UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

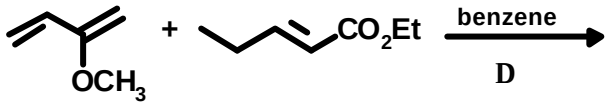
Chemistry 59-331/333 **Apr. 19, 2000**
Final Examination **Time: 3 hours**

Answer all questions in the exam booklet

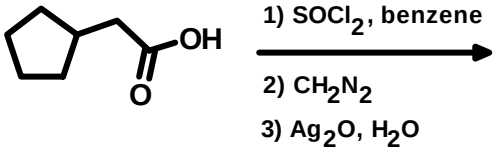
1. Do any eight (8). Total 40 marks

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)



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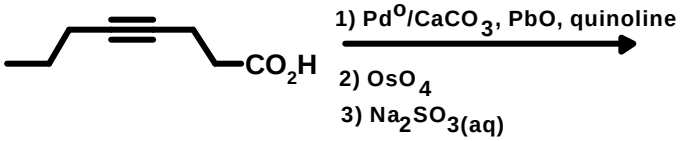

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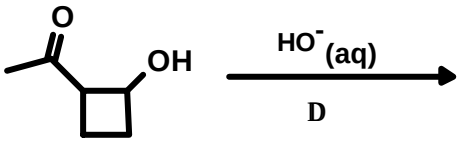

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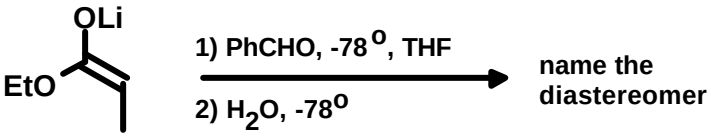

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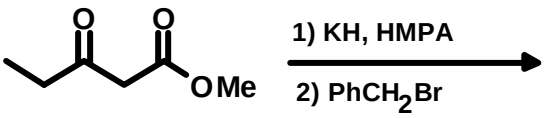
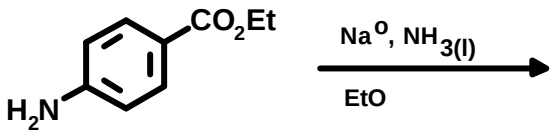
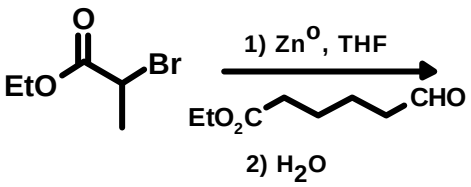


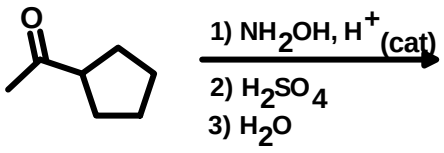
g)



h)

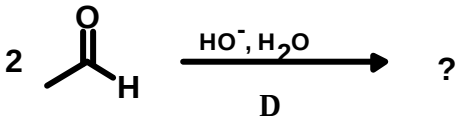


i)



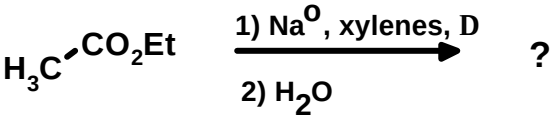
2. Total 20 marks

a) Draw the complete mechanism for the base catalyzed aldol condensation between two molecules of acetaldehyde. 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.

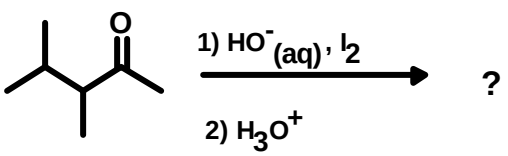


b) Do i) or ii), but not both

i) Show the complete mechanism for the acyloin condensation involving ethyl acetate.

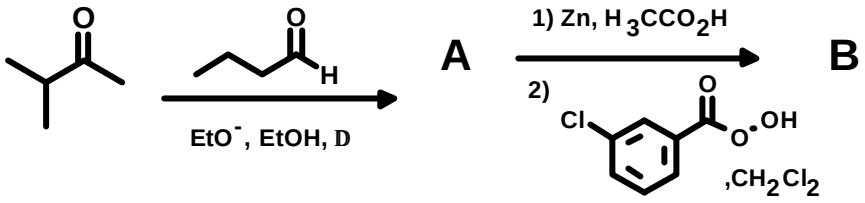


ii) Show the complete mechanism for the following iodoform reaction. Again, show any molecules given off during the reaction. Be sure to explain the features of the intermediates to explain why the reaction goes the way it does.



3. Do any five (5) of the questions (a-f).

a)



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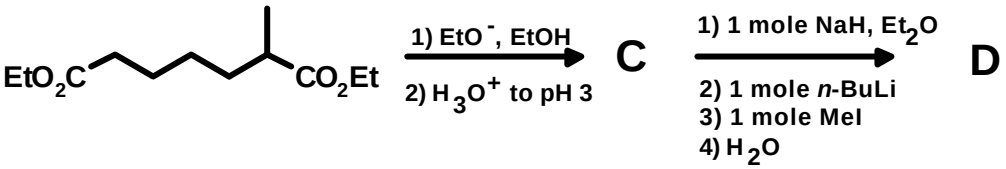

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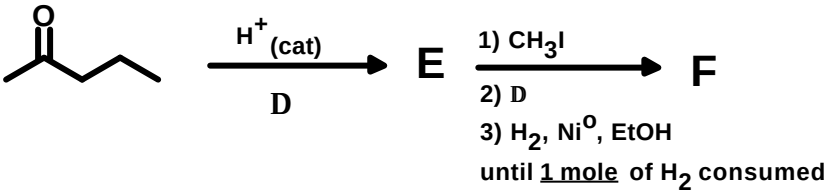
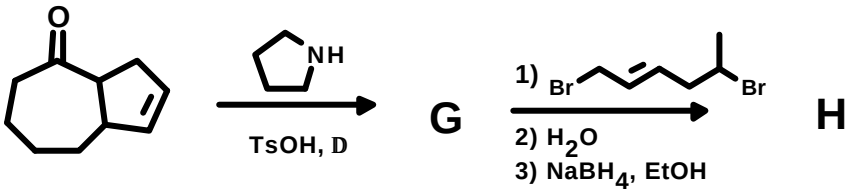
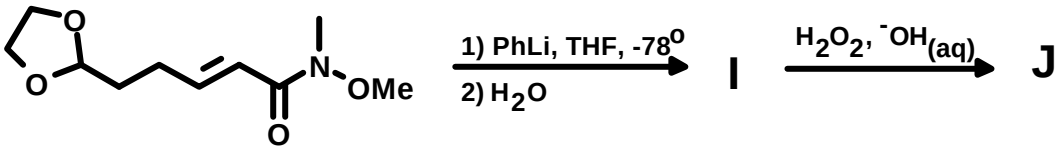


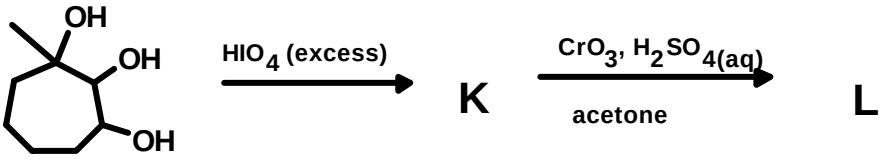
d)



e)



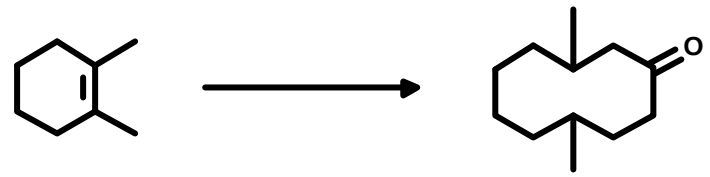
f)



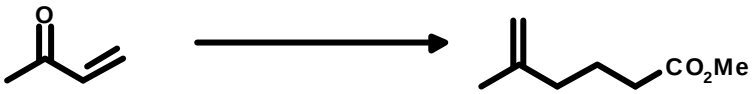
4. Do any seven (7). Total 70 marks

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.

a)



b)



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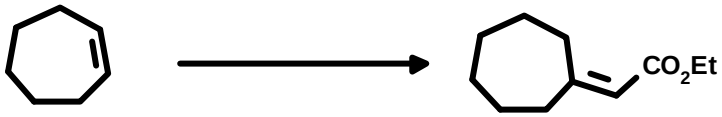
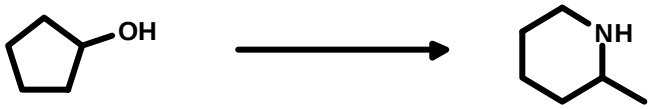
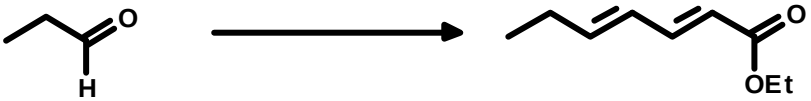


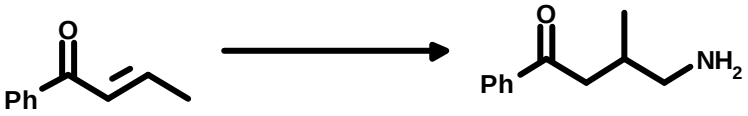
d)



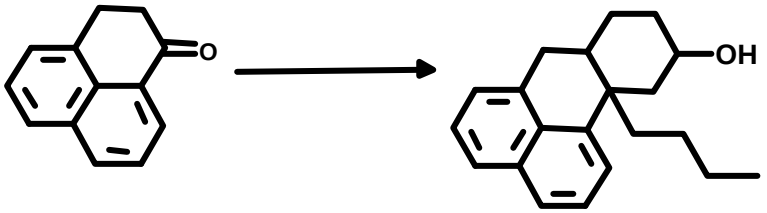
e)



f)



g)



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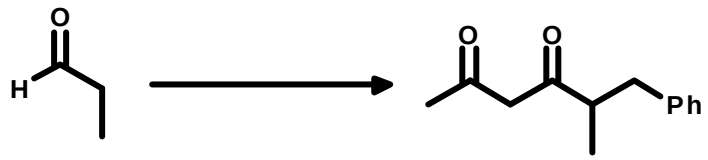

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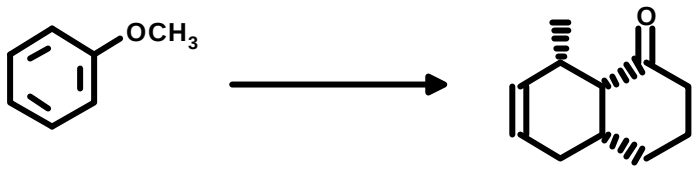
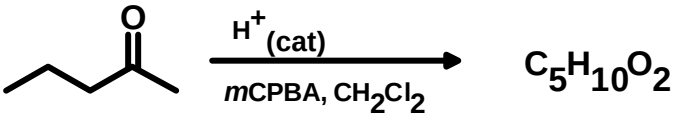


Bonus:

i) There is a least one side product of the Baeyer-Villiger oxidation which is synthetically useful. The product obtained has exactly the same molecular weight as the Baeyer-Villiger product, and can be deduced by putting together various bit of information accumulated in this course. Suggest the identity of this product (worth a little) and how it come about mechanistically (worth more).



ii) As we've seen in this course, stoichiometric formation of aldehyde enolates is very tough, usually due to the susceptibility of the aldehyde carbonyl to nucleophilic attack. Curiously enough, formaldehyde enolate can be generated by treatment of THF with *t*-BuLi, at only slightly elevated temperatures (yes, I've overstated the stability of ethers to alkyllthiums a little). Mechanistically, how does this occur, and what is the relatively small side product not drawn?