

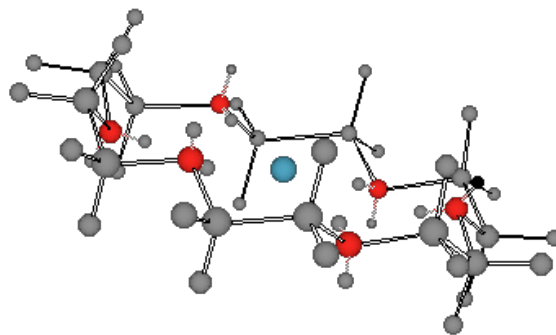
Chem 220a

Problem Set 10

Chapters 12 and 14

Due: Monday, December 5, 2005

Material in this Problem Set will be covered in the final exam.

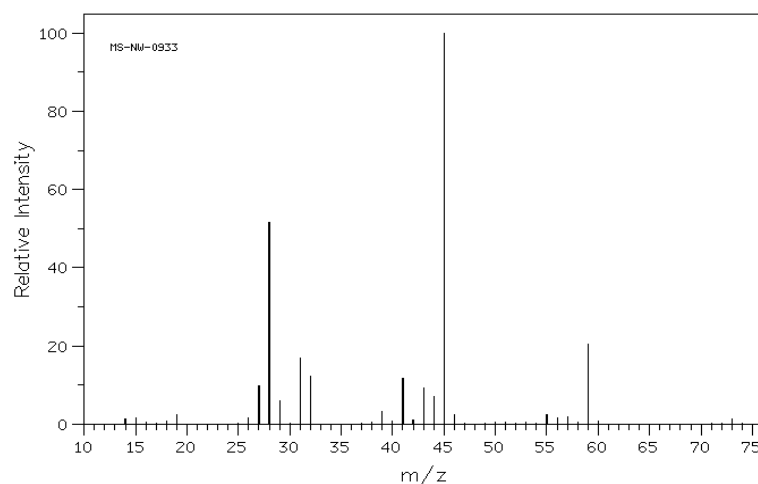
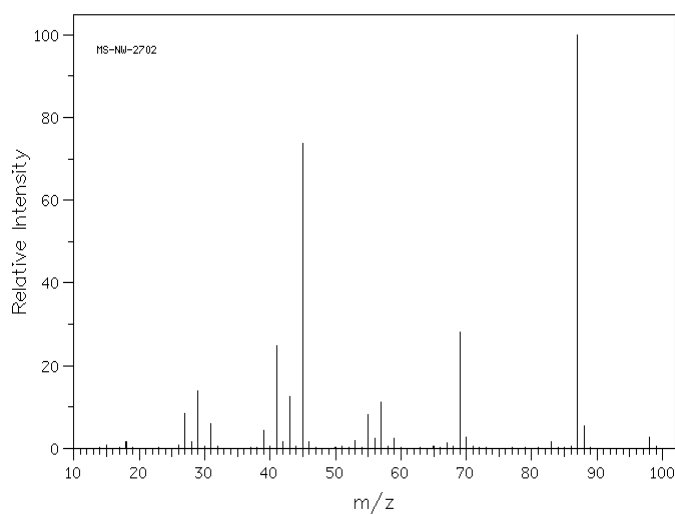


Potassium cation solvated by the cyclic polyether, 18-crown-6 [18-membered ring; 6 oxygen atoms]. Each of the ethano groups is in a staggered conformation with each of the O-C-C-O dihedral angles at $\sim 60^\circ$ [gauche]. For a [Chime™](#) version, [click here](#). Note that the six oxygen atoms occupy the same spatial arrangement as do the six carbon atoms in chair cyclohexane. The discovery of the crown ethers by [Charles Pedersen](#) of DuPont earned him a share in the 1987 Nobel Prize in Chemistry.

1. Compound (*R*)-**A**, $C_7H_{14}O_2$, reacts with excess Grignard reagent **B** to afford two products, **C** [(*R*)- $C_4H_{10}O$] and **D** ($C_7H_{16}O$). Compound **D** is inert to Jones reagent, but it readily reacts with cat. H_2SO_4 to form **only E**, C_7H_{14} . Treatment of compound **E** with cat. OsO_4/HIO_4 produces **F** and **G**. Compound **F** gives **H**, $C_2H_4O_2$, upon exposure to Jones reagent, while compound **G** is inert toward this reagent. What are the structures of **A-H**? Explain $m/z = 45$ and 59 in the mass spectrum of **C**. Why is $m/z = 45$ more intense than 59? Explain the base peak in the spectrum of **D**.

Compound D

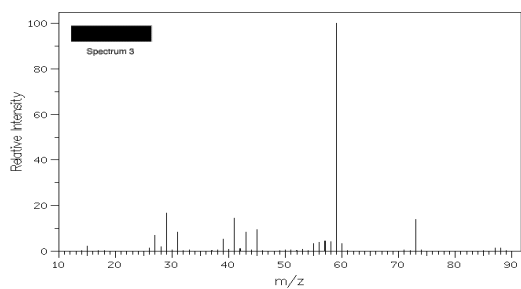
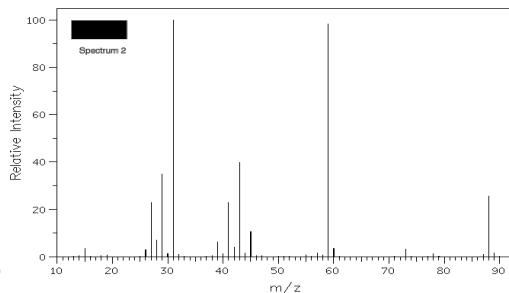
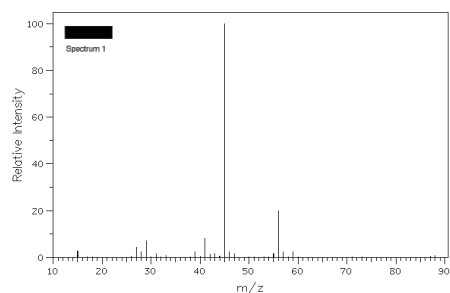
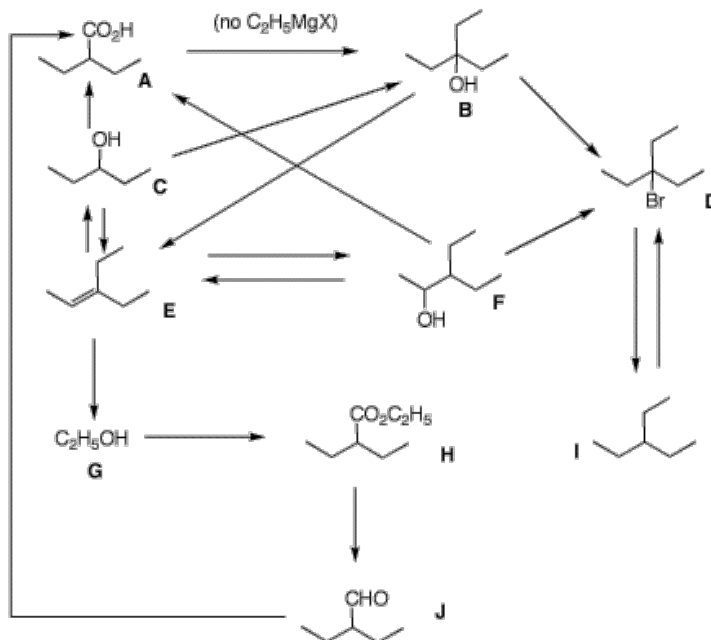
Compound C



2. Provide reagents for the chemical transformations shown on the right. Some conversions may require more than one step.

3. Show how the Grignard reagent RMgX can be parlayed in one step into the following alcohols: RCH₂OH, RCH₂CH₂OH, RCH₂CH₂CH₂OH, and RCH₂C(CH₃)₂OH.

4. Three samples of ethers, ethyl-n-propyl ether, n-butyl methyl ether, and sec-butyl methyl ether, have lost their labels. A student records the mass spectra of the compounds and assigns their structures. Assign the spectra below to its ether based upon your knowledge of β-fragmentation. Click on the spectrum for a blow-up.



5. Explain the molecular ions for trichloroethylene shown in the mass spectrum below. How do the intensities compare with theory? Click on the spectrum for a blow-up.

