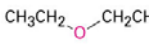
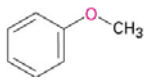
Names and Physical Properties of Ethers

An **ether** has two organic groups (alkyl, aryl, or vinyl) bonded to the same oxygen atom, R–O–R′.



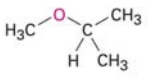
Diethyl ether

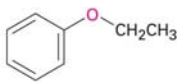


Anisole (methyl phenyl ether)

Tetrahydrofuran

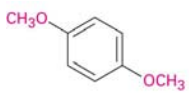
Simple ethers are named by identifying the two organic substituents and adding the word *ether*.

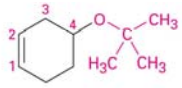


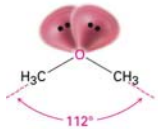


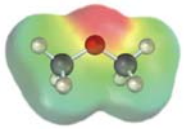
Dioxane

If other functional groups are present, the ether part is considered an alkoxy substituent.







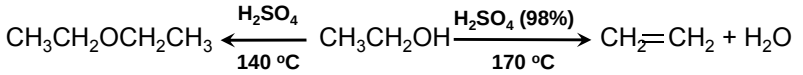


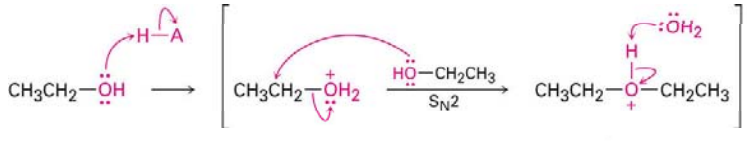
Physical Properties of Ethers

Oxygen atom gives ethers a slight dipole moment, and the boiling points of ethers are often slightly higher than those of corresponding alkanes but much lower than those of isomeric alcohols, due to the absence of H-bonding.

Ether	bp (°C)	Hydrocarbons	bp (°C)	Alcohols	bp (°C)
CH_3OCH_3	-25	$CH_3CH_2CH_3$	-45	CH_3CH_2OH	78.5
THF	65	cyclopentane	49		

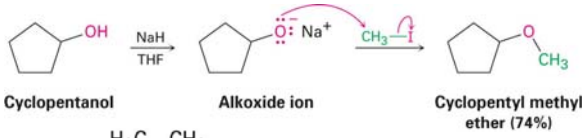
Synthesis of Ether





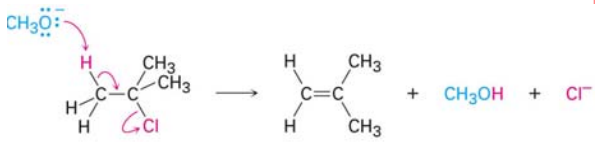
Synthesis of Ether

Williamson Ether Synthesis



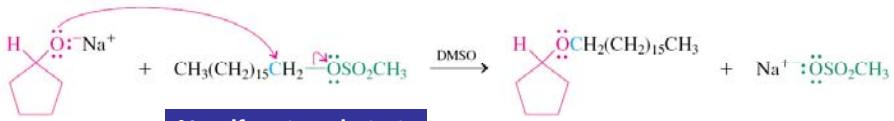
Cyclopentanol — Alkoxide ion — Cyclopentyl methyl ether (74%)

tert-Butoxide — Iodomethane — *tert*-Butyl methyl ether



2-Chloro-2-methylpropane — 2-Methylpropene

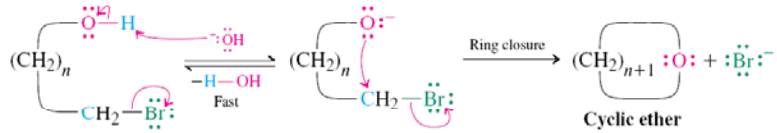
The haloalkane substrate is limited to 1° alkyl halide.

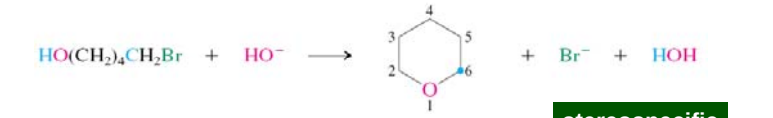


1° sulfonate substrate

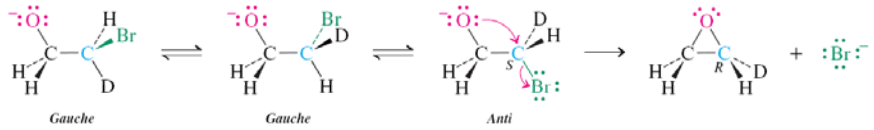
Synthesis of Ether

Cyclic ethers: intramolecular S_N2 reactions





stereospecific



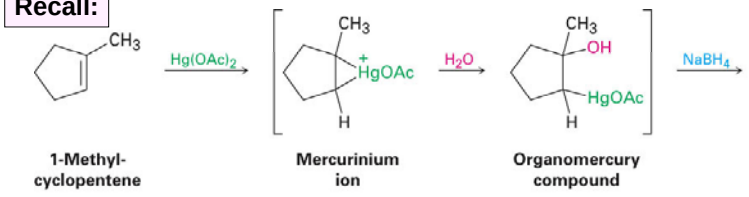
Relative Rates of Cyclic Ether Formation

$$k_3 \geq k_5 > k_6 > k_4 \geq k_7 > k_8$$

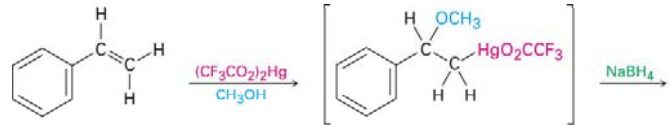
k_n = reaction rate, n = ring size

Alkoxymercuration of Alkenes

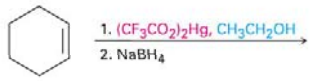
Recall:



1-Methyl-cyclopentene — Mercurinium ion — Organomercury compound



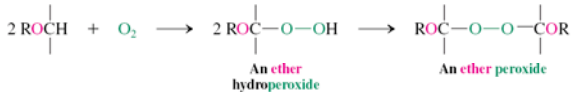
Styrene



Cyclohexene

Reactions of Ethers

Peroxides from Ethers

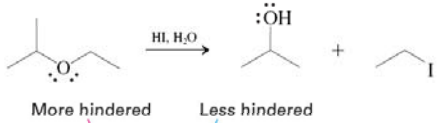


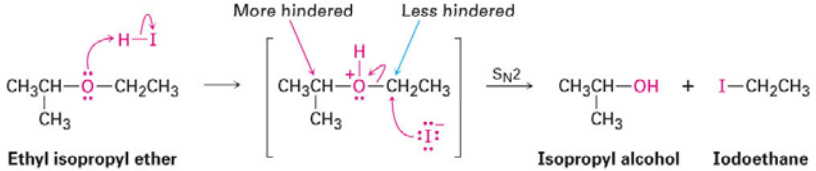
An ether hydroperoxide — An ether peroxide

As peroxides decompose explosively, ethers should not be exposed to air for a long time.

Cleavage by strong acids: HBr & HI

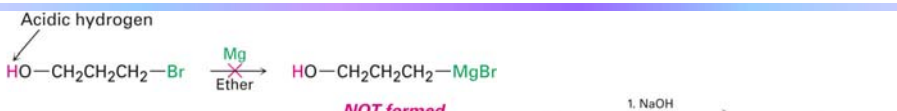
Alkyloxonium ion



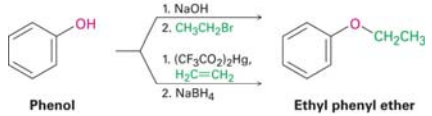


Ethyl isopropyl ether — Isopropyl alcohol — Iodoethane

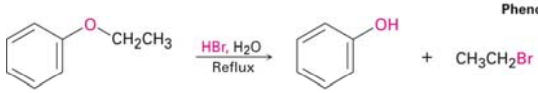
Protection of Alcohols

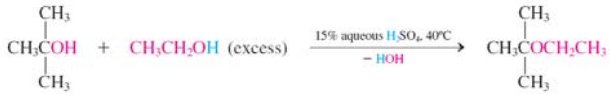


NOT formed

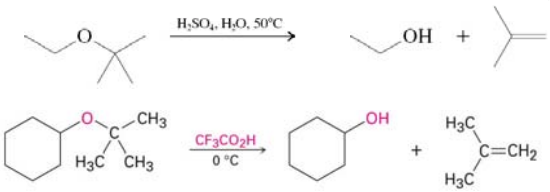


Phenol — Ethyl phenyl ether



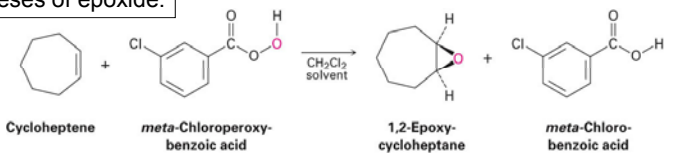


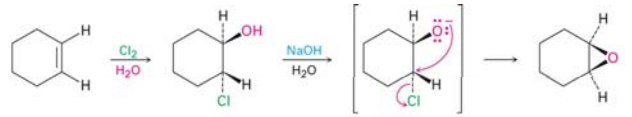
t-Bu may act as a protective group of OH as it can be conveniently removed under acidic conditions afterwards.



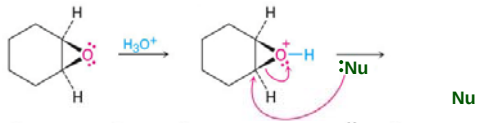
Cyclic Ether: Epoxides

Recall syntheses of epoxide:



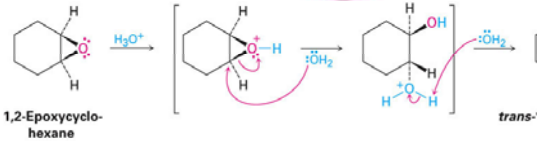


Acid-catalyzed epoxide opening:



trans-product (stereospecific)

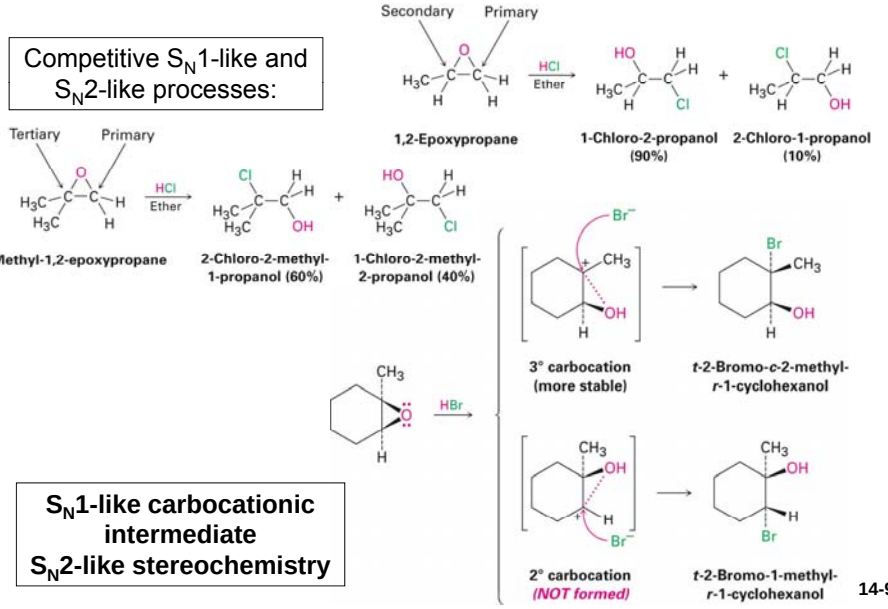
Recall:



1,2-Epoxycyclo-hexane

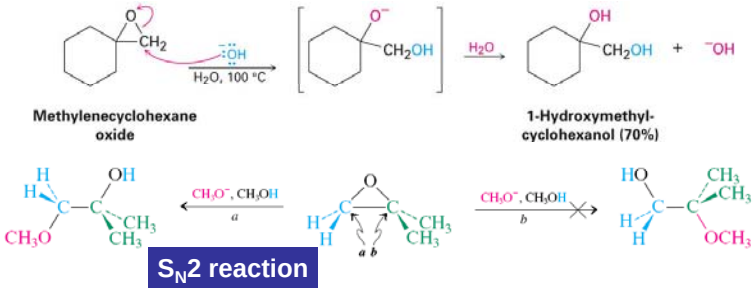
Acid-Catalyzed Ring Opening of Epoxide

Competitive S_N1-like and S_N2-like processes:

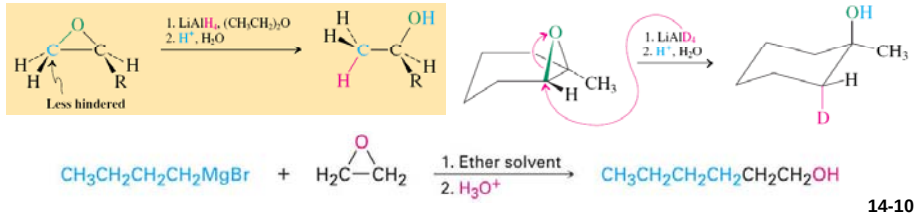


S_N1-like carbocationic intermediate
S_N2-like stereochemistry

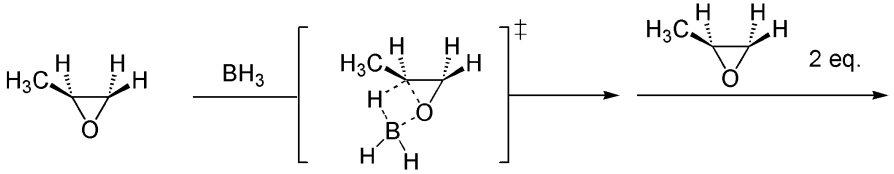
Base-catalyzed Epoxide Opening



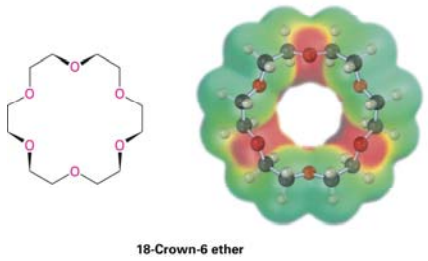
Nucleophile attacks the less hindered carbon center and give *anti*-product.



Reaction of Epoxide with Borane



$(CH_3CH_2CH_2O)_3B \xrightarrow{H_2O} CH_3CH_2CH_2OH$

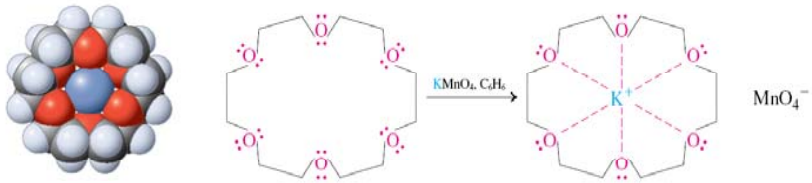


Crown Ether

x*-crown-*y

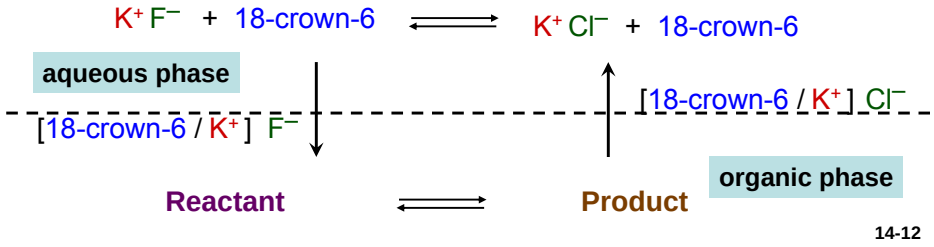
x **total number of atoms**
y **number of oxygen**

Crown Ether

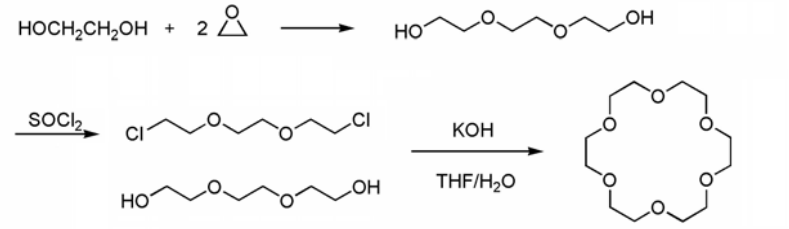


15-crown-5 and 12-crown-4 complex Na+ and Li+, respectively.

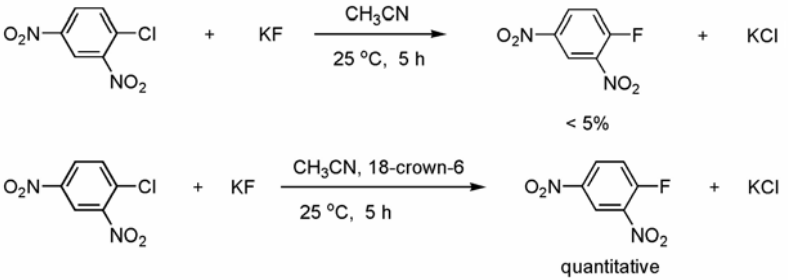
Phase transfer catalyst



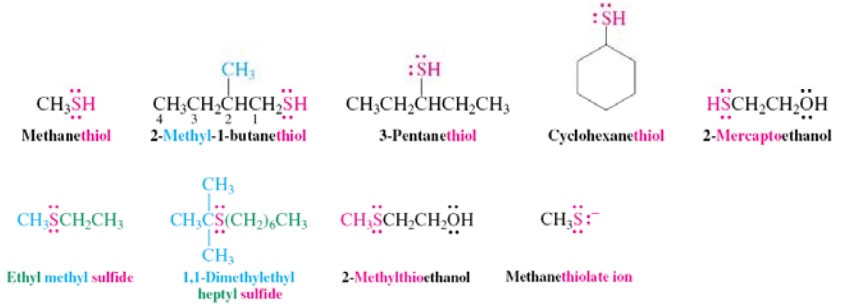
Synthesis and Application of Crown Ethers



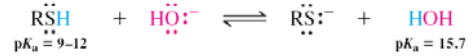
Phase transfer catalyst



Thiols and Sulfide



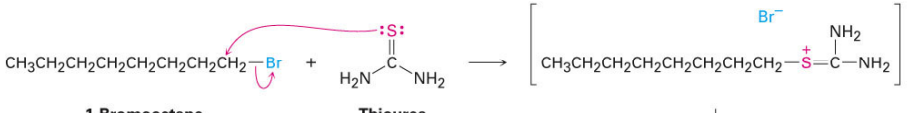
Acidity of Thiols



1-Bromooctane — 1-Octanethiol (83%)

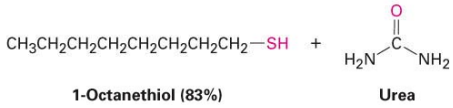
The reaction usually gives a poor yield due to a second S_N2 reaction to give a sulfide as a by-product.

Syntheses of Thiols and Sulfides

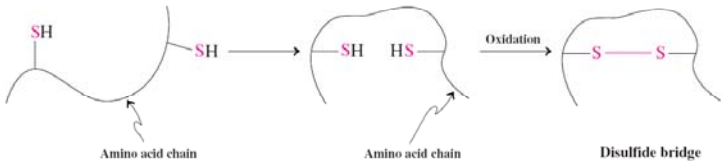


1-Bromooctane — Thiourea

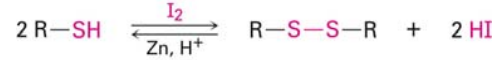
Reversible disulfide formation is important in stabilizing the folding of proteins.



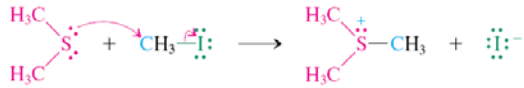
1-Octanethiol (83%) — Urea



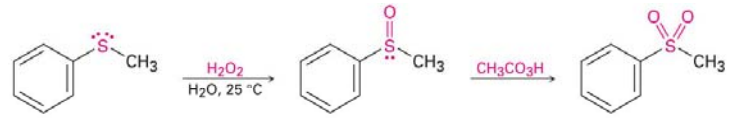
Reactions of Thiols and Sulfides



A thiol — A disulfide



Trimethylsulfonium iodide



Methyl phenyl sulfide — Methyl phenyl sulfoxide — Methyl phenyl sulfone