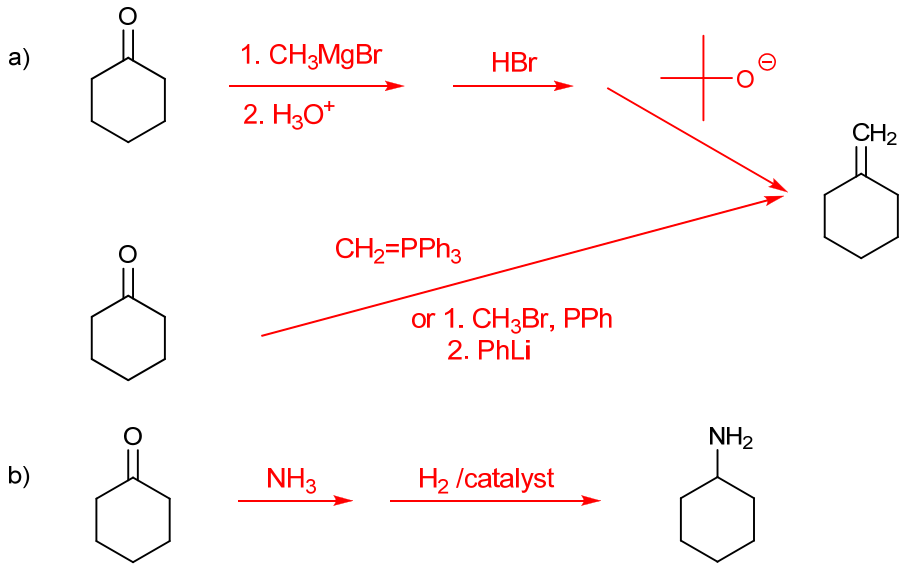
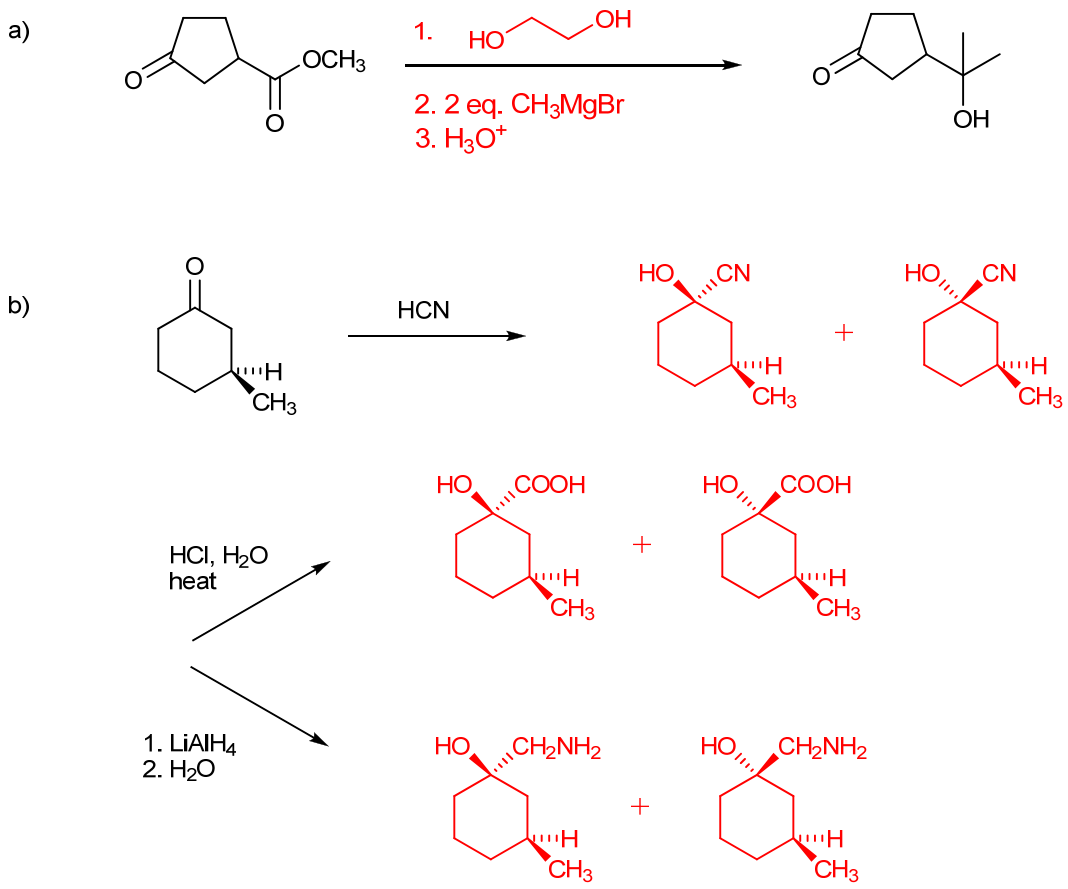
CHE 322 Workshop 6: Part 2
Ketones and Aldehydes I *(Mar. 2-3, 2009)*

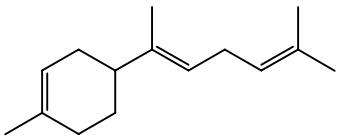
1. Give reactants and/or reagents that would give the following compounds.



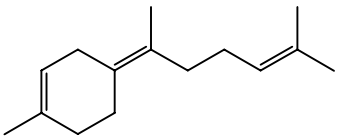
2. Complete the following reaction sequences.



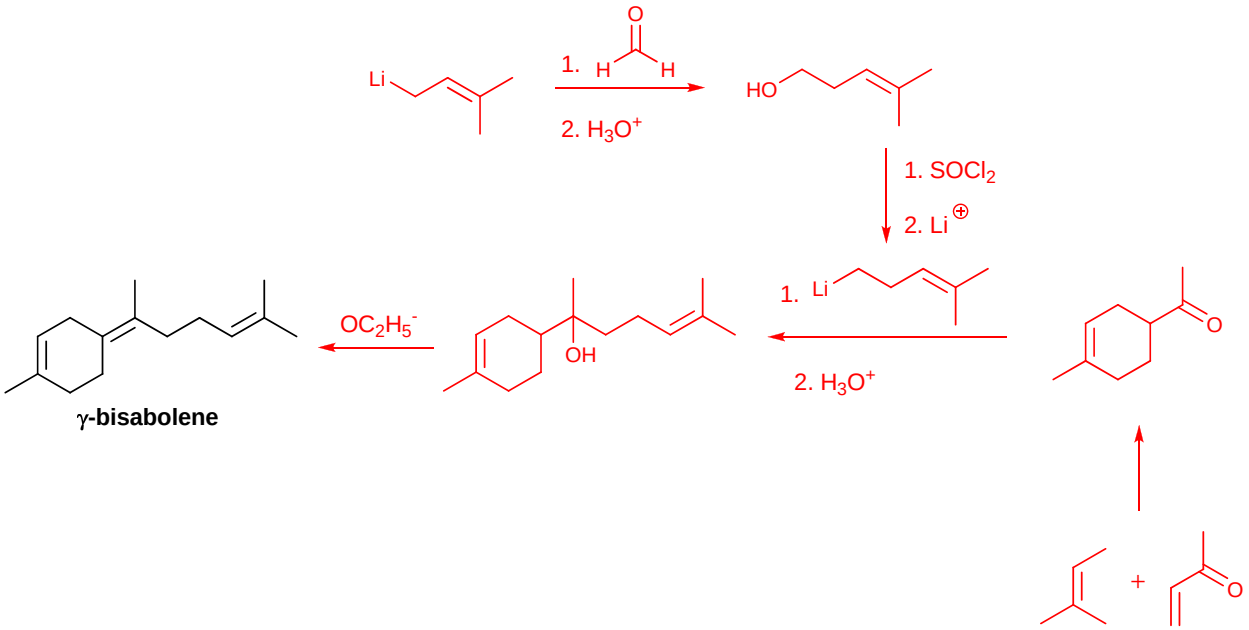
3. α-Bisabolene and γ-bisabolene (shown below) are derived from different types of plants. Synthesize the two bisabolenes using methods you learned from CHE 321. (From compounds of no more than five carbons.) What problems of stereochemistry might occur? Show how your new knowledge of the Wittig reaction would solve the problem and simplify the syntheses.



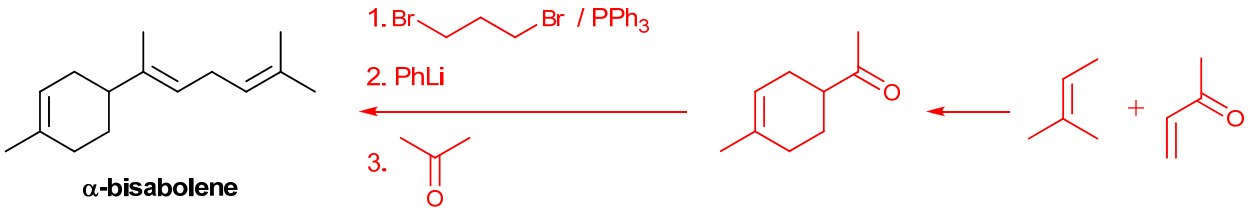
α-bisabolene



γ-bisabolene



Using CHE 321 chemistry, the final elimination step won't result in the double bond in the desired position in α-bisabolene. With Wittig reaction, the position of the double bond can be controlled (see below).



4. A synthesis of ascorbic acid (vitamin C, 1) starting from D-(+)-galactose (2) is shown below (Haworth, W.N., et al., *J. Chem. Soc.*, **1933, 1419–1423**.). Consider the following questions about the design and reactions used in this synthesis:

a) Why did Haworth and co-workers introduce the acetal functional groups in 3?

Protect the OH groups.

b) Write a mechanism for the formation of one of the acetals.

See textbook pages 702-703.

c) Write a mechanism for the hydrolysis of one of the acetals (4 to 5). Assume that water was present in the reaction mixture.

All the steps in the formation of acetals are reversible.

d) The compound 5, which is in equilibrium with an open chain compound, was reduced to compound 6 by the sodium amalgam in the presence of an acid. From what functional group did the reduction actually proceed?

The reduction occurred on an aldehyde functional group.

e) Write a mechanism for the formation of a phenylhydrazone from the aldehyde carbonyl of 7. (Do not be concerned about the phenylhydrazone group at C2. We shall study the formation of bishydrazones of this type [called an osazone] in Chapter 22).

See textbook pages 706 – 709. The formation of phenylhydrazone is similar to that of imine.

f) What reaction was used to add the carbon atom that ultimately became the lactone carbonyl carbon in ascorbic acid (1)?

The addition of HCN to the C=O group (forming a cyanohydrin) resulted in the carbon that ultimately became the lactone carbonyl carbon in compound 1.