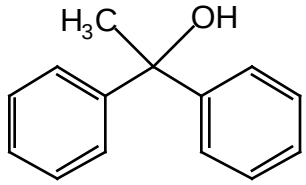
**Hour Examination #2, Chemistry 302-302A, 2004**

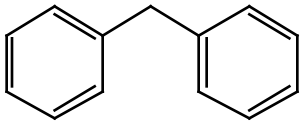
"Problems worthy
of attack
prove their worth
by hitting back."

Piet Hein
(thanks to Josh Schulman)

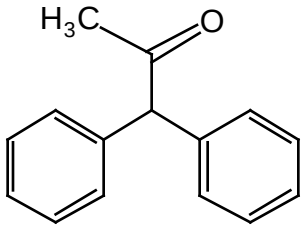
1 (21 points). Devise syntheses for the following molecules. You may use any inorganic reagent, alcohols containing no more than three carbons, benzene, pyridine, thiophene, furan, and...need something else organic? Ask and we'll tell you if you can use it. Mechanisms are not necessary.




(a)



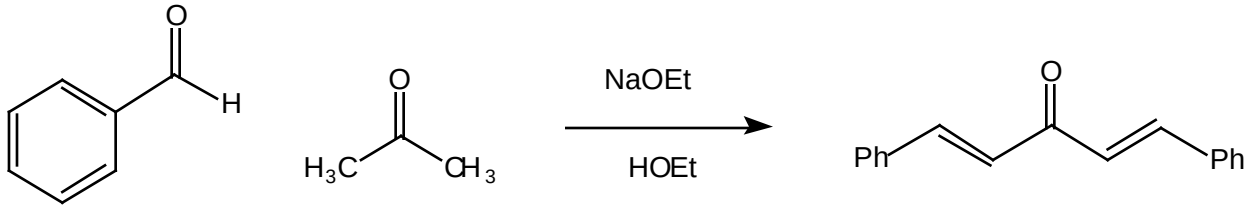
(b)




(c)

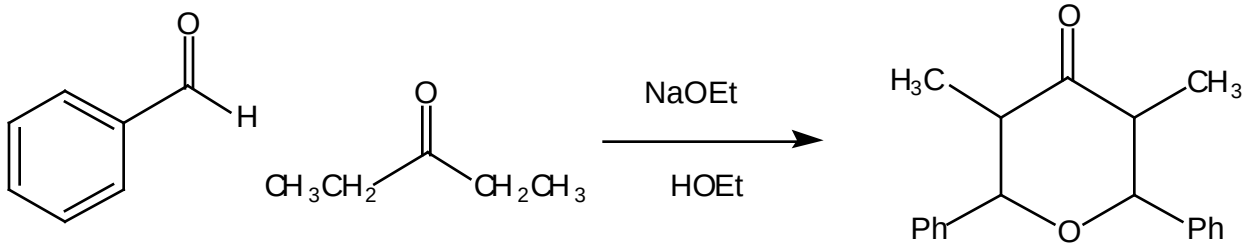
2 (21 points). Provide detailed mechanisms for the following condensation reactions. You do not have to predict or explain stereochemistry for part (b).

(a)




(Ph-CHO)

(b)

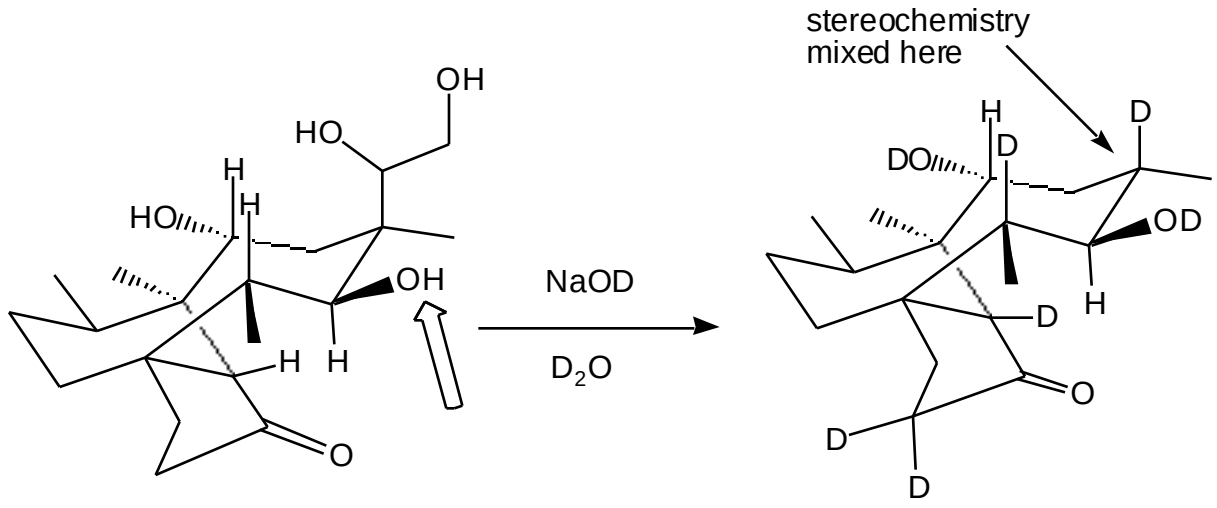



(Ph-CHO)

(c) Now explain why the two reactions take different routes.

3 (18 points). You will have to analyze and think about what steps happen when in this problem. That is, the order in which you do things is very important.

Provide mechanisms for the following transformations. In answering this question, you do not have to draw out the entire molecule over and over. Focus on the relevant parts.




Here is a suggested analysis. What transformations are easy/obvious? Do these first!

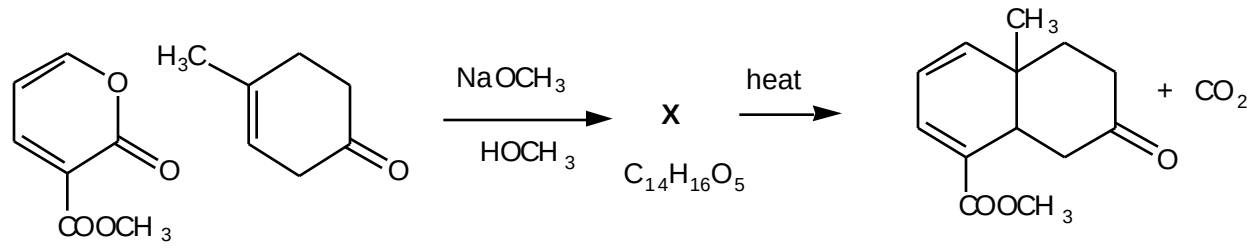
(a) Five hydrogens are easily exchanged for deuterium in this molecule. Which are they? Indicate them with arrows or be very clear in words.

Write a mechanism for one of those “easy” exchanges  at carbon (one only!).

(b) Now what’s hard/mysterious?  One hydrogen that should not exchange does, and a carbon-carbon bond must have broken so that diol in the upper right can be lost to be replaced with a deuterium.

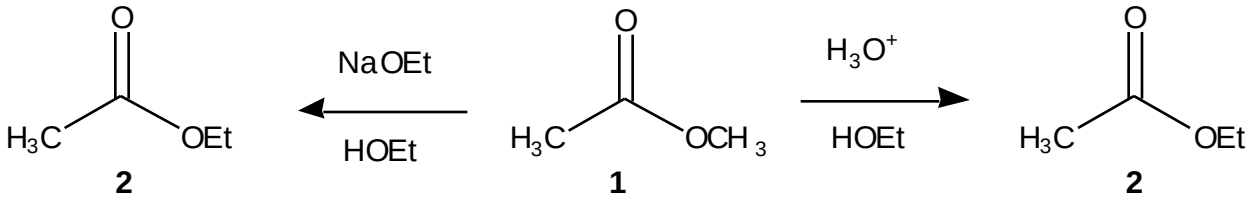
One conversion serves to make both of these “mysterious” reactions possible. Ask yourself what that conversion could be, then write us reaction mechanisms that show how everything happens. Hint: The other stereoisomer of the “arrow” OH does ***not*** lose the diol or exchange the “mysterious” hydrogen.

4 (20 points). Here is a reaction that appears at an early stage of Corey and Watt's synthesis of racemic α-ylangene. Please Note: There is ***no*** reaction in the absence of base! Note that it is possible to work on this question from either end.



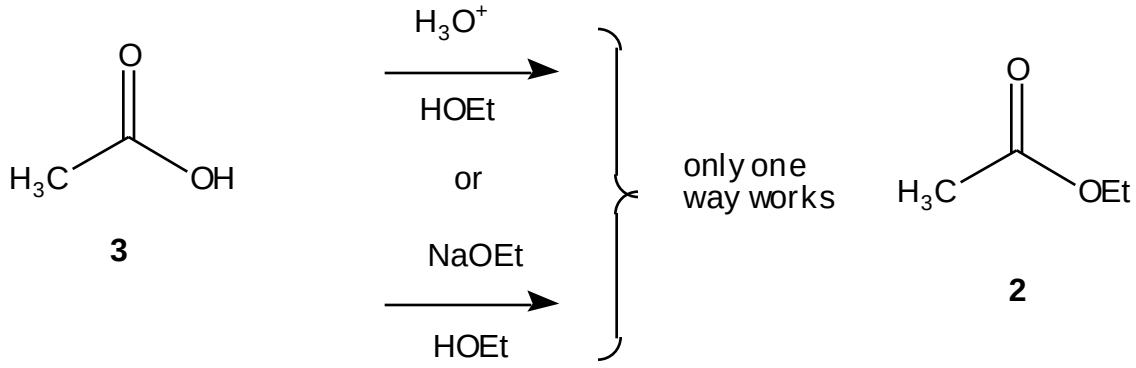

Provide a nice mechanism for this reaction, and a structure for (**X**). Analyze first!

5 (20 points). Methyl acetate (**1**) is transformed in either acid or base into ethyl acteate (**2**).




(a) write mechanisms for both those changes.

In contrast to **1**, acetic acid (**3**) can be made into ethyl acetate under only one of the conditions (either acid or base).




(b) Which reaction works (acid or base)?

(c) explain why the other reaction fails. What product is formed under the other conditions (acid or base)?

"I pledge that I have not violated the Honour Code on this examination."