UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

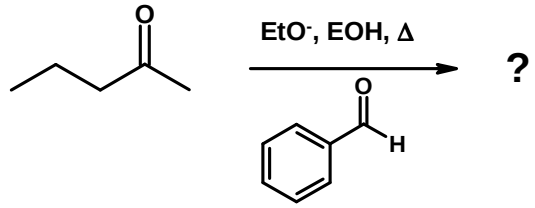
Chemistry 59-331/333 **Apr. 19, 2004**
Final Examination **Time: 3 hours**

Answer all questions in the exam booklet

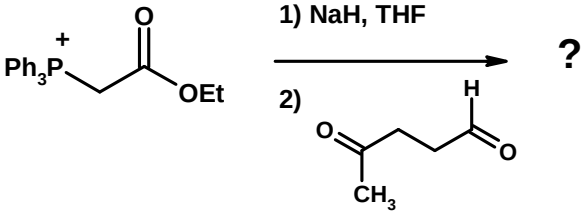
1. Do any eight (8). Total 40 marks

Indicate the structure of the expected major product from each of the following transformations. Mechanisms are not necessary, but showing your work may be a help. Include product stereochemistry where it applies.

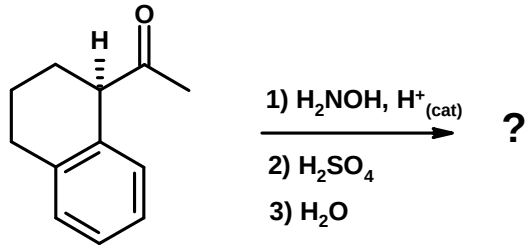
a)



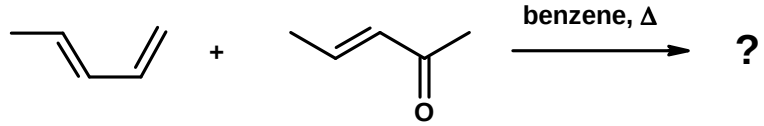
b)



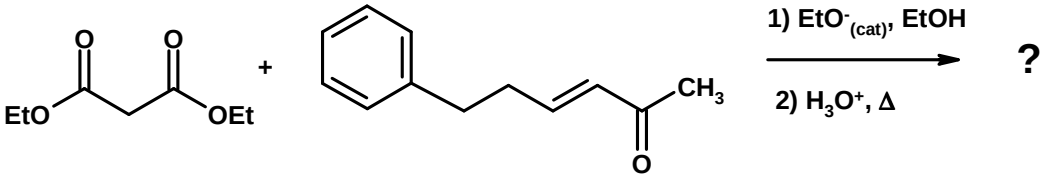
c)



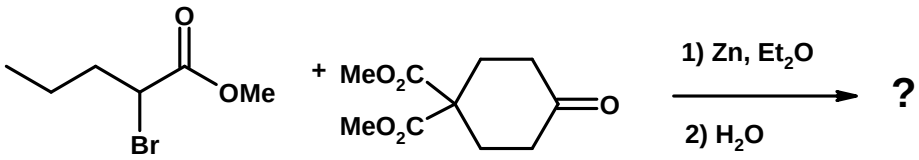
d)



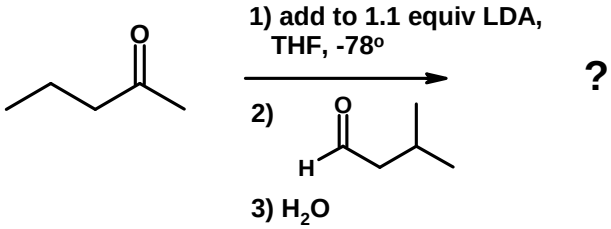
e)



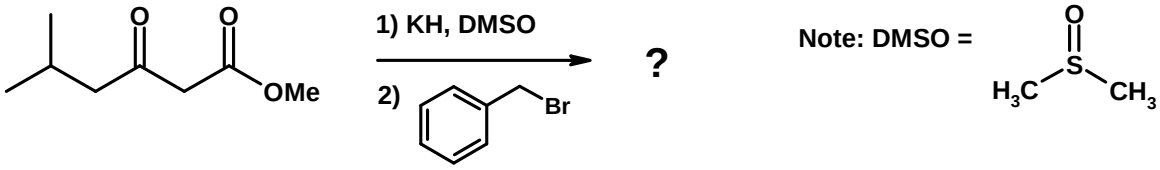
f)



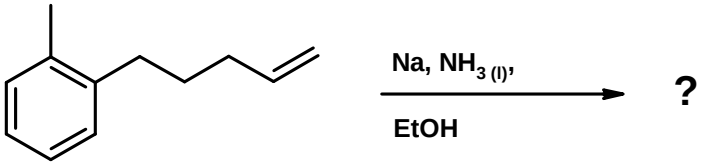
g)



h)

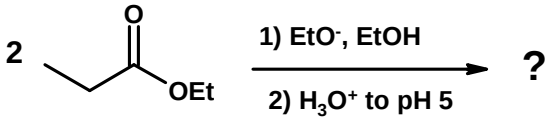


i)



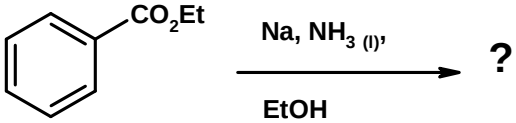
2. Total 20 marks

a) Draw the complete mechanism for the Claisen condensation between two molecules of ethyl propanoate. The complete answer will show any small molecules which 'come off' during the reaction, the appropriate intermediates and final product, and whether each step is reversible or irreversible.

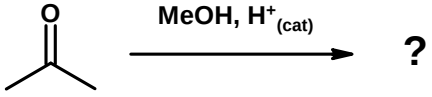


b) Do i) or ii), but not both

i) Show the complete mechanism for the dissolving metal reduction of ethyl benzoate. The stoichiometry of reaction is not implied by what is shown below; it should be apparent from your answer.

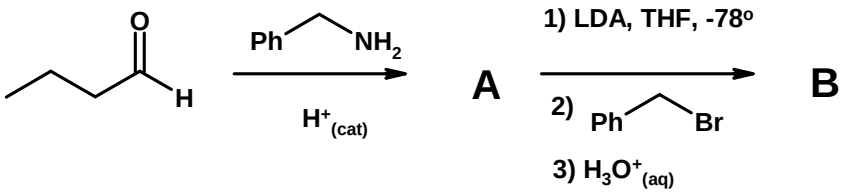


ii) Show the complete mechanism for the 'protection' of acetone by methanol.

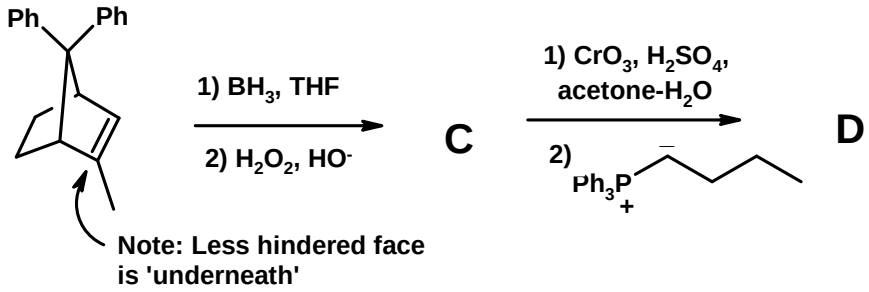


3. Do any five (5) of the questions (a-f). Mechanisms are not necessary, but showing your work may be a help. Include product stereochemistry where it applies.

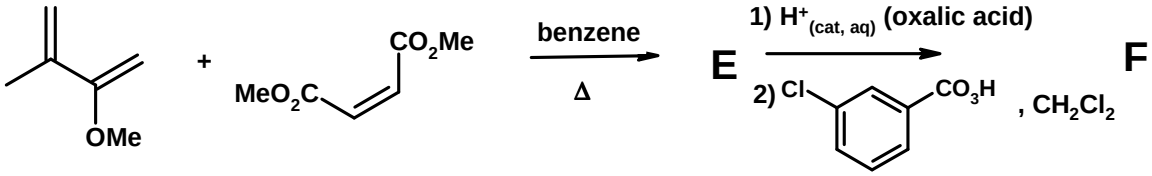
a)



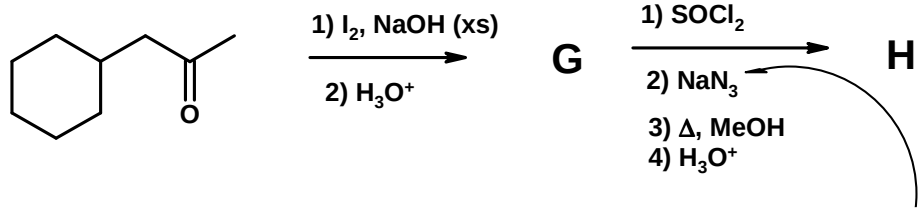
b)



c)

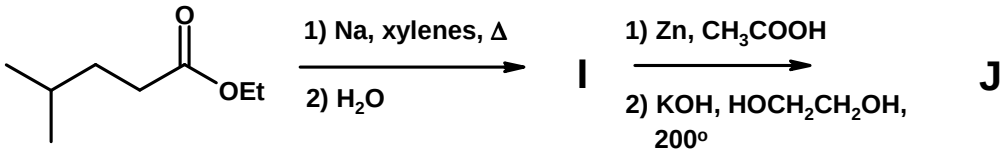


d)

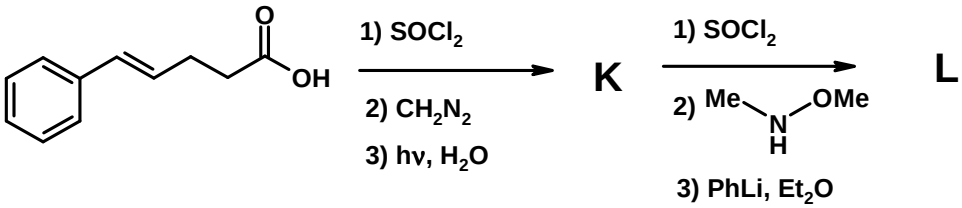


Note: For full marks, I need to also see the structure of the compound after this step, in *any one* of the reasonable resonance forms

e)



f)

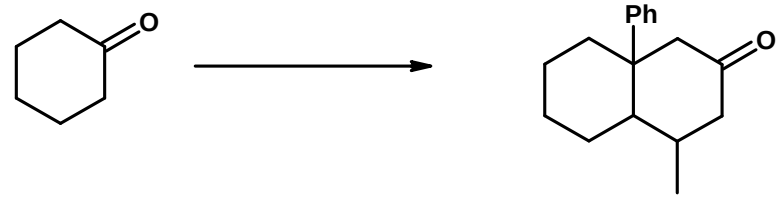


4. Do any seven (7). Total 70 marks

Show by equation how you would prepare the illustrated compounds below from the given starting material. You may use any other reagents you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not

necessary, but showing your work may be a help. Indicate stereochemistry where it applies.

a)



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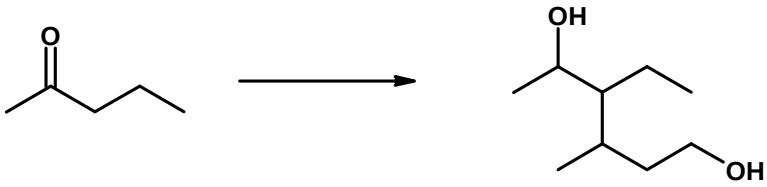
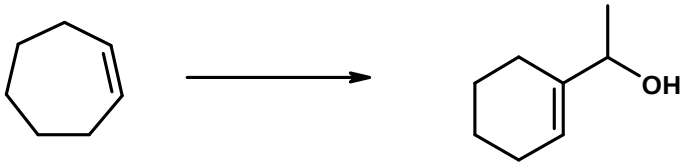
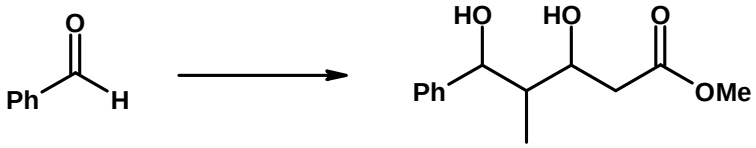


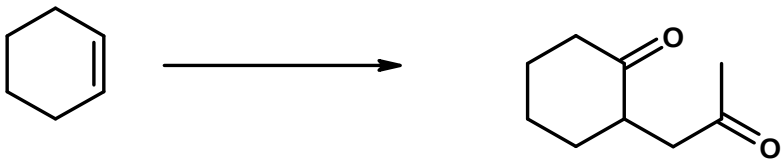
c)



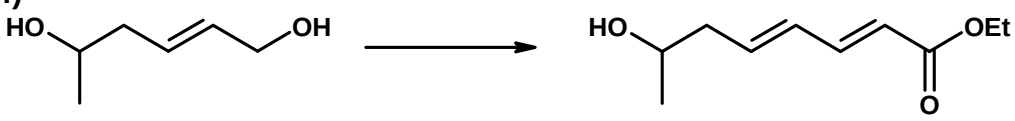
d)



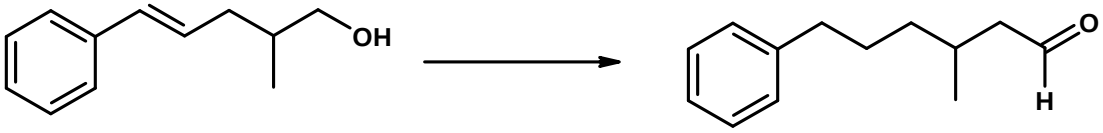
e)



f)

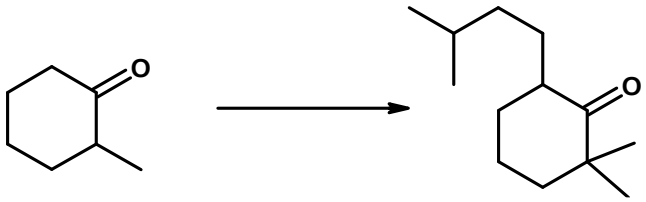


g)



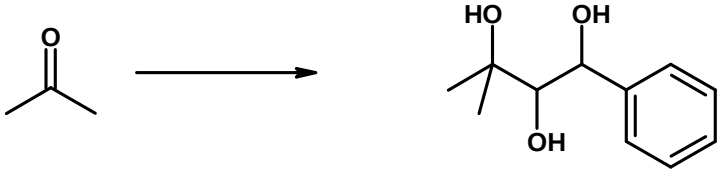
Note: Please count your number of carbons carefully

h)



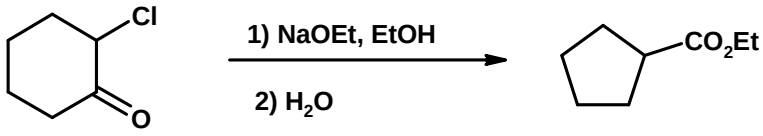
Note: Assume normal ketone enolate polyalkylation is a problem

i)



Bonus:

i**)** Treatment of the following chloroketone by ethoxide ion did not give an aldol type product, but rather the indicated ester. The reaction is called the Favorskii rearrangement. Suggest how this reaction proceeds.



iii) The statement that ethers are forever stable to alkyllithiums is not entirely true. As you have seen, aldehyde enolates are not easily made by direct deprotonation of aldehydes. Indirectly, however, the enolate of acetaldehyde (ethanal) is easily made from tetrahydrofuran and butyllithium, if you warm it up. Suggest a mechanism for this preparation. (Hint: There are a couple volatile organic by-products)