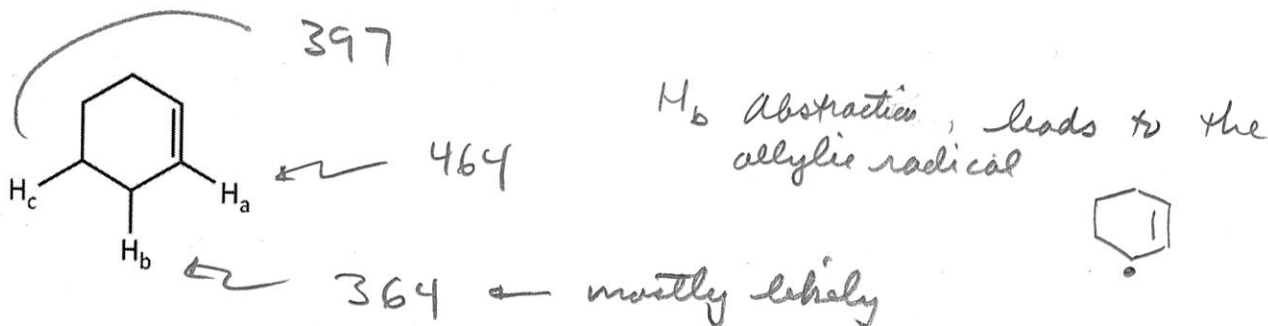
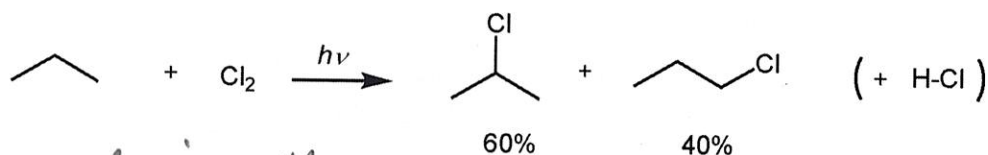


Key

1. For the compound shown below, the carbon-hydrogen bonds to the highlighted hydrogens  $H_a$ ,  $H_b$ , and  $H_c$ , have bond dissociation enthalpies (BDEs) of 397, 364, 464 kJ/mol, *irrespectively*. Assign these values to the correct hydrogens and indicate which one is most likely to be abstracted in a *radical* reaction. (20 points)



2. Explain why the mixture is obtained in the following halogenation reaction. (10 points)

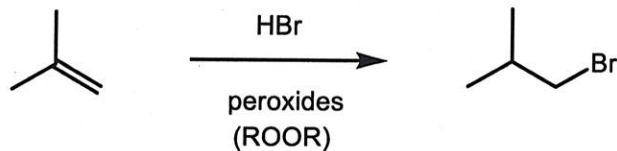


during the propagation step shown below, two different radicals are formed



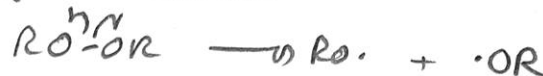
3. In terms of the mechanism of the reaction explain why the addition of peroxides changes the course of the addition reaction shown below. (10 points)

Extra Credit Historically, where did the peroxides come from that led to the discovery of the "peroxide effect"? *form in "old" samples of alkanes due to autoxidation* (5 EC points)

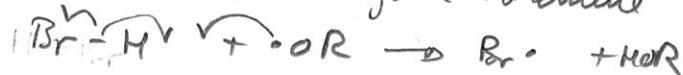


It's the next addition that sets the stereo

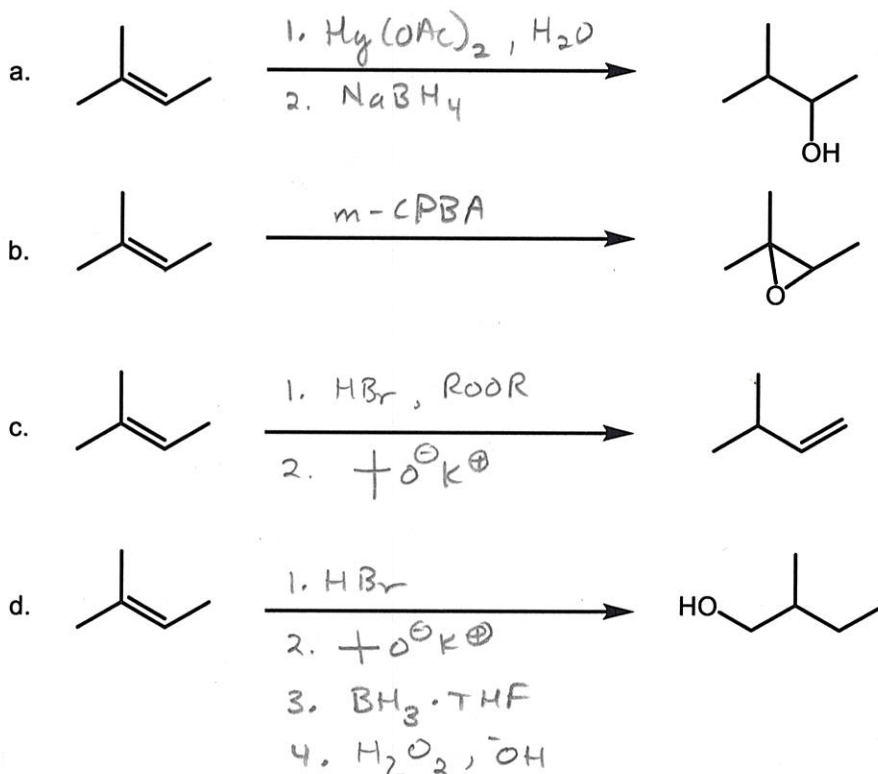
In the presence of peroxides, the peroxide undergoes "easy" bond fragmentation to give a radical



then H-Br reacts with the radical to give bromine

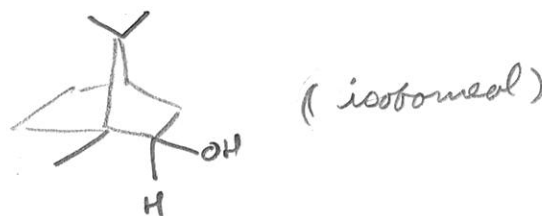


4. Show how to make the following compounds from the given starting materials. Some of the transformations require more than one step. (20 points)

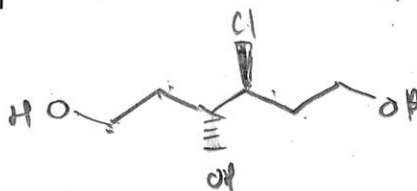


5. Provide structures for the following compounds (don't forget stereochemistry!). (15 points)

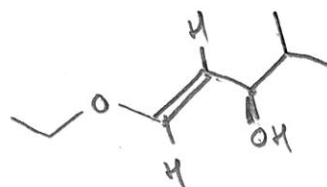
a. (1R,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol



b. (3R,4S)-4-chlorohexane-1,3,6-triol

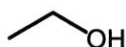


c. (1E,3R)-1-ethoxy-4-methylpent-1-en-3-ol

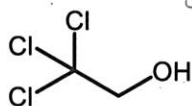


6. Explain the two trends in acidity for the following compounds (10 points)

Trend 1

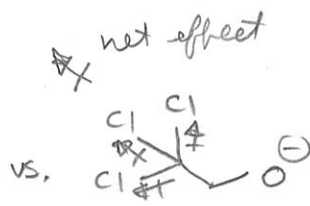
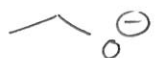


$pK_a = 16$



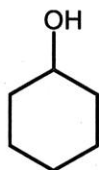
$pK_a = 12.2$

*always consider the conj. bases*

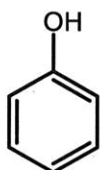


*net effect*  
*more stable due to the inductive effect*

Trend 2



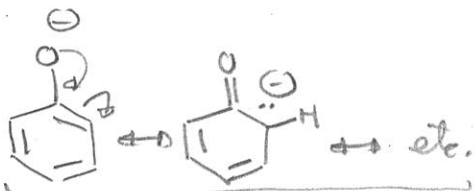
$pK_a = 18$



$pK_a = 10$

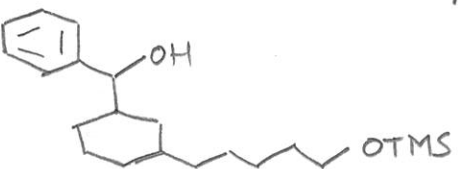
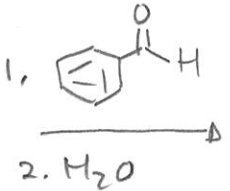
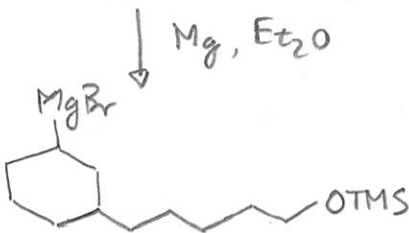
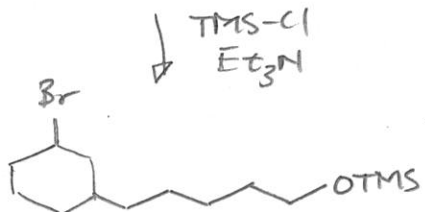
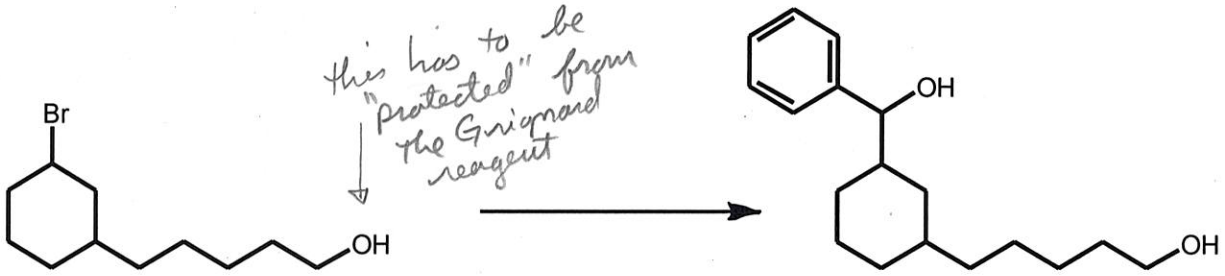


*localized negative charge*



*this conjugate base has lots of resonance stability for the negative charge*

7. Show reagents and conditions to accomplish the following – show all intermediates. (Note that you will need to use a protecting group to be successful) (10 points)

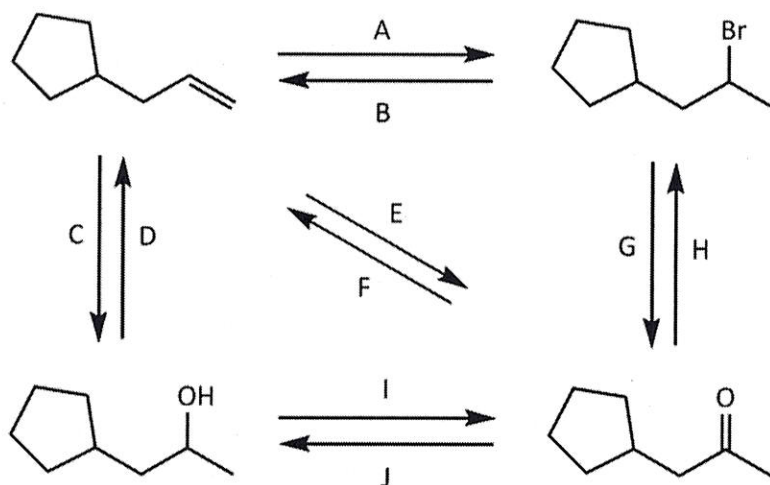


*nBu<sub>4</sub>N F*  
*(deprotection step)*

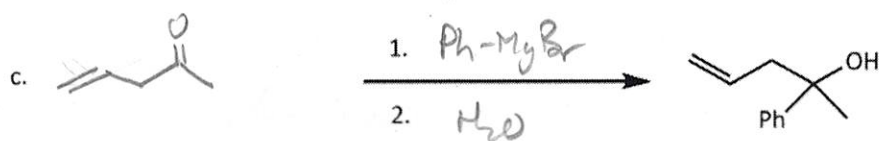
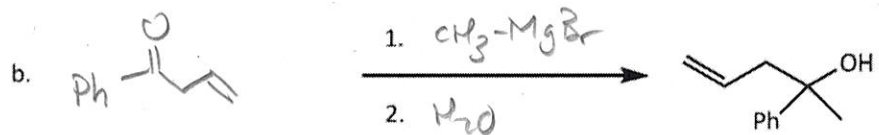
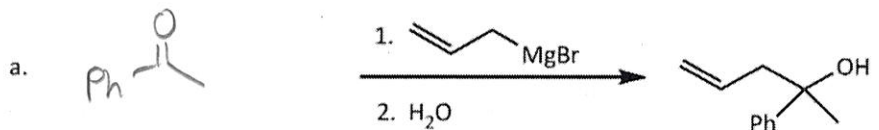
8. For the following series of reactions, fill in the reagents necessary to accomplish each transformation (some of them require more than one step – be sure to use numbers (1, 2., etc) to show separate steps when necessary. You do not need to show any intermediates. Fill in your answers at the left: (50 points)

A.  $\text{HBr}$ B.  $\text{tO}^\ominus \text{K}^\oplus$ C. 1.  $\text{Hg}(\text{OAc})_2$   $\text{H}_2\text{O}$   
2.  $\text{NaBH}_4$ D. 1.  $\text{Ts-Cl}$ , pyridine  
2.  $\text{tO}^\ominus \text{K}^\oplus$ E. step C, then  
PCCF. 1.  $\text{NaBH}_4$   
then DG. 1.  $\text{tO}^\ominus \text{K}^\oplus$ 2.  $\text{Hg}(\text{OAc})_2$   $\text{H}_2\text{O}$  3.  $\text{NaBH}_4$  4. PCCH. 1.  $\text{NaBH}_4$  2.  $\text{PBr}_3$ 

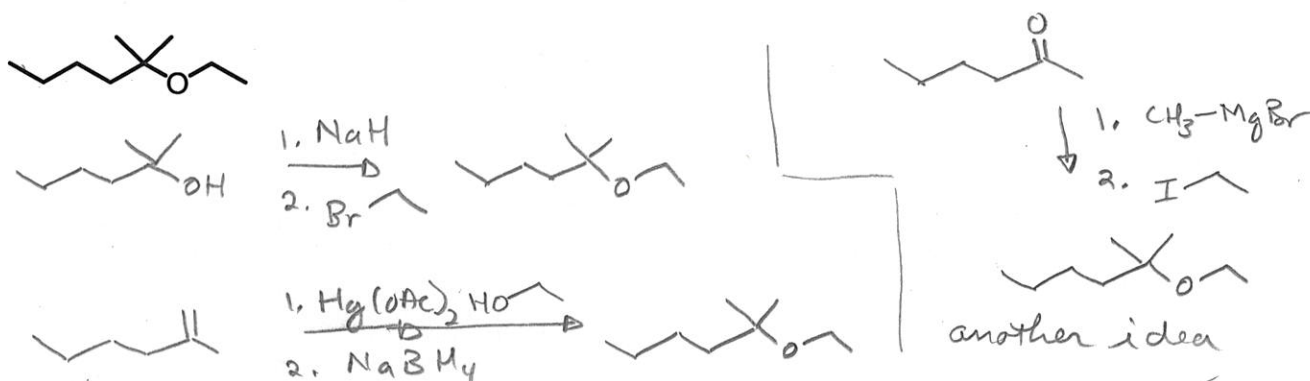
I. PCC

J.  $\text{NaBH}_4$ 

9. Show all three possible methods to prepare the product alcohol using the using a Grignard reaction (a hint is given for the first case. (25 points)



10. Show two (2) different syntheses of the following compound. One of the syntheses should be a Williamson ether synthesis, but there are several correct possibilities for the other. (10 points)

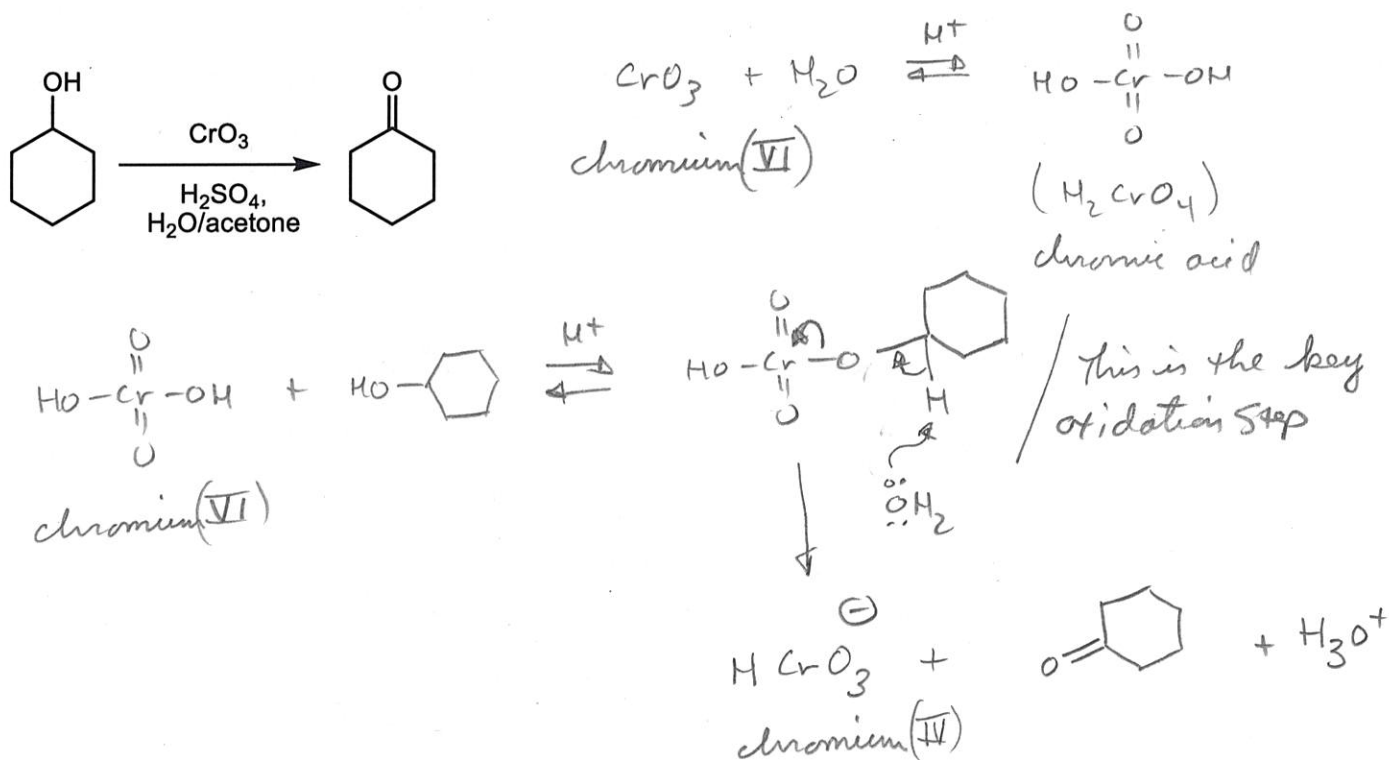


11. Name the product shown in Questions 9 and compound shown in Question 10. (10 points)

Question 9 2-phenylpent-4-en-2-ol

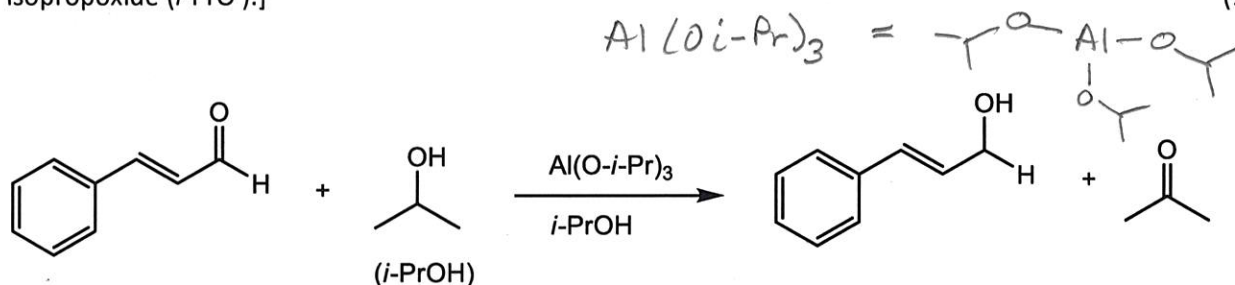
Question 10 2-ethoxy-2-methylhexane

12. Show the mechanism for the oxidation of cyclohexanol to cyclohexanone using Jones' reagent. (Hint: consider what the chromium looks like in water in the presence of strong acid) (10 points)





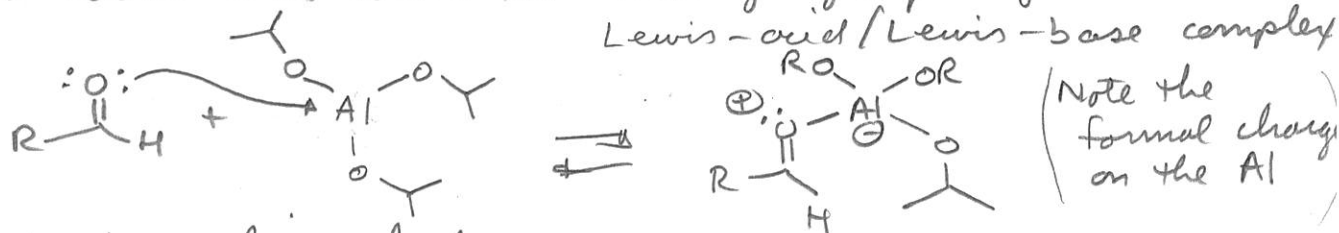
- [Notice the reactant, isopropyl alcohol (*i*-PrOH) is involved also as a solvent and is attached to the aluminum as isopropoxide (*i*-PrO<sup>-</sup>).] (10 points)



In the  $\text{NAD}^+/\text{NADH}$  reaction discussed in Klein and in lecture, the key step is the "hydride transfer" step from the alcohol to a pyridinium ion. This is the opposite direction of electron-flow compared to chromium oxidations



In the MPV reaction, the aluminum acts as a Lewis acid and coordinates with the carbonyl group to give a Lewis-acid/Lewis-base complex



then by pushing electrons,  
a hydride transfer takes place.

