Answers to Hour Examination #2, Chemistry 302X - 2006

1. R = CH3C H2C H2

(a)

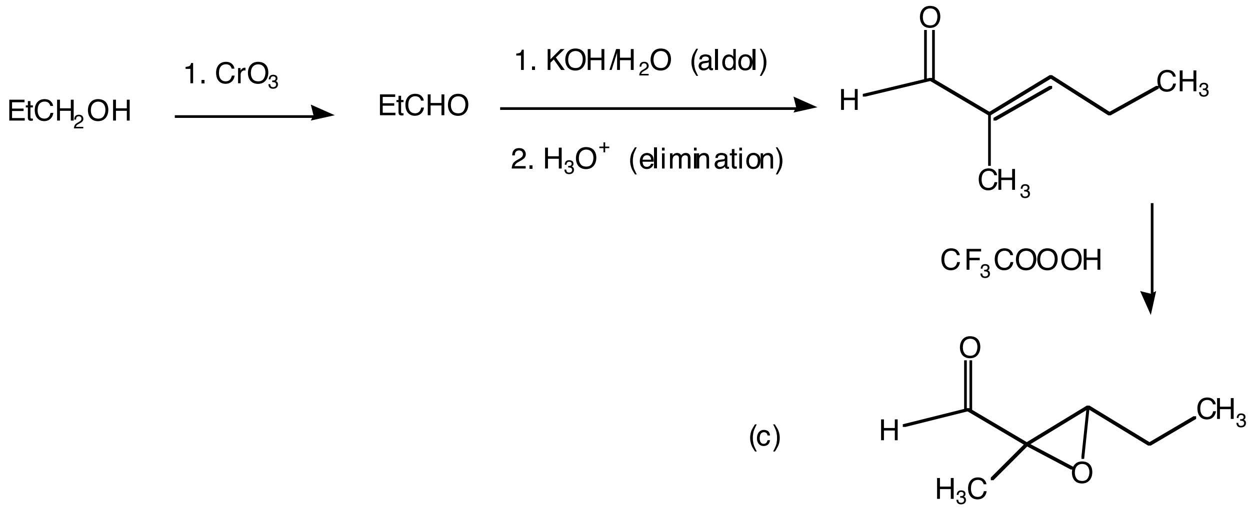
$$\mathrm{ROH} + \mathrm{HCl} \longrightarrow \mathrm{RCl} \xrightarrow{\mathrm{Li}} \mathrm{RLi} \xrightarrow[\text{2. } H_2O]{\text{1. } H_2C=O} \mathrm{RCH_2OH}$$

$$\mathrm{RCH_2OH} \xrightarrow[\text{2. RLi; 3. } H_2O]{\text{1. } CrO_3} \mathrm{R_2CHOH} \xrightarrow[\text{2. RLi; 3. } H_2O]{\text{1. } KMnO_4} \text{(a)}$$

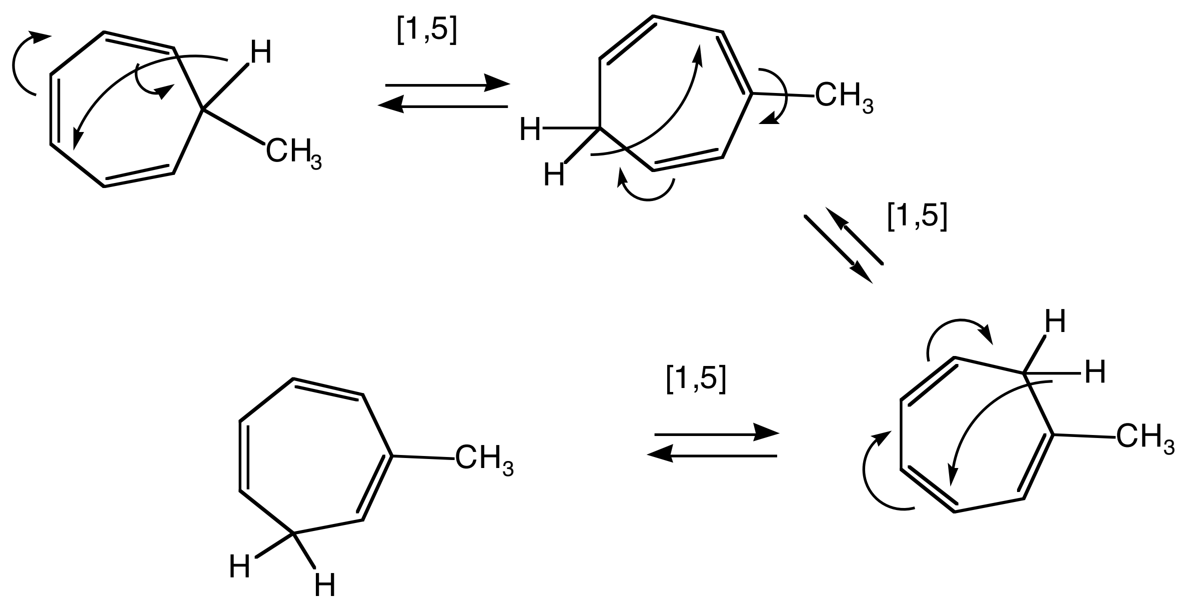
(b)

$$\text{(a)} \xrightarrow[\text{2. Li; 3. } H_2O]{\text{1. HCl}} \text{(b)}$$

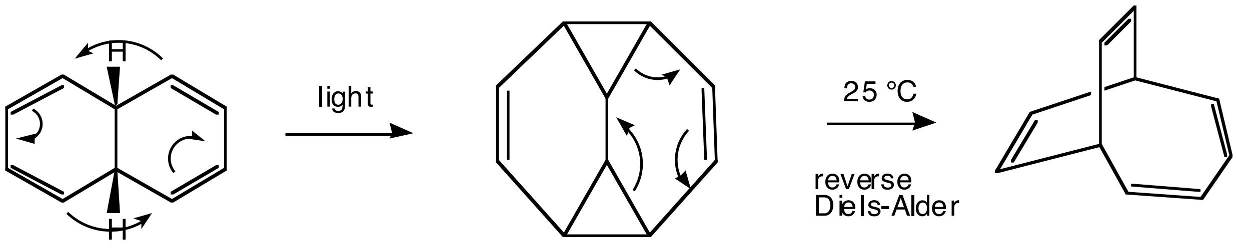
(c)



2. A series of [1,5] hydrogen shifts interconverts all the possible isomers.



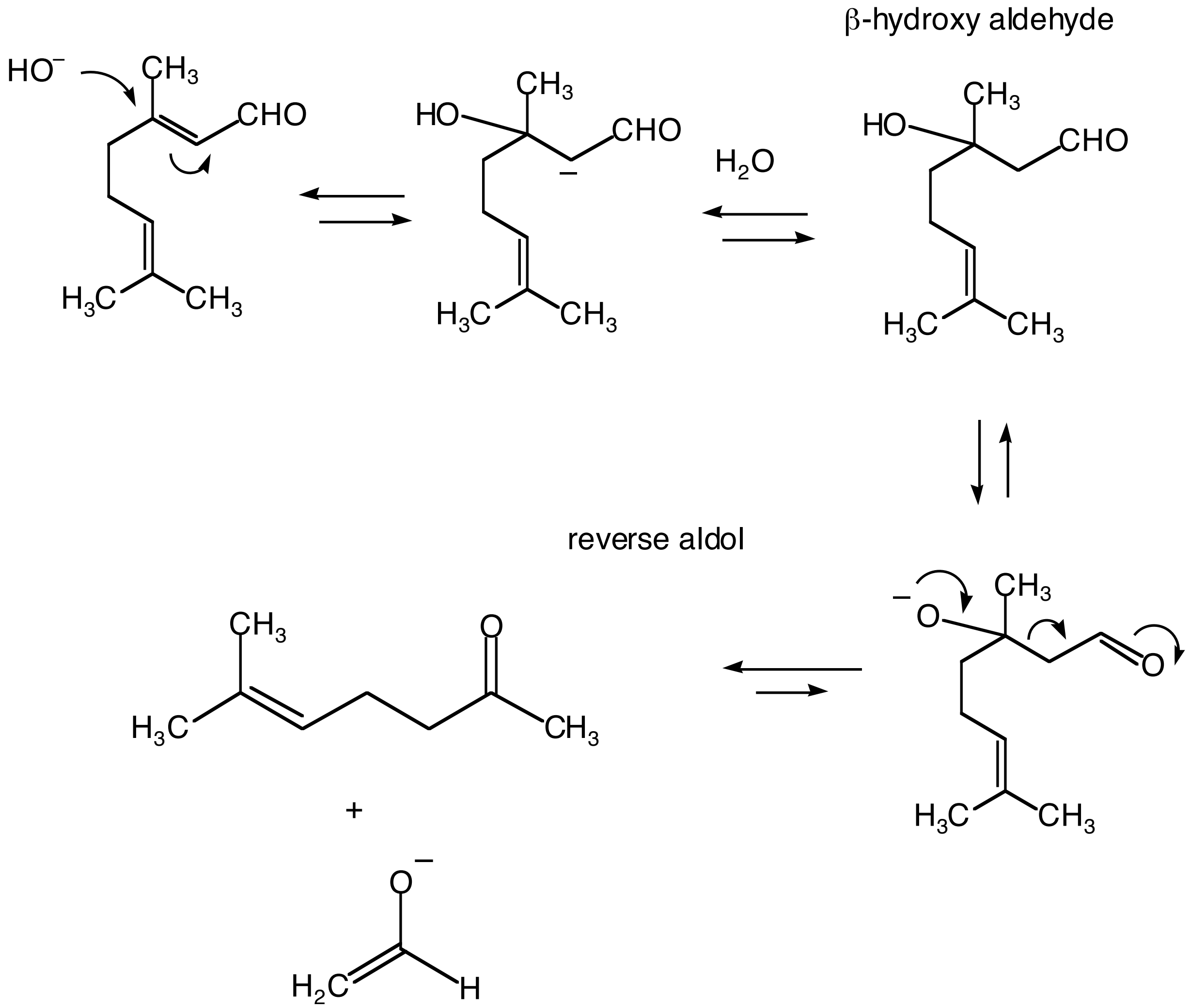
b.



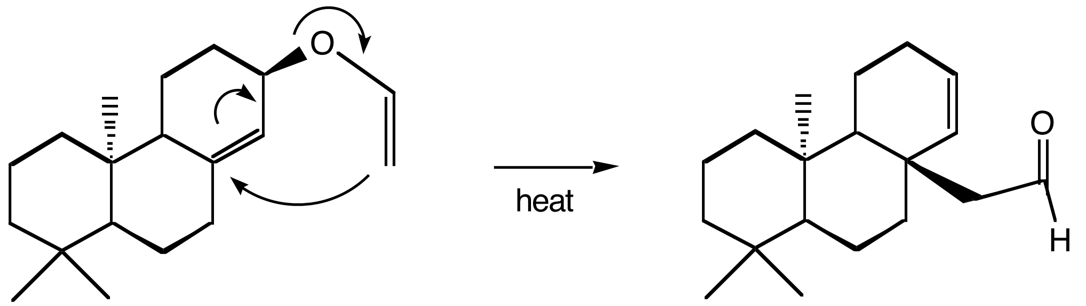
Z = light - it is a 4 + 4 (4n)
cycloaddition

A

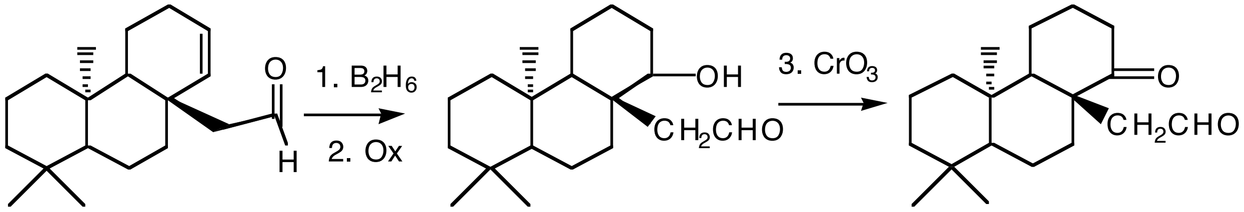
3. Michael followed by a reverse aldol.



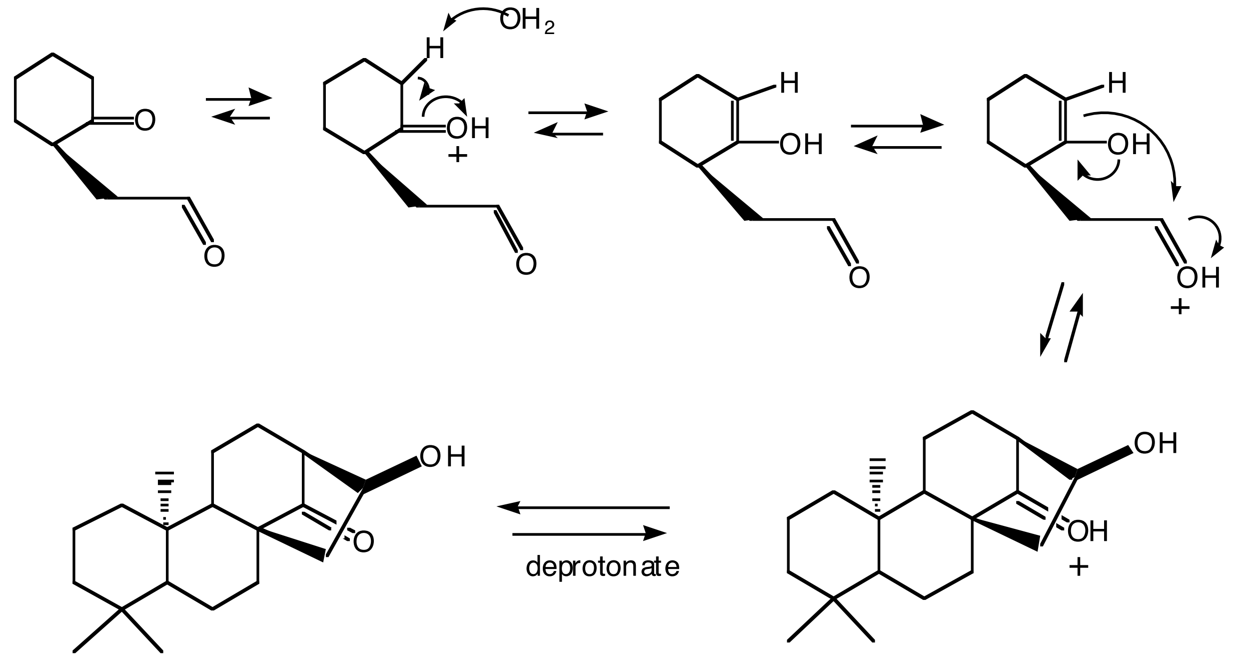
4. We begin with a Claisen variation of the Cope rearrangement. Sorry we drew the molecule in such an uninformative way, but it wouldn’t fit on the page otherwise.



Now a sequence of hydroboration/oxidation, CrO_3 oxidation, and an acid-catalyzed aldol finishes off the problem.

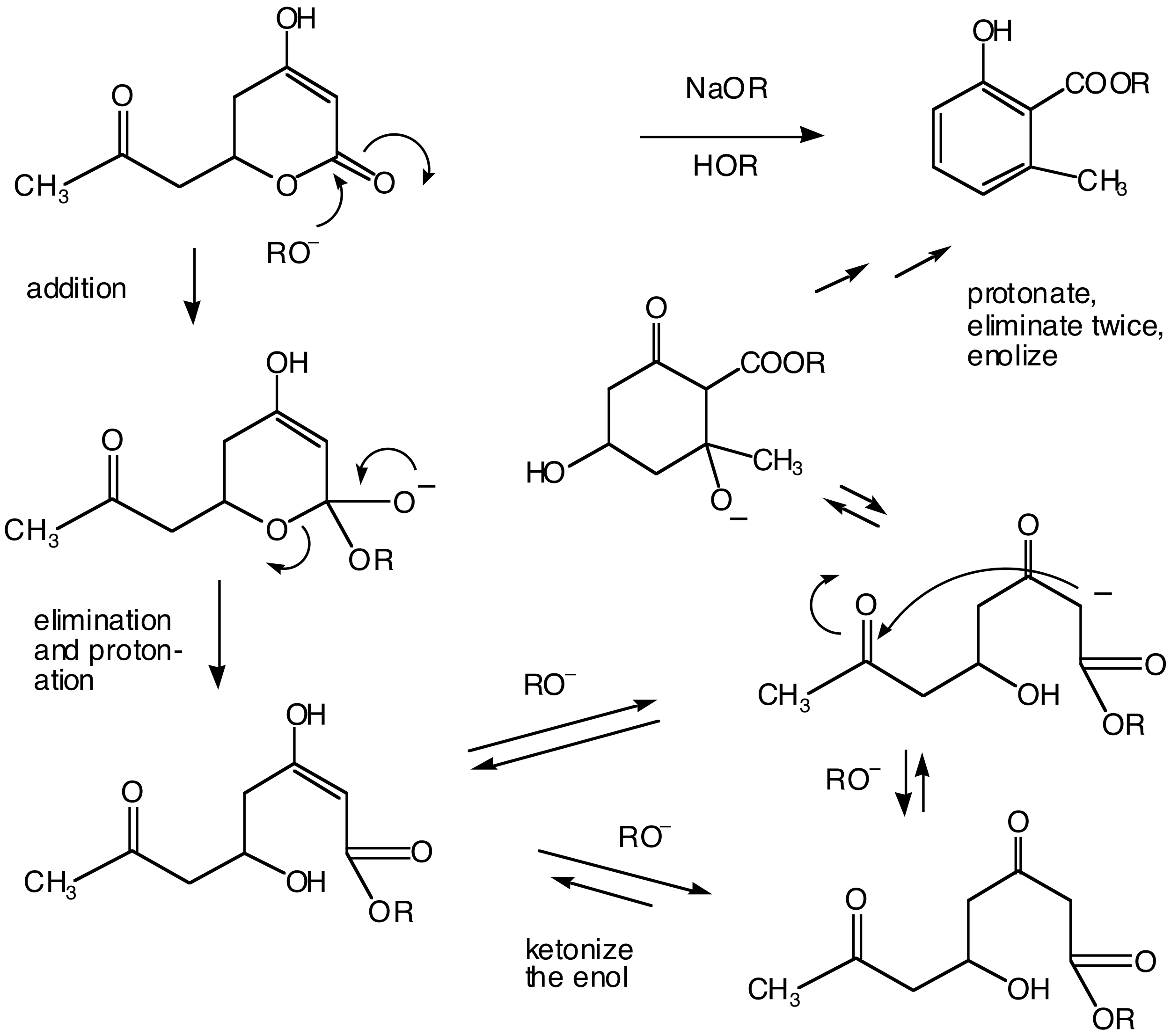


acid-catalyzed aldol:



It is hard to justfy the direction of hydroboration (there are, of course, two possibilities) other than by saying that the one shown leads to product. Perhaps the proximate carbonyl donates electrons into the empty 2*p* orbital of boron - it is a six-membered ring. Elimination would give either an unconjugated or (ugh) a bridgehead double bond.

5.



Note that many other openings of the lactone are possible, but they inevitably give a corboxylate ($RCOO^-$) not an ester.

6. CH_3COO^- ^+Na and CH_3OH