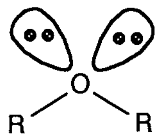
Bean-2
Chem 3332

CHAPTER 14: Ethers, Epoxides, Sulfides

Importance:

Structure / Polarity / Physical Properties

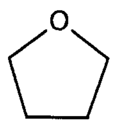


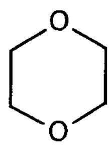
	CH_3-O-CH_3	$CH_3CH_2CH_3$	CH_3CH_2-O-H
dipole moment			
boiling point			

Ethers as Solvents:

- limited reactivity
- not as toxic as chlorinated solvents such as CCl_4 / $CHCl_3$ / CH_2Cl_2
- low boiling, so easily removed
- large dipole moments and H - bond acceptors, so dissolve polar substances
- no H-bonds between ether molecules, so dissolve nonpolar substances (no H-bonds to disrupt)
- no acidic hydrogens, so can serve as solvents under strong basic conditions

CH_3CH_2—O—CH_2CH_3





18-crown-6

CH_3—O—CH_2CH_2—O—CH_3

Ether Complexes:

a. Grignard reagent -

b. Boron reagents -

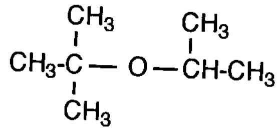
c. Crown ether / cations -

Nomenclature of Ethers

I. Acyclic Ethers - 2 accepted systems

A. As alkyl alkyl ether: Name each alkyl group attached to oxygen in alphabetical order and add "ether." (common name)

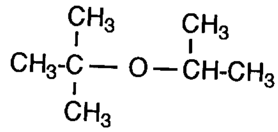
$CH_3CH_2CH_2-O-CH_2CH_3$



$CH_3CH_2CH_2-O-CH_2CH_2\text{-}OH$

B. As alkoxy alkane: Name the RO- group as an alkoxy group. The larger or more complex group is chosen as the parent name.

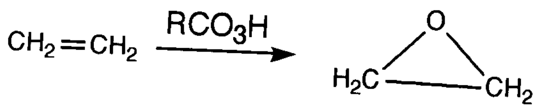
$CH_3CH_2CH_2-O-CH_2CH_3$

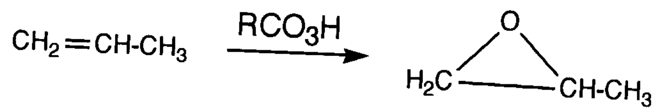


$CH_3CH_2CH_2-O-CH_2CH_2\text{-}OH$

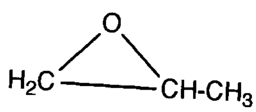
II. Cyclic ethers (Epoxides) - 3 accepted systems

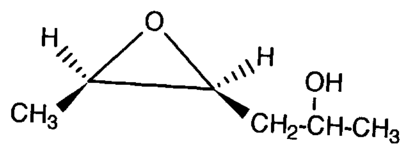
A. Common name: Name of alkene used to form the epoxide plus "oxide." (industry uses)



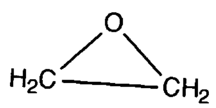


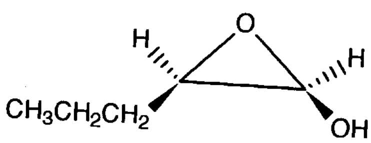
B. Name the oxygen of the epoxide ring as an epoxy substituent. Use both numbers of the carbons bonded to oxygen to designate position.

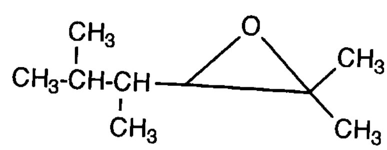




C. Name as derivative of oxirane.

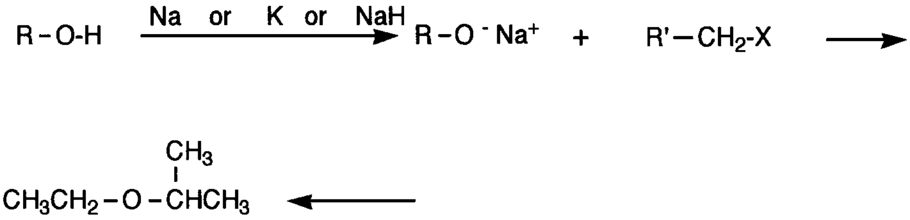


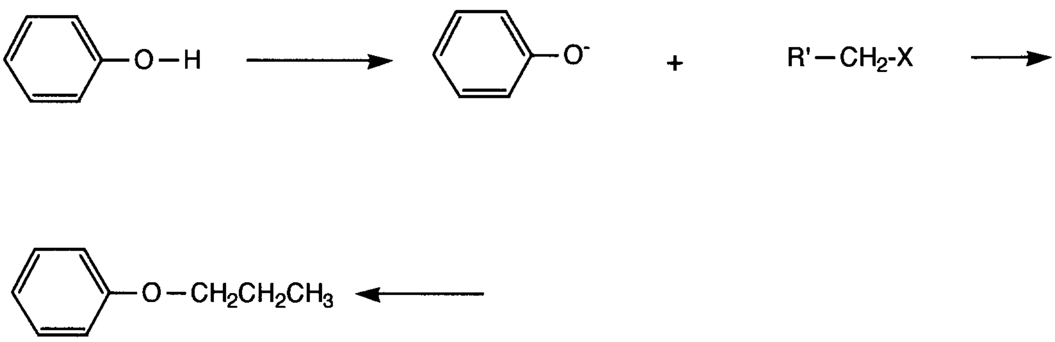




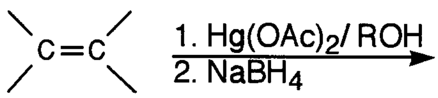
SYNTHESIS OF ETHERS

I. Williamson Ether Synthesis

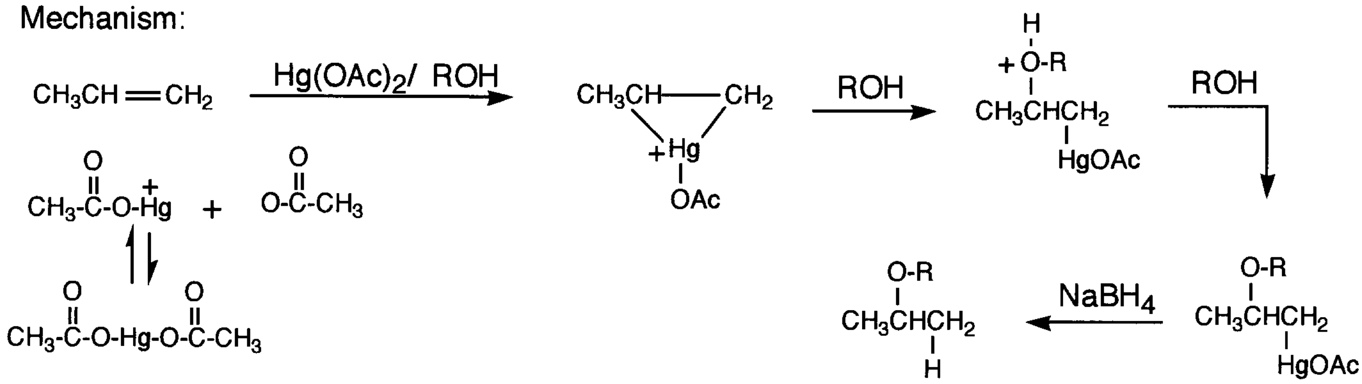
A.


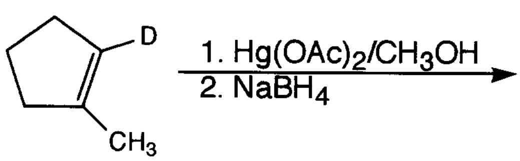
B.


II. Alkoxymercuration/demercuration



Mechanism:



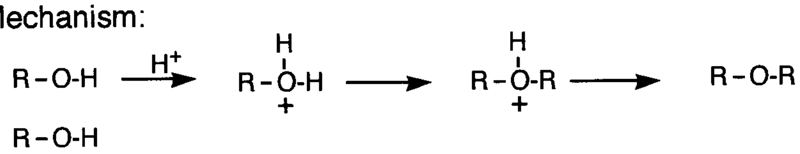


III. Symmetrical ethers through intermolecular dehydration of 1° alcohols

$$R-O-H \quad + \quad H-O-R \xrightarrow[-\,H_2O]{H^+}$$

EX: $2\ CH_3CH_2-O-H \xrightarrow[140^\circ C]{H_2SO_4}$

Mechanism:



NOT for unsymmetrical ethers! $CH_3CH_2-O-H \quad + \quad CH_3-O-H \xrightarrow[140^\circ C]{H_2SO_4}$

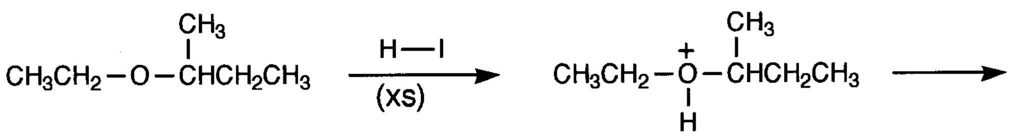
REACTIONS OF ETHERS

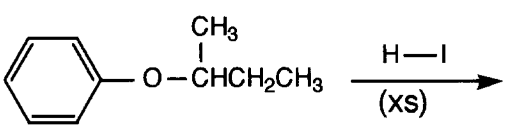
- ethers are unrective to many organic reagents
- ether bond (C-O) is stable to

I. Cleavage by strong acids (HI and HBr, not HCl)

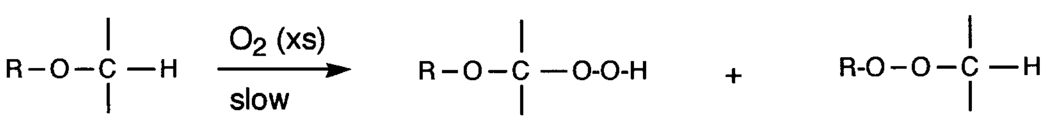
$$R-O-R' \xrightarrow[\text{heat}]{\text{HI or HBr (XS)}}$$

Mechanism:



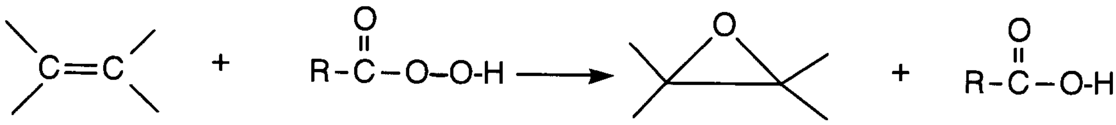


II. Autoxidation (DANGER!!)

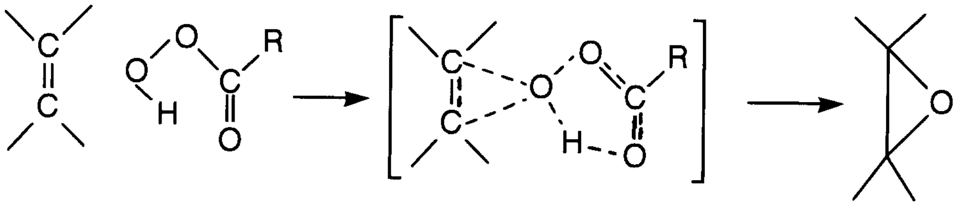


Synthesis of Epoxides:

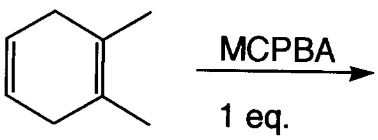
I. Epoxidation of alkenes with peroxyacids:



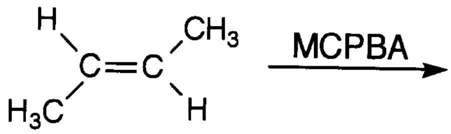
Mech: a concerted process



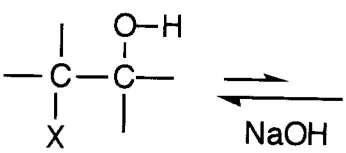
Electron rich π bonds react fastest:

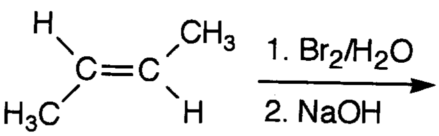


Stereochemistry of the alkene is maintained:

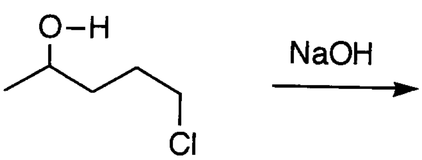


II. Intramolecular Williamson



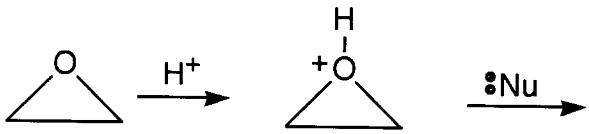


Larger cyclic ethers can also be formed:

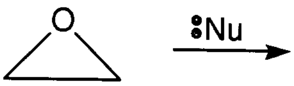


REACTIONS OF EPOXIDES

I. Acid - catalyzed cleavage

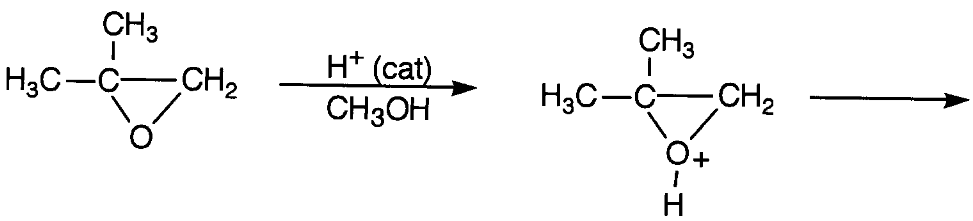


II. Base - catalyzed cleavage

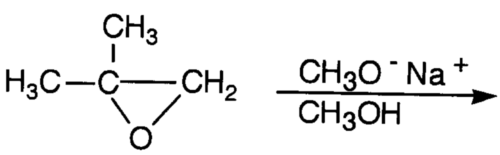


If the epoxide is symmetrical, the results of acid cat. and base cat. are the same.
Consider each process with asymmetrical epoxides:

I. Acid - catalyzed cleavage



II. Base - catalyzed cleavage



Summary:

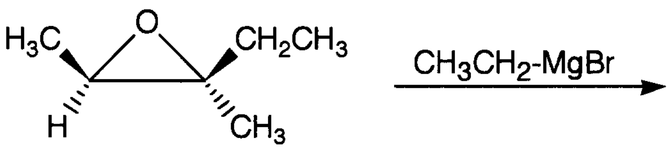
1. Weak nucleophiles (H_2O, ROH, Cl^-) only react with protonated epoxide.

2. Strong nucleophiles (OH^-, RO^-, NH_2^-, CN^-, carbanions) react with unprotonated epoxide.

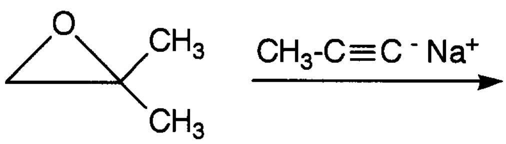
3. Acid - cat. process: Nu attacks the more substituted carbon.

4. Base cat. process: Nu attacks the less substituted carbon.

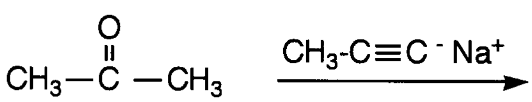
III. Reaction of Epoxide with Grignard/Organolithium Reagents



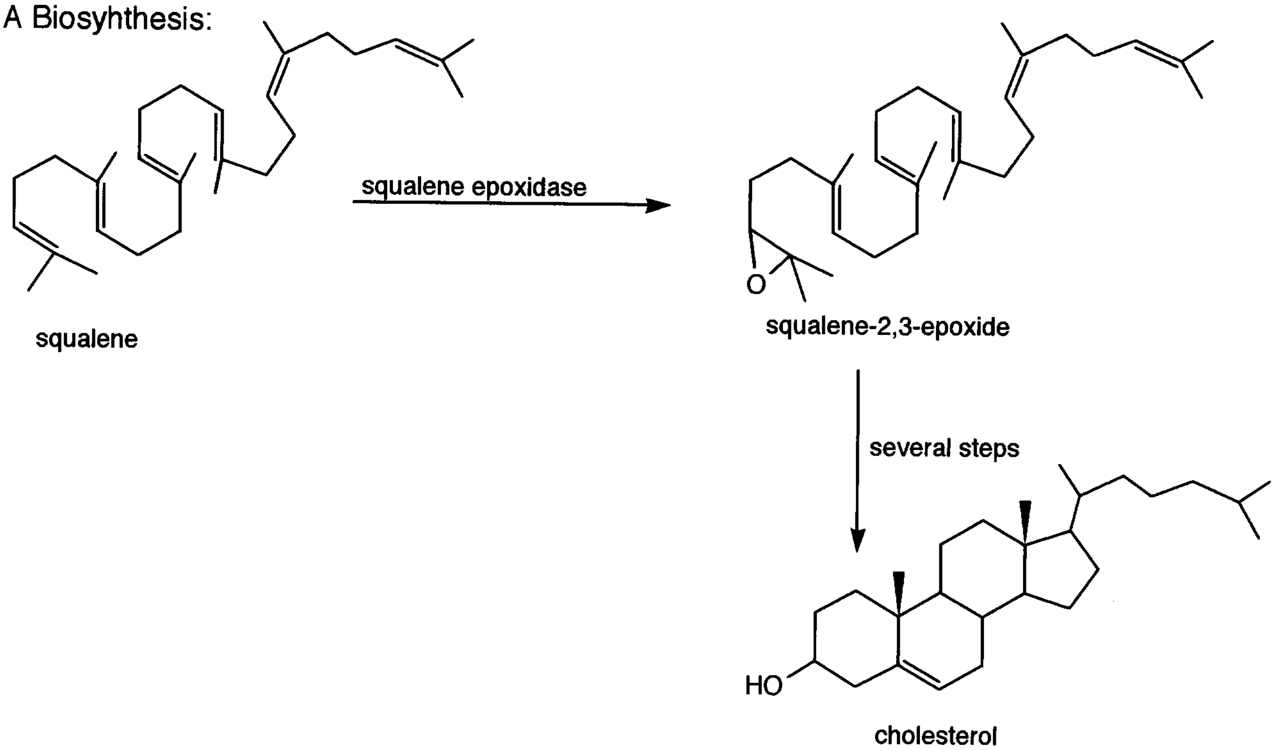
IV. Reaction of Epoxide with Acetylide Ion



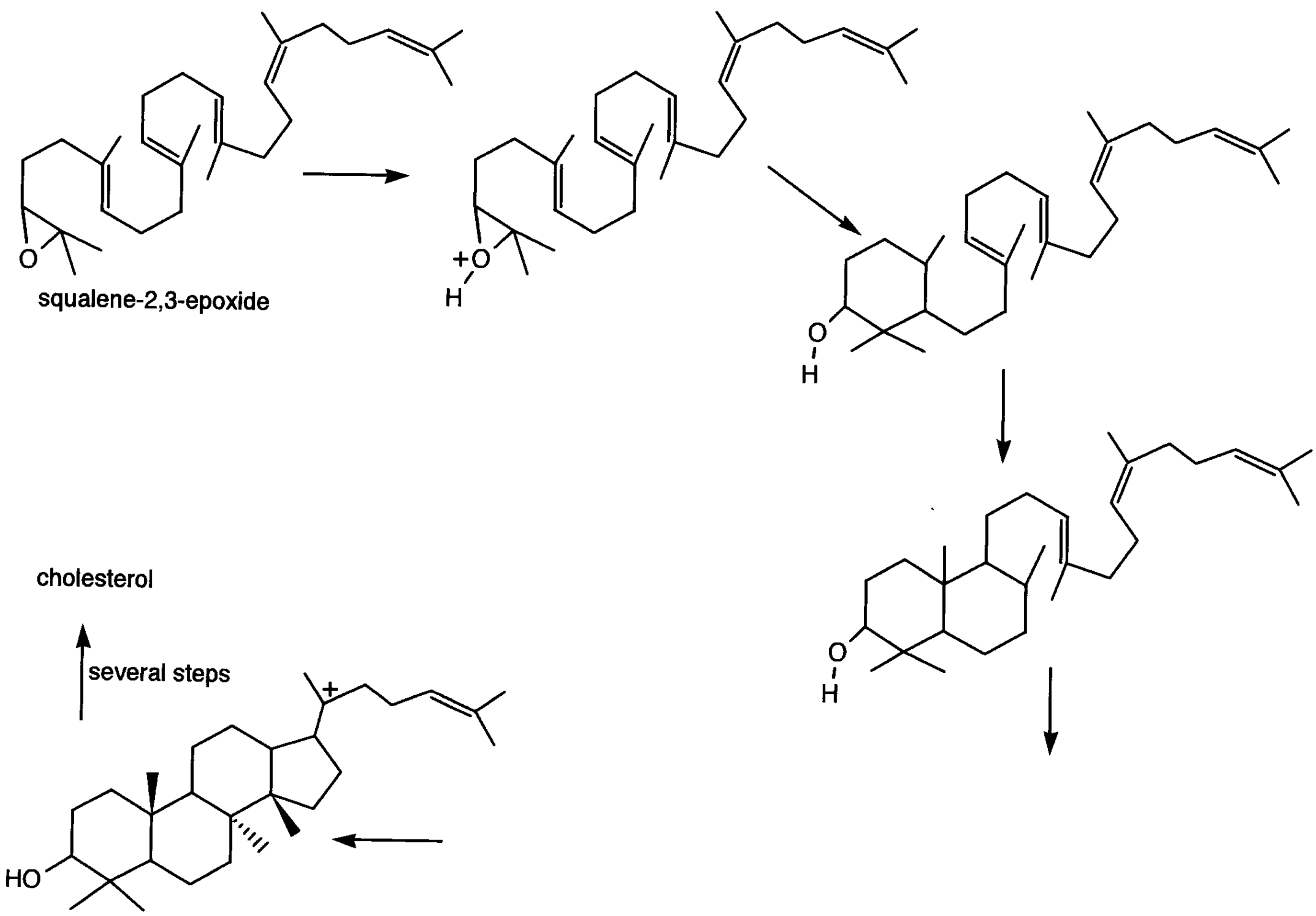
Compare to:



A Biosyhthesis:

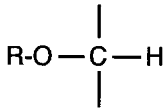


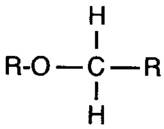
The organic chemist's mechanism:



Spectroscopy of Ethers

IR: absence of 0-H stretch (alcohols) and carbonyl C═O stretch (aldehyde/ketone/acids)
C-O stretch between 1050-1150 cm^{-1} is usually strong

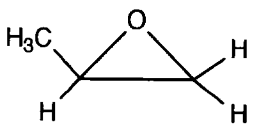
^{1}H NMR:  3.4 - 4.5 δ

^{13}C NMR:  65 - 90 δ

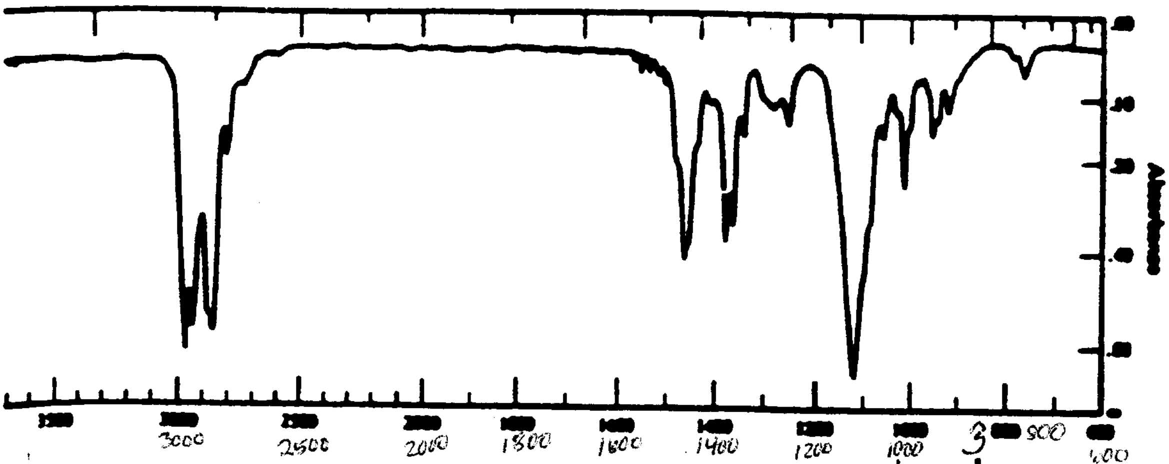
CH_3—O—CH_2-CH_2-CH_3

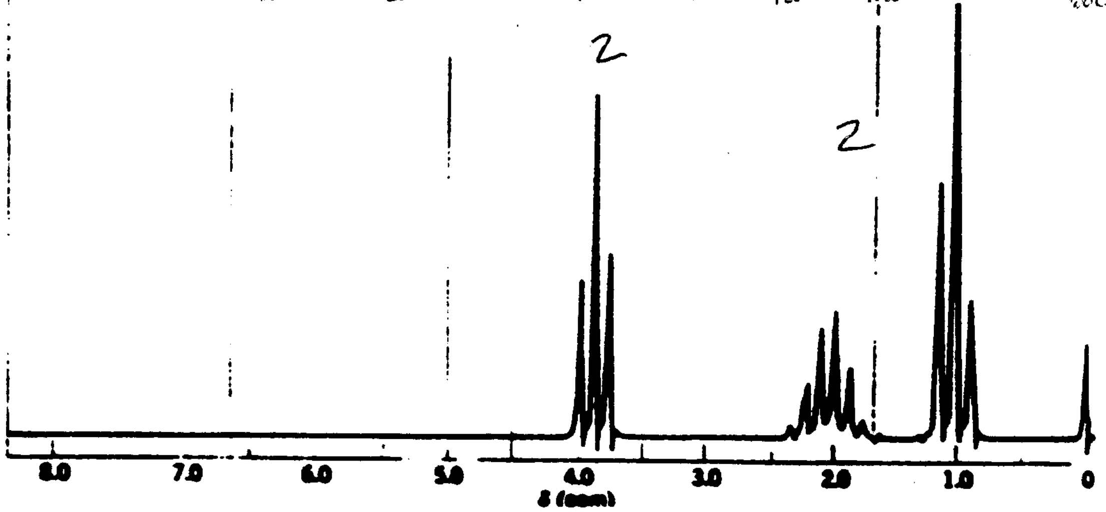
Spectroscopy of Epoxides

^{1}H NMR: protons of carbons adjacent to epoxide oxygen slightly higher field (upfield) than those of of other ethers - 2.5 - 3.5 δ



Unknown Example: $C_6H_{14}O$





1H NMR Spectrum of 1,2-epoxypropane