Ethers

General

Naming

Preparation

Cleavage Reactions

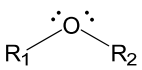
Ref 11 : 1, 10 - 14

Prob HMWK #05

Adv Rdg 16: 1 - 5

General

sp^3 O

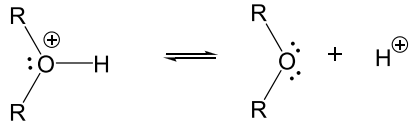


R = alkyl, vinyl, or aryl

• cannot act as acid

• can act as base (both Lewis & B.-L.),

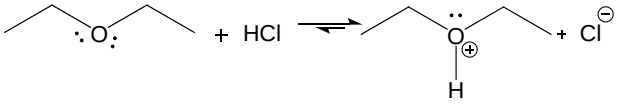
very similar to ROH



"oxonium ion"

pK_a = ~ – 4 (similar to ROH_2^+);

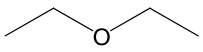
e.g.



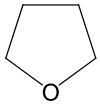
Occurrence, Common Names

commonly used as solvent for rxns,

such as



"ether", diethylether



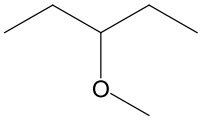
THF, tetrahydrofuran

Systematic Naming

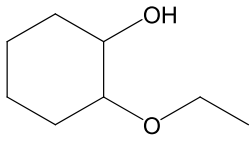
1.)" alkoxyalkane method"

smaller R larger R

Examples

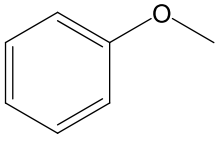


3 - methoxypentane



2 - ethoxycyclohexanol

2.) "alkyl alkyl ether method" ; used commonly;
e.g.,



methyl phenyl ether

Prep

1.) ROH + mineral acid

2.) alkene + peracid
→ epoxide

} *seen before*

3.) Williamson synthesis

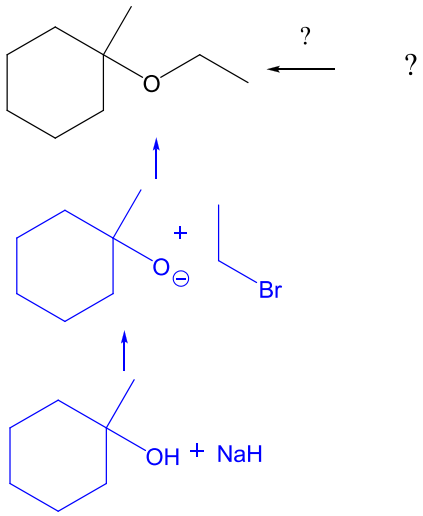
typical S_N2 rxn:

halide/tosylate (1° / 2°) + alkoxide → ether

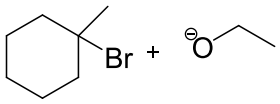
(substrate) (nucleophile)

Note : Ideally, substrate should be 1°

Example:



Alternative:

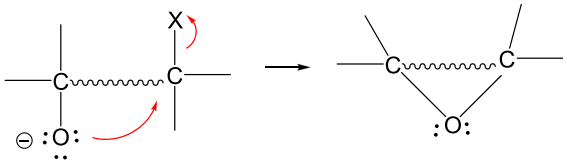


would not work; would get elimination product

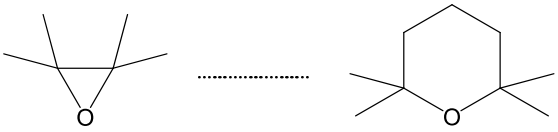
Internal Williamson Rxn

produces cyclic ethers;

general scheme:



can make :



(see HMWK #05 for practice)

Rxns

generally relate to C-O bond breakage

1.) Trtmt w/ strong base

normally no S/E rxn b/c ^-OR poor L.G.

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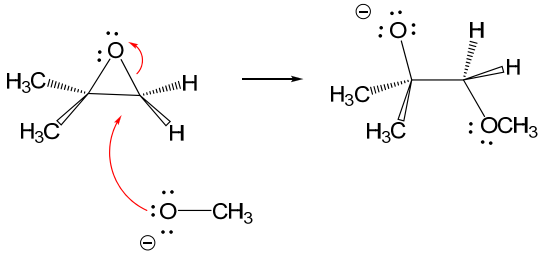
except for epoxides;

which have extra angle strain;

base attacks at less substituted C (better access),

S_N2 style; i.e., inversion of configuration

e.g.



2.) Acidic Cleavage

w/ strong acid, such as $HCl_{(aq)}$, $HBr_{(aq)}$

works b/c oxonium ion is formed
which contains a good L.G. (ROH)

Where does C – O – C split?
Depends on structure of ether!

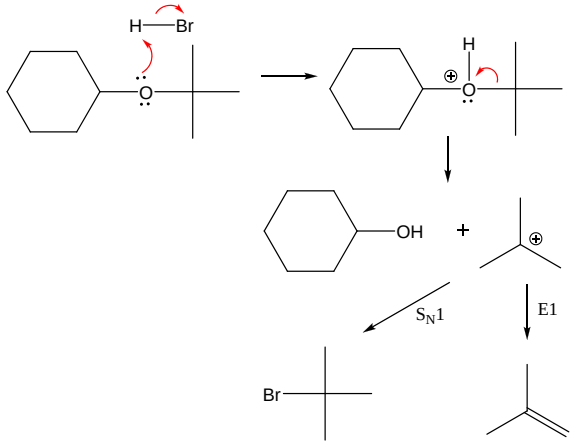
3 different cases:

a.) "tertiary C" present

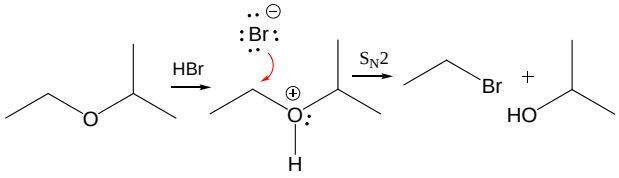
b.) only "primary & secondary C's" present

c.) epoxides

a.) if 3° / allylic C / benzylic C present,
cleaves at that site by S_N1/E1
e.g.,



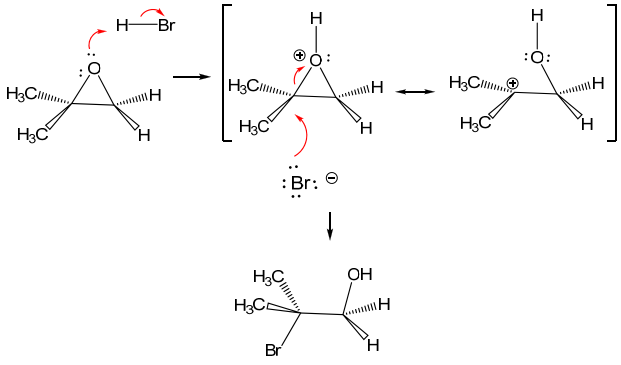
b.) if only 1° / 2° C present,
cleaves by S_N2 at less substituted site
e.g.,



c.) in acidic cleavage of **epoxides**
get both regio- & stereocontrol:

- cleaves at more substituted site &
- forms trans product (*may not be apparent*)

e.g.



Br & OH attached in anti fashion;
inversion of config. takes place at "attack site"