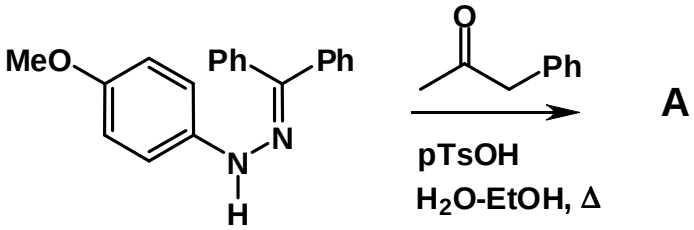
UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

Chemistry 59-531/431 **Dec. 11, 2010**
Final Examination **Time:3 hours**

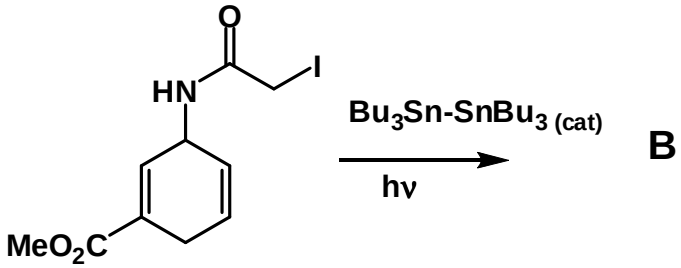
Answer all questions in the exam booklet.

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).**

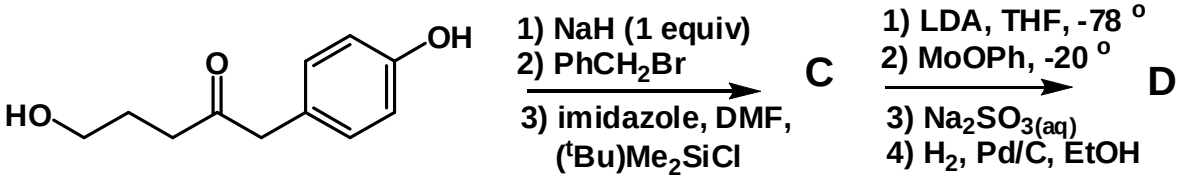
a)



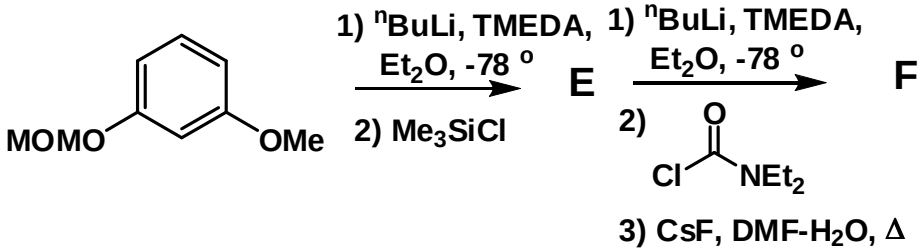
b) Note: I am not looking for >1 cyclization. The complete answer will classify the reaction according to Baldwin's Rules.



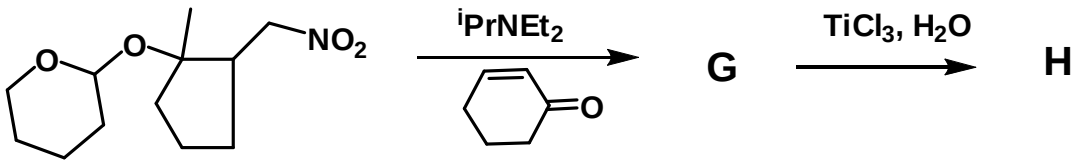
c)



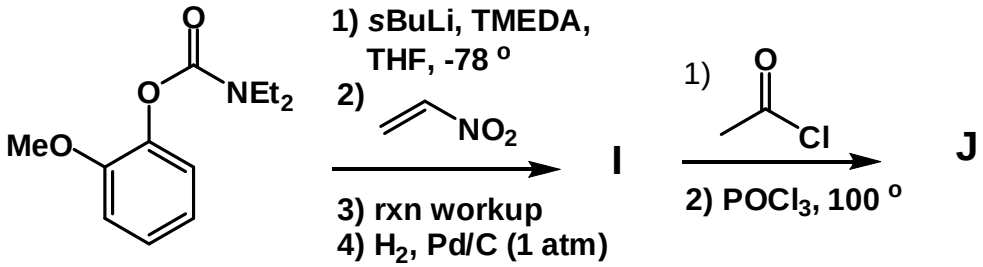
d) The complete answer will have 'OMOM' drawn out at least one time.



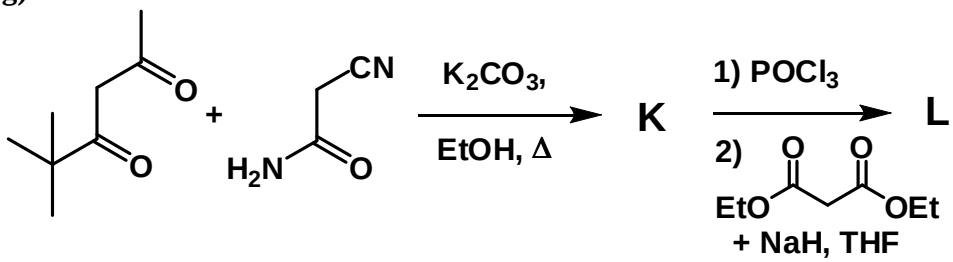
e) Do not worry about stereochemistry here, but I want to see one valence bond structure for the nitro group for full marks.



f) Note: Carbamates are very stable with respect to hydrogenation and Lewis acids.

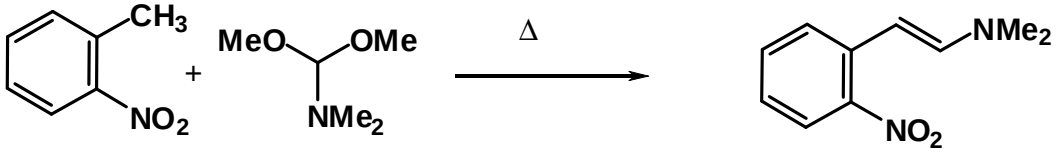


g)



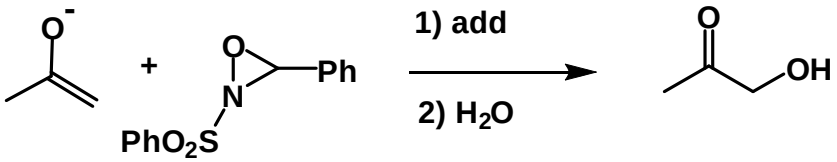
2. (**Total 30 marks**)

a) The most common indole syntheses involves reaction of an ortho methyl nitrobenzene and 'DMFDMA' to give an aryl enamine, which is then reduced. Show by way of mechanism the enamine synthesis. I do want to see at least one valid valence bond (resonance) structure for the nitro group in your answer.



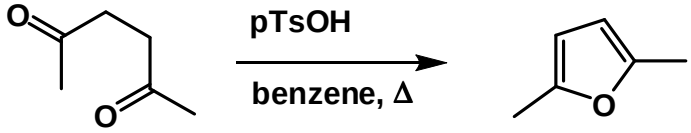
b) **Do *either* i) *or* ii) (but not both) and iii) (10 marks each).**

i) One of the most common ways for formation of 1,2-dioxygenated compounds is by way of reaction of an enolate with an oxaziridine. Show the mechanism of the transformation. Full marks will include the source of the most common side product (especially with lithium enolates of ketones).



ii) The palladium mediated cross coupling reaction of aryl halides and aryl organometallics (we'll use the Grignard for simplicity) is *the* most common method for biaryl synthesis. Provide the mechanism for this transformation.

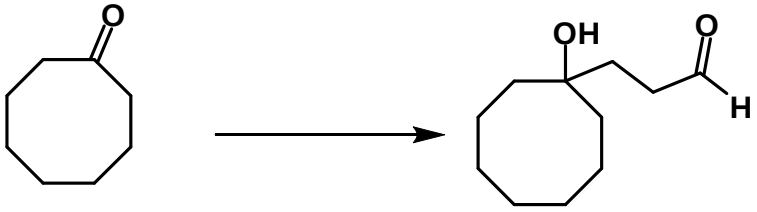
iii) The most common method for the synthesis of furans 'from scratch is the acid catalyzed reaction of 1,4-diketones, called the Paal-Knorr. Provide a reasonable mechanism for this reaction. The perfect answer will include the structure of p-TsOH.



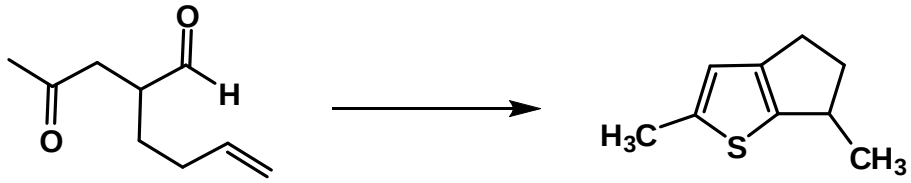
3. Do any five (5) of the following.

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; show the structures of all acronyms used (at least once), other than for solvents. Mechanisms are not necessary, but may be a help. (**Total 50 marks**)

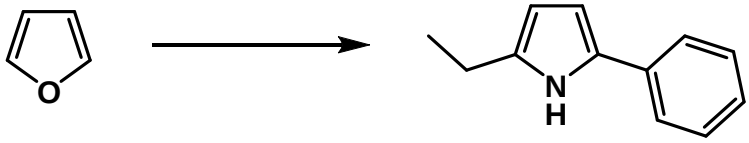
a)



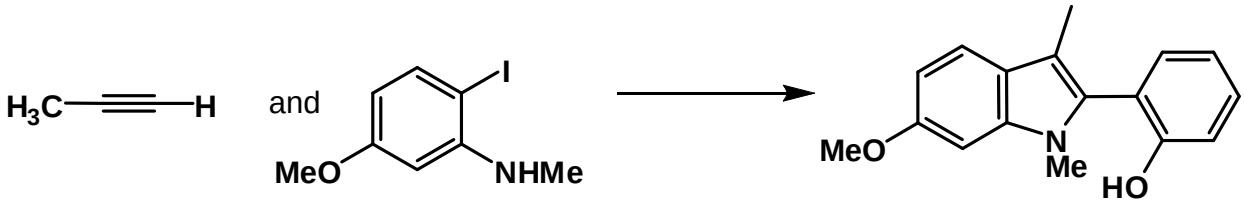
b)



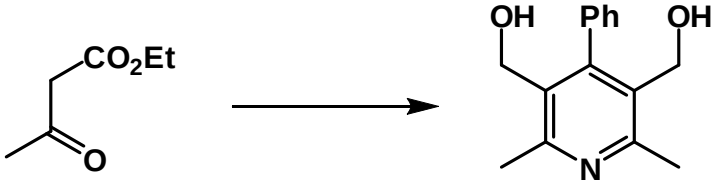
c)



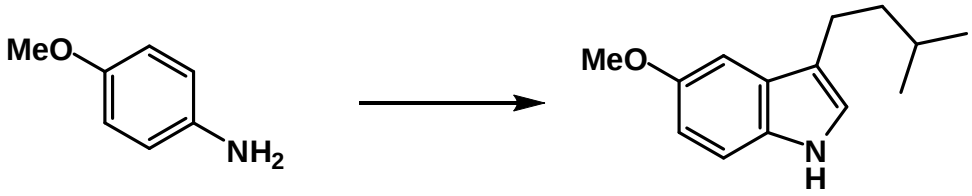
d)



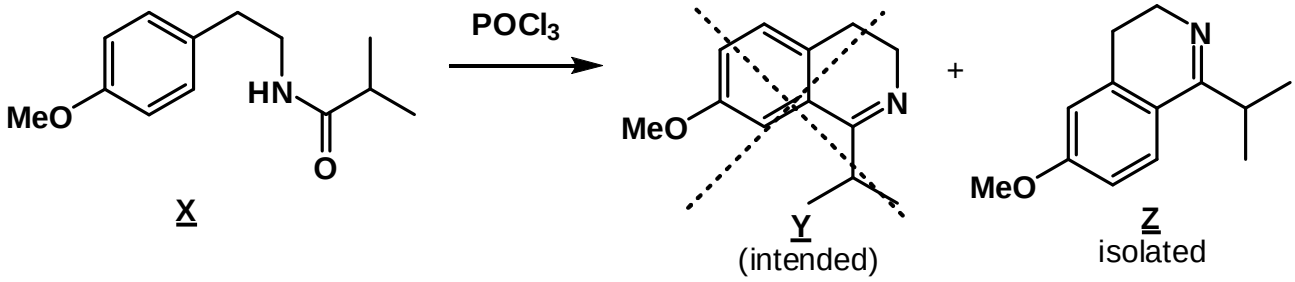
e) Please indicate stoichiometry of your reaction steps carefully in the following case.



f)



Bonus: In an attempt to do a Bischler-Napieralski reaction to prepare the indicated isoquinoline (**Y**), aryl amide **X** was subjected to conventional conditions. What was isolated, however, was an unexpected dihydroisoquinoline **Z**. Can you propose by mechanism what happened here??



Assorted Cheat-sheet info

Baldwin's Rules for Ring Closure

For tetrahedral substrates:

a) 3- to 7- exo-tet favoured
b) 5- to 6- endo-tet disfavoured

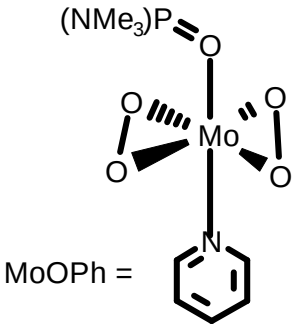
For trigonal substrates

a) 3- to 7- exo-trig favoured
b) 3- to 5- endo-trig disfavoured
c) 6- to 7- endo-trig favoured

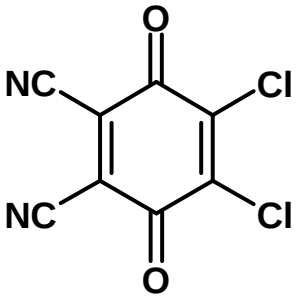
For digonal substrates

a) 3- to 4- exo-dig disfavoured
b) 5- to 7- exo-dig favoured
c) 3- to 7- endo-dig favoured

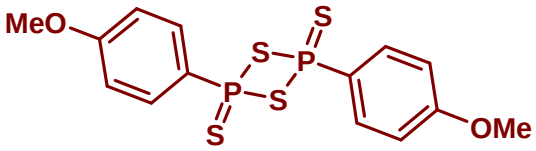
The structure of MoOPh is:



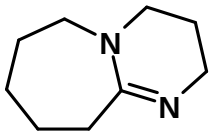
The structure of DDQ is



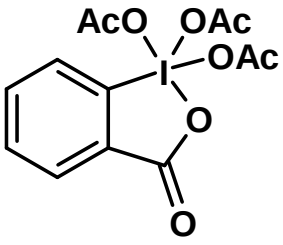
The structure of Laweson's reagent is



DBU (diazabicycloundecane) is



DMP (Dess-Martin periodinane) is



The structure of josiphos is