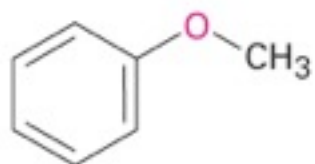


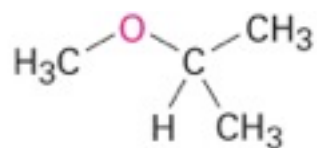
Diethyl ether



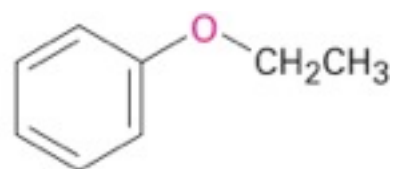
Anisole
(methyl phenyl ether)



Tetrahydrofuran

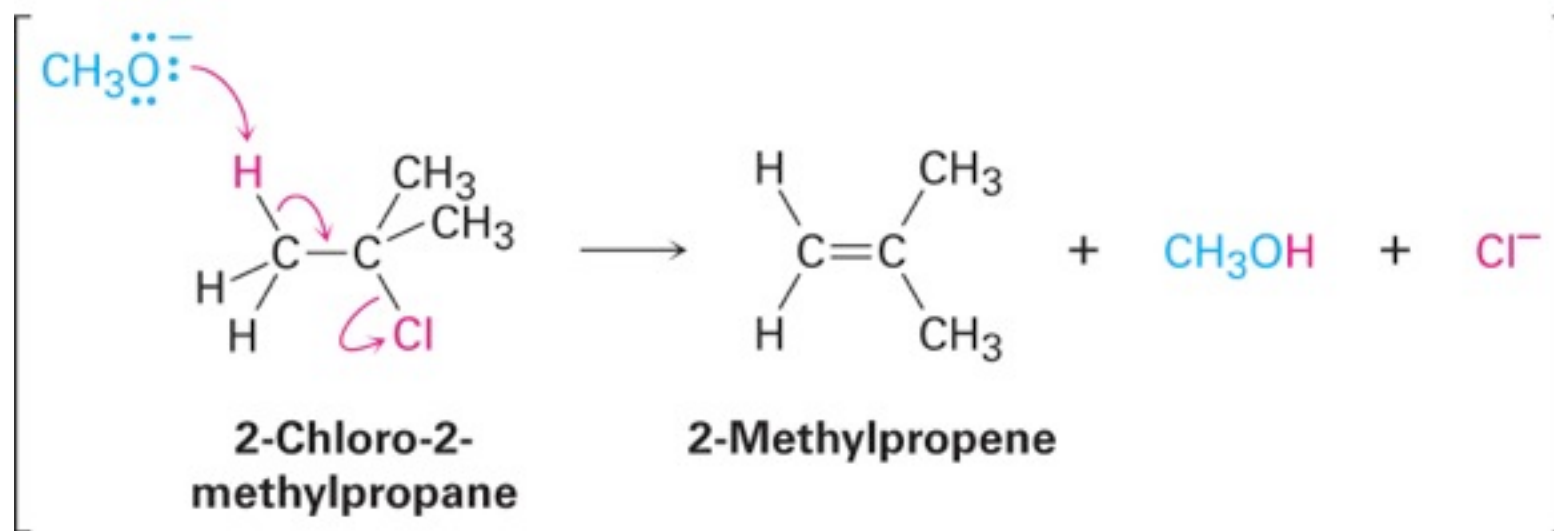
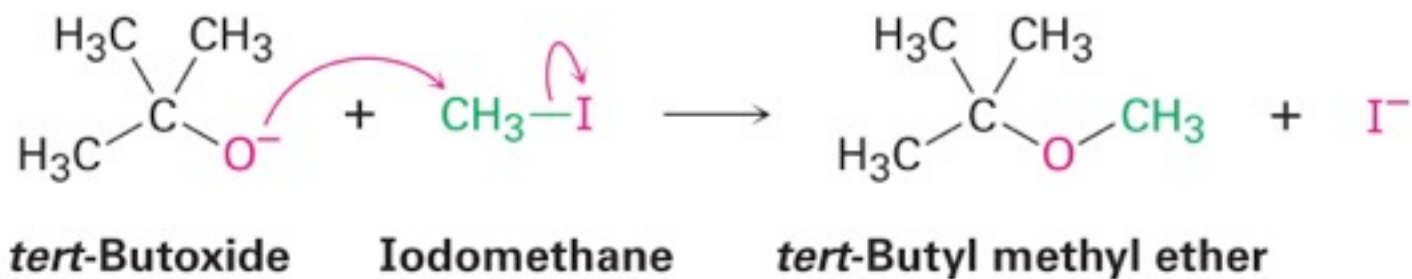


Isopropyl methyl ether

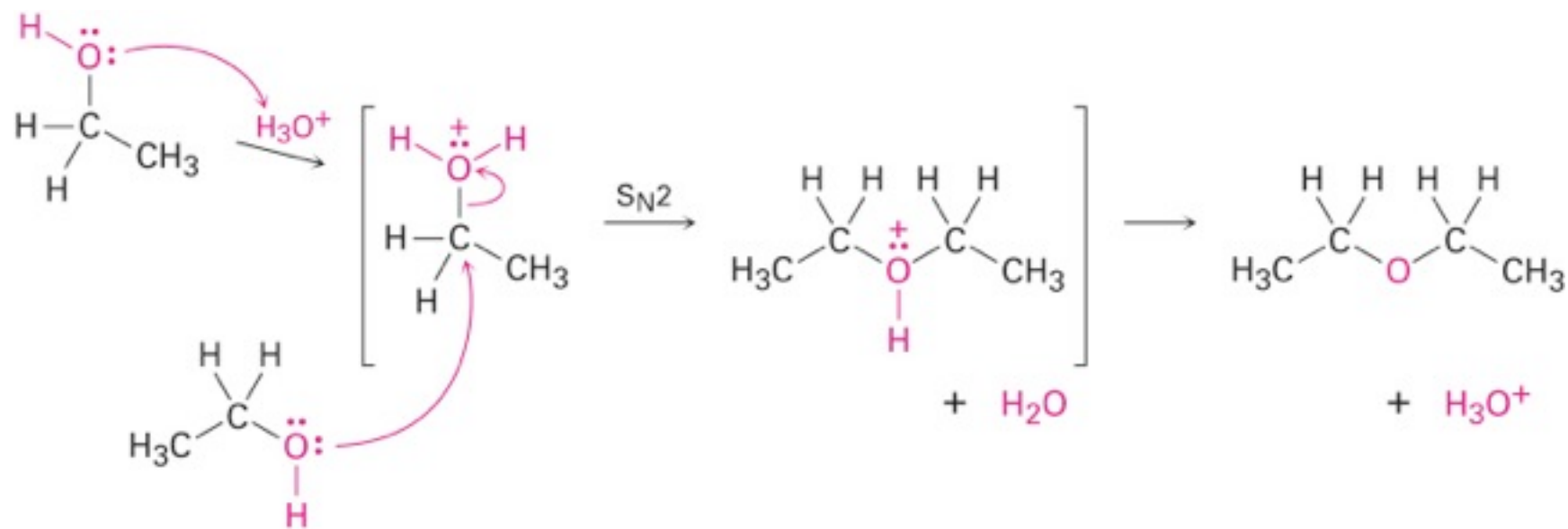


Ethyl phenyl ether

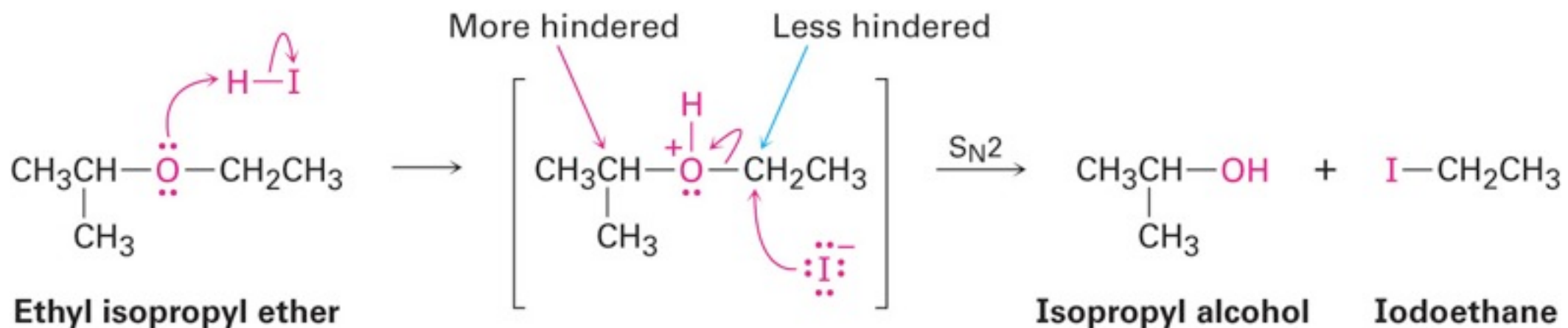
Sterically hindered - good base



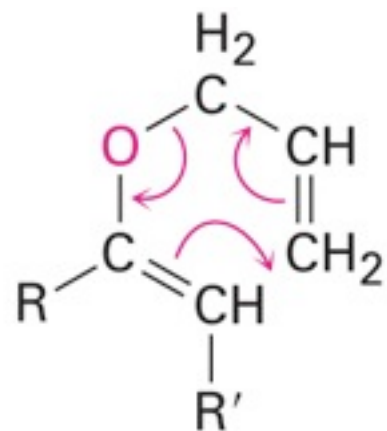
Dimerization



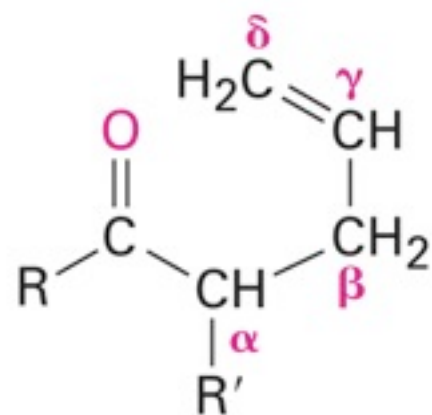
- Ethers are generally unreactive
- Strong acid will cleave an ether at elevated temperature
- HI, HBr produce an alkyl halide from less hindered component by S_N2 (tertiary ethers undergo S_N1)



Claisen Rearrangement

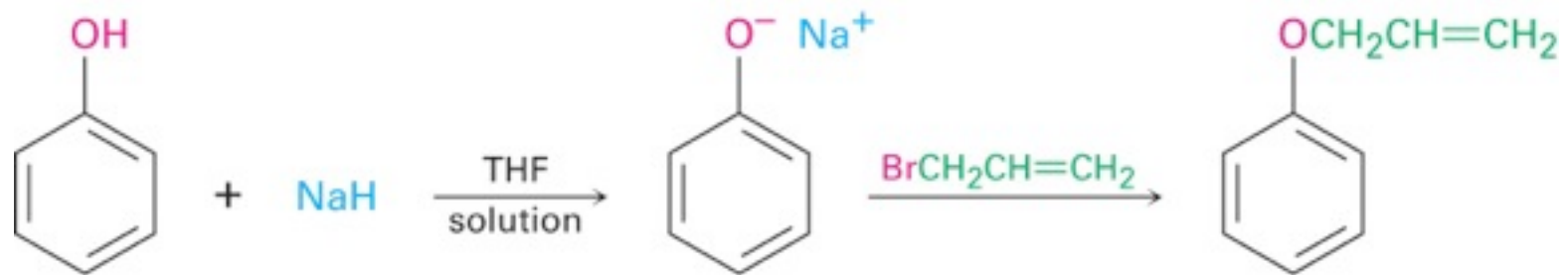


An allyl vinyl ether



A γ,δ unsaturated ketone

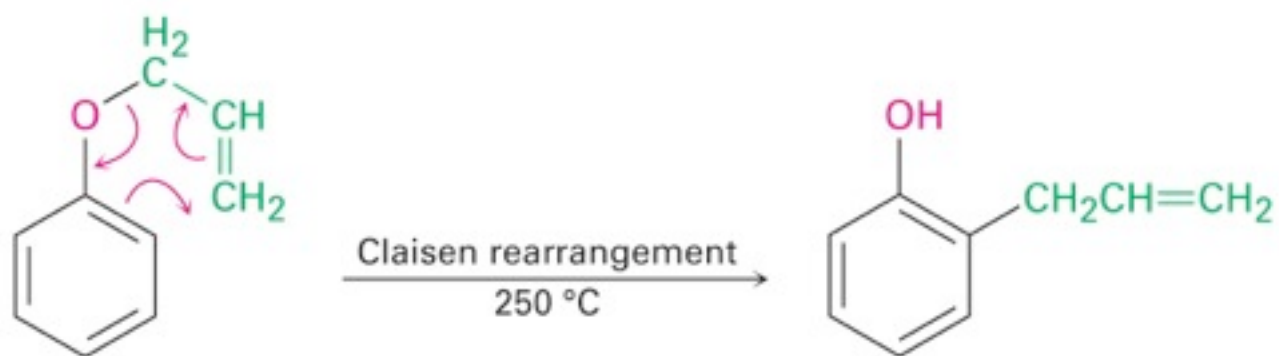
Claisen Rearrangement



Phenol

Sodium phenoxide

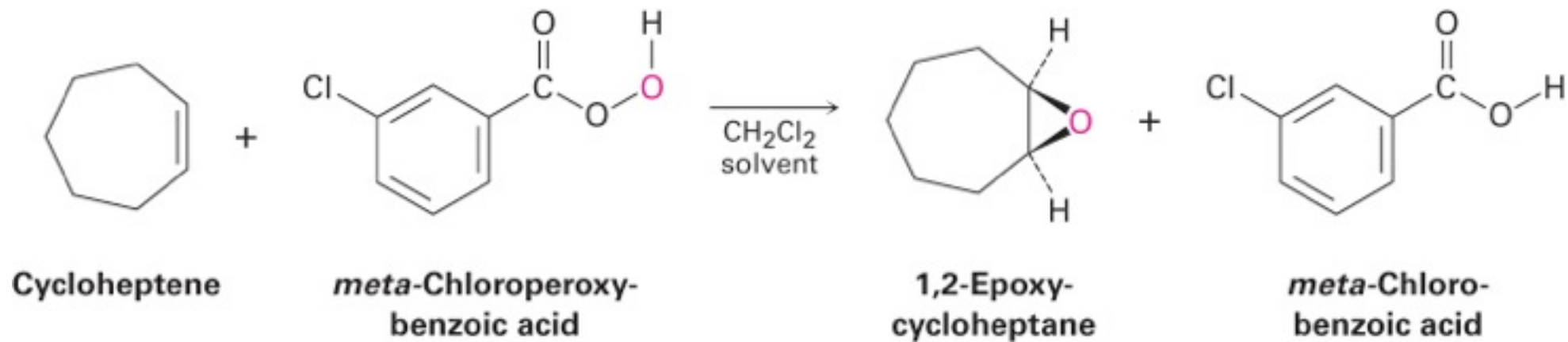
allyl vinyl ether



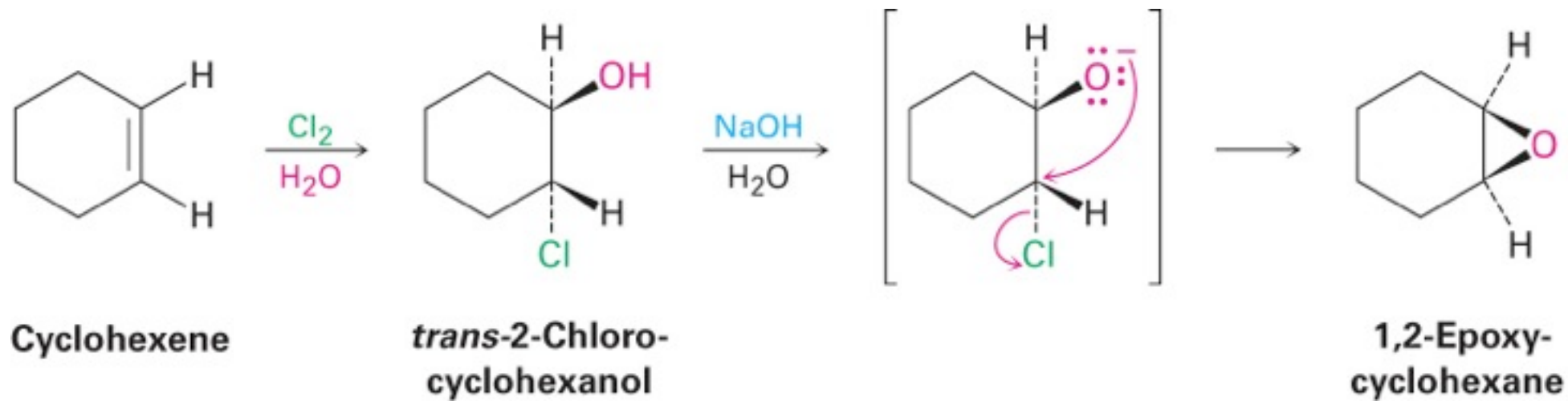
allyl vinyl ether

o-Allylphenol

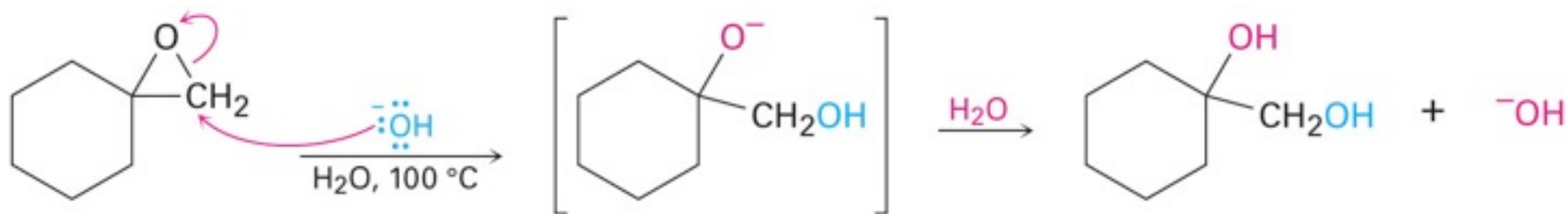
Epoxides via peracids



Epoxides via α -halo-alcohols (halohydrin)



Nucleophilic ring-opening



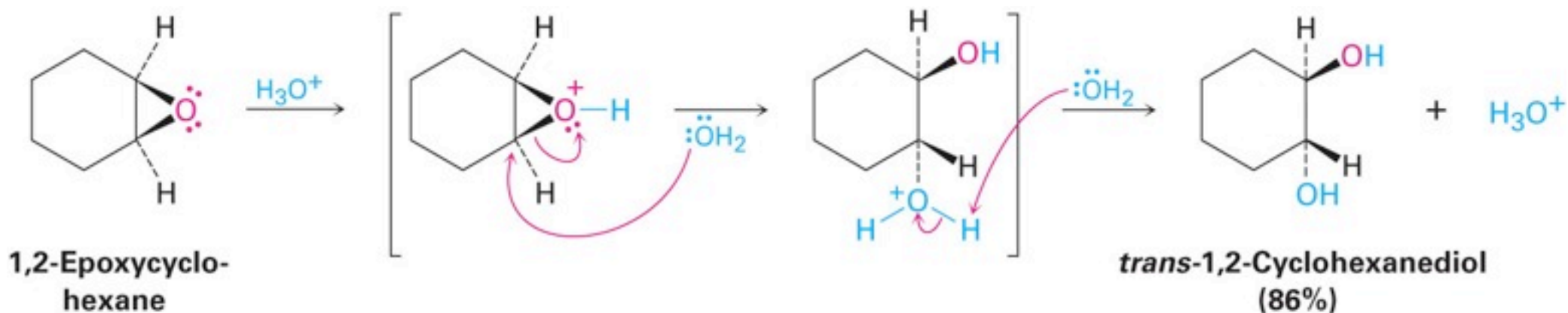
Methylenecyclohexane
oxide

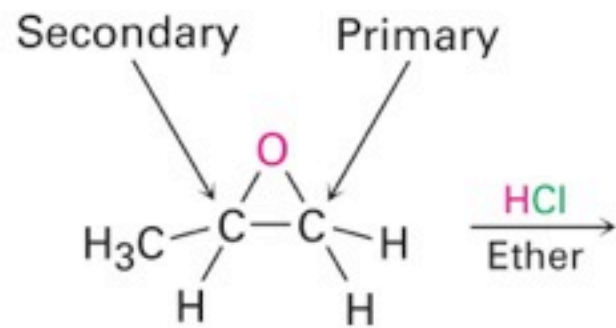
1-Hydroxymethyl-
cyclohexanol (70%)

attack at sterically most accessible carbon ($\text{S}_{\text{N}}2$)

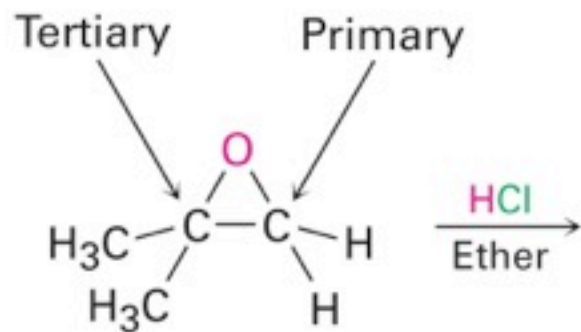
Acid-catalyzed ring-opening

- Water adds to epoxides with dilute acid at room temperature
- Product is a 1,2-diol (on adjacent C's: *vicinal*)
- Mechanism: acid protonates oxygen and water adds to opposite side (*trans* addition)





1,2-Epoxypropane

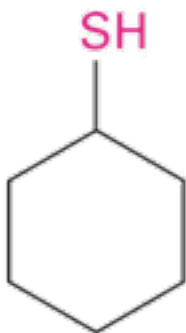


2-Methyl-1,2-epoxypropane

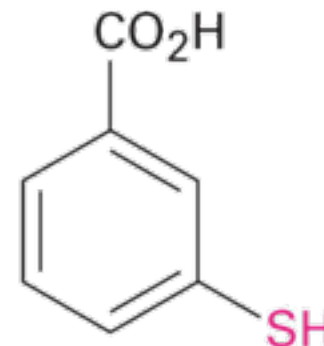
- **Thiols (RSH)**, are sulfur analogues of alcohols
 - Named with the suffix *-thiol*
 - SH group is called “mercapto group” (“capturer of mercury”)



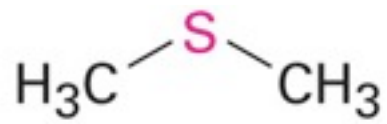
Ethanethiol



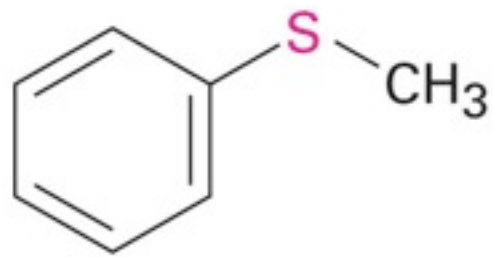
Cyclohexanethiol



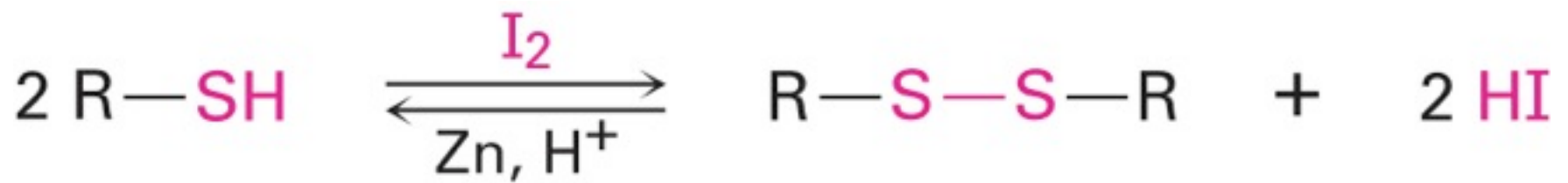
m-Mercaptobenzoic acid



Dimethyl sulfide

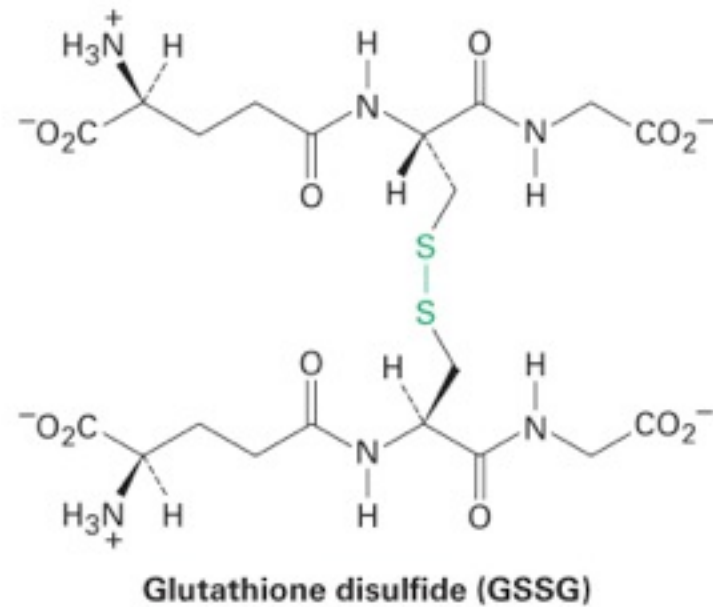
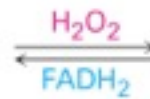
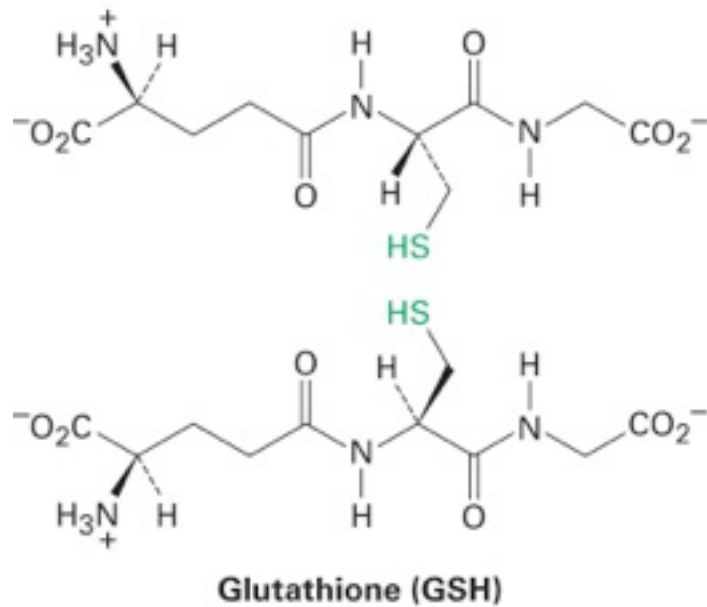


Methyl phenyl sulfide

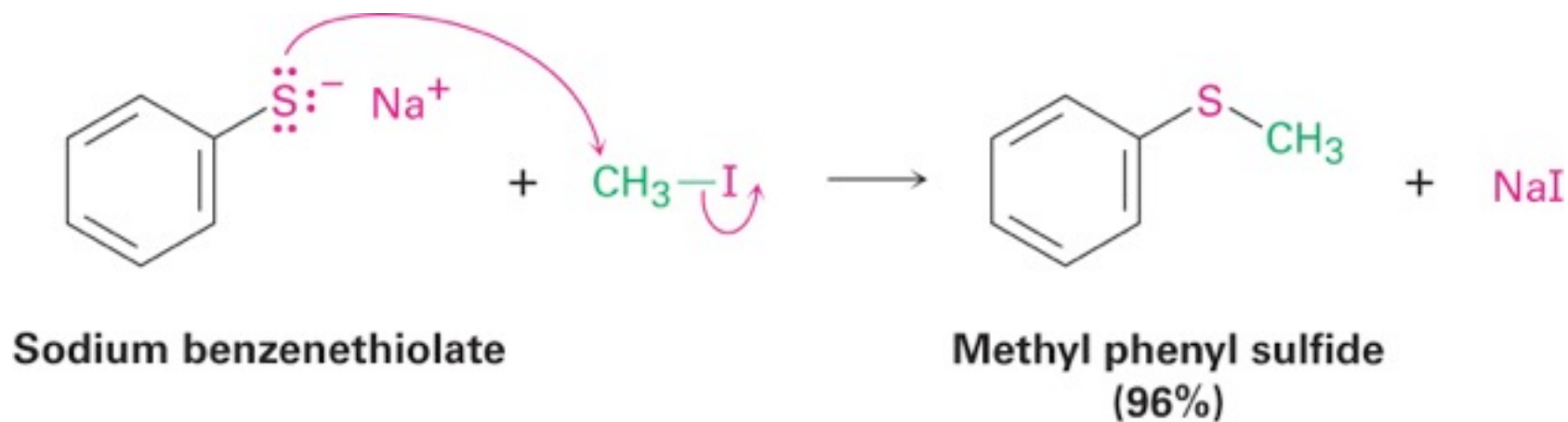


A thiol

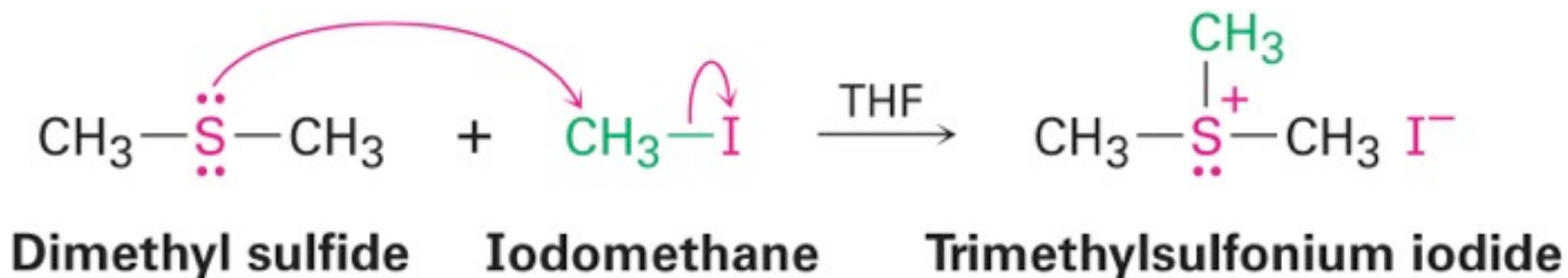
A disulfide

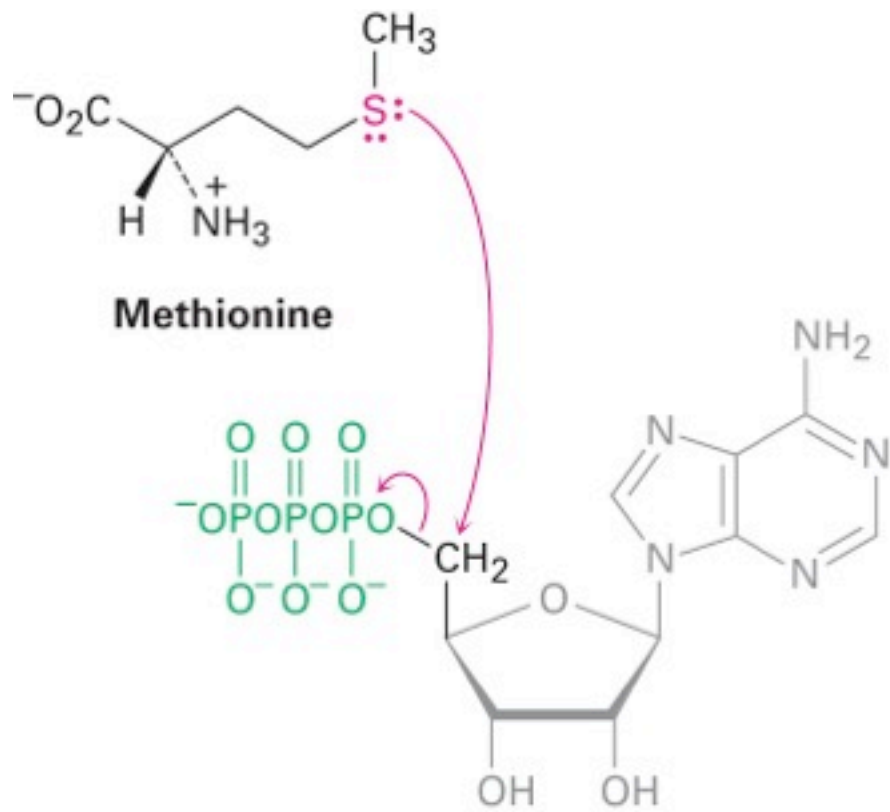


- **Thiolates (RS⁻)** are formed by the reaction of a thiol with a base
- Thiolates react with primary or secondary alkyl halide to give sulfides (RSR')
- Thiolates are excellent nucleophiles and react with many electrophiles

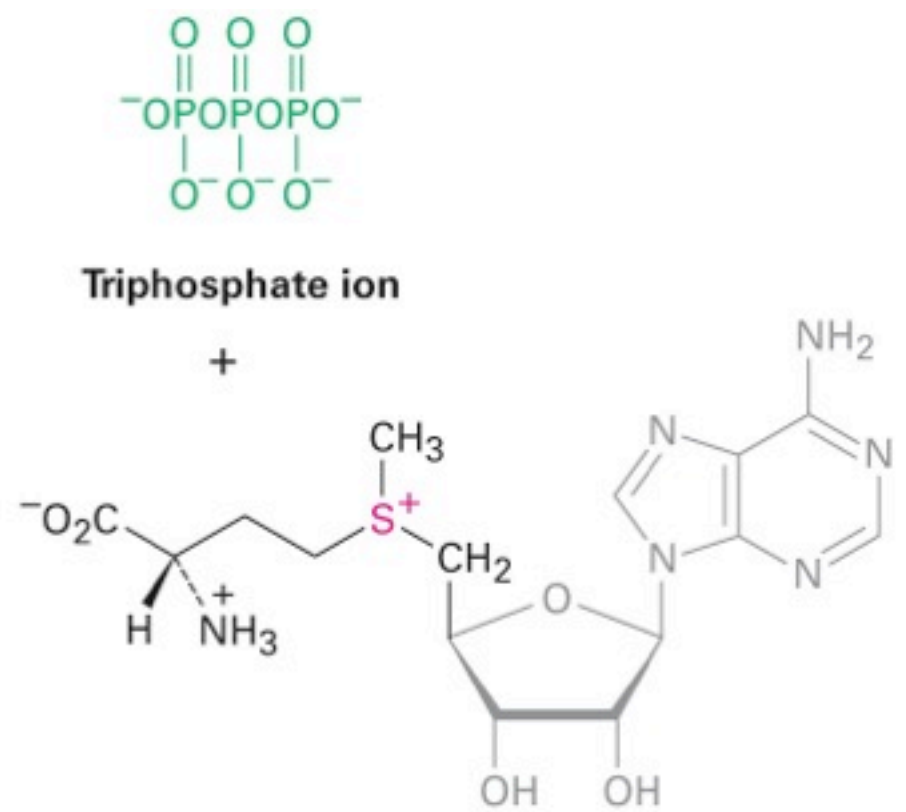


- Sulfur compounds are more nucleophilic than their oxygen-compound analogues
 - 3p valence electrons (on S) are less tightly held than 2p electrons (on O)
- Sulfides react with primary alkyl halides (S_N2) to give trialkylsulfonium salts (R₃S⁺)





S_N2



- Sulfides are easily oxidized with H_2O_2 to the sulfoxide (R_2SO)
- Oxidation of a sulfoxide with a peroxyacid yields a sulfone (R_2SO_2)
- Dimethyl sulfoxide (DMSO) is often used as a polar aprotic solvent

