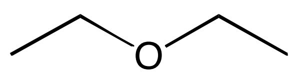
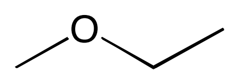
Ethers

Ethers are organic compounds with two alkyl groups attached to an oxygen
(water has no alkyl groups attached and alcohols have one alkyl group attached)

the two alkyl groups can be the same group or different



symmetrical

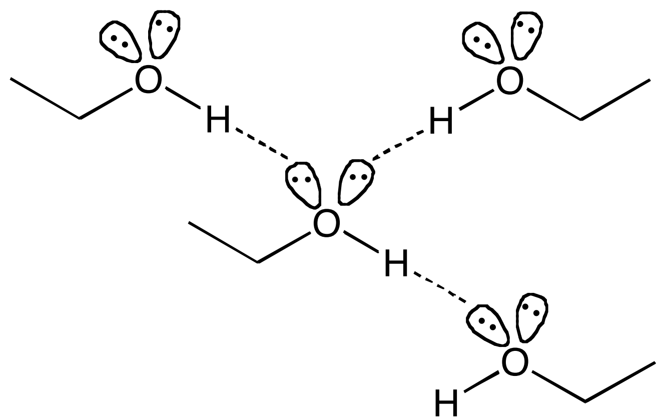


unsymmetrical

The lack of a labile hydrogen causes ethers to have vastly different properties than alcohols

1) boiling point

O-H bond allows alcohols to form hydrogen bonding (each H-bond is ~4-5 Kcal/mol)

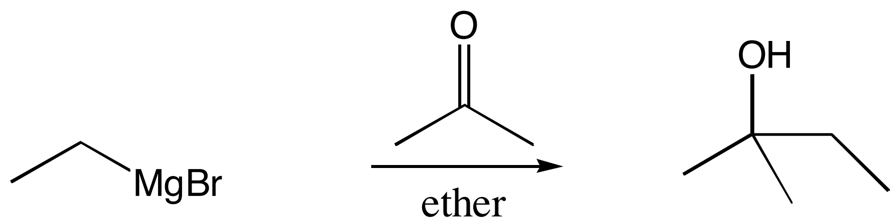


with the lack of these H-bonds, ethers have much lower boiling points

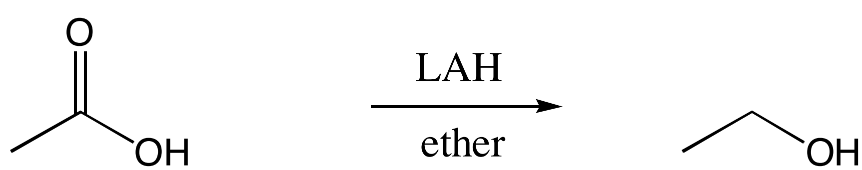
2) pKa

with no labile hydrogens ethers have no acidic hydrogens to abstract

this fact allows ethers to be used in many organic reactions where alcohols would be imposible to use due to pKa of alcohol



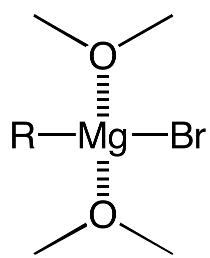
Grignard reaction



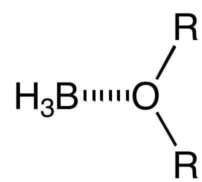
LAH reduction

3) complexation

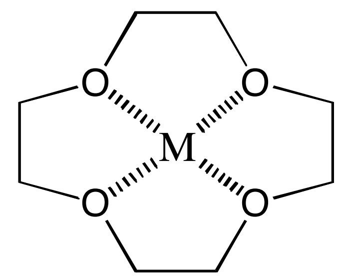
the lone pair of electrons on oxygen can be used to form
Lewis acid type complexes with various π acceptors



Grignard



boron complexes



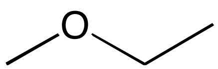
crown
ethers

Nomenclature

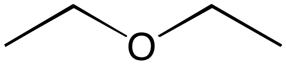
There are many different ways to name ethers

-common names

use alkyl alkyl ether system



ethyl methyl ether



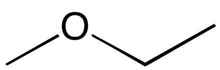
diethyl ether

-IUPAC names

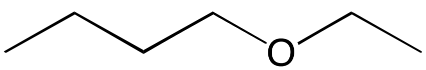
alkoxy alkane system

find longest contiguous chain with the alkoxy substituent,

name using same rules for alkanes learned previously



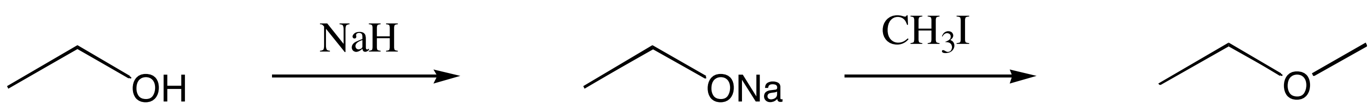
methoxy ethane



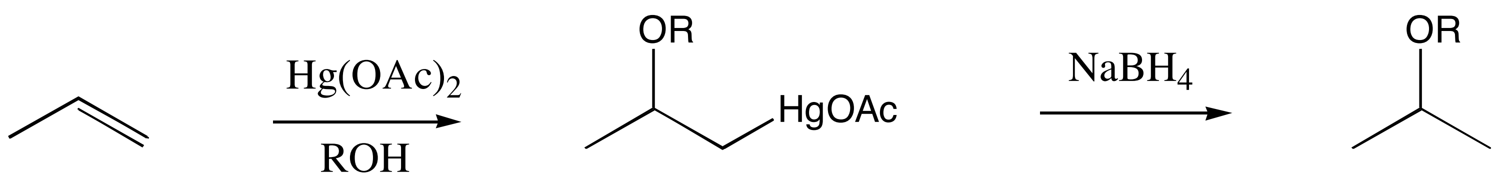
1-ethoxy butane

Synthesis

We have already seen the most common methods to synthesize ethers



Williamson Ether Synthesis



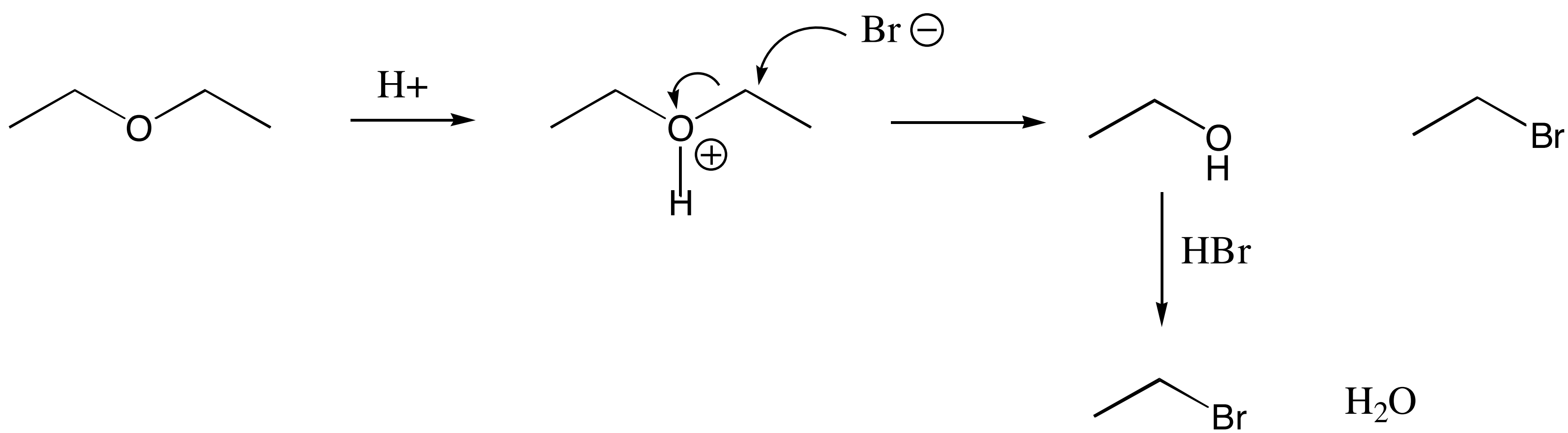
addition to alkenes

Reactions of Ethers

Ethers are relatively unreactive

- main reason that they are commonly used as solvents for organic reactions

one of the few reactions that they can undergo is alkyl cleavage with HI or HBr



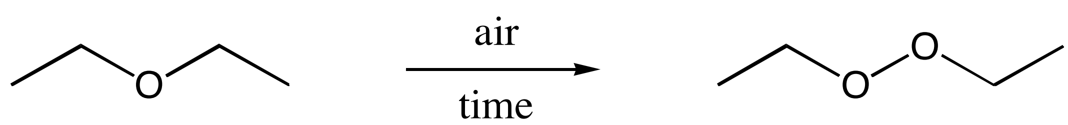
very similar to alcohol reactions observed in chapter 11

HI > HBr >>HCl

Autoxidation

Serious issue with ether solvents!

Over time the ether can be oxidized to a peroxide



these peroxides are potentially explosive

therefore ether solvents should not be kept in open containers for long periods

and especially DO NOT distill these solvents after long periods of time

Cyclic Ethers

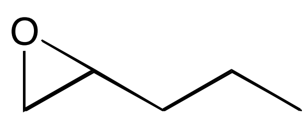
There are many types of cyclic ethers depending upon the ring size

We have already seen three membered ring ethers called EPOXIDES

Either named from starting alkene used to synthesize with OXIDE

propene propene oxide

Or the EPOXY nomenclature is used to designate the substituent



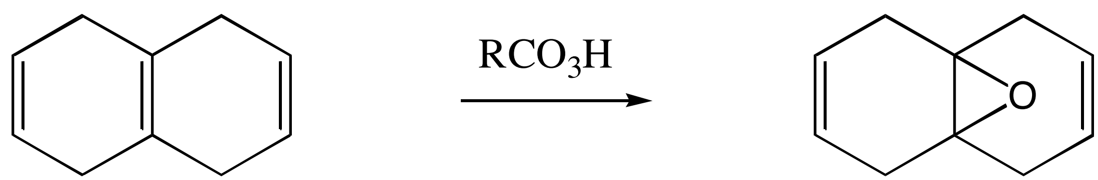
1,2-epoxy pentane

Selectivity in Epoxide Formation

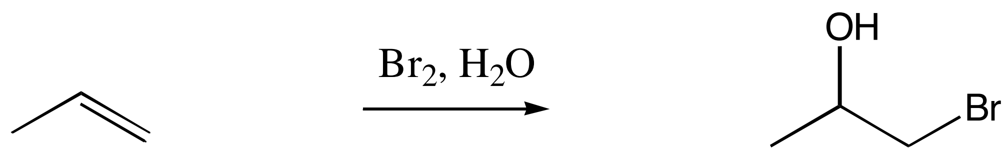
When synthesizing an epoxide from an alkene with peracid

The peracid is acting as a source of an electron deficient oxygen

Therefore the most electron rich double bond will react preferentially

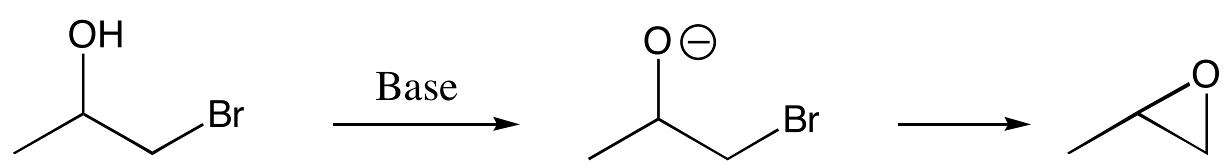


Epoxides can also be synthesized from Halohydrins



remember regio- and stereochemistry
from chapter 8

the halohydrin can react through an intramolecular Williamson ether synthesis

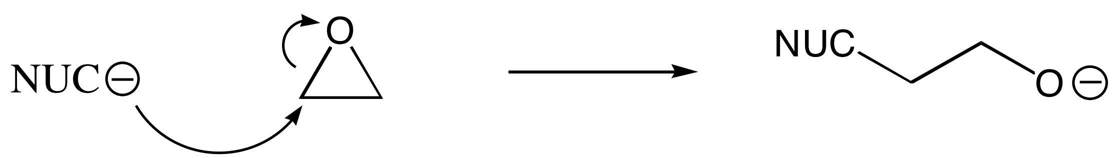


Reaction of Epoxides

Unlike straight chain ethers, epoxides react readily with good nucleophiles

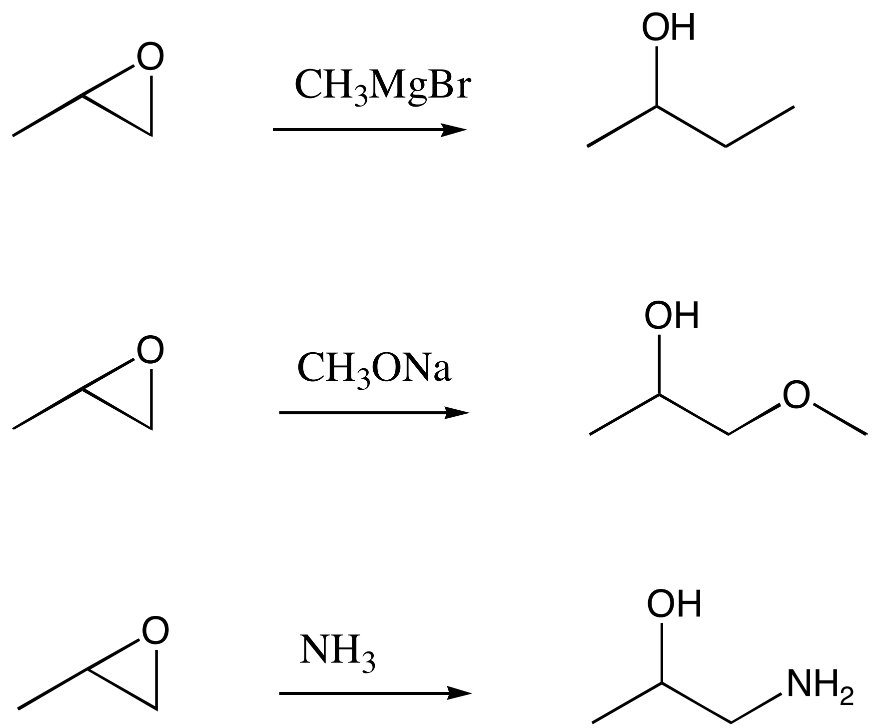
Reason is release of ring strain in 3-membered ring

(even with poor alkoxide leaving group)



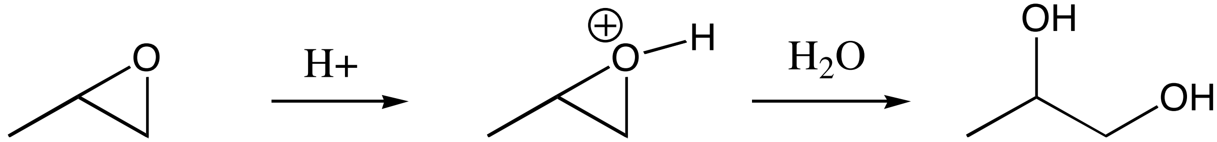
same reaction would never occur with straight chain ether

Most GOOD nucleophiles will react through a basic mechanism



all products
after work-up

Epoxides will also open under acidic conditions



can use weaker nucleophiles in this manner since we have a better leaving group

common examples of nucleophiles include water or alcohols

Differences in Regiochemistry

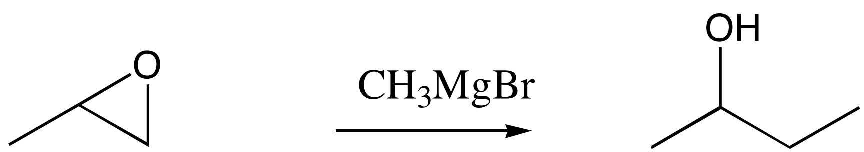
The base catalyzed opening of epoxides goes through a common S_N2 reaction

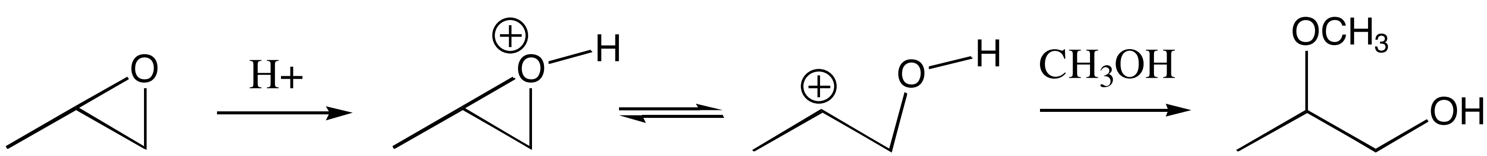
Therefore the nucleophile attacks the least hindered carbon of the epoxide

In the acid catalyzed opening of epoxides the reaction first protonates the oxygen

This protonated oxygen can equilibrate to an open form

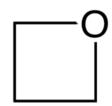
The open form would favor the site that can best stabilized the carbocation





4-Membered Ring Ethers

called Oxetanes



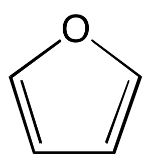
oxetane

least common cyclic ether

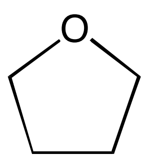
5-Membered Ring Ethers

the saturated version is called tetrahydofuran (THF)

hydrogenated form of conjugated furan



furan

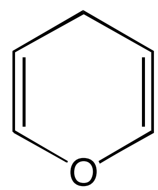


tetrahydrofuran (THF)

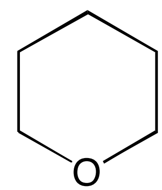
6-Membered Ring Ethers

conjugated version is called pyran

saturated version is tetrahydropyran (THP) (also called oxane)



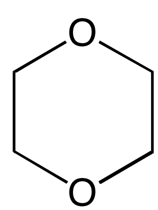
pyran



tetrahydropyran

Some versions have two oxygen ethers

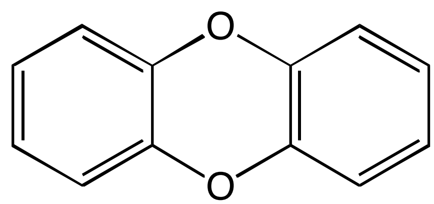
Called dioxane



1,4-dioxane

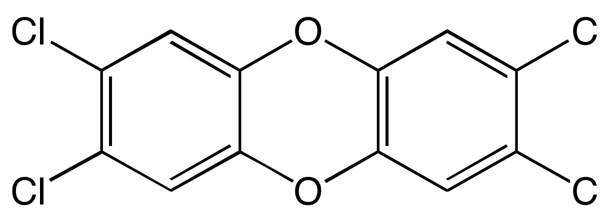
1,4-Dioxane is related to Dioxin

(dibenzodioxin)



dioxin

Unfortunately the media incorrectly names a chlorinated version of dioxin



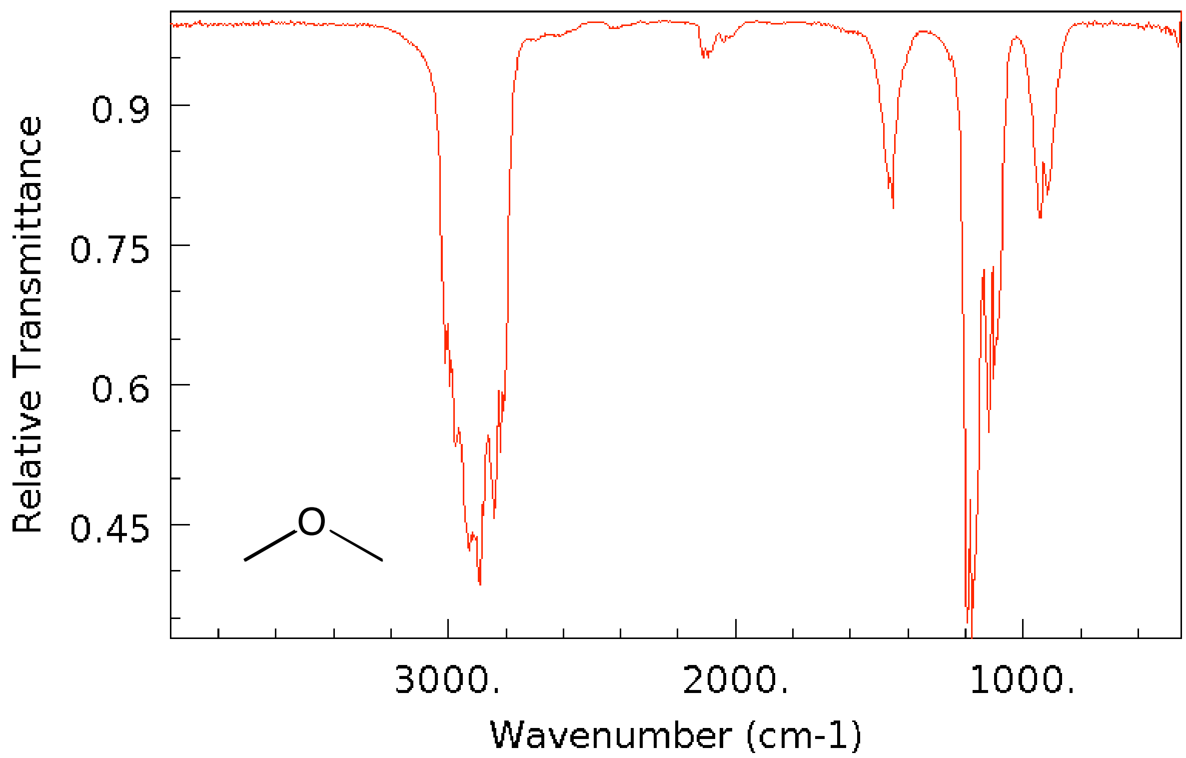
2,3,7,8-tetrachlorodibenzodioxin (TCDD)

TCDD is a toxic substance
Used recently (2004) to poison new Ukrainian president
He was poisoned with TCDD, NOT dioxin as media reports

Spectroscopy of Ethers

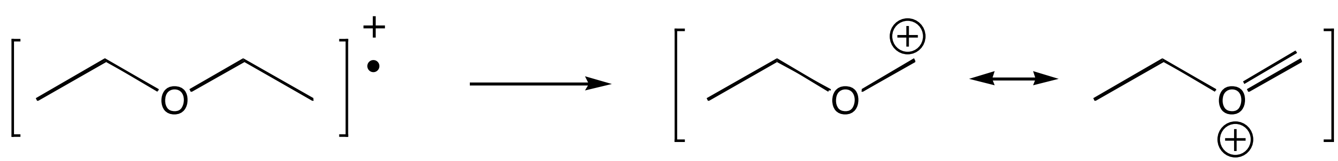
IR

The IR spectrum does not have many diagnostic peaks for an ether

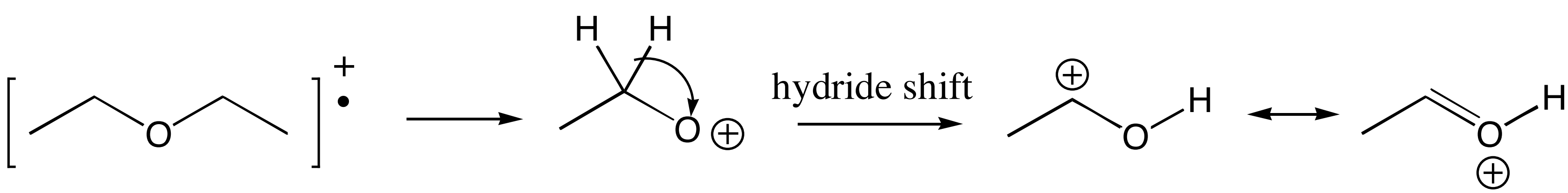


Mass Spectrometry

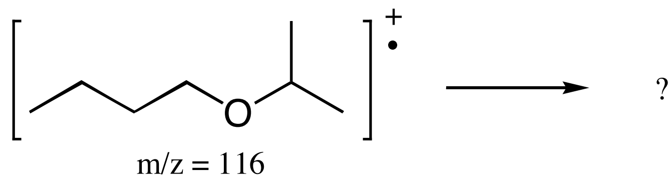
Common fragmentation of ethers is an α-cleavage

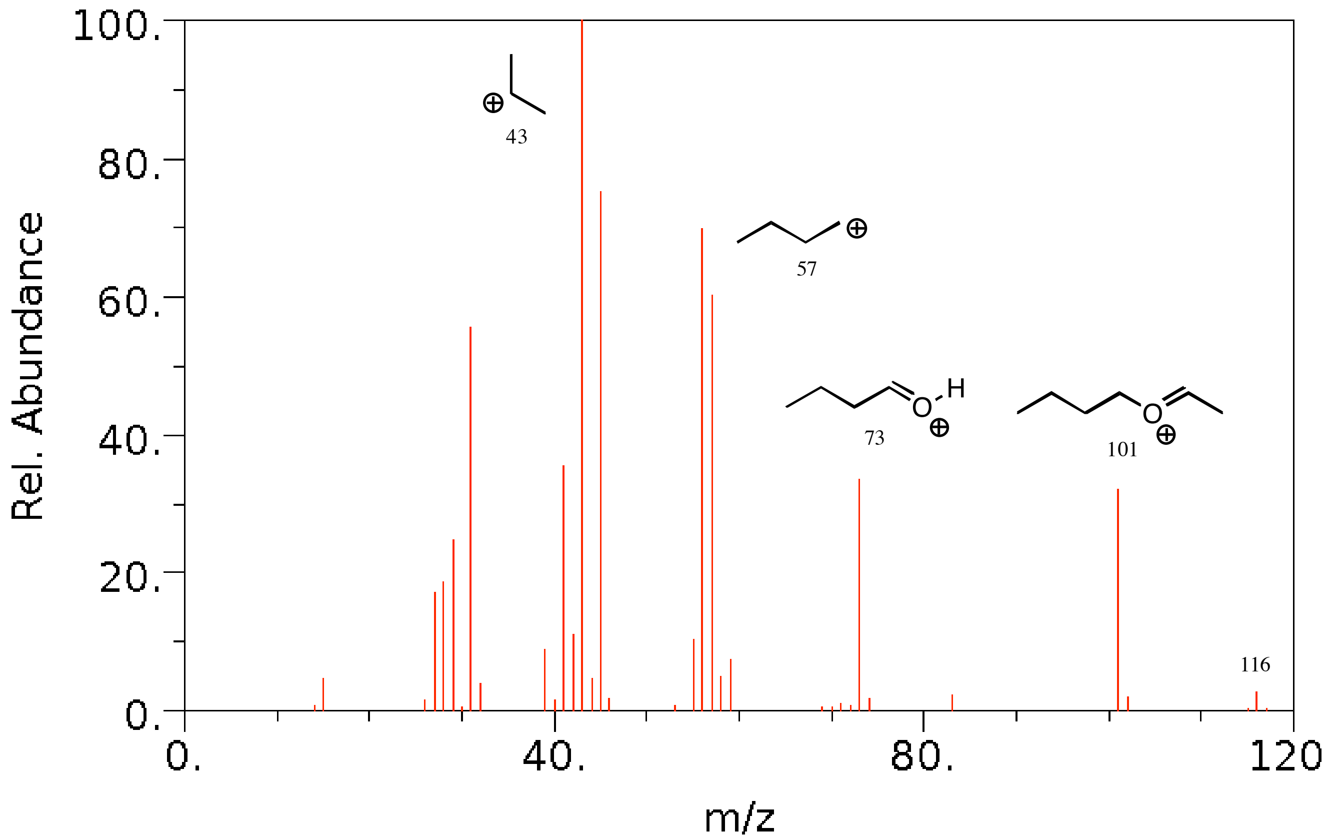


or loss of alkyl group adjacent to oxygen



both fragmentations result in a resonance stabilized oxonium ion


+
O
?
m/z = 116


100.
80.
60.
40.
20.
0.
Rel. Abundance
0.
40.
80.
120.
m/z
43
57
O
H
73
O
101
116

NMR Spectroscopy

Remember position of shifts in ^{1}H and ^{13}C for ether compounds