

UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

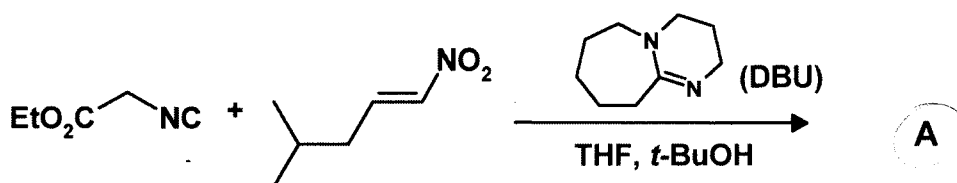
Chemistry 59-531/431
Final Examination

Apr. 17, 2007
Time: 3 hours

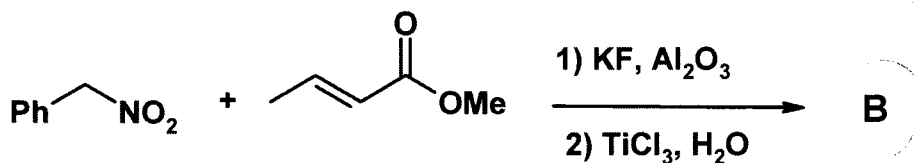
Answer all questions in the exam booklet.

1. Do any nine (9) 'letters'. (45 marks) Provide the major reaction product in each of the following transformations. Include stereochemical (relative and or absolute) information where it is relevant. I do wish you to show any intermediates that could be isolated. Mechanisms are not necessary, but showing your work may be a help. A warning, though...if you do the 1st letter of a series, you must do them all (i.e. you can't do C but not D / E or I but not J).

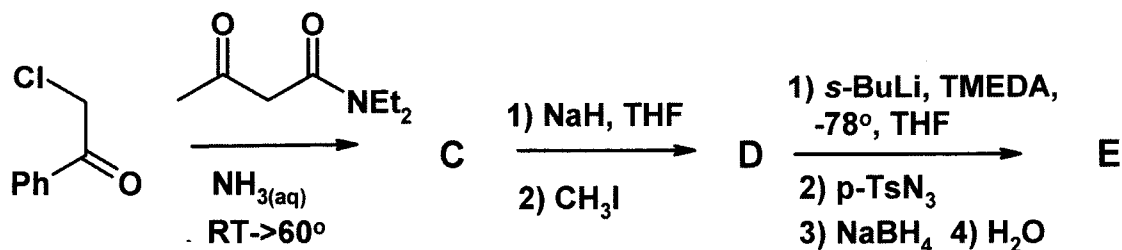
a)



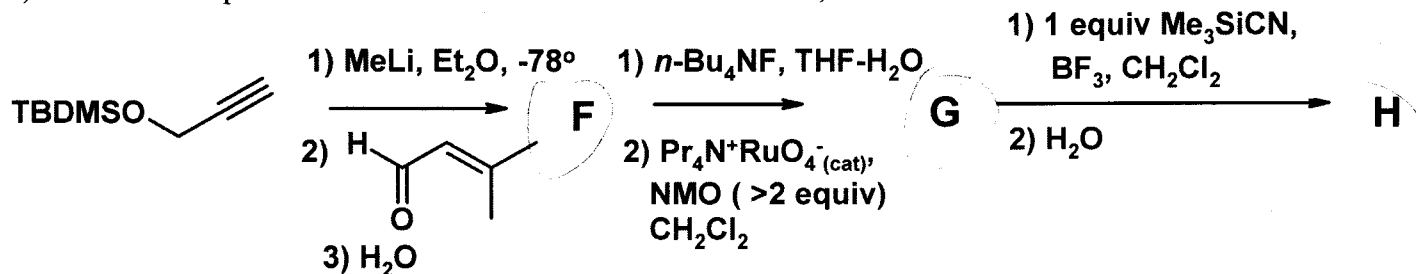
b)



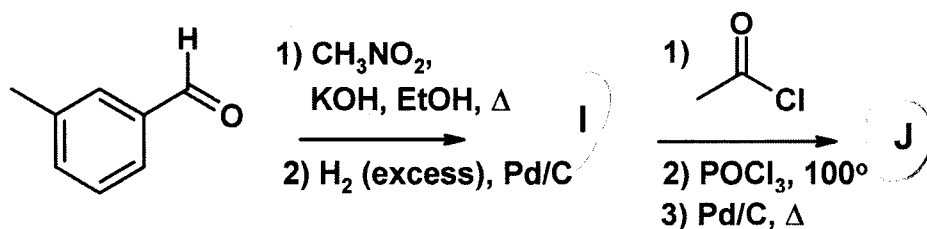
c)



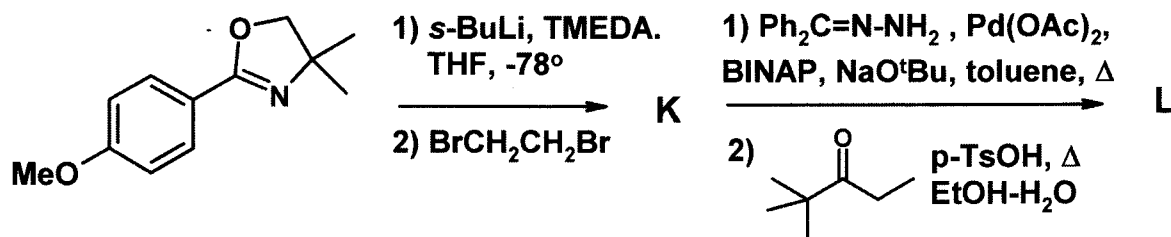
d) Note: the complete answer includes the structure of TBDMS, at least once.



e)

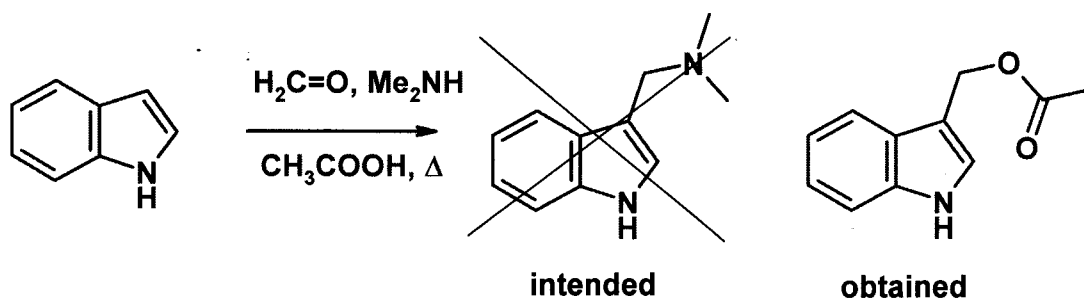


f)



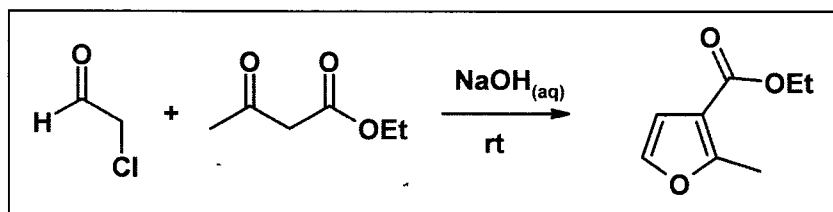
2. (Total 30 marks)

a) A student with limited experience in research attempted to make a simple gramine (2-dimethylaminomethylindole), and in order to make sure the reaction went to completion, heated the mixture overnight. Instead of the gramine, he obtained the 'benzylic' acetate and an angry supervisor. Mechanistically what happened here – I am looking for the entire mechanism.

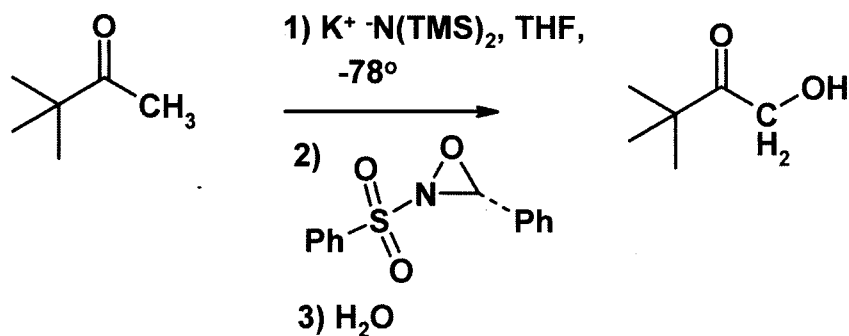


b) Do i) and either ii) or iii), but not both (10 marks each).

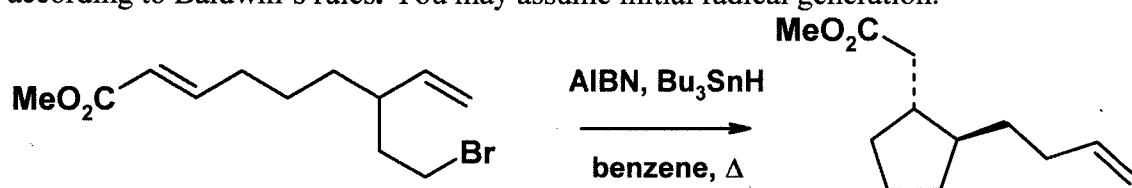
i) Give the complete mechanism of the following transformation



ii) One of the most important methods of α -hydroxycarbonyl formation occurs by reaction of enolates with N-sulphonyloxaziridines. Outline the mechanism of this process. For full marks, what side product do you get if it sticks with lithium enolates?



iii) The following apparently non-conventional cyclization reaction occurred under very conventional conditions. Show how this occurred in step by step fashion, and classify each cyclization step according to Baldwin's rules. You may assume initial radical generation.



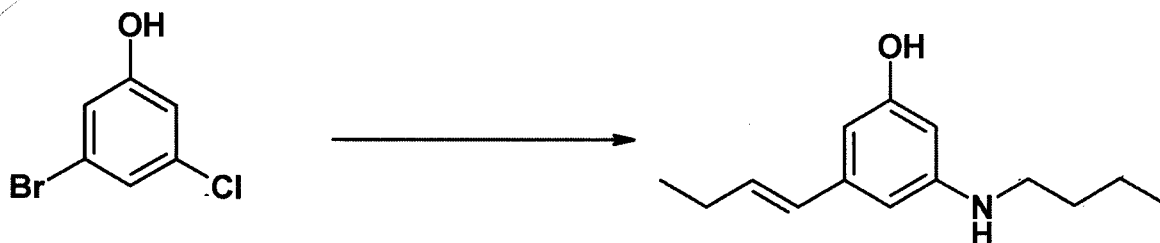
3. Do any five (5) of the following.

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 50 marks)

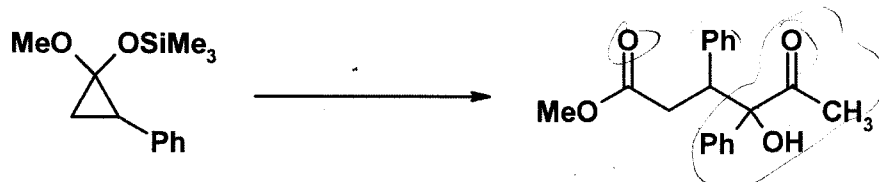
a)



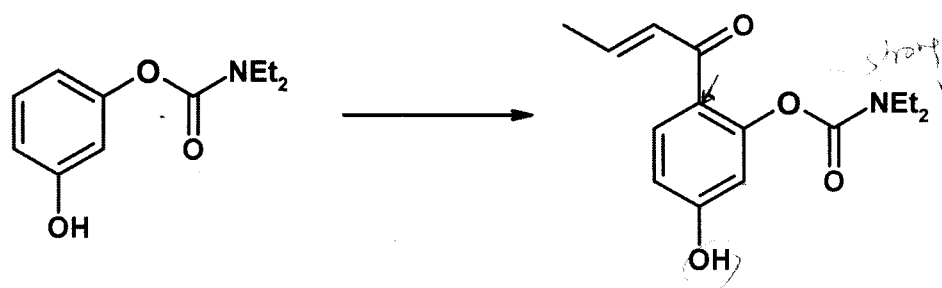
b)



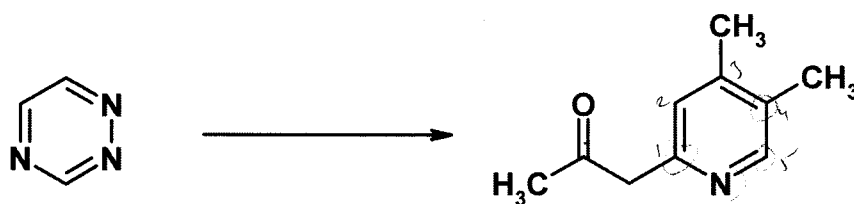
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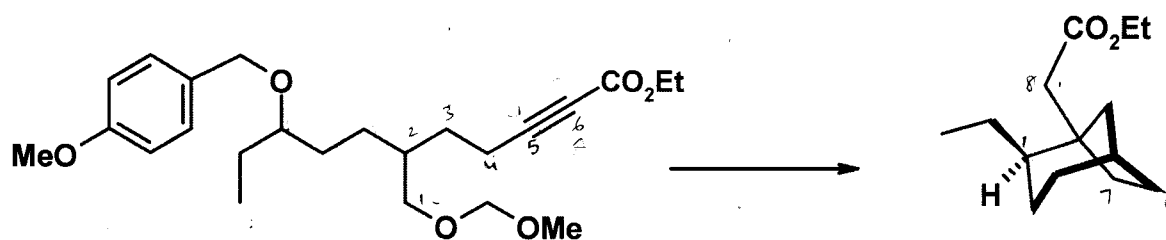
d)



e)



f)



Bonus: In order to make a tricarbonyl compound, the following furanyl alkenoic acid was subjected to conventional conditions. What was obtained however was not an aldehyde/ketone/ester but a ketodiester. How does this “internal redox” reaction proceed?

