Ethers

General

Naming

Preparation

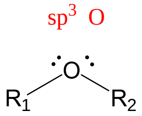
Cleavage Reactions

Ref 11 : 1, 10 – 14

Prob HMWK #05

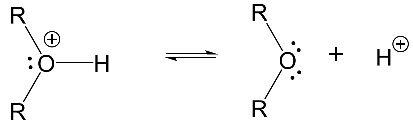
Adv Rdg 16: 1 - 4

General



R = alkyl, vinyl, or aryl

- cannot act as acid
- can act as base (both Lewis & B.-L.), very similar to ROH



"oxonium ion"

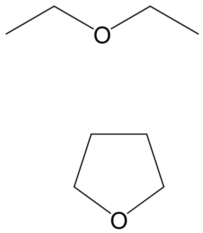
pK_a = ~ – 4 (similar to ROH_2^+);

e.g.

Occurrence, Common Names

commonly used as solvent for rxns,

such as

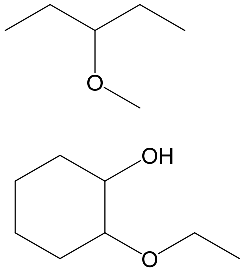


Systematic Naming

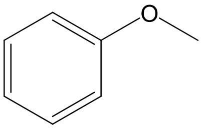
1.)” alkoxyalkane method”

↑ smaller R ↑ larger R

Examples



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



Prep

1.) ROH + mineral acid

seen before

2.) alkene + peracid

→ epoxide

3.) Williamson synthesis

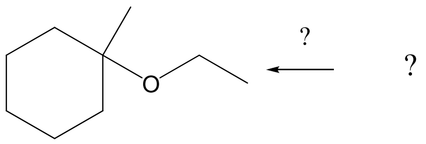
typical S_N2 rxn:

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

(substrate) (nucleophile)

Note : Ideally, the substrate should be 1°

Example:



Internal Williamson Rxn

produces cyclic ethers;

general scheme

(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

2.) Acidic Cleavage

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

works b/c oxonium ion is formed
which is a good L.G.

Where does C – O – C split?

3 different cases:

a.) “tertiary C” present

b.) only “primary & secondary C’s” present

c.) epoxides

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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.,

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

- cleaves at more substituted site &
- forms trans product