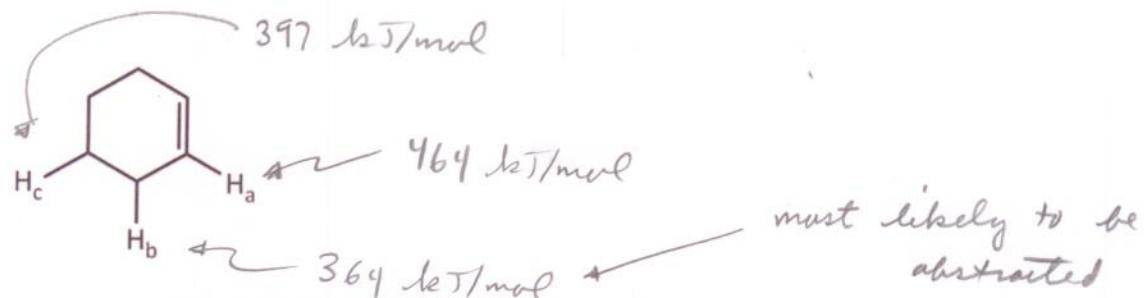
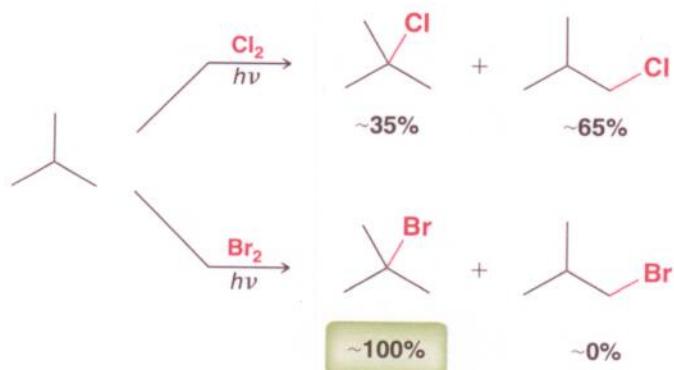


1. For the compound shown below, the carbon-hydrogen bonds to the highlighted hydrogens H_a , H_b , and H_c , have bond dissociation enthalpies (BDEs) of 397, 364, 464 kJ/mol, irrespectively. Assign these values to the correct hydrogens and indicate which one is most likely to be abstracted in a radical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



2. Provide an explanation for the dramatic difference in the ratio of products produced below. (10 points)

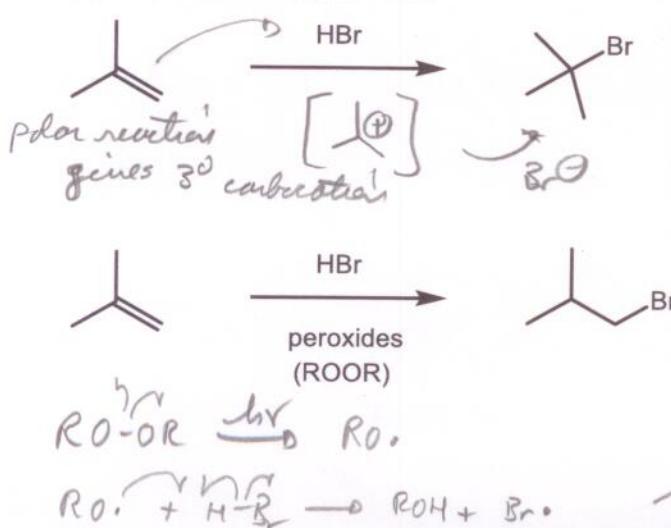


Bromination is more selective because the first propagation step is endothermic and discriminates for the 3° radical over the 1° radical much better than the chlorination reaction, where the first step is exothermic. The radical stability is more important in the bromination step than in chlorination.

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)

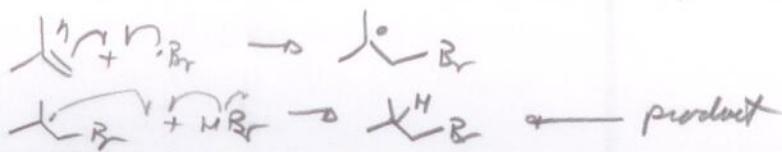
Extra Credit Historically, where did the peroxides come from that led to the discovery of the "peroxide effect"?

Markovnikov addition

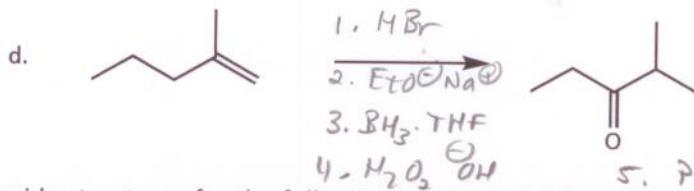
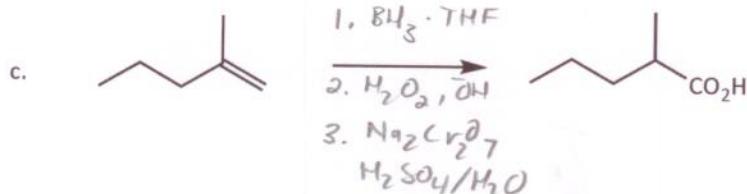
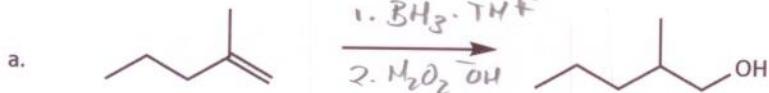


peroxides were formed in alkene samples that were "old" through autoxidation w/ O_2 present in air. (5 EC points)

In the presence of ROOR, the reaction follows a radical mechanism. The initiation step produces a radical which rapidly results in the formation of bromine radical which undergoes addition to the alkene to give the most stable radical, 3°

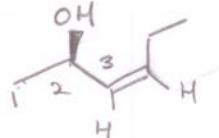


4. Show how to make the following compounds from the given starting materials. Some of the transformations require more than one step. (20 points)

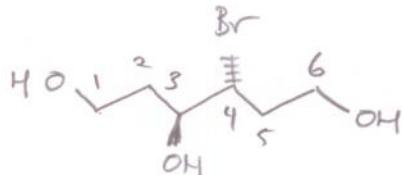


5. Provide structures for the following compounds (don't forget stereochemistry!). (15 points)

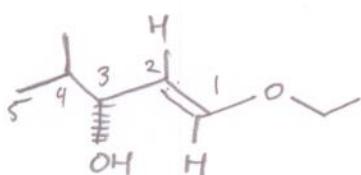
a. (2*R*,4*Z*)-hex-3-en-2-ol



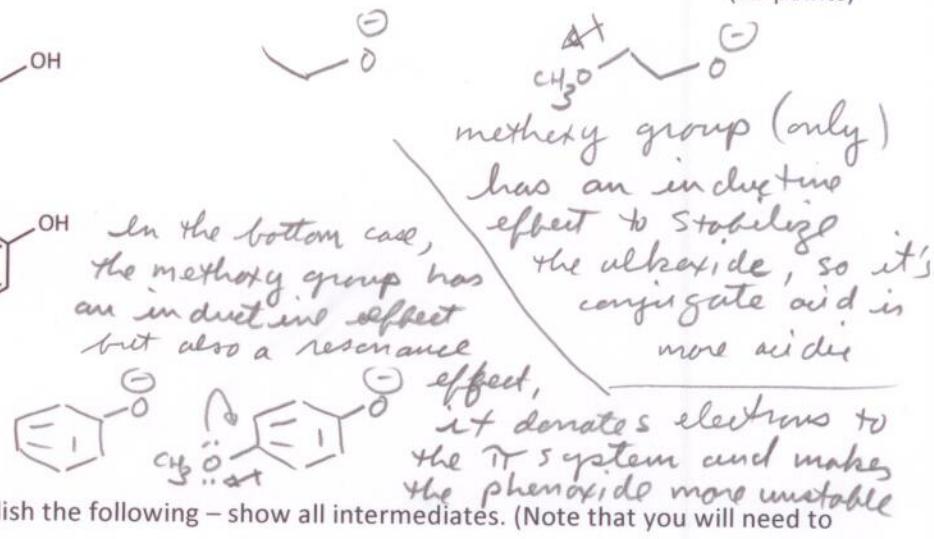
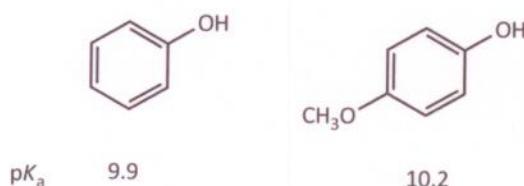
b. (3*S*,4*R*)-4-bromohexane-1,3,6-triol



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



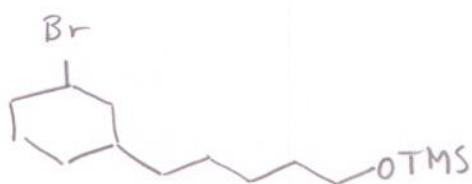
6. Compared to ethanol, 2-methoxyethanol is nearly 100 times more acidic. However, 4-methoxyphenol is slightly less acidic than phenol. Explain why the methoxy group has the "opposing" effect on acidity in the two cases. (10 points)



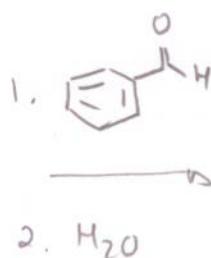
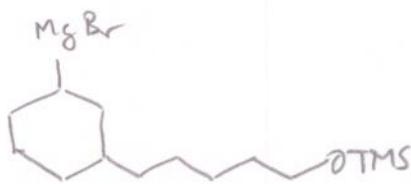
7. Show reagents and conditions to accomplish the following – show all intermediates. (Note that you will need to use a protecting group to be successful) (10 points)



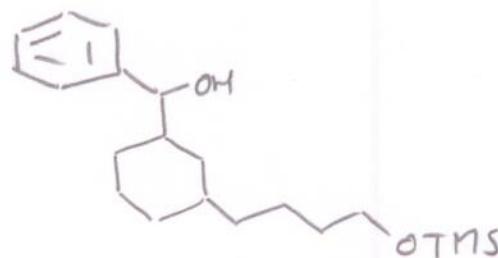
TMS-Cl, pyridine



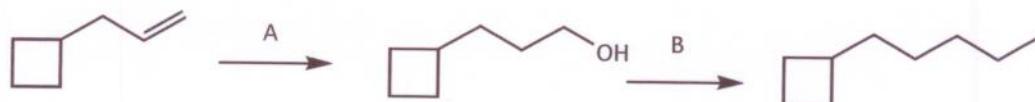
Mg, Et₂O



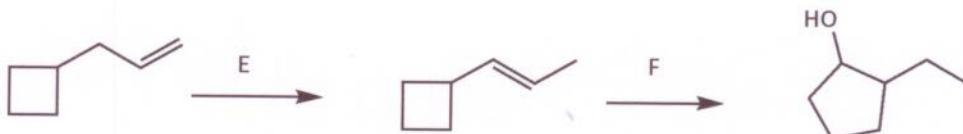
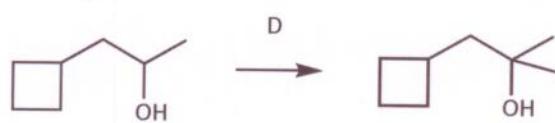
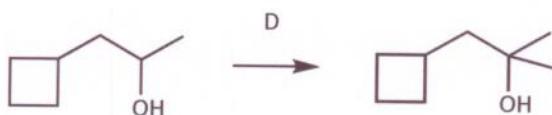
TBAF



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 below by the letter.) (60 points)



C
↓



A. 1. $BH_3 \cdot THF$
2. H_2O_2 / OH^-

B. 1. $TsCl$ pyridine
2. $HgCl \cdot Na^+$ 3. H_2 , Pt

C. 1. $Hg(OAc)_2$, H_2O
2. $NaBH_4$

D. 1. PCC
2. $MeMgBr$ 3. H_2O

E. 1. HBr 2. $NaOEt$, $HOEt$

F (challenging).

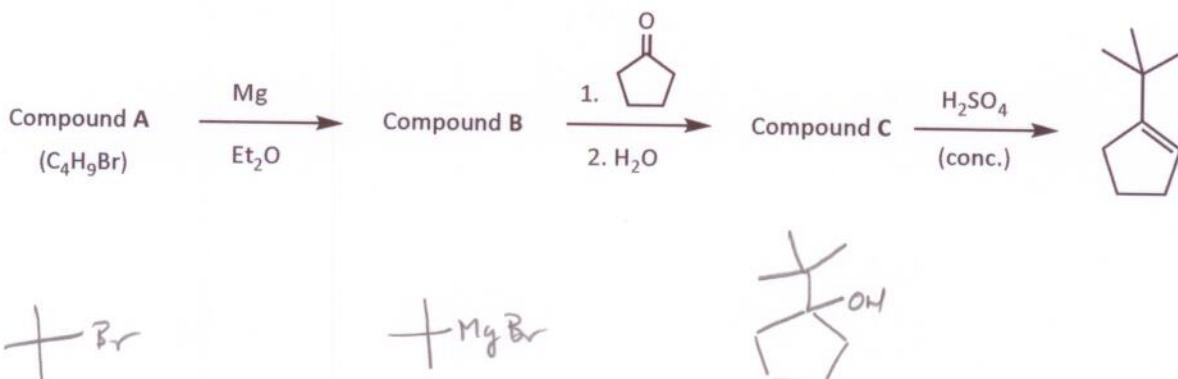
dilute H_2SO_4 (will give product + others) – worth some points

1. H_2 , Pd/C
2. Br_2 , $\lambda\gamma$
3. $NaOEt$
4. $BH_3 \cdot THF$
5. H_2O_2 / OH^-

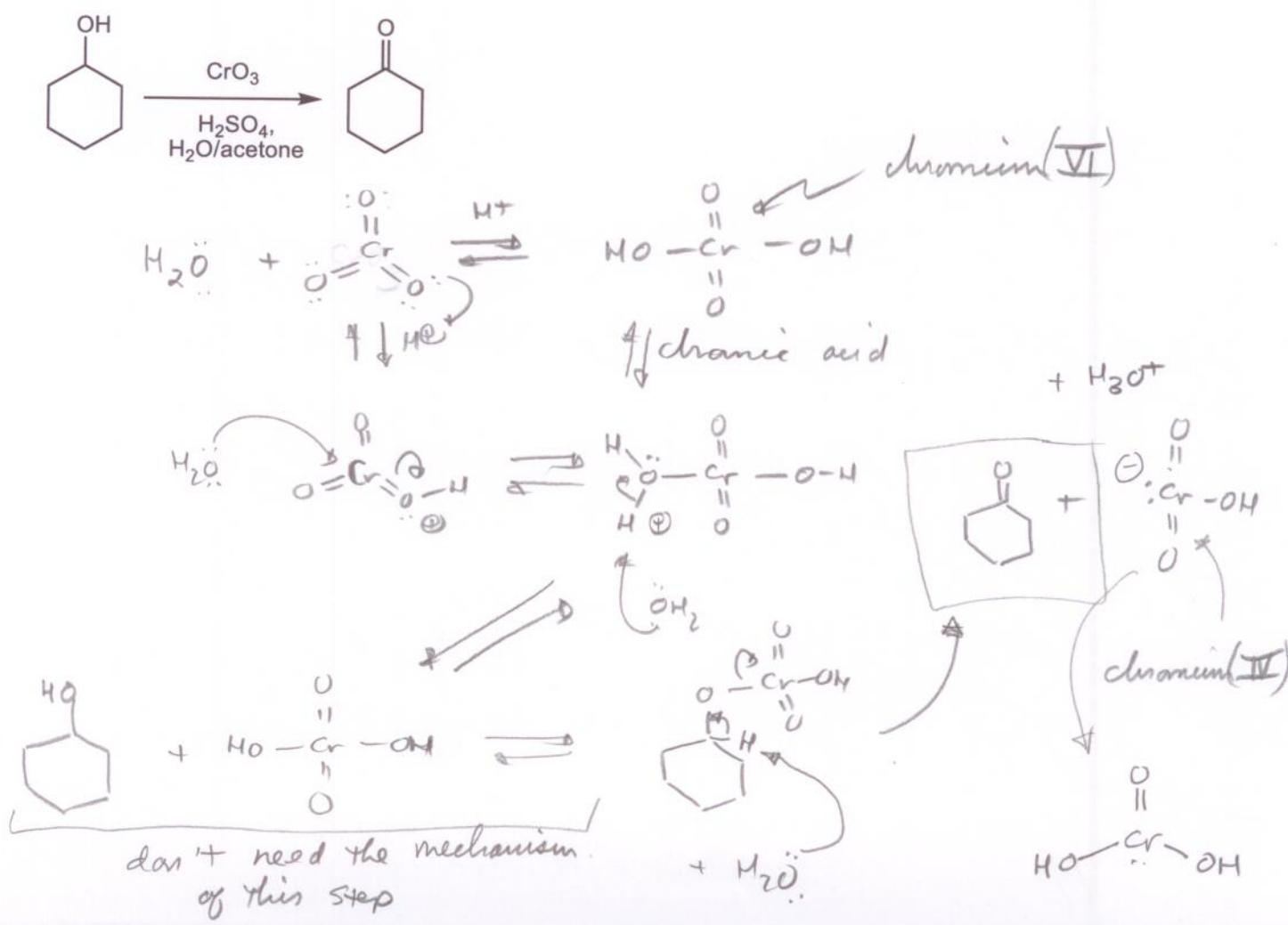
6. dilute H_2SO_4 , Δ

9. Show the structure of all three Compounds A-B in the following synthesis.

(15 points)



10. 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)



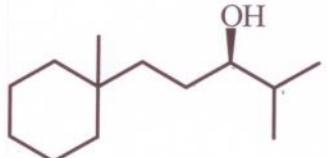
NAME _____

Key

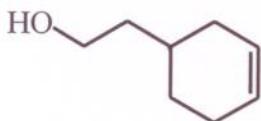
This is the supplement for make-up Exam 1

11. Name the following compounds

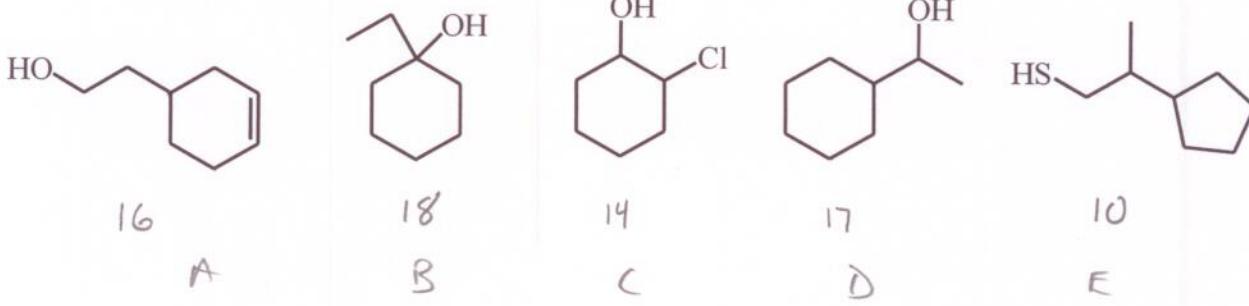
(20 points)

 $(2S,8Z)$ -dec-8-en-3-yn-2-ol $(3R)$ -4-methyl-1-(1-methylcyclobutyl)-pentan-3-ol12. Estimate the pK_a for each compound (be precise) and explain the variation in their pK_a .

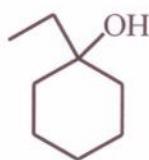
(25 points)



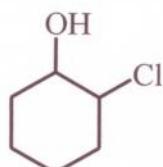
16



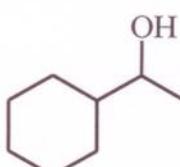
A



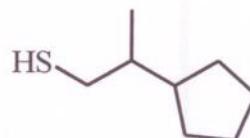
18



14



17



10

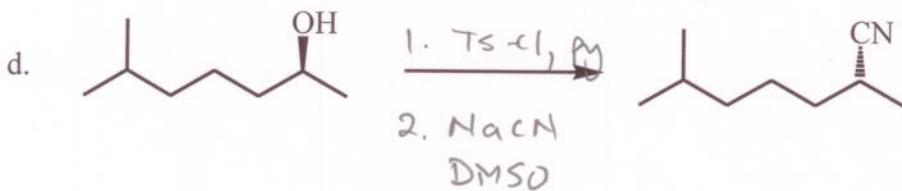
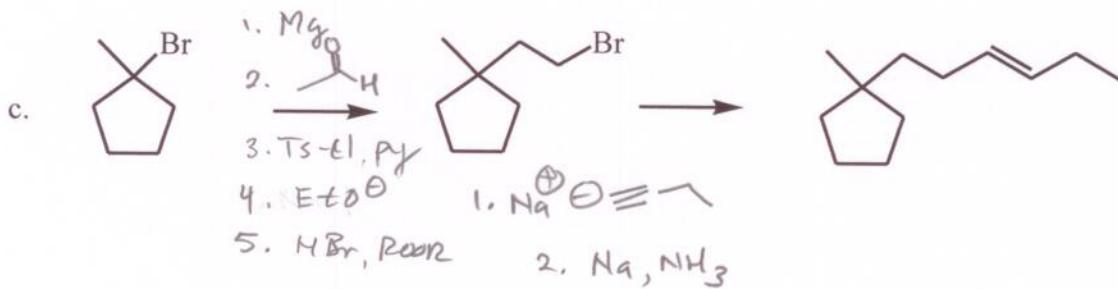
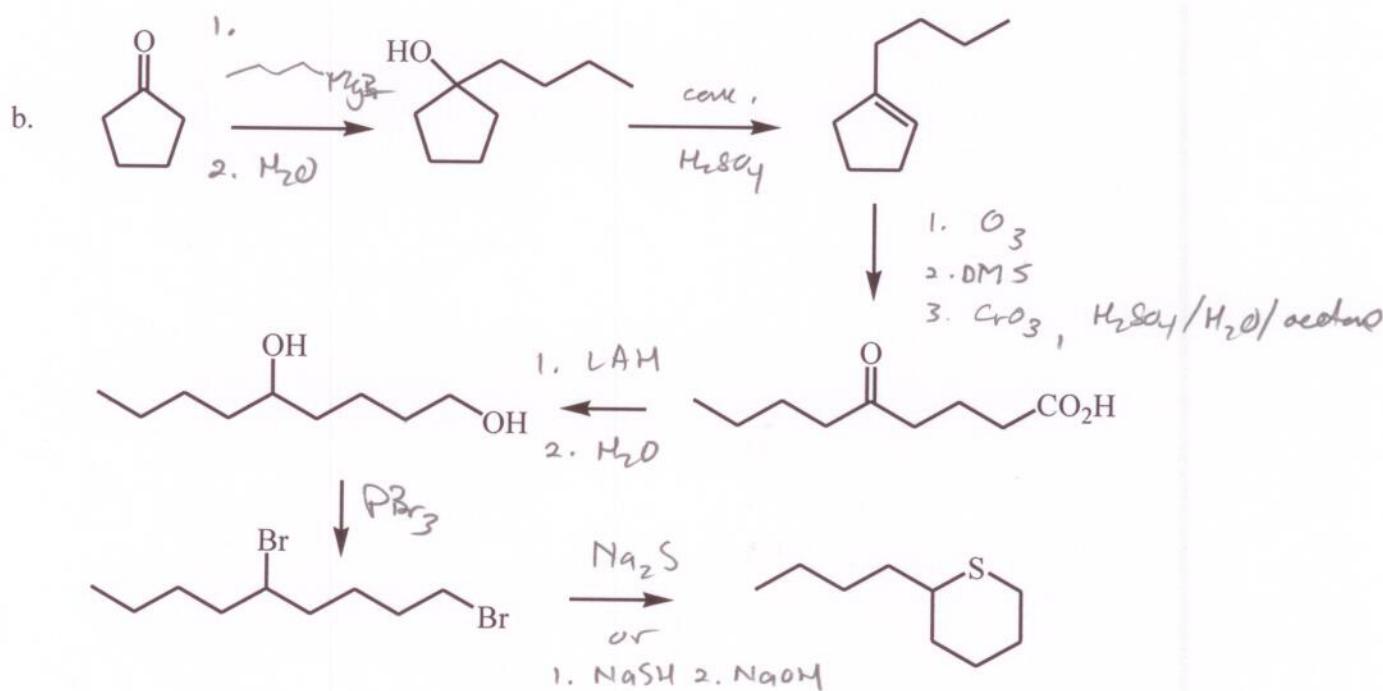
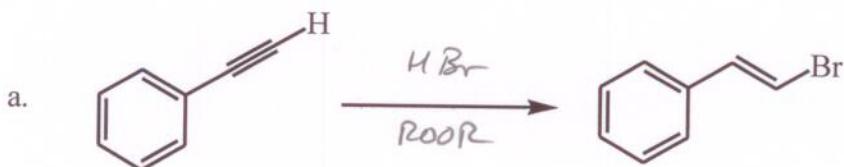
*E - thiols more acidic than alcohols - atom effect
acidity*

*A > B > C - more substituted alcohols less acidic due to lack
of solvation*

*C > D - both are 2° alcohols, but chlorine inductive
effect stabilizes conjugate base from C, so it's more
acidic*

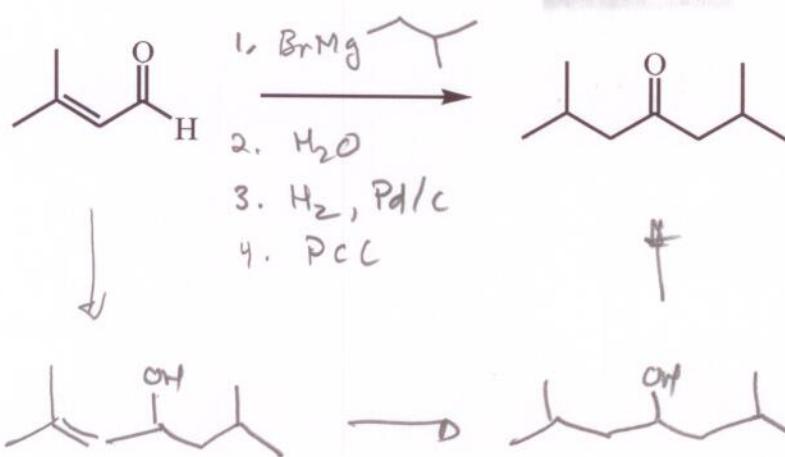
13. Provide reagents and conditions to accomplish each of the synthetic transformations shown below. Several of the transformations require more than one step.

(90 points)



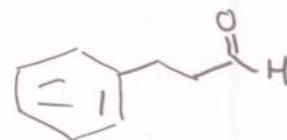
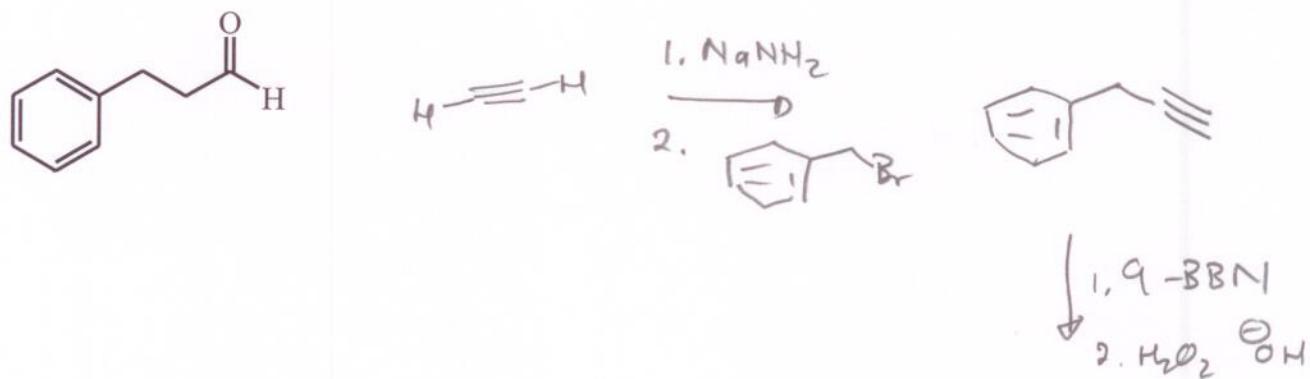
14. Show the reagents necessary to accomplish the following transformation – show all intermediates.

(15 points)



15. Show how to prepare the following compound starting from acetylene (C_2H_2) and any other reagents.

(15 points)



✗