

# Ch. 14 - Wade

## Ethers, Epoxides & Sulfides

Read 14-1 to 14-2

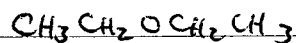
### Nomenclature

General Structure  $R-O-R'$

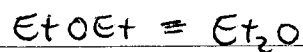
#### Simple Systems

- Name both sides ~~then~~ + ether

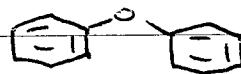
ie.,



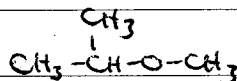
diethyl ether



"Ether"



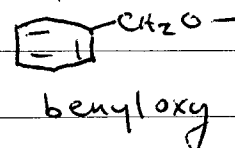
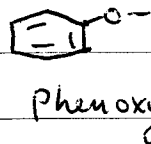
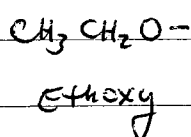
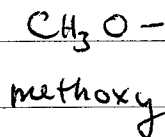
diphenyl ether



isopropyl methyl ether

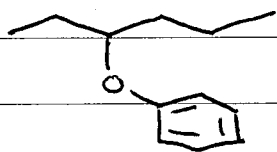
#### More complex systems

- Name as a subst.

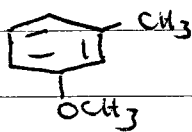


alkoxy groups

Aryloxy group



3-phenoxy hexane



1-methoxy-3-methyl benzene  
3-methoxy toluene

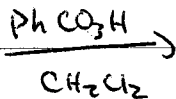
### Cyclic ethers

-heterocyclic compds - cyclic molecule w/ atom other than "C" in ring

### Epoxides



recall,

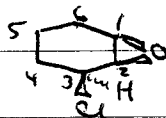


cyclohexene oxide

→ name of cycloalkene + oxide

Also (IUPAC) → name as alkene/ane + epoxy

i.e.)

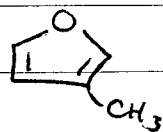
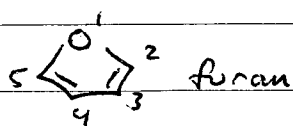


cis - 3-chloro - 1-epoxy cyclohexane

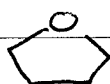
### Oxetanes



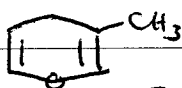
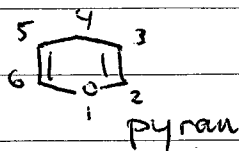
5-6 membered rings



3-methyl furan



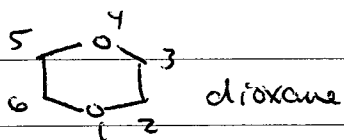
tetrahydrofuran (THF)



3-methyl pyran

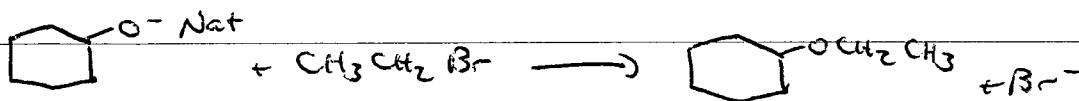
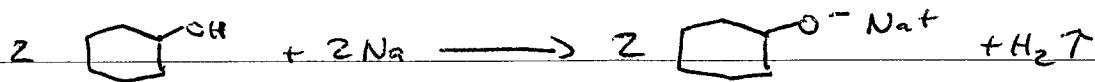


tetrahydropyran



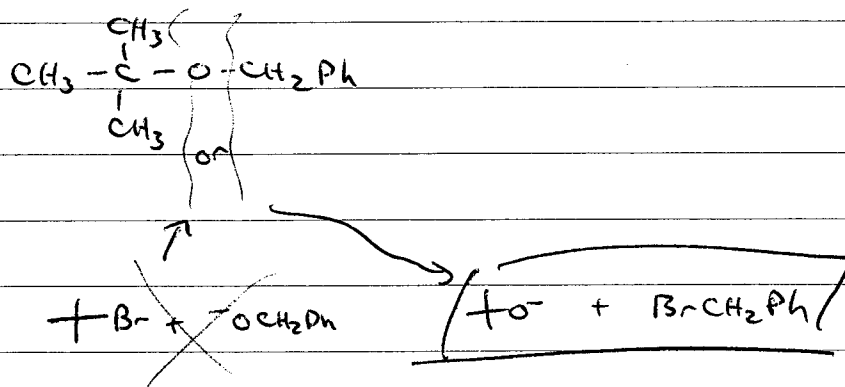
## Ether Synthesis - Alkoxide anions as nucleophiles

### Williamson Ether synthesis

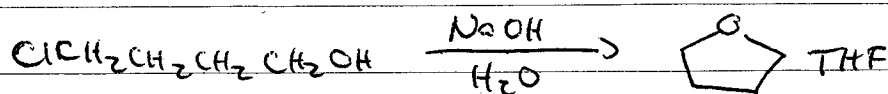


Generally want to use 1° alkyl halides as electrophiles  
↳ avoids E2 eliminations

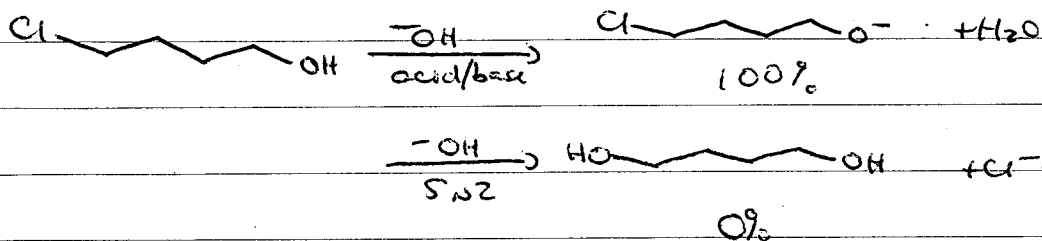
How to make  $(\text{CH}_3)_3\text{COCH}_2\text{Ph}$ ?



Intramolecular Rxns of Alkoxides: Cyclizations

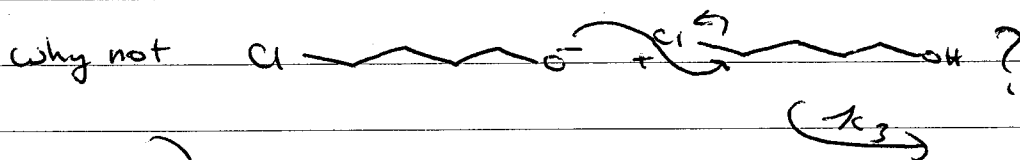
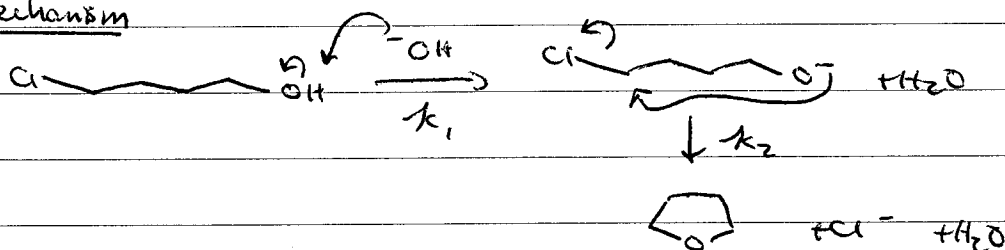


2 competing Rxns:



Acid base Rxns Always faster

Mechanism

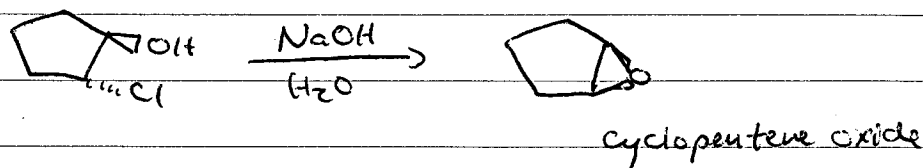


Intramolecular Rxns are ALWAYS faster than intermolecular rxns

$\therefore k_1, k_2 \gg k_3$

Skip 4-6, 4-7

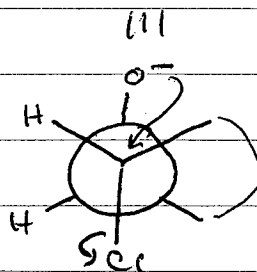
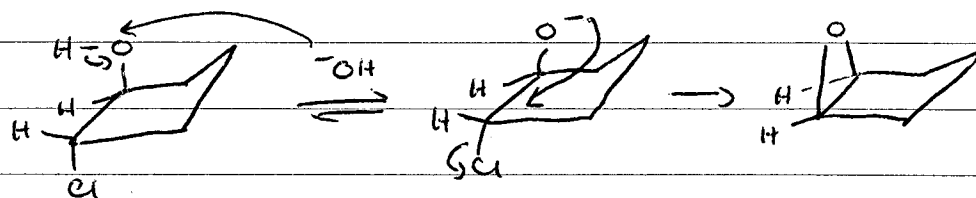
Formation of epoxides can also be accomplished in this manner;



Notice stereochem!

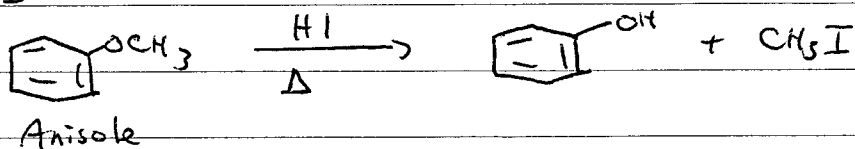


Mechanism

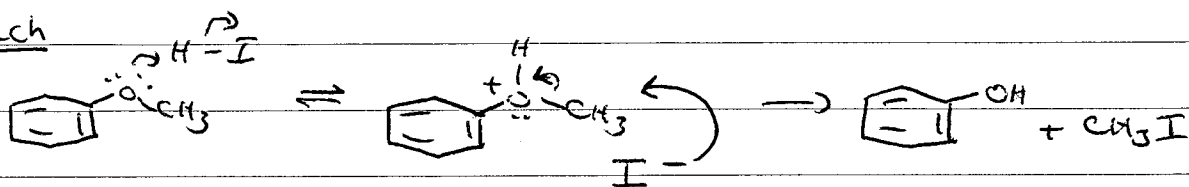


# Ether cleavage w/ HBr, HI

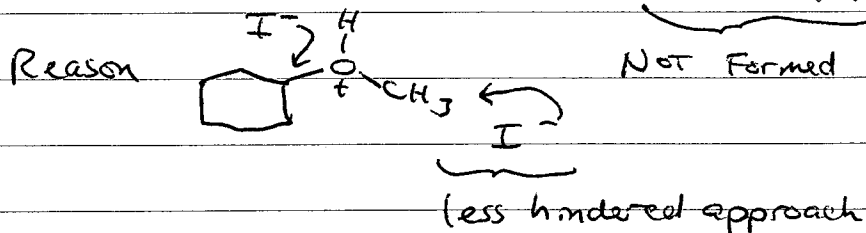
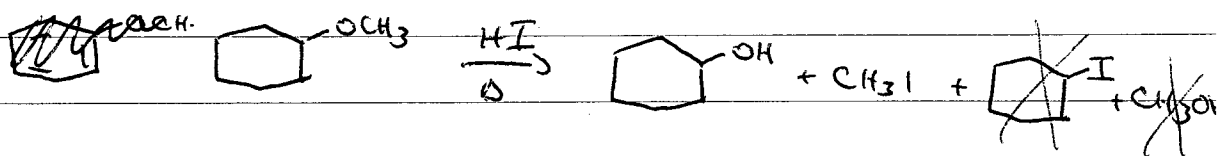
1) HI



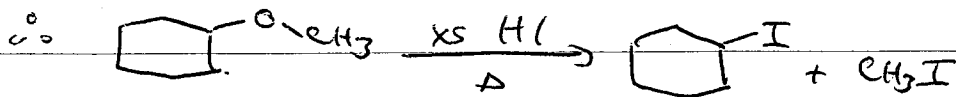
Mech



Also,

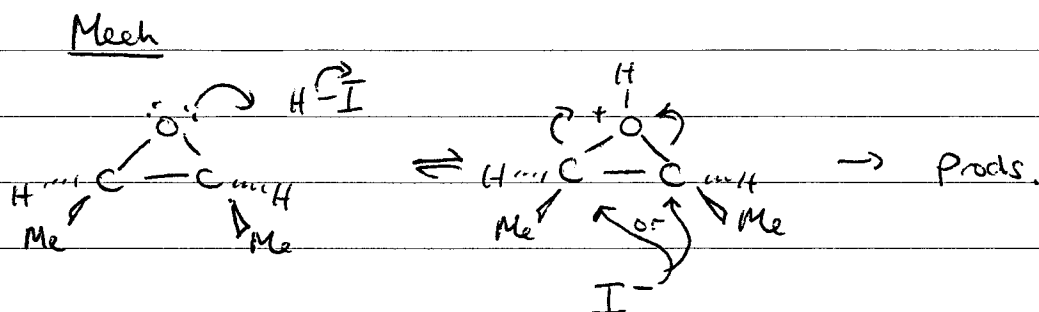
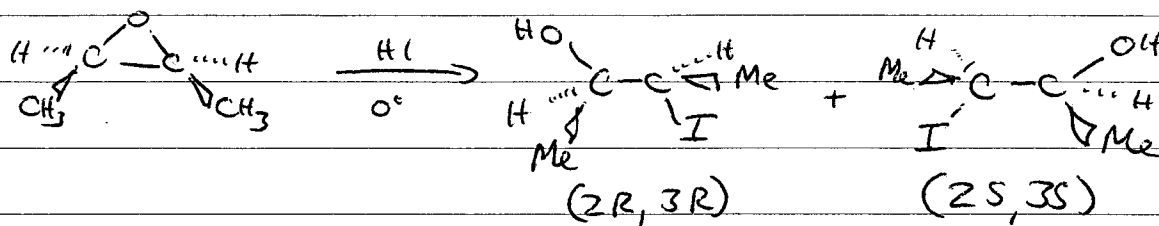


If enough HI, will get RI + R'I



NOTE: Oc1ccccc1  $\xrightarrow{HI}$  NR

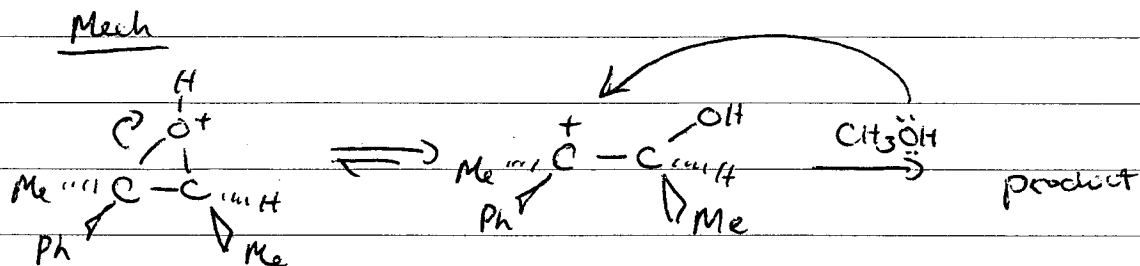
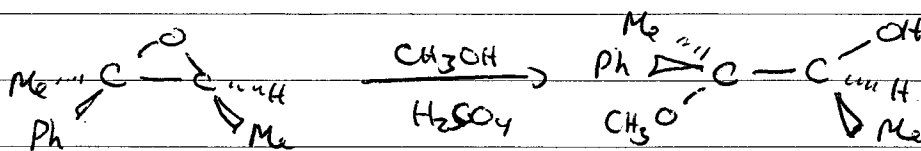
Acid cat. Rxns: Ring opening rxns of epoxides



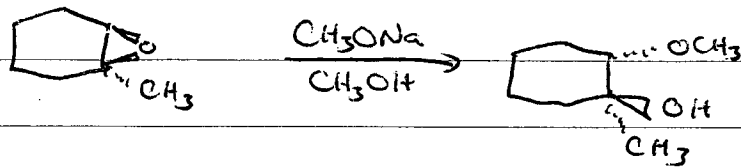
HBr, HCl are similar, except  $HI > HBr >> HCl$

Skip 14-9, 14-10 (read this though!)

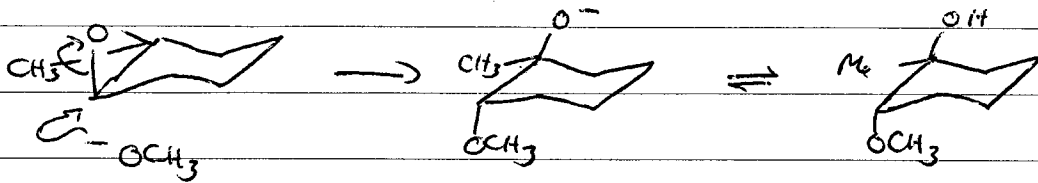
## Asymmetric Epoxide Ring openings



## Ring opening Rxns of epoxides w/ Nucleophiles



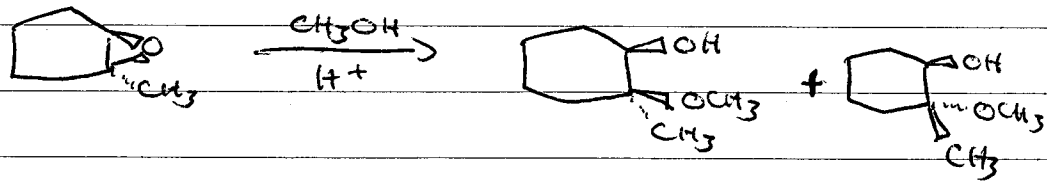
Mech



Rxn occurs at least subst carbon

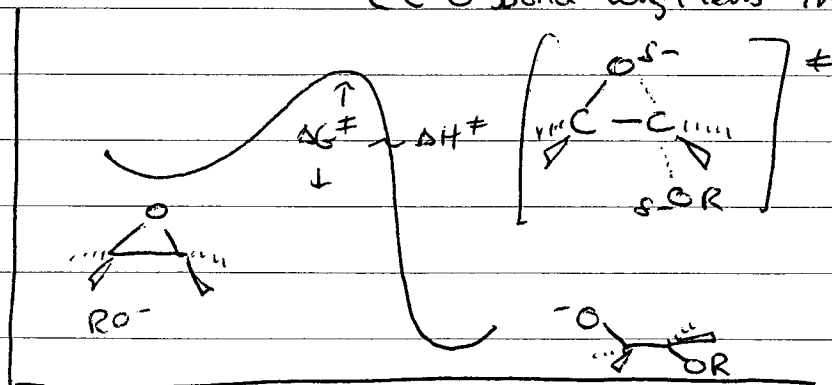
Notice  $^- \text{OH} / \text{OCH}_3$  (Nu) are anti

Notice:  $\text{H}^+$ -cat. rxn goes w/ opposite regiochemistry

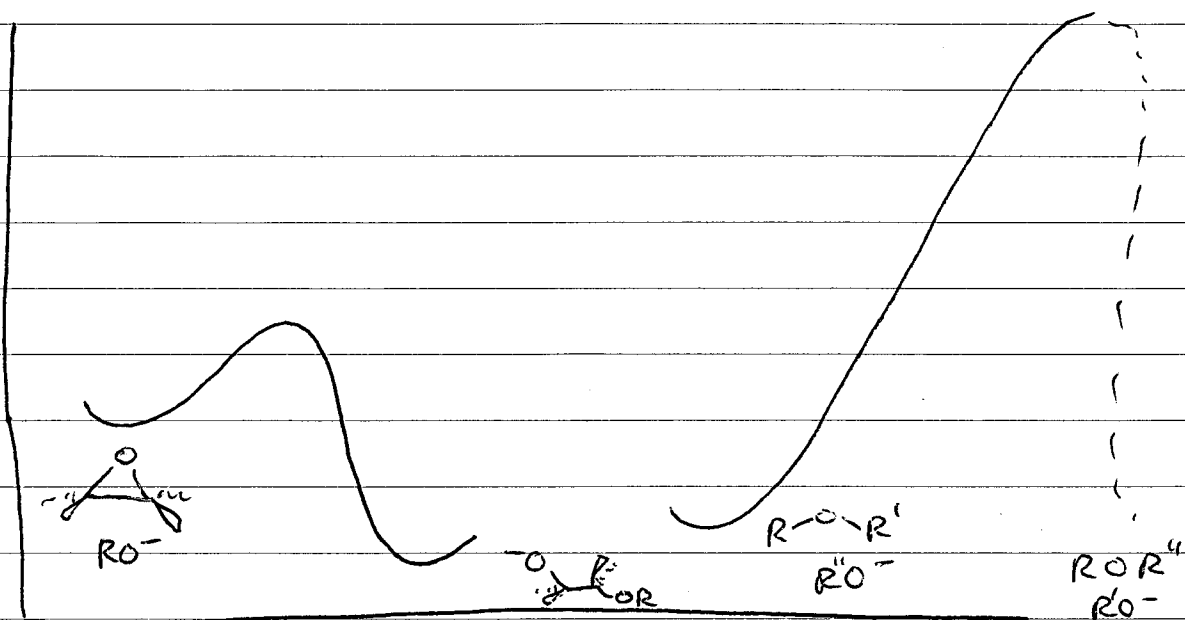
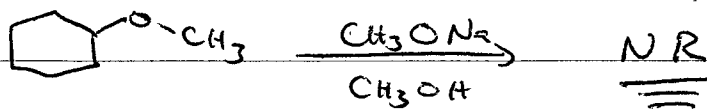


Why does base catalyzed rxn occur?

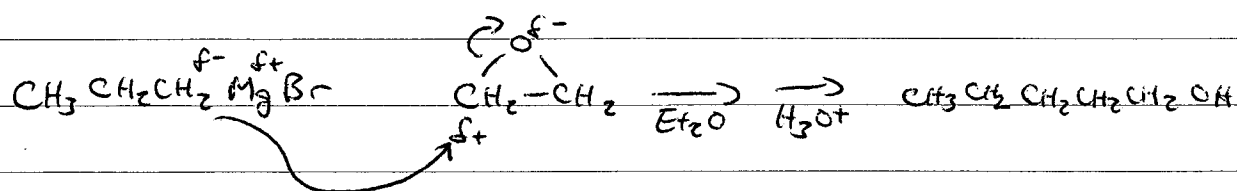
- 1) Relieves strain energy of 3-member ring ( $\Delta H_f = "-"$ )
- 2)  $\Delta H^\ddagger$  is lowered as remove ring strain  
(C-O bond lengthens in TS)



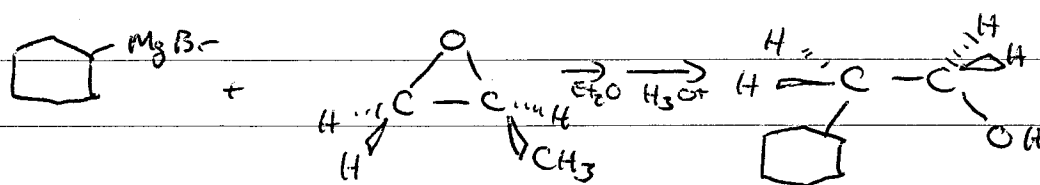
Compare w/ acyclic systems:



# Rxns of Organometallic reagents w/ Epoxides as Electrophiles



also,



Skip 14-16