UNIVERSITY OF WINDSOR
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

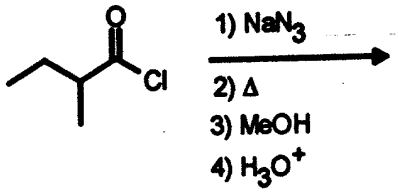
Chemistry 59-331/333 **Apr. 21, 1997**
Final Examination **Time: 3 hours**

Answer all questions in the exam booklet.

1. Do any eight (8)

Indicate the structure of the expected major product from each of the following reactions. Mechanisms are not necessary, but showing your work is likely to be a help. Indicate product stereochemistry where it applies. **(Total 40 marks)**

a)



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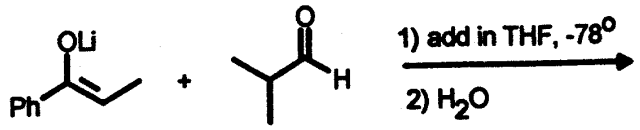

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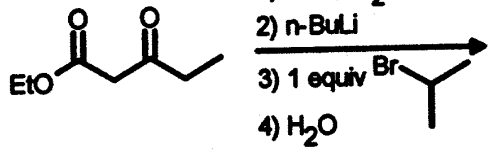

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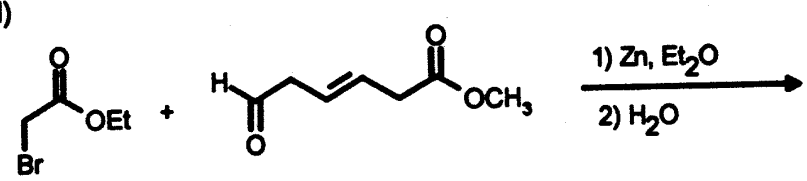

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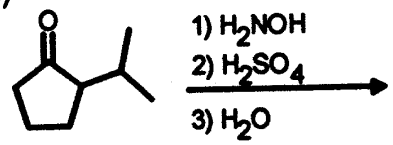

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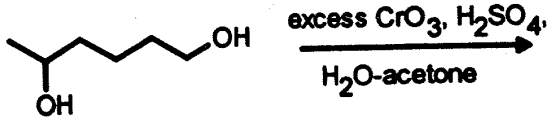
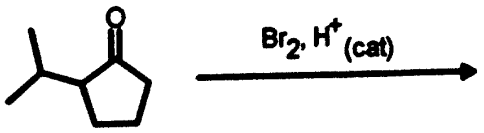
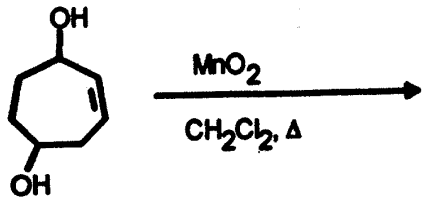


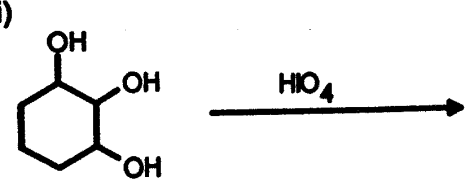
g)



h)

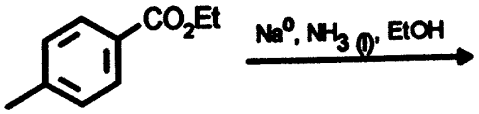


i)



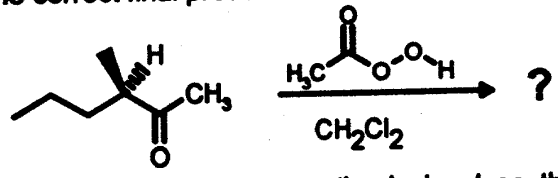
2. (Total 20 marks)

a) Draw the mechanisms for the dissolving metal reduction of the ethyl 4-methylbenzoate. The complete answer will indicate the regiochemistry of the reduction.

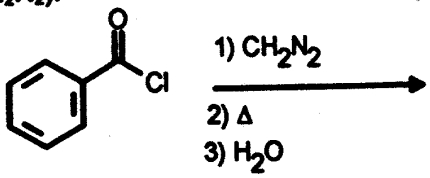


b) **Do i) or ii), but <u>not</u> both.**

i) Give the mechanism for the Baeyer-Villiger oxidation of the indicated ketone. The correct final product should be indicated in the answer.



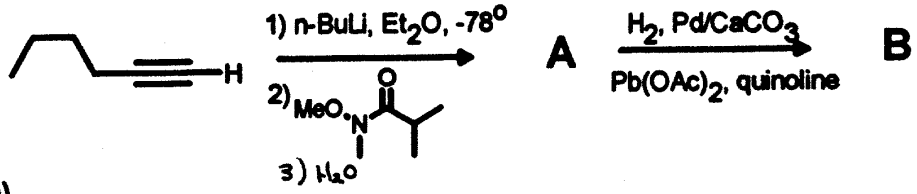
ii) The Arndt-Eistert synthesis involves the reaction of an acid chloride with a diazoalkane, followed by thermal (or photochemical or Ag^+ induced decomposition) of the first generated intermediate. Outline the mechanistic steps of this reaction. At least one resonance form of each diazo compound must be drawn (i.e., something more than CH_2N_2).



3. Do any 5 of the question parts, accounting for 10 compound letters.

Give the expected compounds corresponding to the letters below. Indicate stereochemistry where it applies. Mechanisms are not necessary. **(Total 50 marks)**

a)



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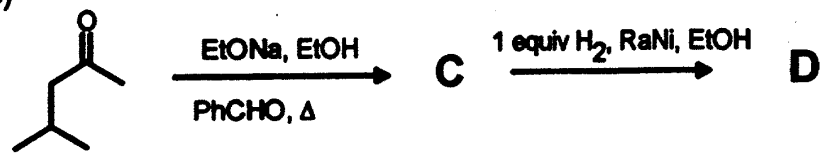

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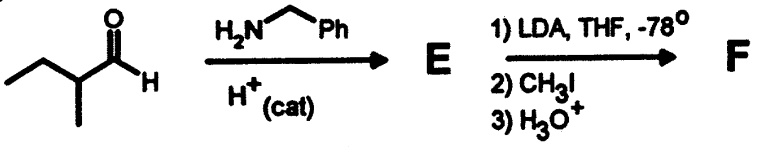

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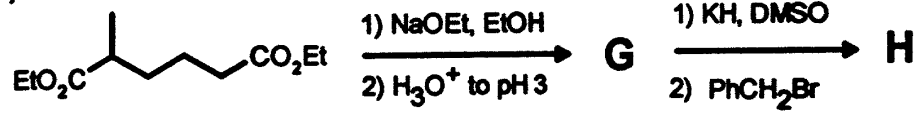

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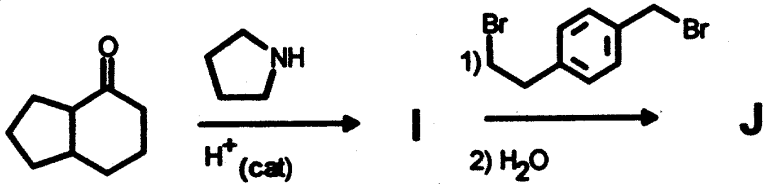

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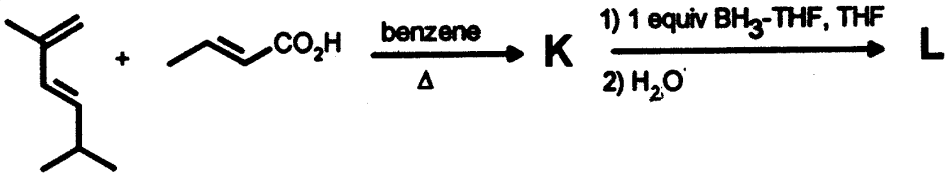
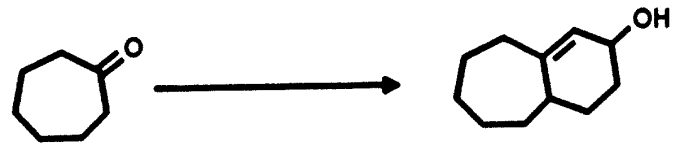


4. Do any seven (7) of the following

Show by equation how you would prepare the illustrated below from the given starting material. You may use any other reagents which you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not necessary, but may be a help. **(Total 70 marks)**

a)



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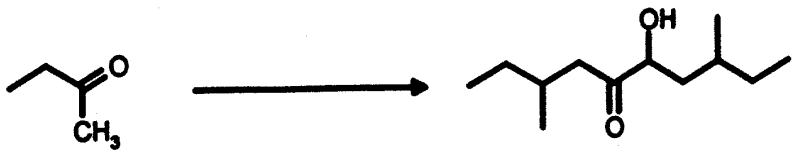

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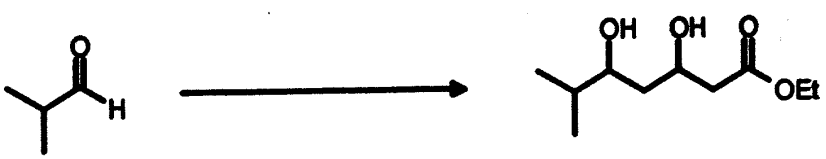
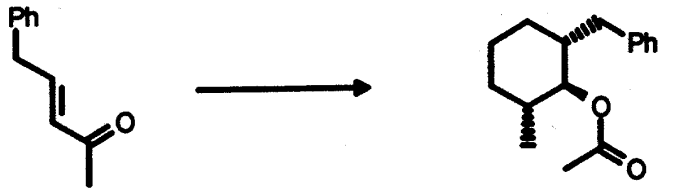
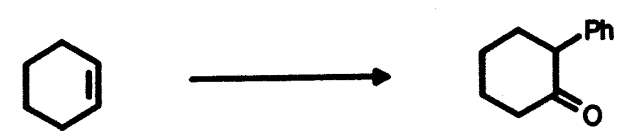


d)



e)



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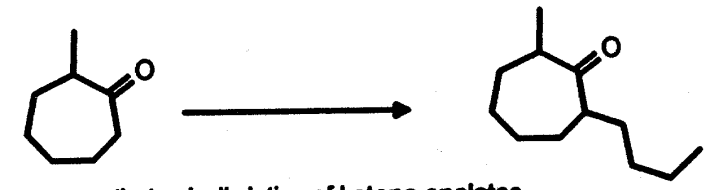
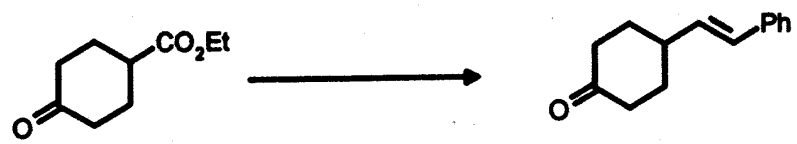
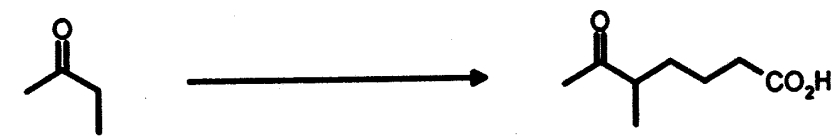


assume that polyalkylation of ketone enolates is a problem

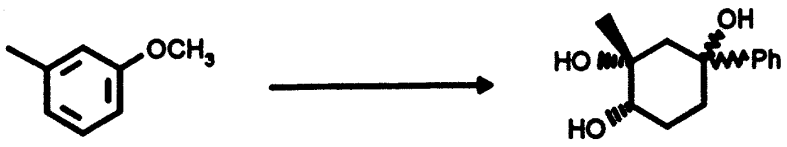
g)



h)

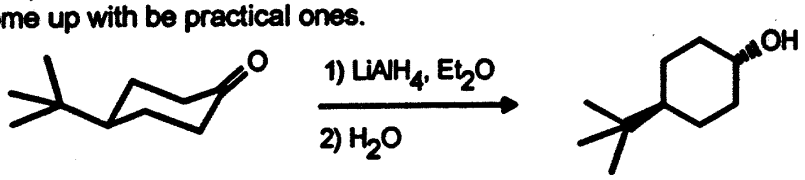


i)

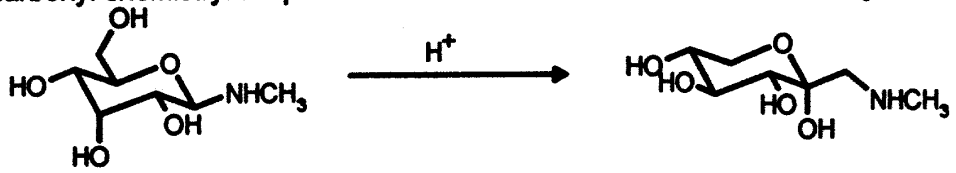


Bonus: (up to 10 marks):

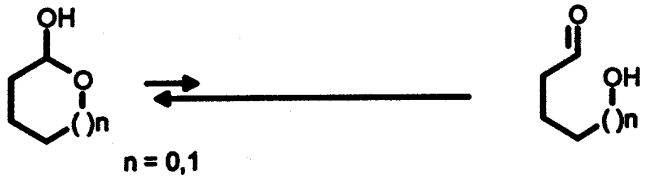
a) Here's a chance to be creative. The following ketone reduction gives the alcohol product with the OH 'trans' to the bulky tert-butyl group. Knowing what you do about cyclohexane conformational analysis, suggest a way in which you could get the other ('cis') diastereomer of alcohol. It is not absolutely necessary that the reagents you come up with be practical ones.



b) The Wendy Wong question. A biochemically important reaction, called the Amadori rearrangement, involves the rearrangement of certain amino substituted aldoses (a type of cyclic hemi acetal) to an isomeric amino substituted ketose (another hemi acetal). This reaction may be acid or base catalyzed (we'll focus on the acid catalyzed one). Stripped of all the excess hydroxy groups, what is going on is very simple carbonyl chemistry. Propose of reasonable mechanism for this rearrangement.



Note: Unlike acyclic hemi acetals, cyclic hemi acetals are thermodynamically stable, i.e.



n = 0,1