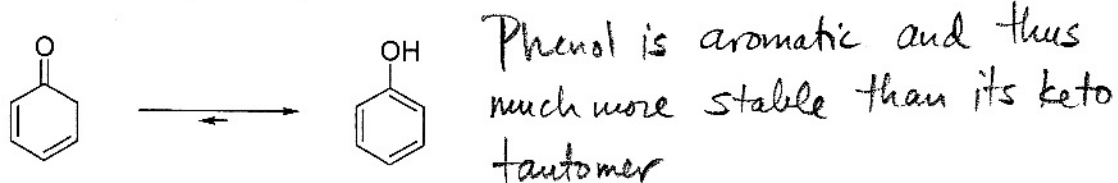
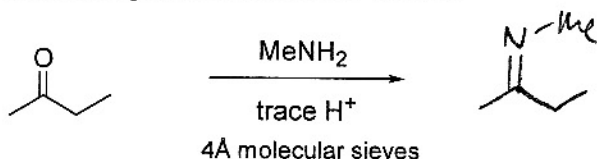


Provide short (2-3 sentences MAX) answers to each of the following questions (16 pts).

1a) Most ketones exist primarily in the *keto* form, but phenol exists exclusively in the *enol* form. Explain why.



1b) In the formation of an imine, we typically use a trace of a carboxylic acid and something called *molecular sieves*.



Draw the imine product that results from this reaction, then answer the following:

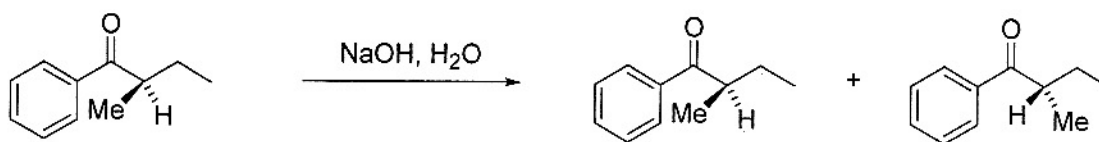
Why does the pH of the reaction have to be carefully controlled, i.e., must be  $\leq 5$ ?

To avoid protonation of the amine, which would render it non-nucleophilic.

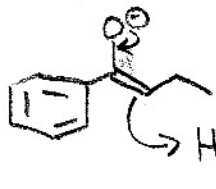
What is the purpose of the molecular sieves?

To remove water formed in the reaction so the eqbm position favors products (i.e., imine)

1c) Why does an optically active solution of (*R*)- $\alpha$ -methylbutyrophenone form a racemic mixture when aqueous base is added to the solution?

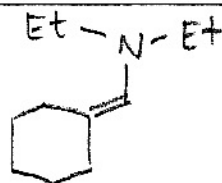
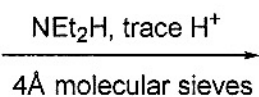
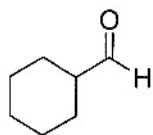
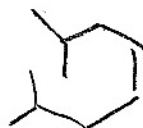
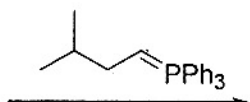
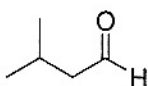
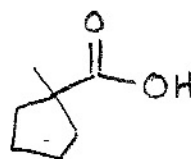
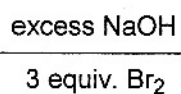
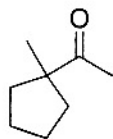
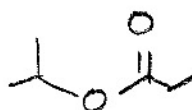
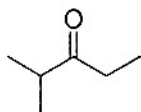
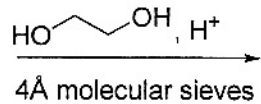
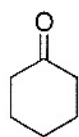


The enolate that forms under these conditions is planar:

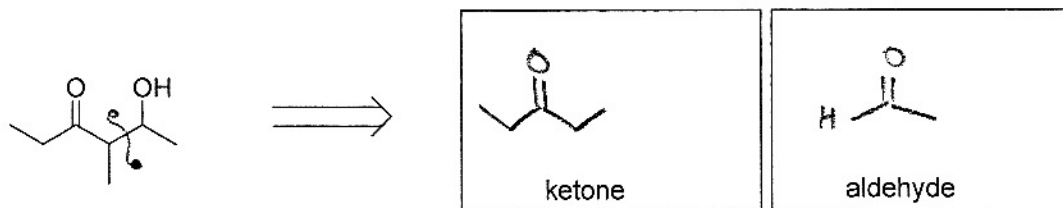


and can be reprotonated by  $H_2O$  from either face with no preference, resulting in an equal mixture of the two enantiomers of  $\alpha$ -methylbutyrophenone.

2) Predict the major organic product of each of the following reactions. Assume aqueous workup for all reactions. (20 pts).

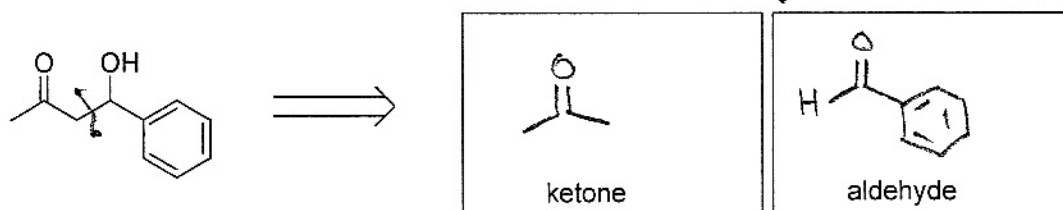


3a) Indicate the starting aldehydes and ketones that reacted to form each of the aldol products shown and propose enolate formation conditions (base, equivalents, relative temperature, relative reaction time) that you would use in each case. (16 pts)



Enolate formation conditions:

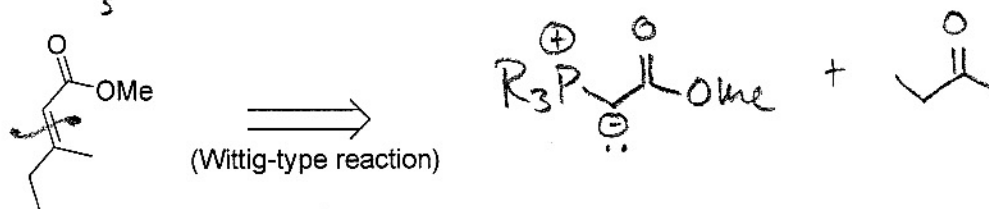
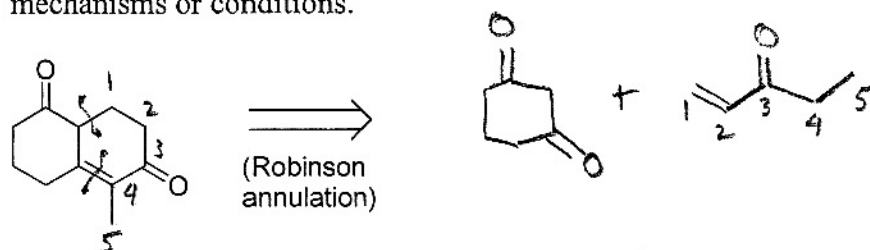
NaH or KH, 0.95 equiv, longer reaction times, relatively higher T (or  $\rightarrow O^{\ominus}K^{\oplus}$ , or LDA, 0.95 equiv)



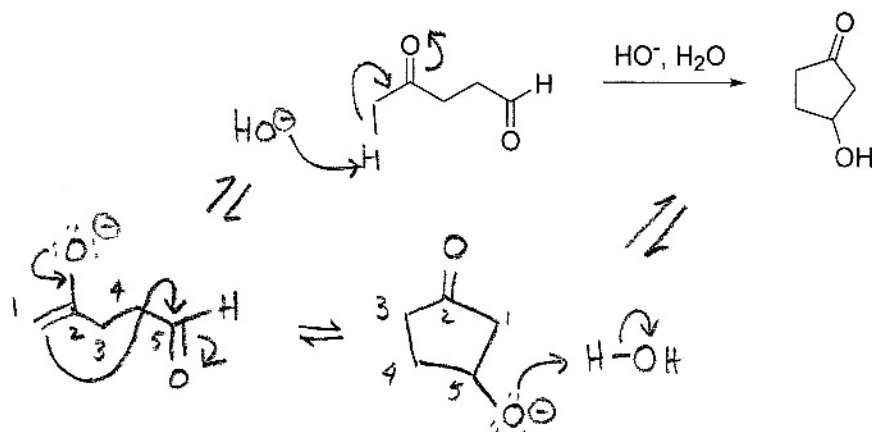
Enolate formation conditions:

LDA, THF,  $-78^{\circ}C$ , short reaction times

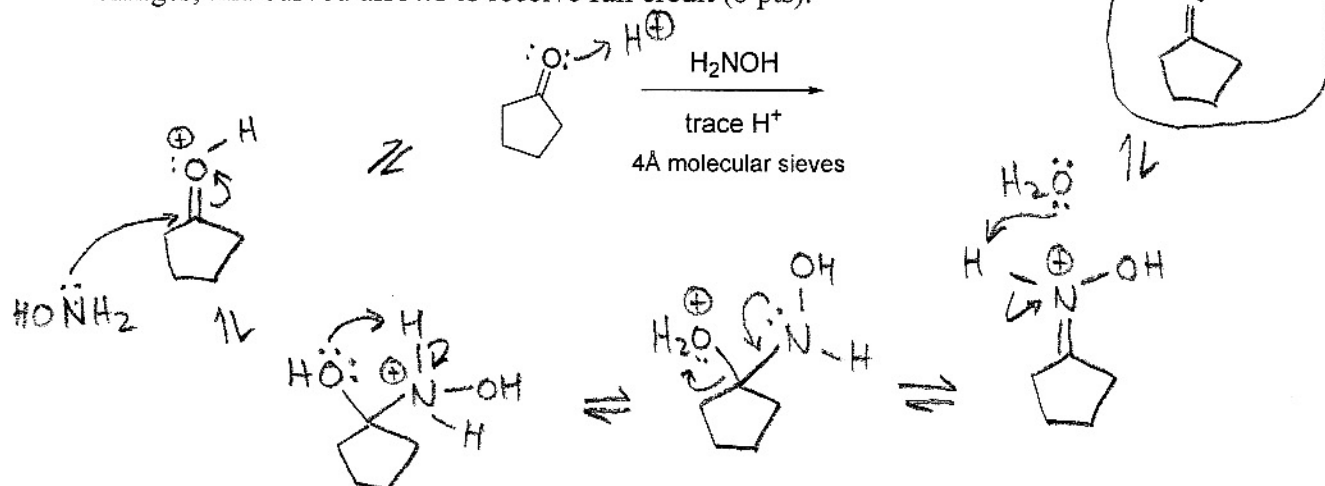
3b. Indicate how you would form the following molecules using the indicated reaction by showing the necessary starting materials. You do not have to draw any mechanisms or conditions.



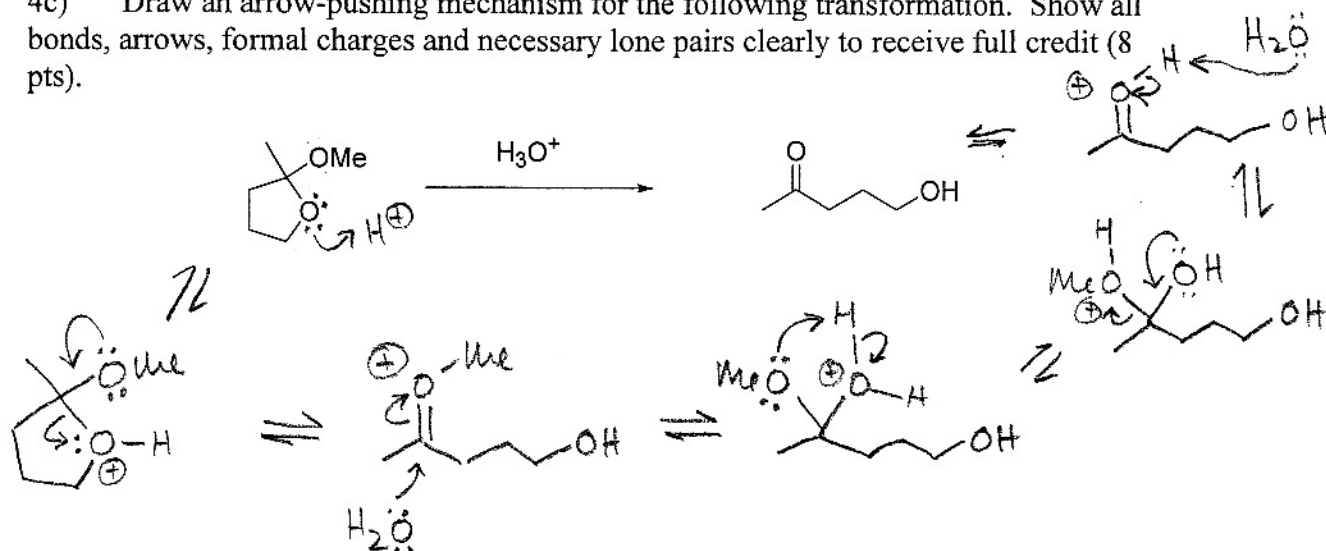
4a) Provide an arrow-pushing mechanism for the formation of the product in the following transformation. Show all necessary lone pairs, formal charges, and curved arrows to receive full credit (8 pts).



4b) Predict the product and provide an arrow-pushing mechanism for the formation of the product in the following transformation. Show all necessary lone pairs, formal charges, and curved arrows to receive full credit (8 pts).



4c) Draw an arrow-pushing mechanism for the following transformation. Show all bonds, arrows, formal charges and necessary lone pairs clearly to receive full credit (8 pts).



CC=CC  $\xrightarrow{\text{1. Hg(OAc)}_2, \text{H}_2\text{O}}$  CC(O)CC  $\xrightarrow{\text{2. NaBH}_4}$  CC(O)CC  $\xrightarrow{\text{PCC, CH}_2\text{Cl}_2}$  CC(=O)CC  $\xrightarrow{\text{Me}_2\text{NH, tr. H}^+, \text{4 A m.s.}}$  CC(=CC)N(C)C

