

## Chapter 13

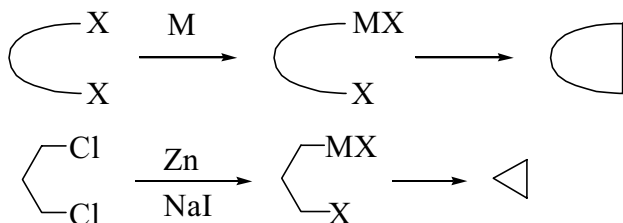
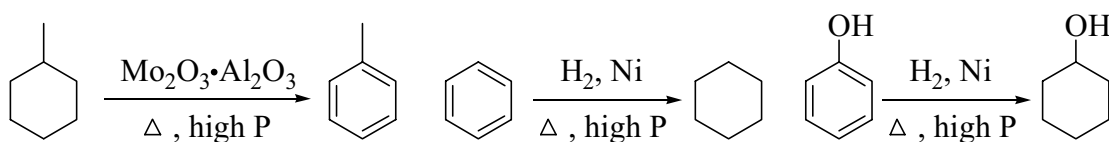
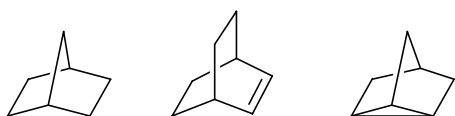
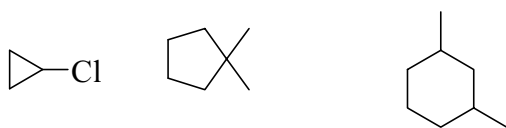
comps to form chains : open-chain comps

comps to form ring : cyclic comps  $\longrightarrow$  alicyclic comps



chemistry is similar  
to open-chain comps

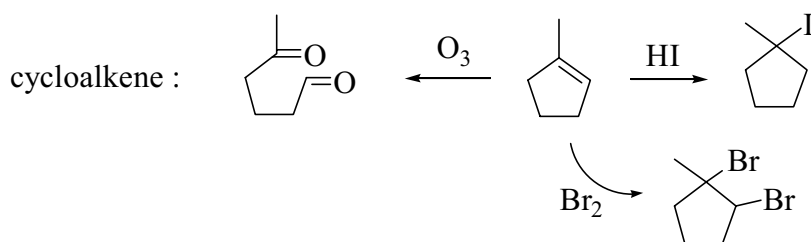
nomenclature

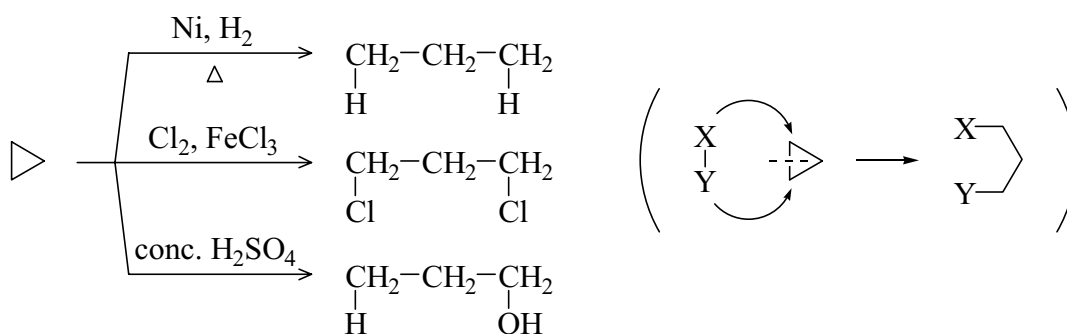


intramolecular rxn cf) intermolecular rxn

cycloaddition

cycloalkane : halogenation by free radical mechanism





general trend  
for addition rxn      alkene > cyclopropane > cyclobutane

Baeyer : strain theory  $\rightarrow$  deviation from  $109.5^\circ$   
 cyclopropane :  $109.5 - 60 = 49.5^\circ$   
 cyclobutane :  $109.5 - 90 = 19.5^\circ$

heats of combustion  $\rightarrow$  relative stabilities  $\rightarrow$   $-\text{CH}_2-$  group of open-chain alkane  
 157.4 kcal

↓  
 Table 13.2  $\leftarrow$  compare with Baeyer theory  $\leftarrow$  rings are flat?  $\leftarrow$  puckered  
 ↓  
 cyclopropane : planar

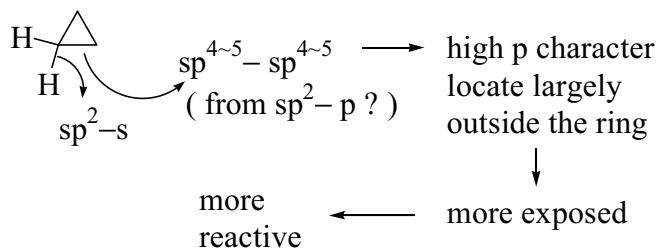
cyclobutane : puckered in spite of increased angle strain  
 cyclopentane

↓  
 large rings are stable  $\rightarrow$  Is it easy to synthesize them?  $\rightarrow$  No

↓  
 Why?  $\leftarrow$  the larger ring  $\leftarrow$  (intramolecular rxn, intermolecular rxn)  $\leftarrow$  high dilution  
 ↓  
 the longer chain  
 ↓  
 the less likely the two ends of the chain approach each other

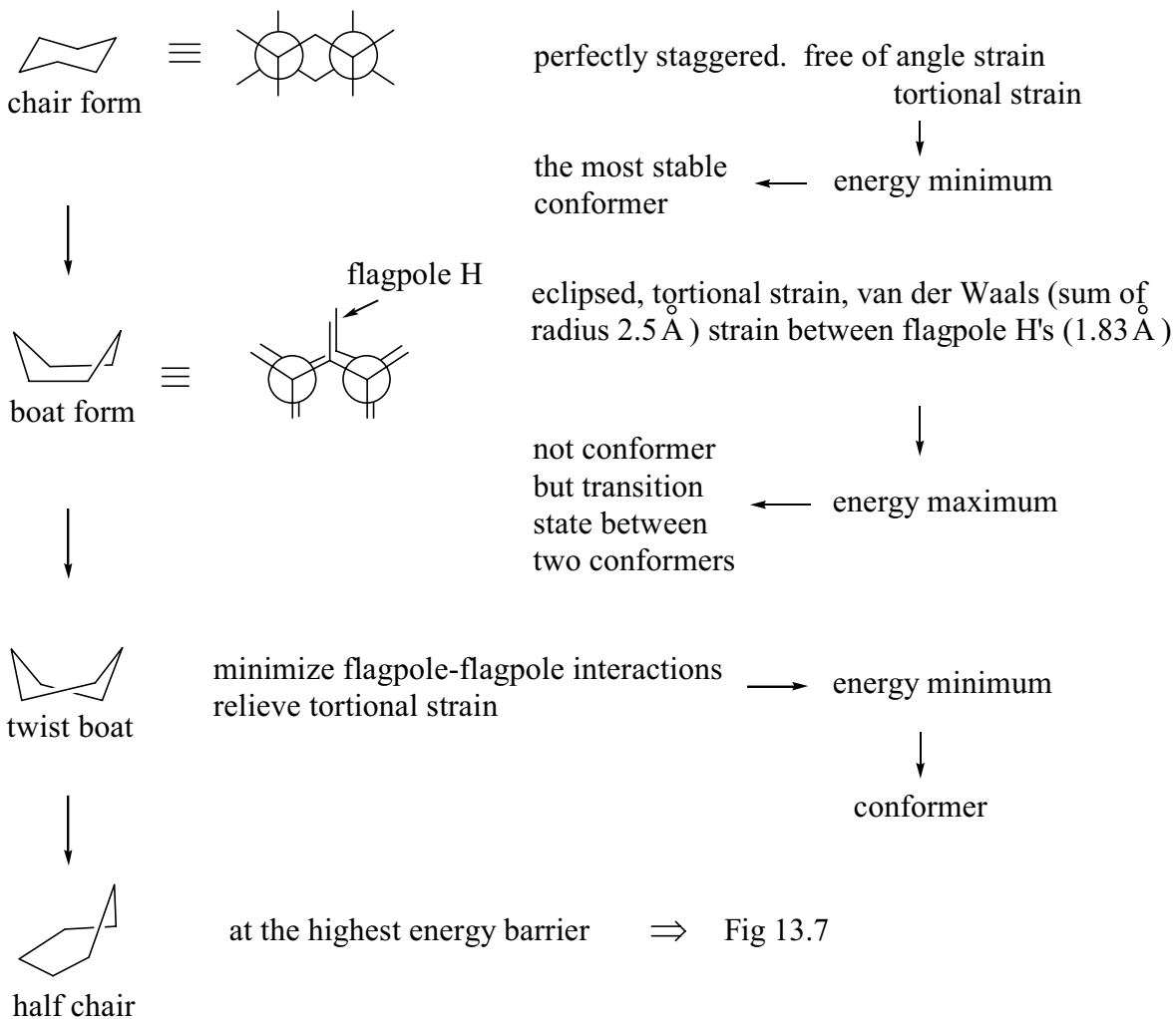
the greater overlap of atomic orbital  $\rightarrow$  the stronger bond  $\rightarrow$  C :  $109.5^\circ$   
 for the strongest bond  
 higher reactivity  $\leftarrow$  weaker bond  $\leftarrow$  less overlap (Fig 13.3)  $\leftarrow$  for cyclopropane  $60^\circ$   $\leftarrow$  bond

quantum mechanics :



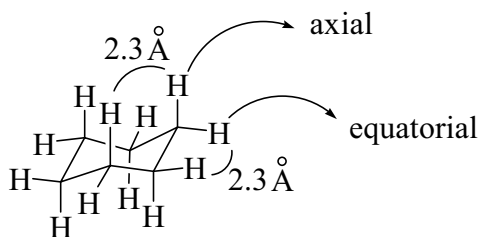
chemistry of cyclic compd  $\Rightarrow$  conformational analysis  $\Rightarrow$  angle strain, torsional strain, van der Waals strain (steric strain)  
 dipole-dipole interaction

cyclohexane

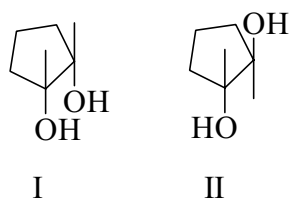
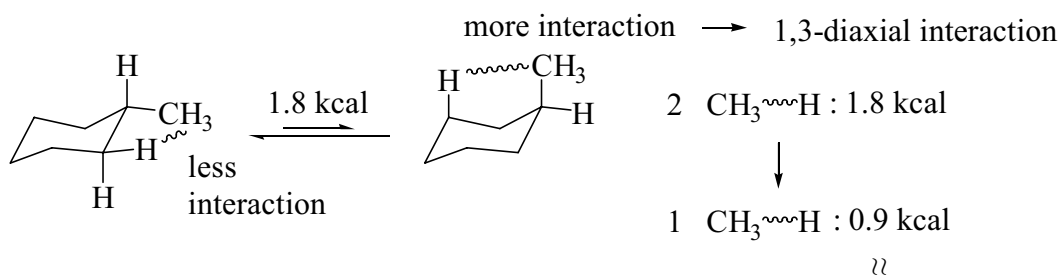


cyclopentane  $\longrightarrow$  puckered at the cost of angle strain due to torsional strain

cyclobutane  $\longrightarrow$  puckered at the cost of angle strain due to torsional strain



2.3 Å is favorable distance



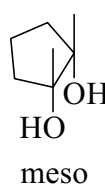
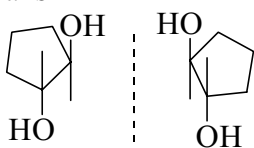
different orientation in space → stereoisomer

not conformational isomer but configurational isomer ← no interconversion by rotation

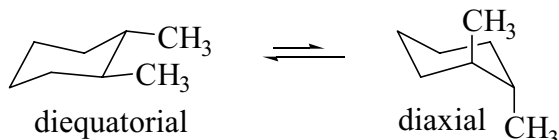
diastereomer ← not mirror image

I : cis

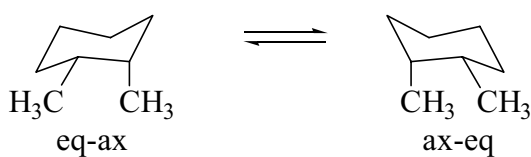
II : trans



trans -1,2-dimethylcyclohexane

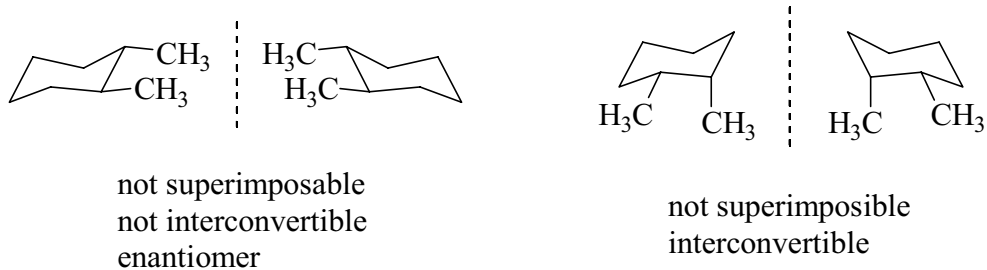


cis-1,2-dimethylcyclohexane

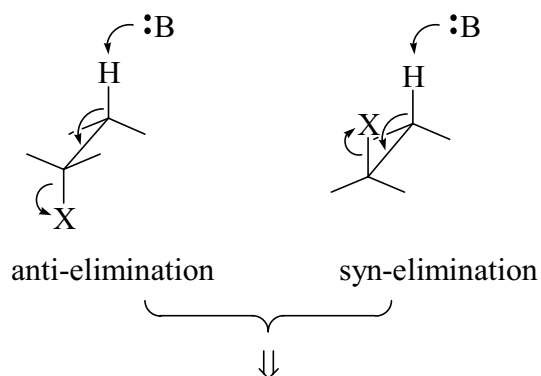


trans is more stable than cis : the same distance between methyl groups.  
the difference is 1,3-diaxial interactions.  
~ 1.8 kcal/mole is more stable.

t-Butyl group locks the molecule in a single conformation.

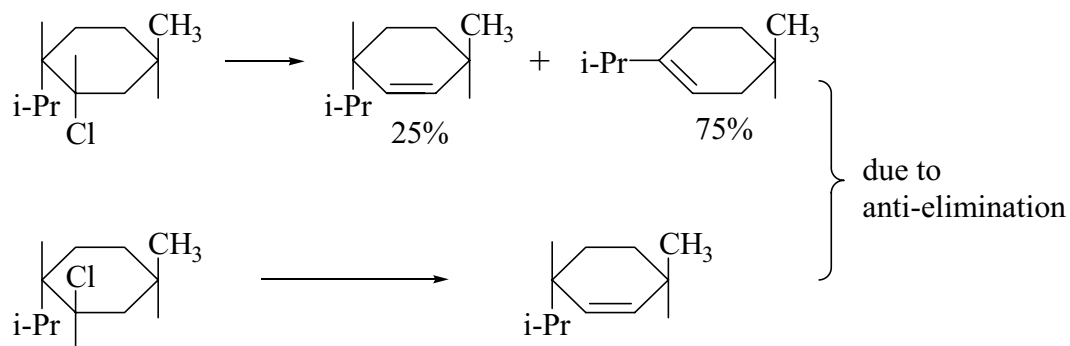


### Elimination



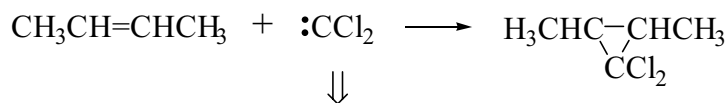
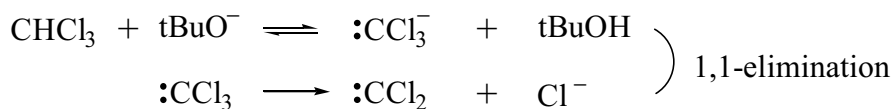
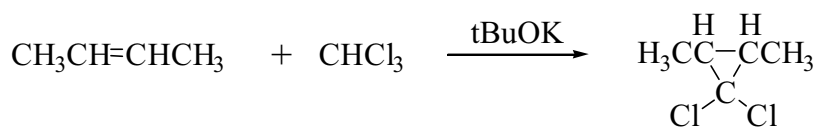
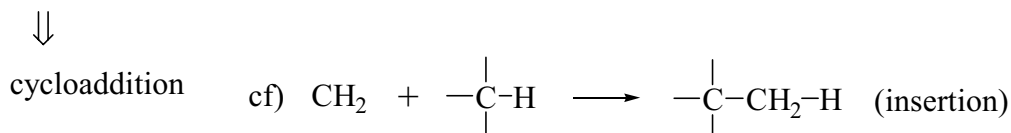
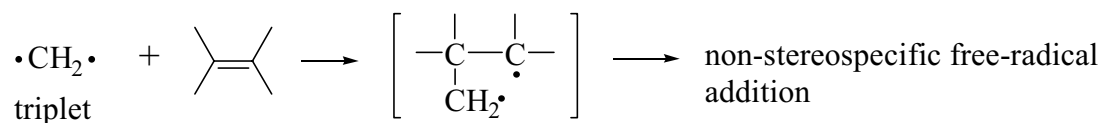
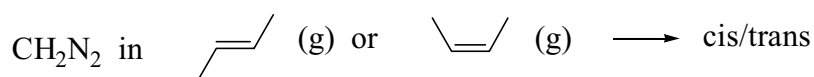
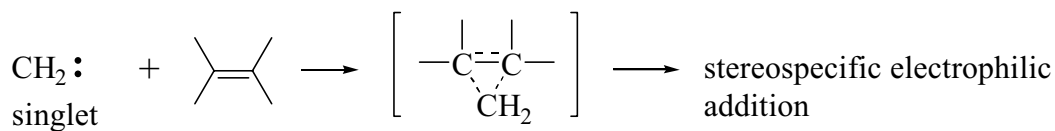
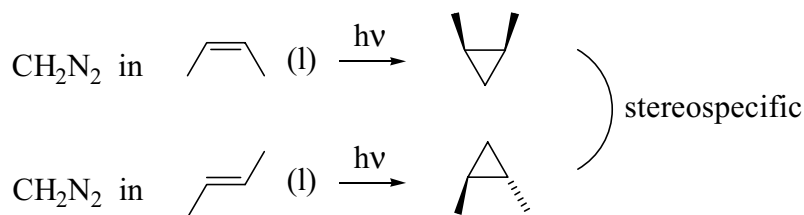
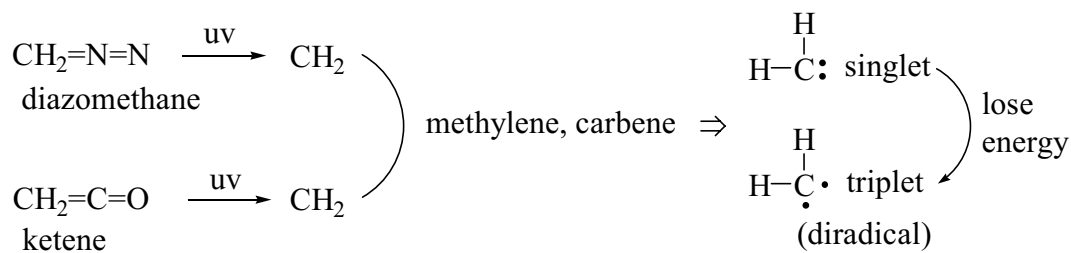
electronically periplanar eliminations are the most favorable.

anti-elimination is more favorable due to conformational effects

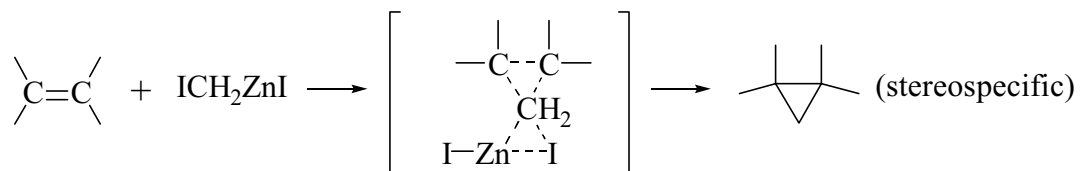
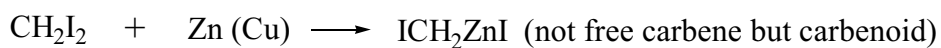


cyclohexane : syn-elimination → difficult

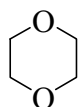
cyclopentane : syn-elimination → easy



$\Downarrow$   
 believed to be singlet  $\Rightarrow$  stereospecific addition (syn)



cyclic ethers



1,4-dioxane



furan

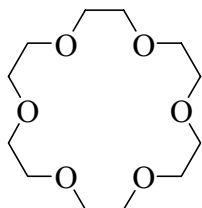


tetrahydrofuran (THF)

18-crown-6 :



18 atoms in the ring  
6 oxygen atoms



interior : hydrophilic

exterior : lipophilic

hole : 2.7 Å diameter



K<sup>+</sup> : 2.66 Å diameter



loose ion pair  $\leftarrow$  potassium salt can be delivered into organic layer  $\leftarrow$  fit to 18-crown-6



anion is very reactive

18-crown-6 : host

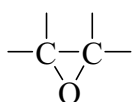
15-crown-5  $\Rightarrow$  Na<sup>+</sup>

K<sup>+</sup> : guest

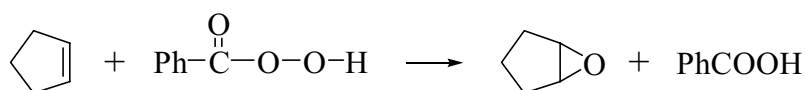
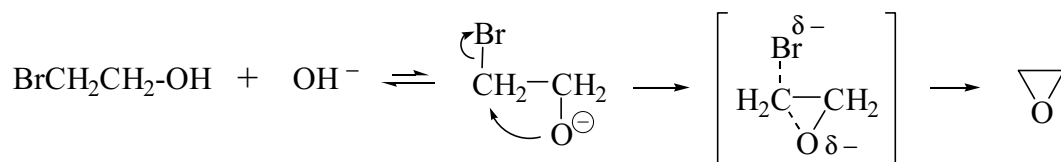
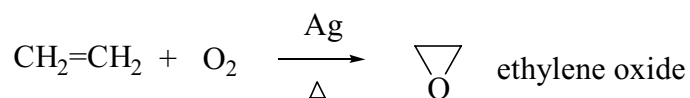
12-crown-4  $\Rightarrow$  Li<sup>+</sup>

)  $\Rightarrow$  antibiotics

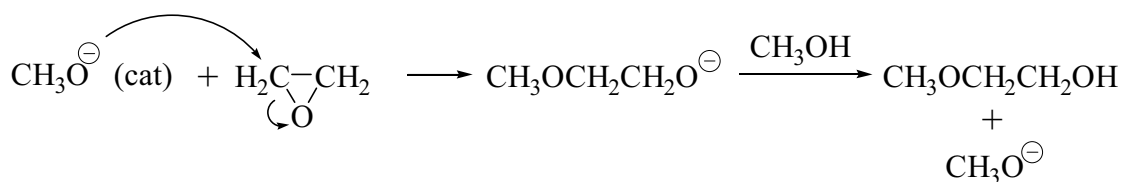
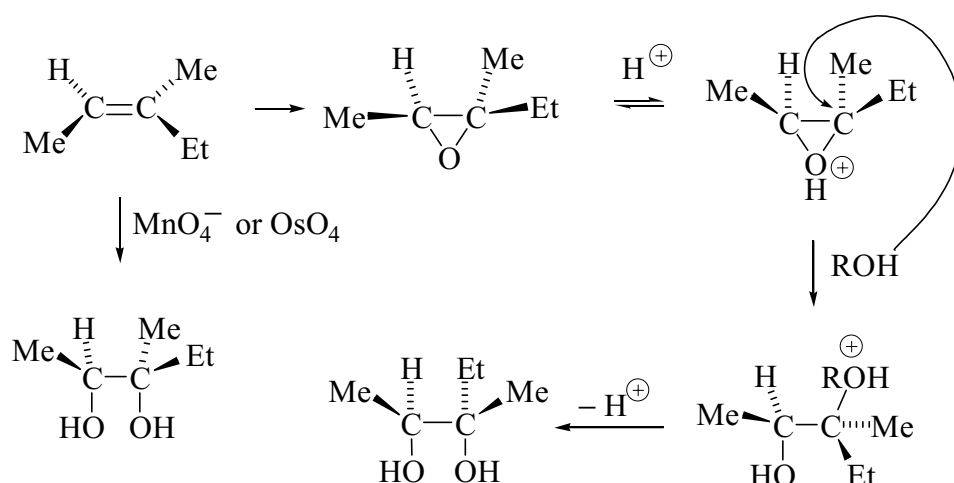
epoxide :



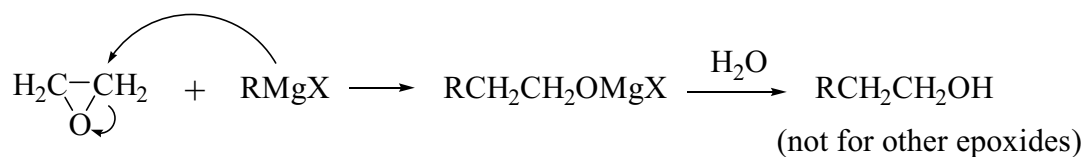
(oxirane)

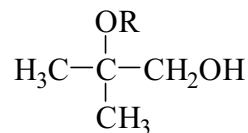
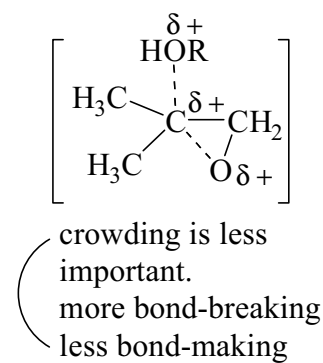
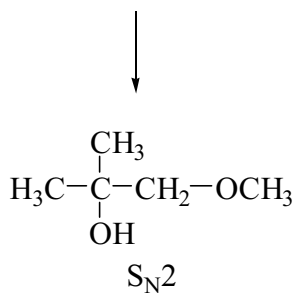
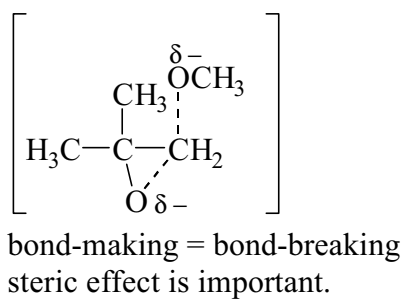
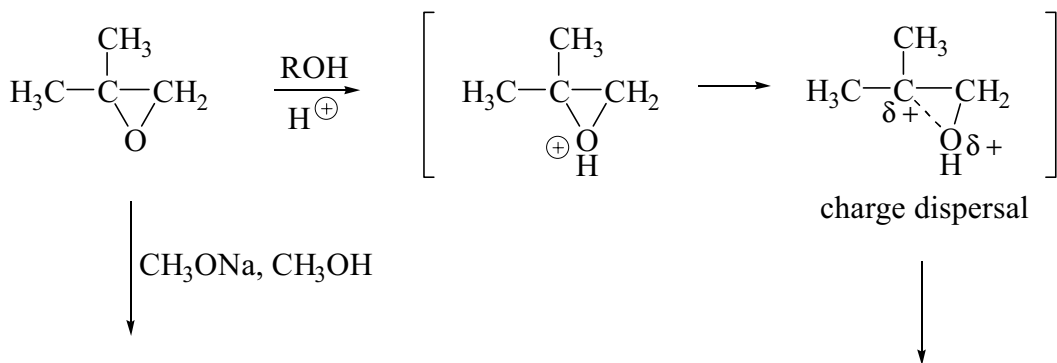


epoxide is reactive due to angle strain.



(require strong Nu under alkaline conditions)





( not S<sub>N</sub>1  
S<sub>N</sub>2-like )



( olefin + Br<sub>2</sub> + H<sub>2</sub>O  
+ IN<sub>3</sub> or BrN<sub>3</sub> )

