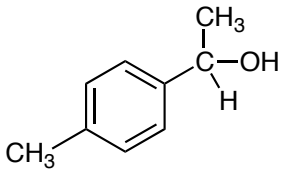
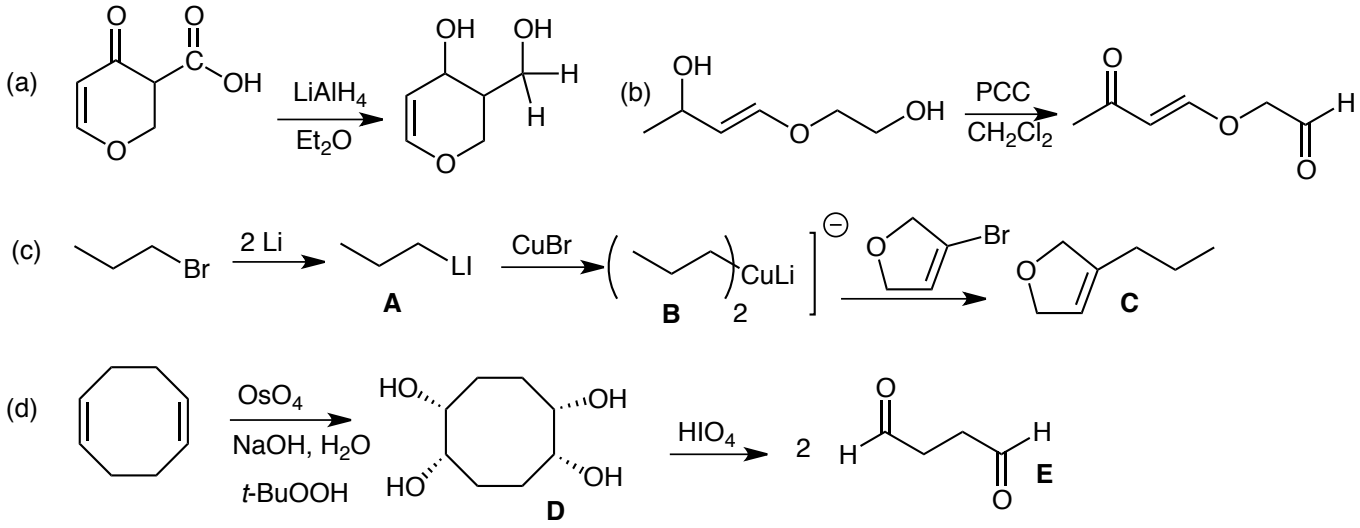
Long Island University, Department of Chemistry

Chem. 122, Sect 012, Exam 1, 100 pts, Spring, 2011

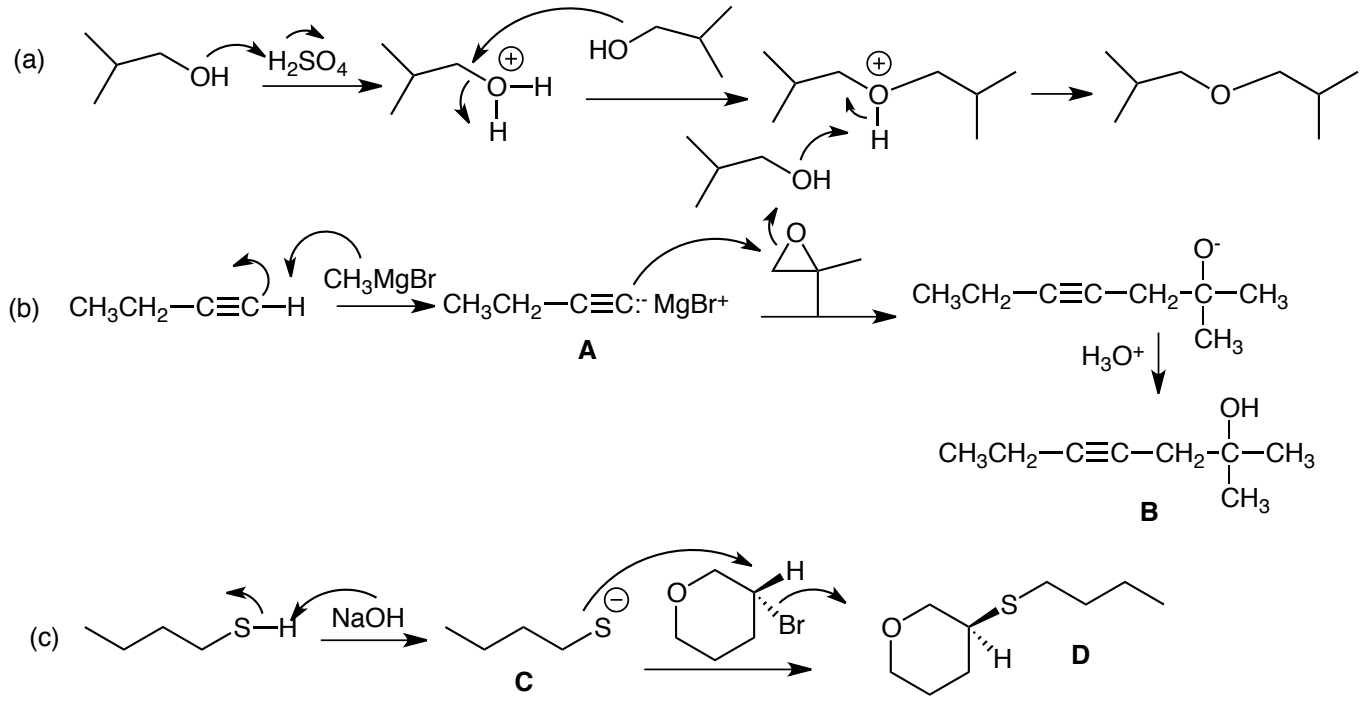
1. Identify the following molecule based on its, formula ($C_9H_{12}O$), IR and proton NMR. IR: 3500 - 3200 cm^{-1}. ^1H NMR: δ 1.62, 3H, doublet; 2.2, 3H, singlet; 4.2, 1H, singlet; 4.85, 1H, quartet; 7.2, 2H, doublet,; 7.4, 2H, doublet. (10 pts)



2. Give the product of the following reactions. It is not necessary to show the full mechanism. Be sure to show the stereochemistry where appropriate. (40 pts)



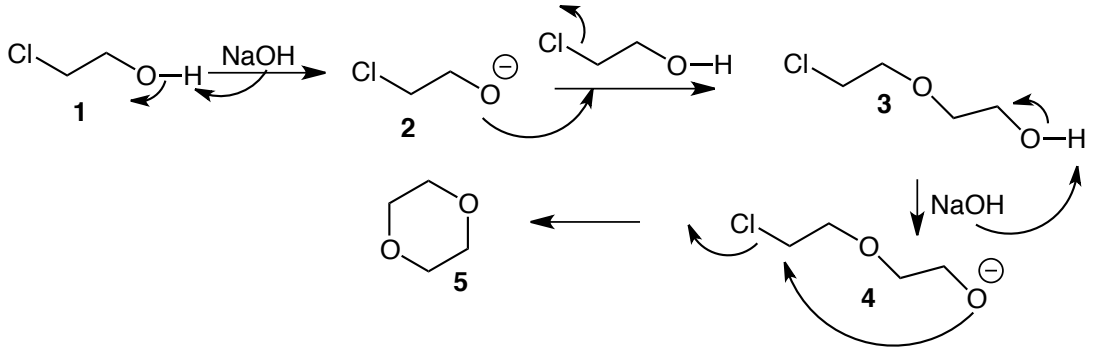
3. For the following reactions, give the product(s) and the complete reactions mechanisms by which they are formed. Pay careful attention to stereochemistry where appropriate. (30 pts)



With the relatively mildly basic sulfur anion, we get mainly S_N2 substitution, even with a secondary substrate.

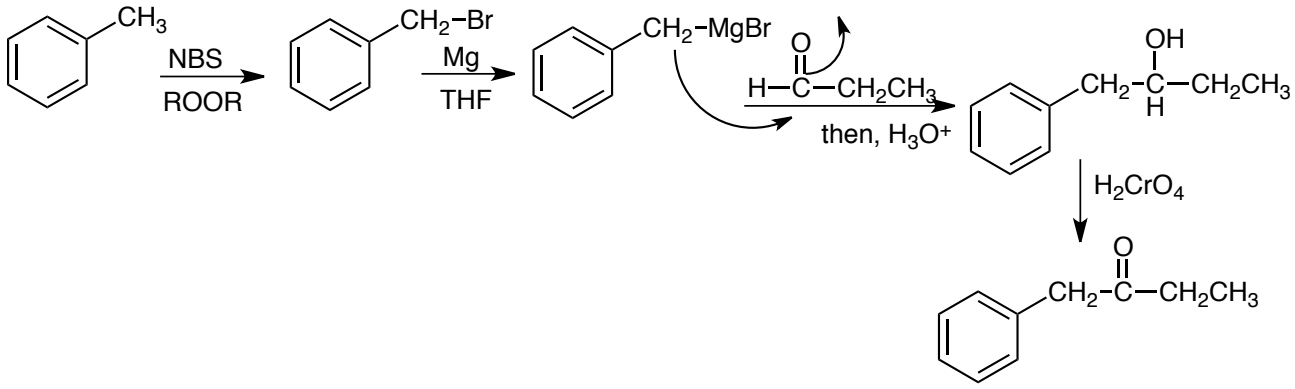
4. Show how the following transformation occurs, giving all of the steps of the mechanism. (10 pts)

What we have is a double Williamson synthesis. The alcohol 1 is not a strong enough nucleophile to attack another molecule of itself without activation by a base such as sodium hydride. The anion **2** then attacks another molecule of **1** in a simple S_N2 reaction to give **3**. This must be deprotonated again by the base to give the anion **4** which does an intramolecular S_N2 attack on the $–CH_2$-Cl to give the ether. Remember, that intramolcular attack is very favorable for the formation of 5- and 6-membered rings.

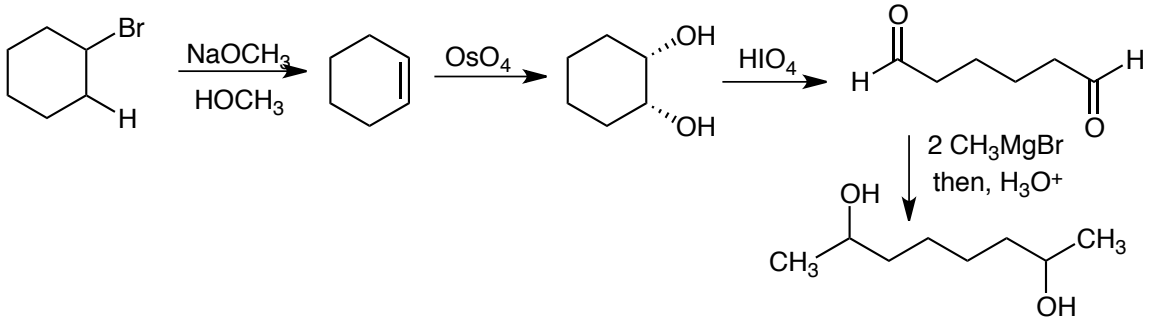


5. Synthesize **two** of the following three molecules as shown. For extra credit do all three. (20 pts)

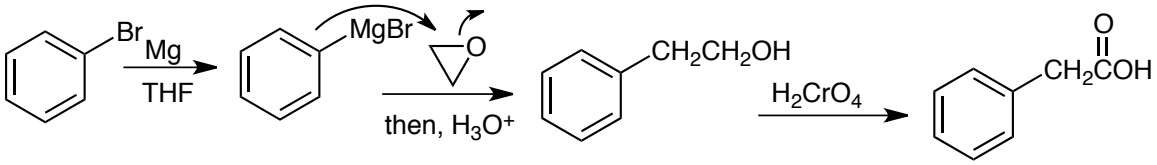
(a)


CH3
NBS
ROOR
CH2–Br
Mg
THF
CH2–MgBr
O
H–C–CH2CH3
then, H3O+
OH
CH2–C–CH2CH3
H
H2CrO4
O
CH2–C–CH2CH3

(b)


Br
H
NaOCH3
HOCH3
OsO4
OH
OH
HIO4
O
H
H
O
2 CH3MgBr
then, H3O+
OH
CH3
CH3
OH

(c)


Br
Mg
THF
MgBr
O
then, H3O+
CH2CH2OH
H2CrO4
O
CH2COH