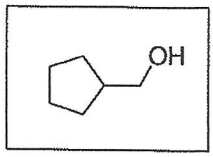
Key - 3331 Summer 08
Exam 2 Mingen

For each of the following questions, circle the *best* answer. (4 pts each, 20 total)

1a. Which of the following best describes the mechanism of the Williamson ether synthesis?

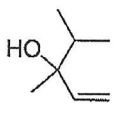
S_N1 (circled) S_N2 E1 E2 Nucleophilic addition

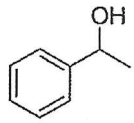
1b. Which of the following reagents would convert the alcohol in the box to a carboxylic acid?

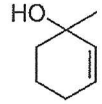


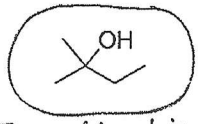
PCC DMSO, $(COCl)_2$, Et_3N (Swern) (circled) H_2CrO_4, H_2O, acetone (Jones) CrO_3 pyridine (Collins)

1c. Which of the following alcohols could have been made from reacting a Grignard reagent with an ester?

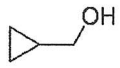




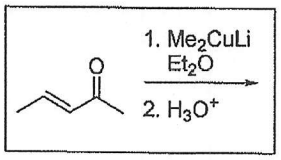


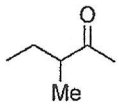


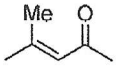
Two identical R groups

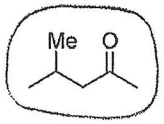


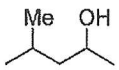
1d. Which of the following is the correct product of conjugate addition of Me_2CuLi to the enone shown in the box?

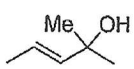




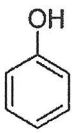


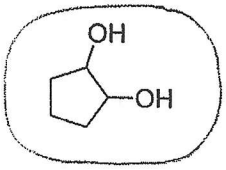


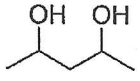


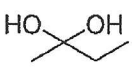


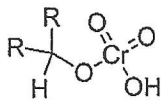
1e. Which of the following is a *vicinal diol*?



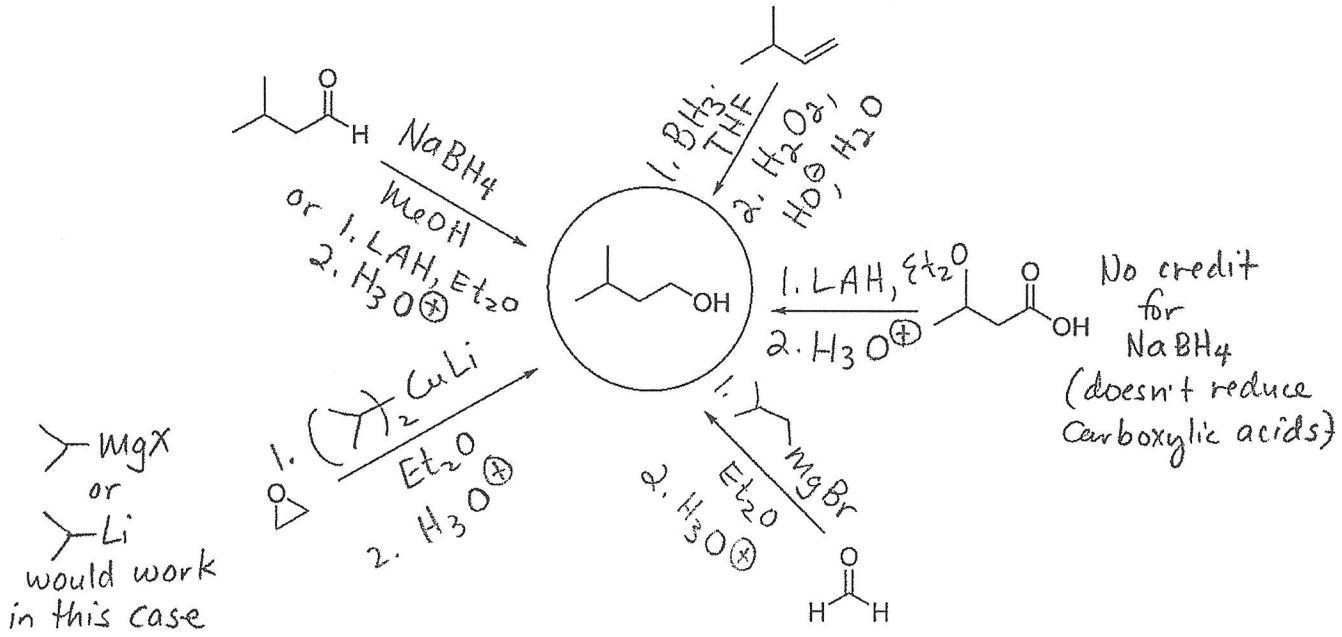




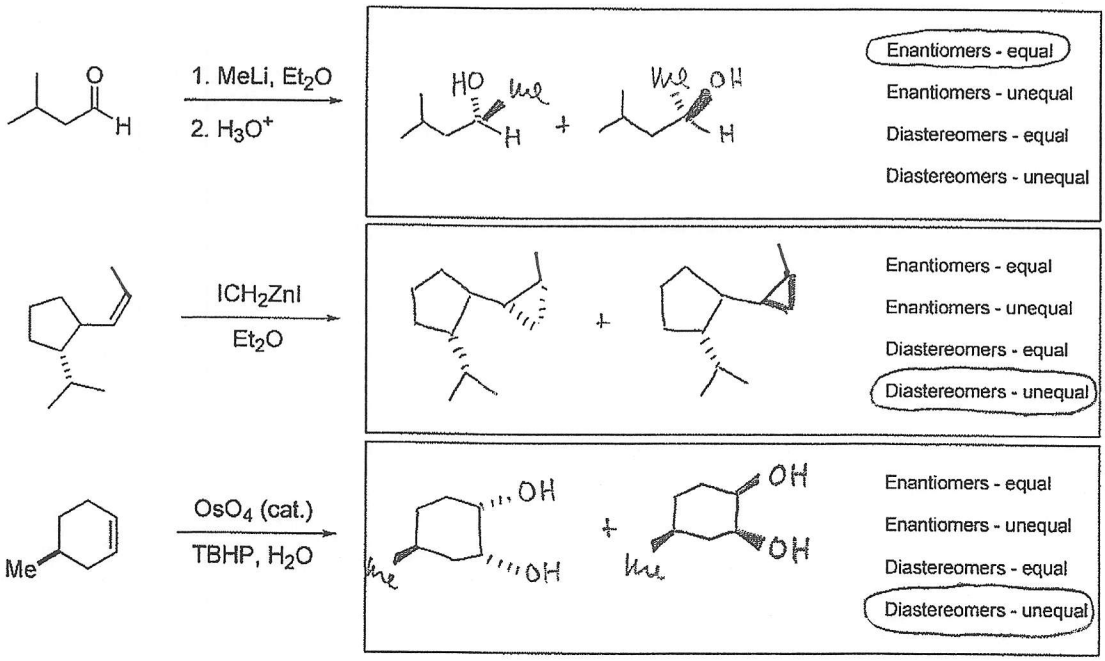




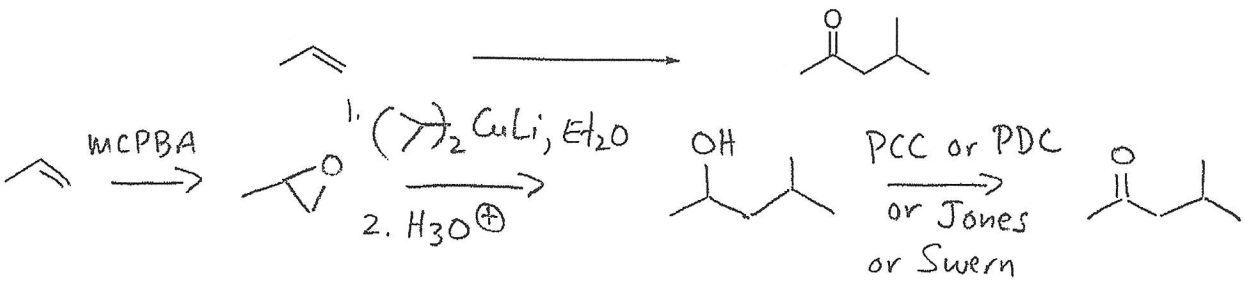
2a. The alcohol shown in the circle can be accessed from each of the starting materials shown. Provide the missing reagents for each transformation. Write them over the arrows (15 pts).



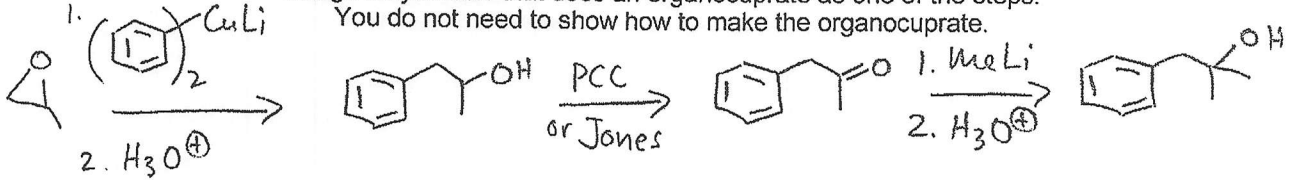
2b. Predict all organic products for each of the following transformations, showing stereochemistry by using wedge and dash notation. If more than one product forms, indicate the stereochemical relationship of the products and whether they are formed in equal or unequal amounts by circling the correct choice in the box. (18 pts)



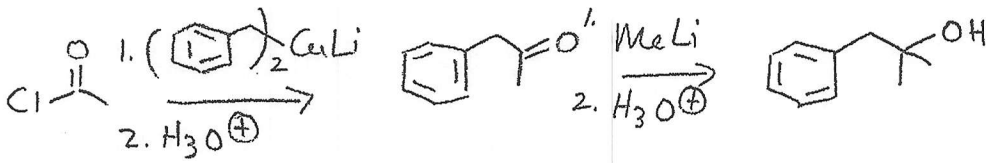
3. For each of the following, outline a synthesis of the target molecule from the indicated starting material and any organic or inorganic reagents. **For full credit, show the reagents and the product of each step, and observe any special conditions required in each synthesis. Do not draw any mechanisms.** (18 pts)

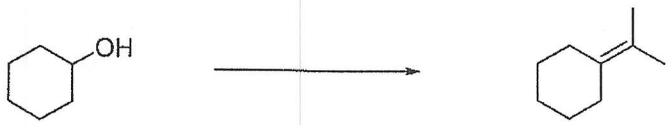


Using either one of the starting materials shown (your choice), design a synthesis that uses an organocuprate as one of the steps. You do not need to show how to make the organocuprate.

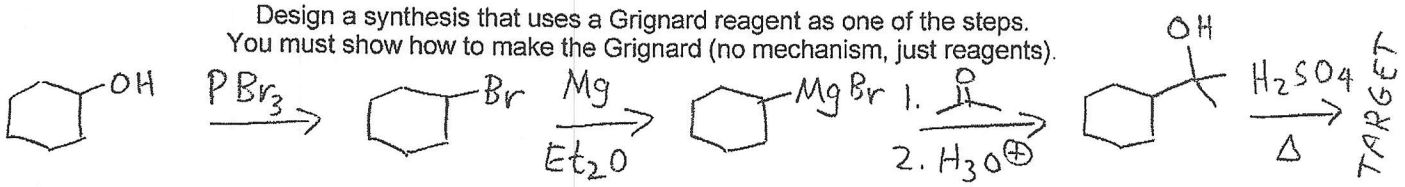


OR

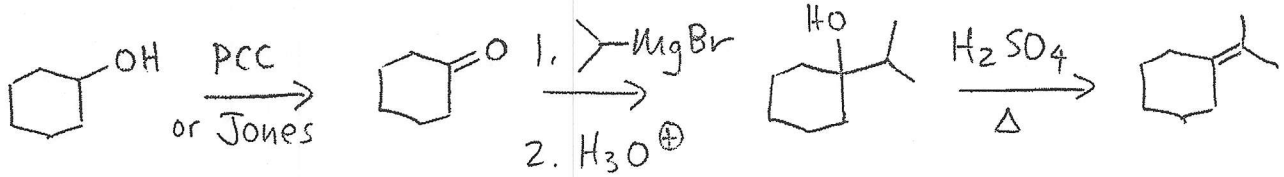




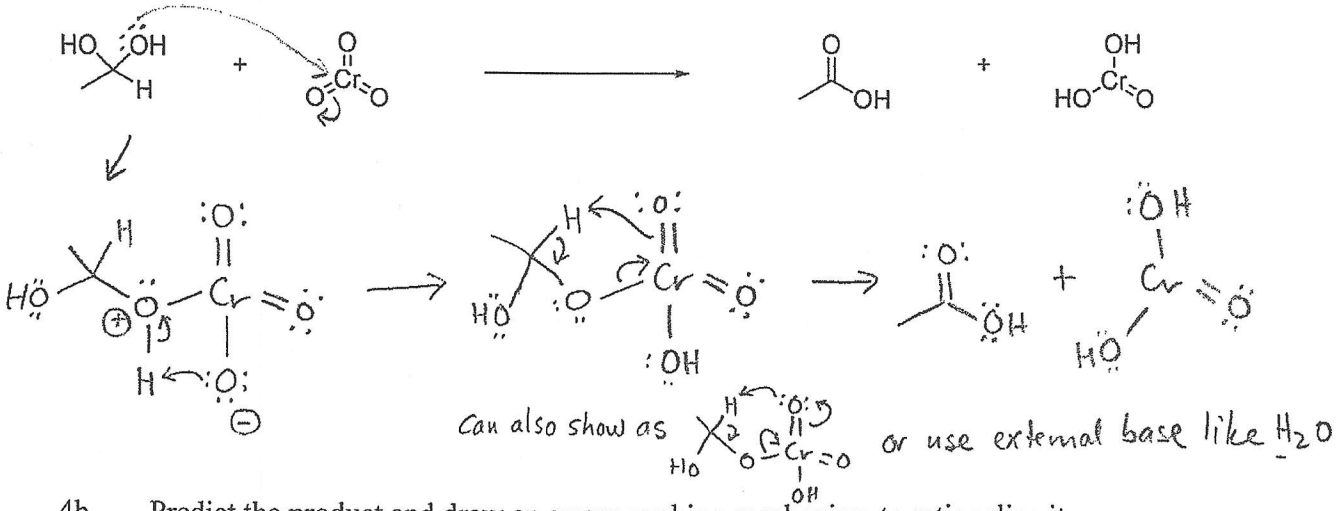
Design a synthesis that uses a Grignard reagent as one of the steps. You must show how to make the Grignard (no mechanism, just reagents).



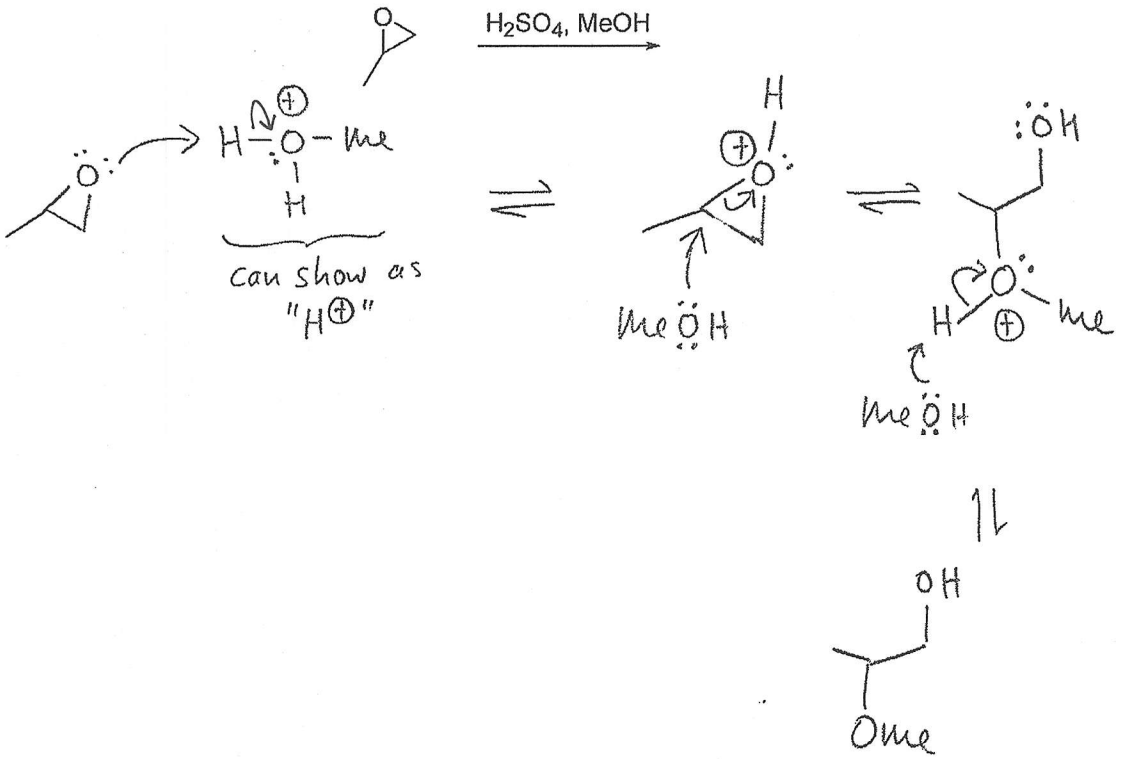
OR



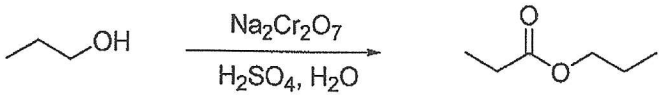
4a. Draw an arrow-pushing mechanism to rationalize the formation of the organic product of the following transformation. Show all bonds, curved arrows, non-zero formal charges, necessary lone pairs and intermediates clearly to receive full credit (10 pts).



4b. Predict the product and draw an arrow-pushing mechanism to rationalize its formation under the following conditions. Show all bonds, curved arrows, non-zero formal charges, necessary lone pairs and intermediates clearly to receive full credit (10 pts).

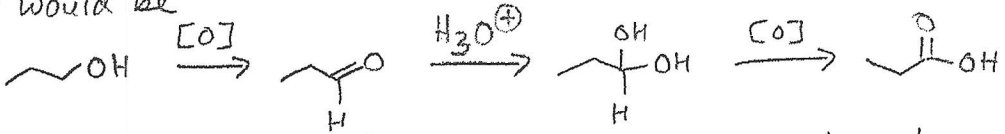


5. When propanol is warmed gently in an acidic, aqueous solution of sodium dichromate, the following result is observed:



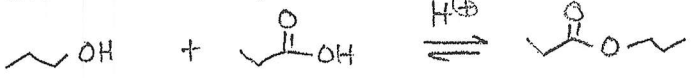
Provide an explanation for how this transformation occurs. **You do not have to draw any mechanisms, but to receive credit you must include key structures to support your explanation.** (9 pts).

Based on chemistry you knew when you took the exam, a reasonable answer would be

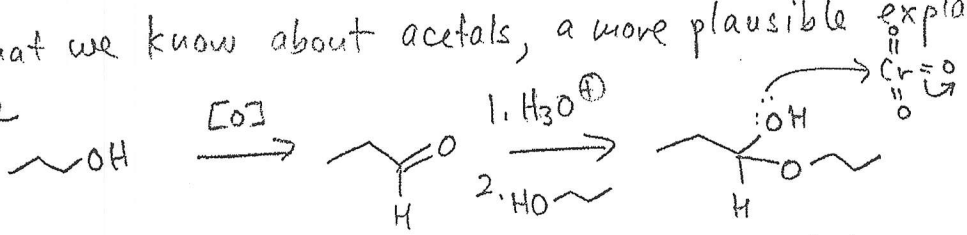


The alcohol is oxidized first to the aldehyde, which becomes hydrated under the reaction conditions. The hydrate is then oxidized to the carboxylic acid.

The carboxylic acid and the alcohol can then undergo a Fischer esterification under the reaction conditions:



Now that we know about acetals, a more plausible explanation would be



Under the reaction conditions, hemiacetal the aldehyde reacts with propanol to form the hemiacetal. The hemiacetal can then be oxidized, giving the ester: