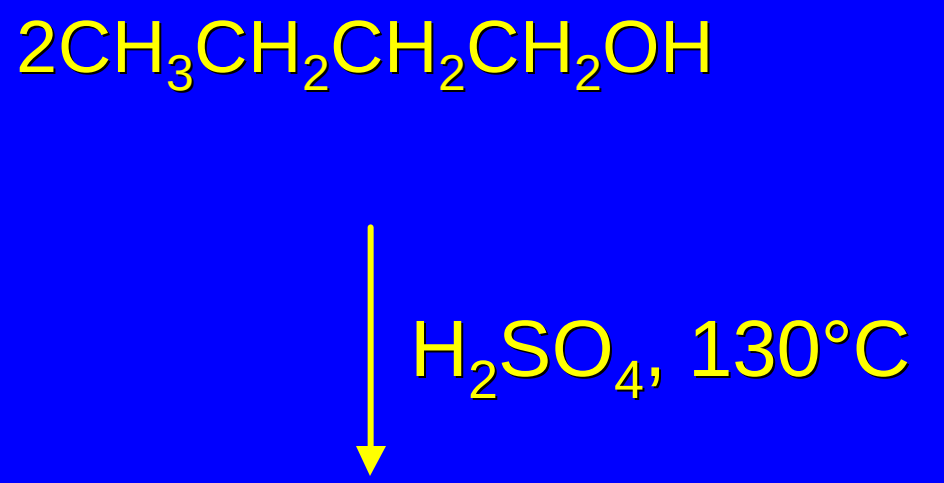
Only catalytic quantities of 18-crown-6 are needed

Example



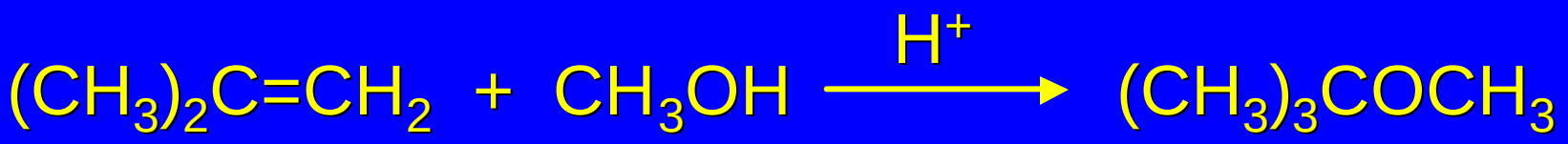
16.5
Preparation of Ethers

*Acid-Catalyzed Condensation of Alcohols**



*Discussed earlier in Section 15.7

Addition of Alcohols to Alkenes



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.

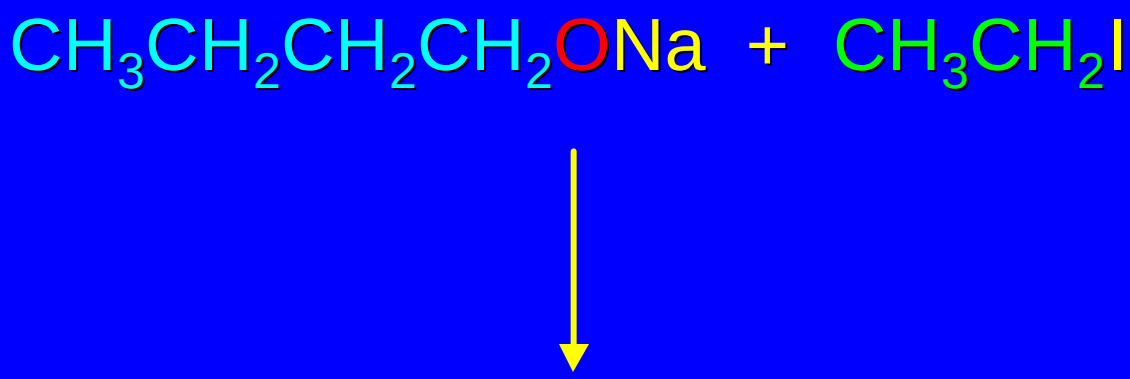
16.6

The Williamson Ether Synthesis

Think S_N2!

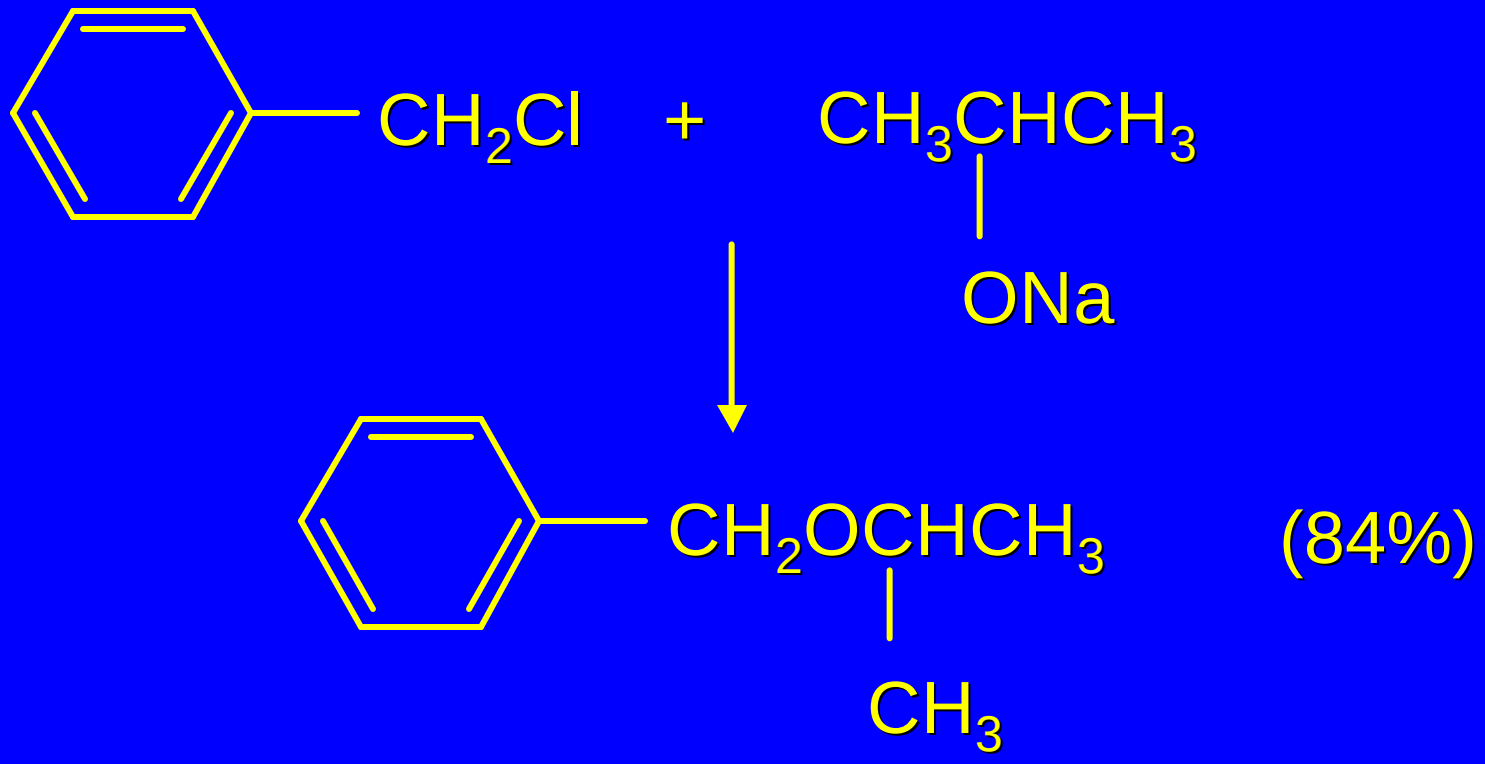
primary alkyl halide + alkoxide nucleophile

Example



(71%)

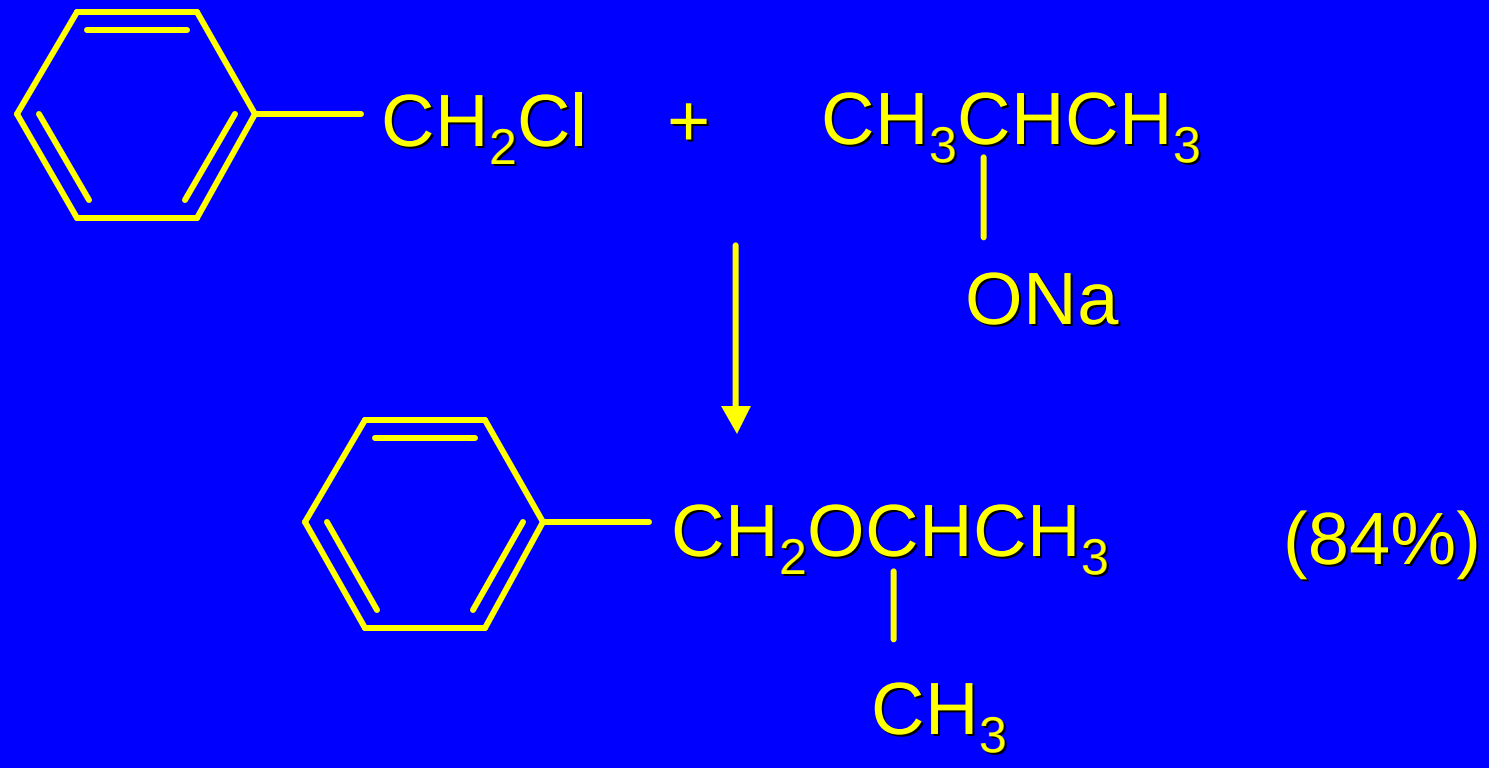
Another Example



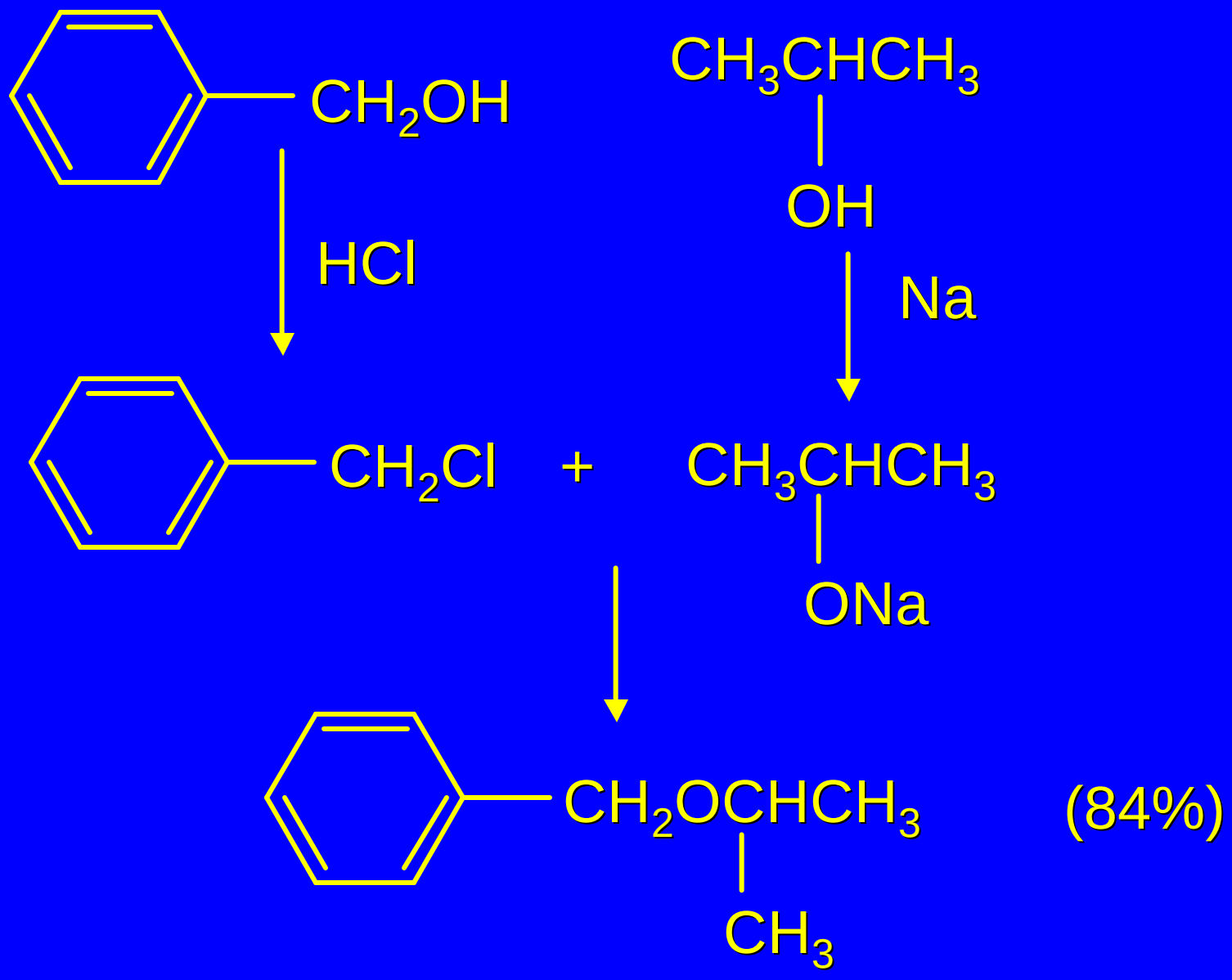
Another Example

Alkyl halide must be primary

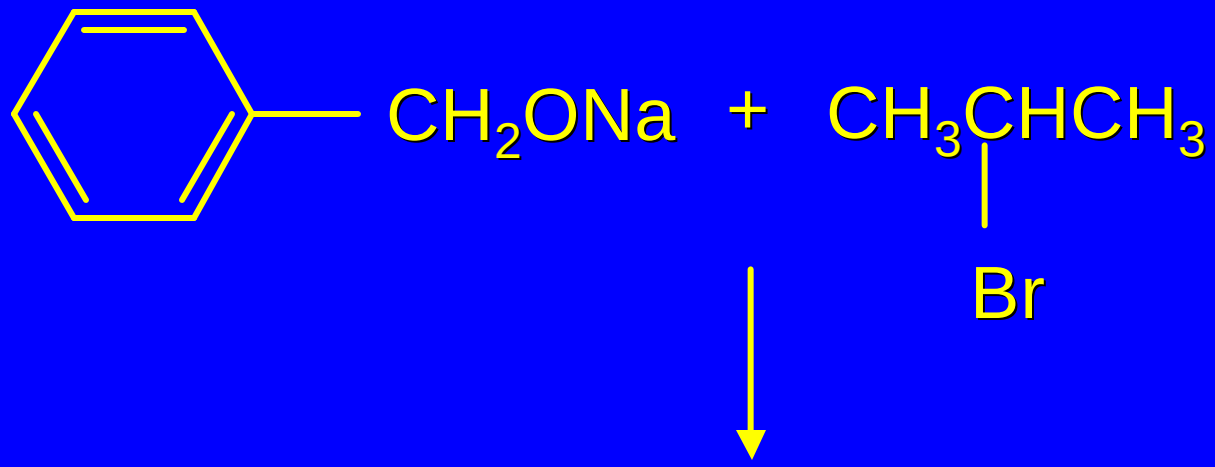
Alkoxide ion can be derived from primary, secondary, or tertiary alcohol



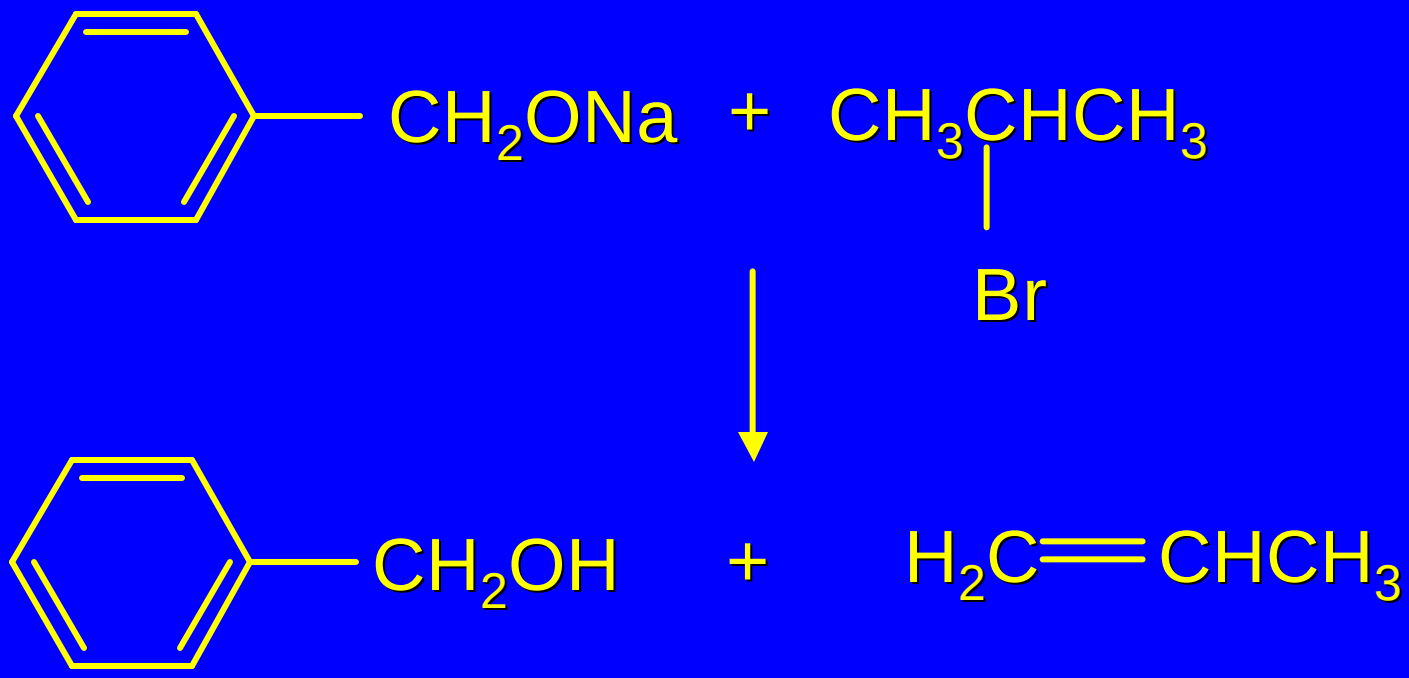
Origin of Reactants



What happens if the alkyl halide is not primary?



What happens if the alkyl halide is not primary?



Elimination by the E2 mechanism becomes the major reaction pathway.

16.7
Reactions of Ethers:
A Review and a Preview

Summary of reactions of ethers

No reactions of ethers encountered to this point.

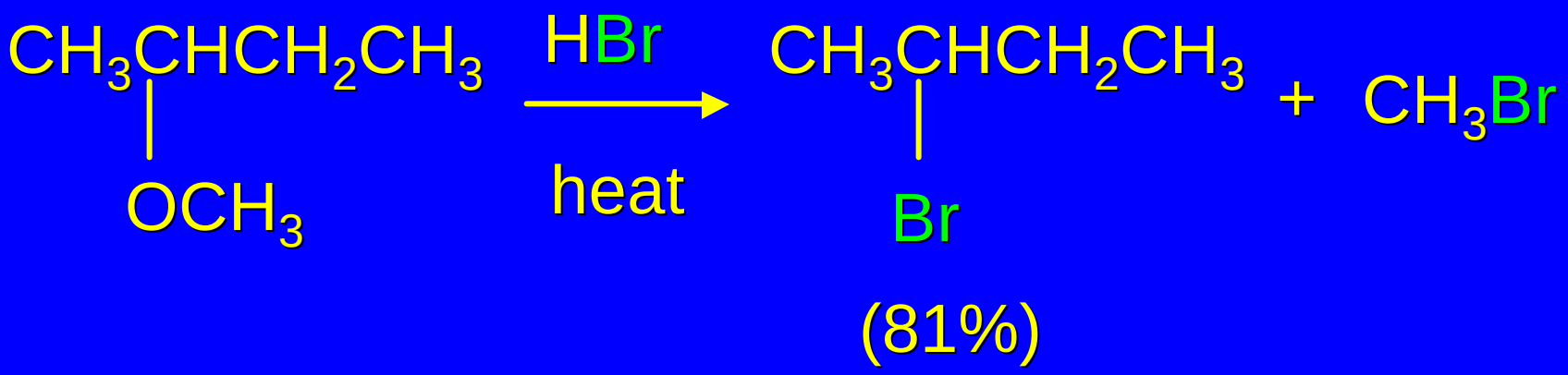
Ethers are relatively unreactive.

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

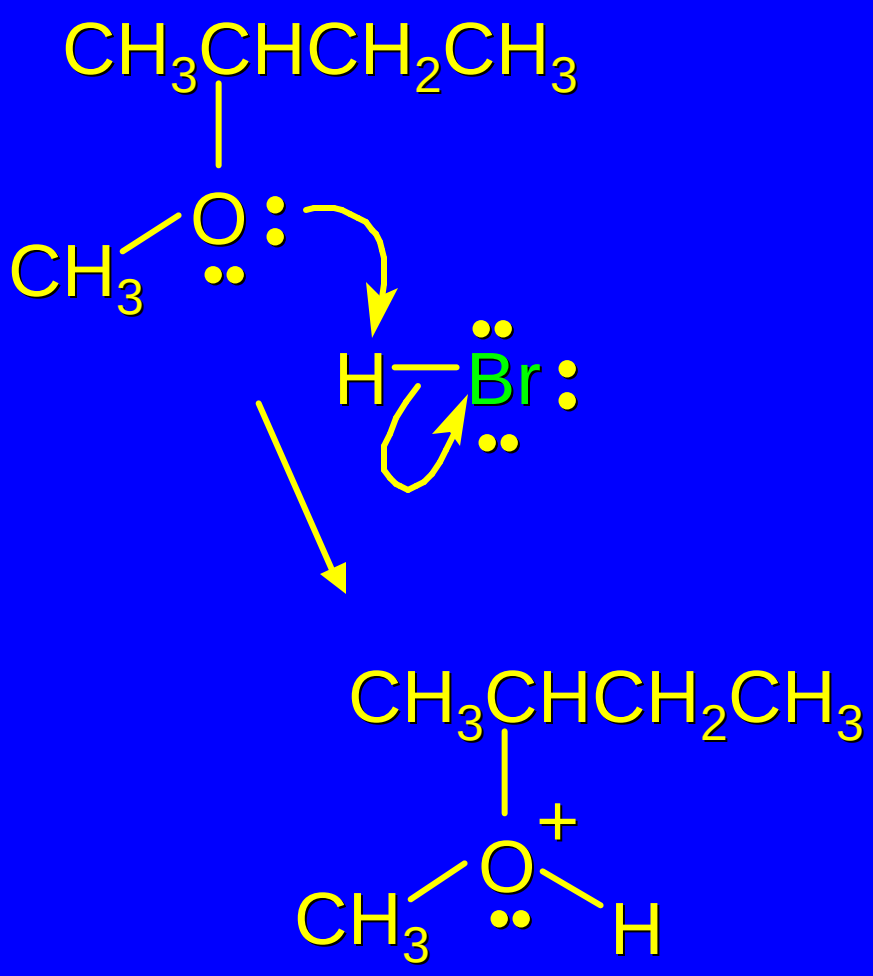
Ethers oxidize in air to form explosive hydroperoxides and peroxides.

16.8
Acid-Catalyzed Cleavage of Ethers

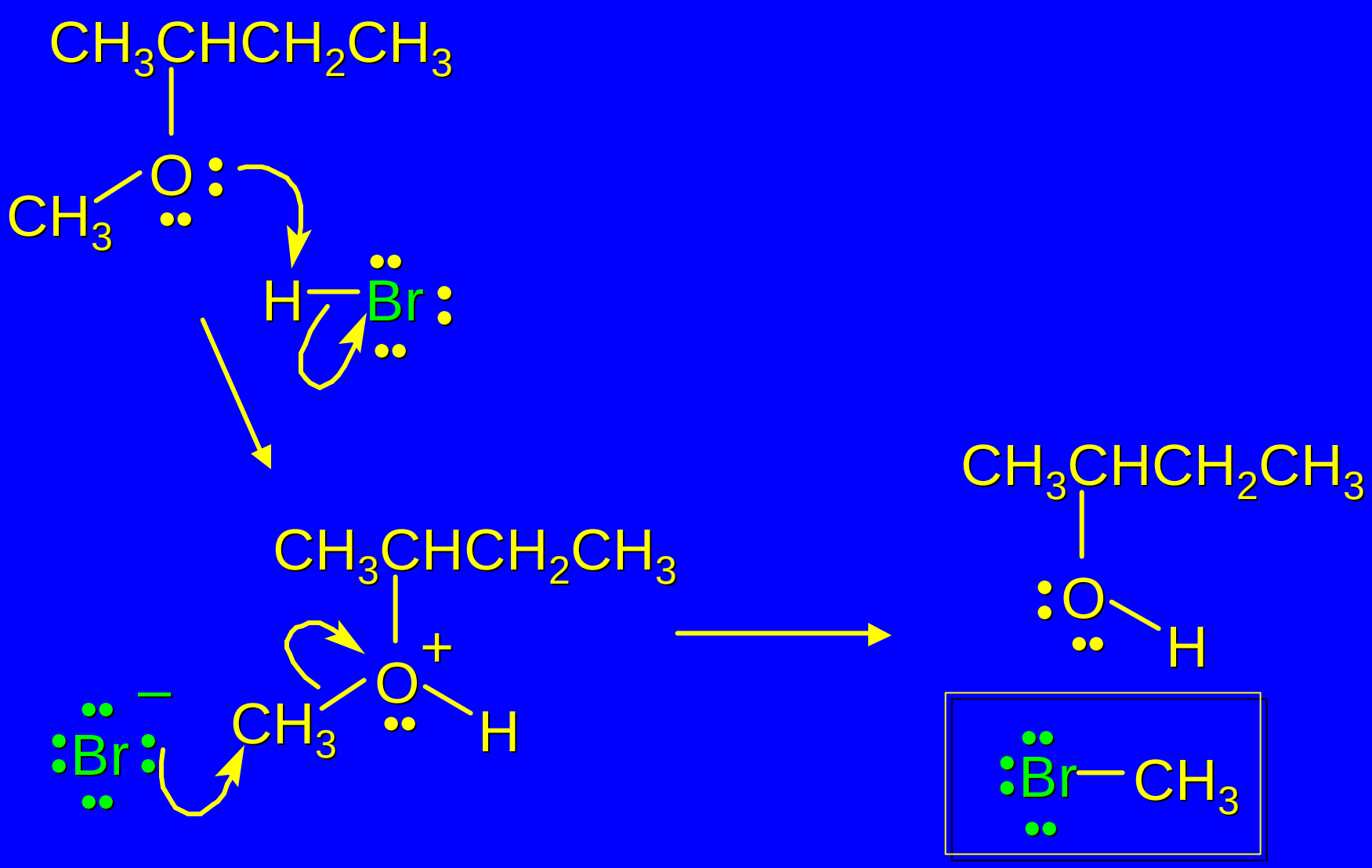
Example



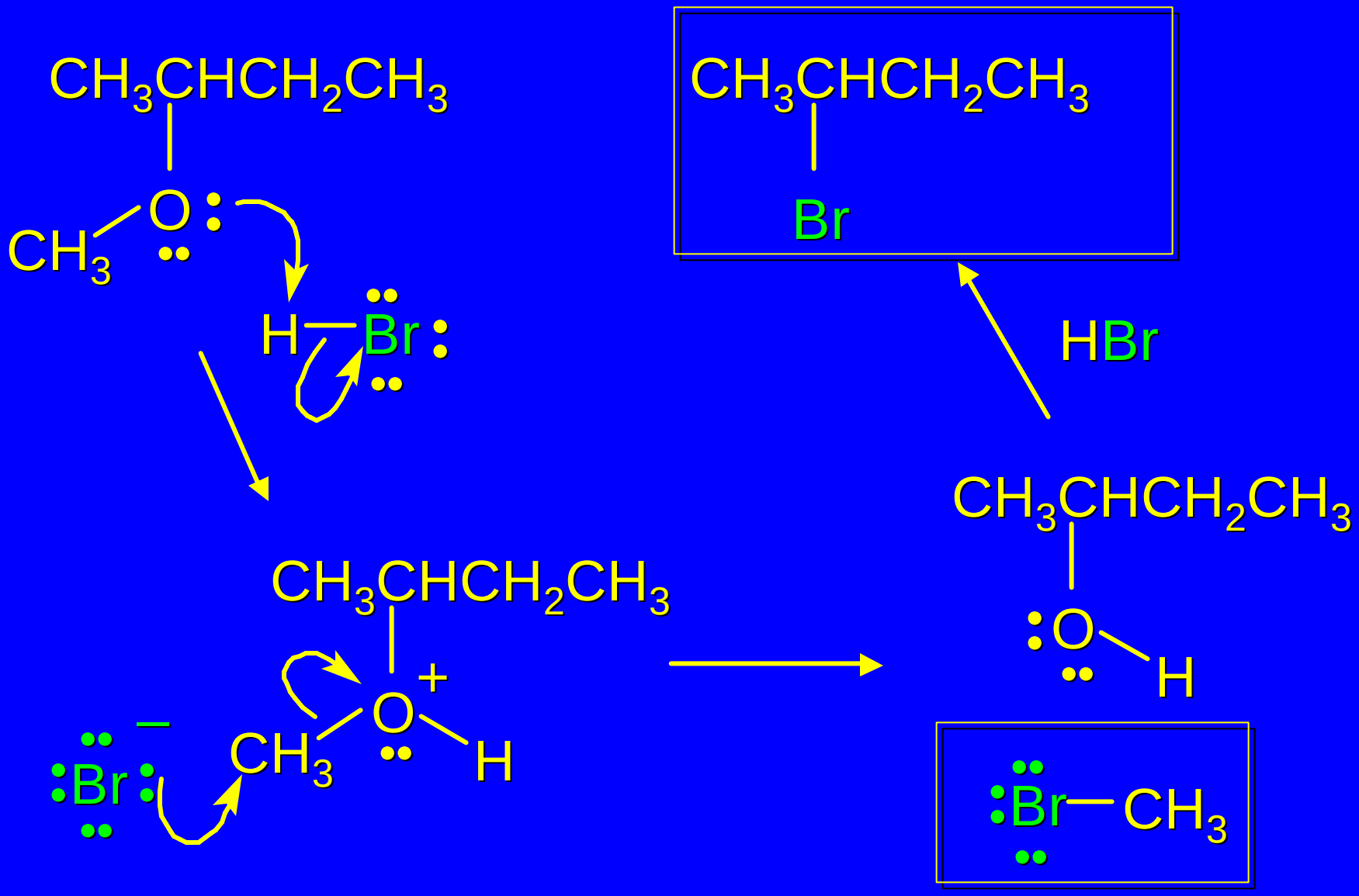
Mechanism



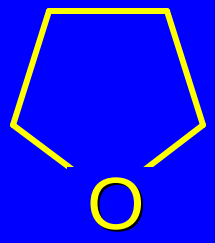
Mechanism


CH3CHCH2CH3
O
CH3
H
Br
CH3CHCH2CH3
O
+
CH3
H
Br
–
CH3CHCH2CH3
O
H
Br
CH3

Mechanism


CH3CHCH2CH3
O
CH3
H
Br
CH3CHCH2CH3
Br
HBr
CH3CHCH2CH3
O
H
CH3CHCH2CH3
O
+
CH3
H
Br
Br
CH3

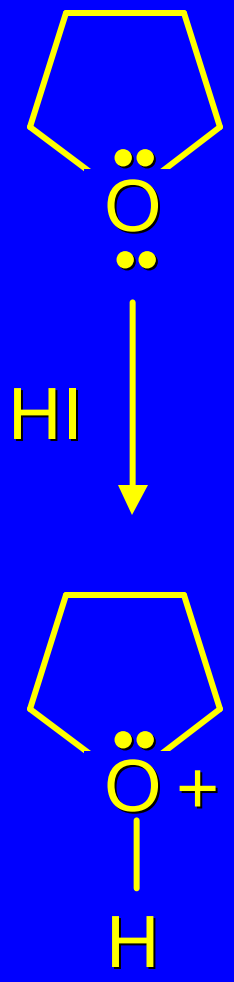
Cleavage of Cyclic Ethers



$$\xrightarrow[150^\circ C]{HI} ICH_2CH_2CH_2CH_2I$$

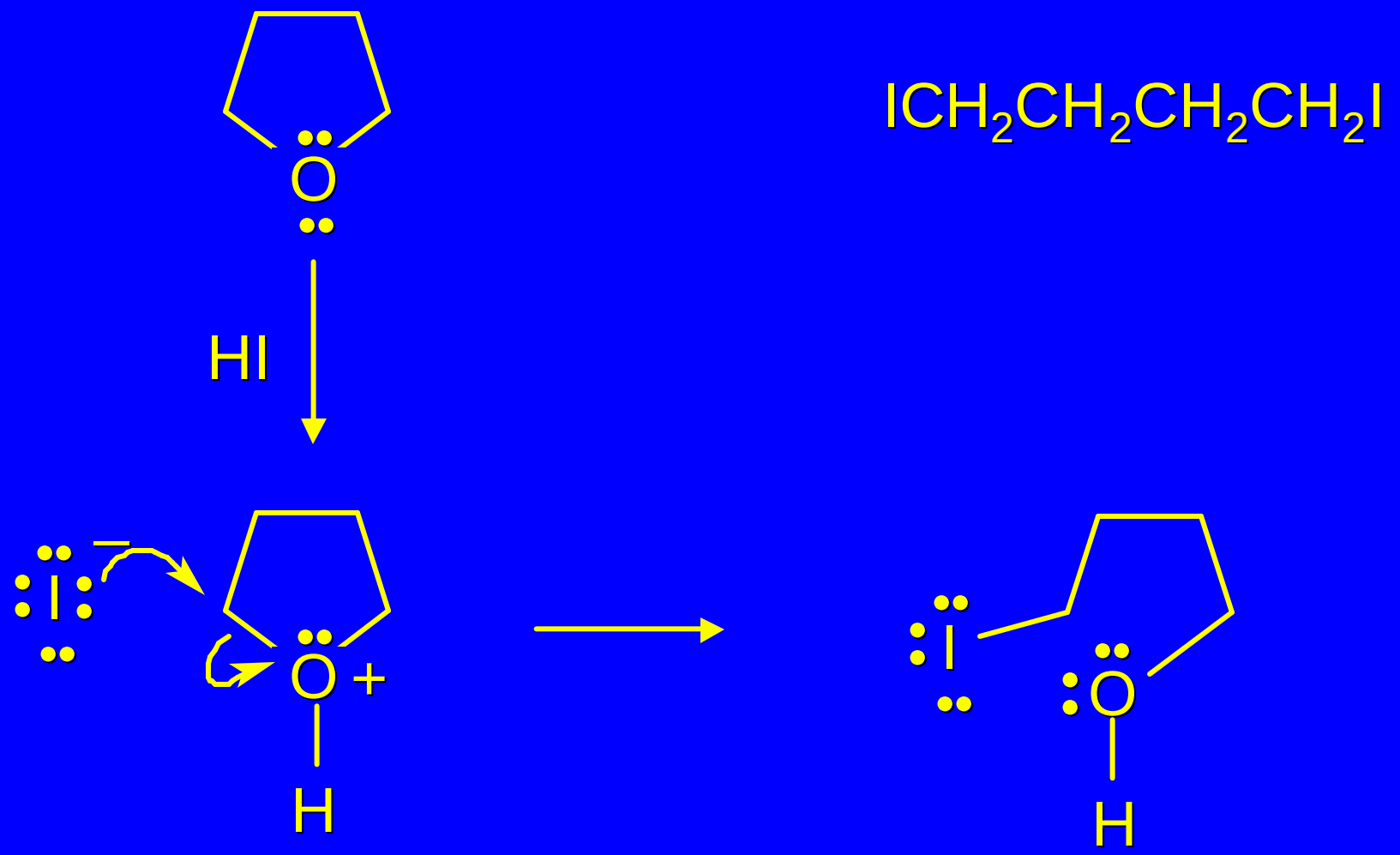
(65%)

Mechanism



$ICH_2CH_2CH_2CH_2I$

Mechanism



$ICH_2CH_2CH_2CH_2I$

Mechanism