

**UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY**

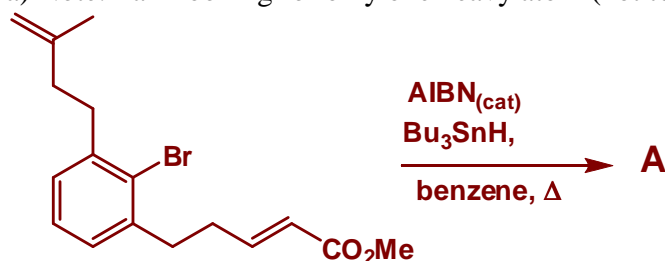
**Chemistry 59-531/431
Final Examination**

**Dec. 9, 2011
Time: 3 hours**

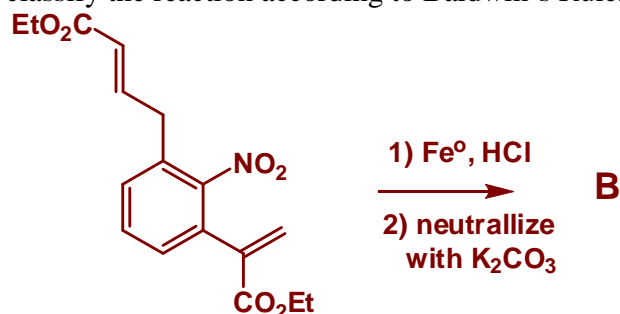
Answer all questions in the exam booklet.

1. Do any ten (10) '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**).

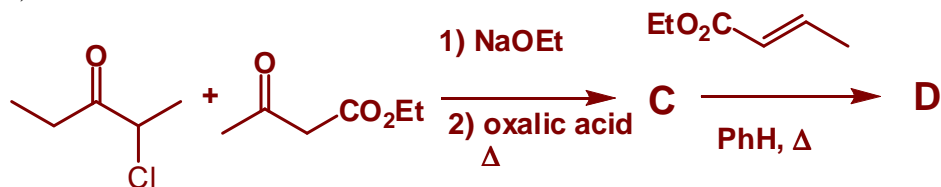
a) Note: I am looking for only one heavy atom (not to H) bond formation.



b) Note: I am not looking for >1 heavy atom (not to H) bond formation. The complete answer will classify the reaction according to Baldwin's Rules.

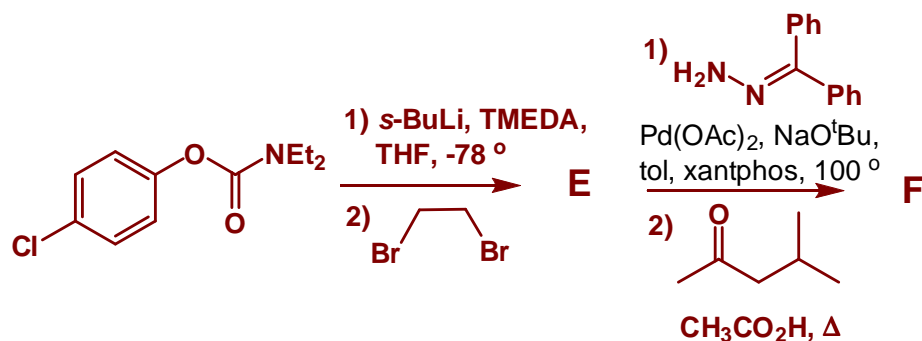


c)

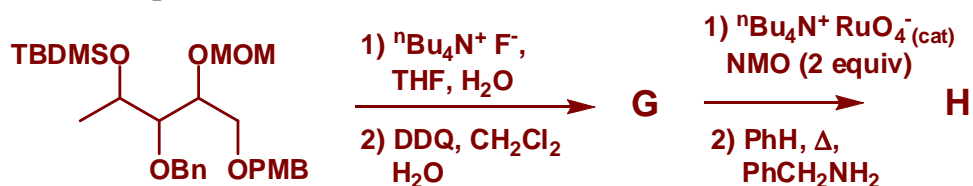


Consider any stereochemistry in **C** to **D** to follow 'normal' rules, and frontier MO's to be in accordance with δ^+ and δ^- electron densities

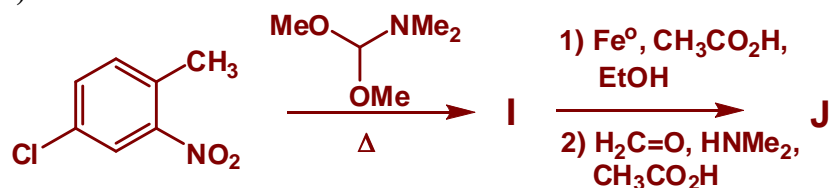
d) Note: Carbamates are very stable with respect to NaO^tBu and weak acid like $\text{CH}_3\text{CO}_2\text{H}$.



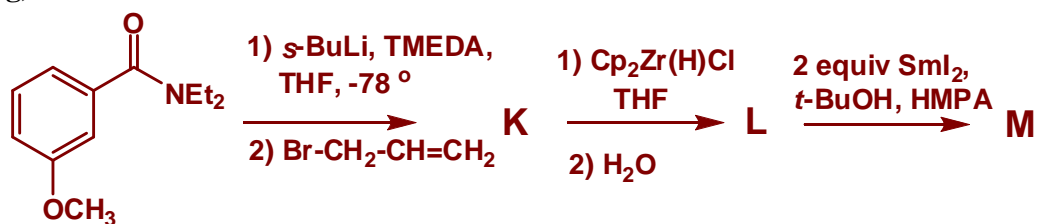
e) The complete answer will show the structures of TBDMS, BN, MOM and PMB at least once



f)

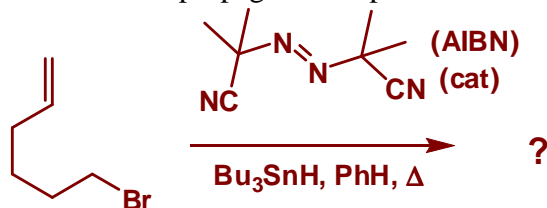


g)



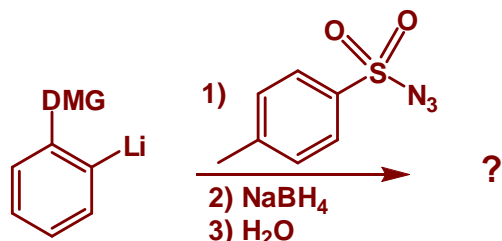
2. (Total 30 marks)

a) Give the complete mechanism of the following 5-hexenyl radical cyclization, showing plausible initiation and propagation steps.

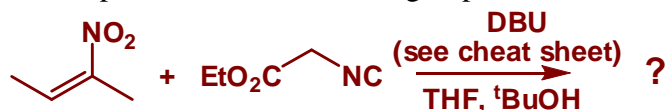


b) **Do either i) or ii) (but not both) and iii) (10 marks each).**

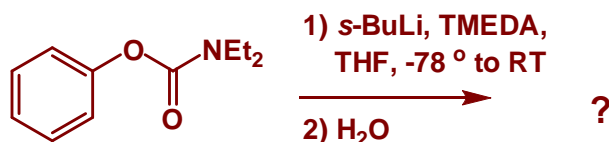
- i) One of the less obvious electrophile incorporations used during directed lithiation is an N^+ equivalent, commonly done by addition of tosyl azide to the aryllithium, followed by the addition of borohydride. Give the mechanism for this reaction sequence; it will be necessary to include proper valence bond structures for the azide.



- ii) One of important pyrrole forming reactions involving an isonitrile is called a Barton Zard, which involves an activated isonitrile (usually by an ester) and a nitroalkene. Give the complete mechanism of the following example; the complete answer will include the final product and a valence bond representation of the nitro group and the isonitrile (at least once).



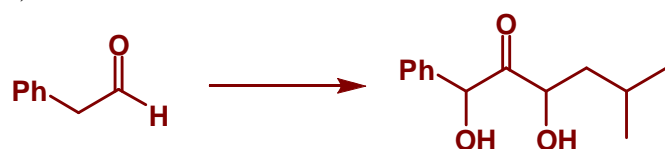
- iii) Aside from being a powerful metallation directing group (DMG), carbamates are quite capable of rearrangement upon warming. Please show the mechanism of the following, along with all intermediates that could have even a short lifetime.



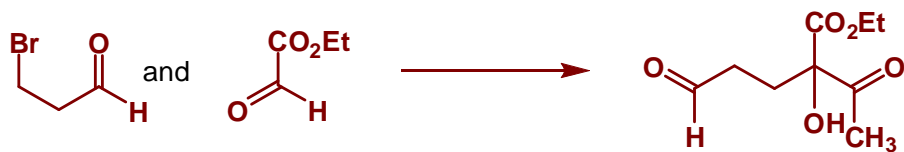
3. **Do any five (5) of the following.**

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, as long as they are chemically stable. 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)**

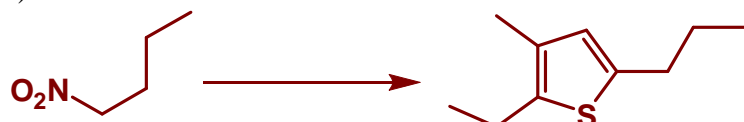
a)



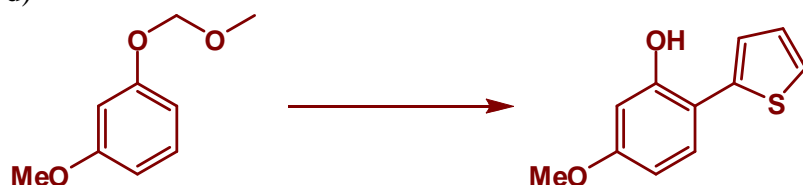
b)



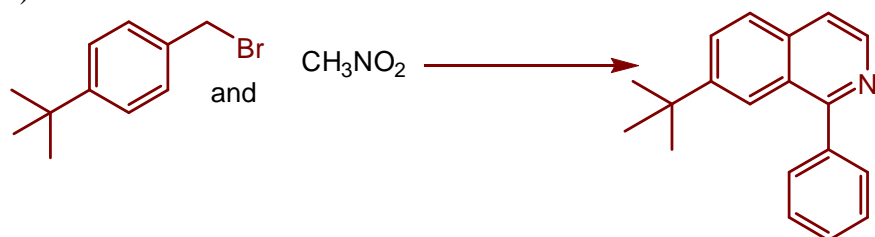
c)



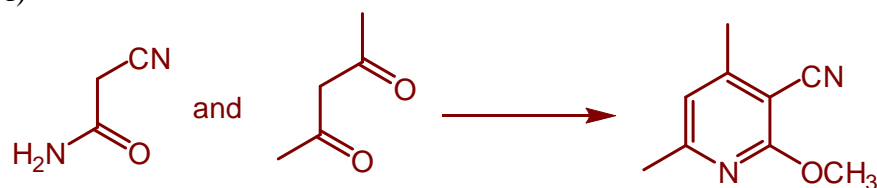
d)



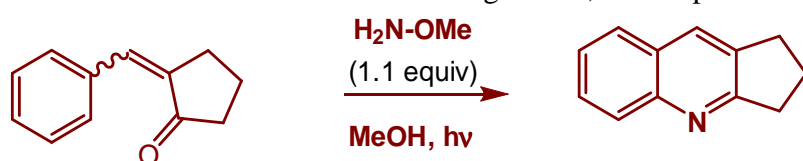
e)



f)



Bonus: A low yielding but interesting quinoline preparation was recently reported by Pratt. Can you propose a reasonable mechanism for this transformation? I would have predicted that this reaction would have required heating, but it does not. The photolysis is to ensure that there is a useful concentration of alkene in the Z- configuration, so that productive reaction can occur.



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

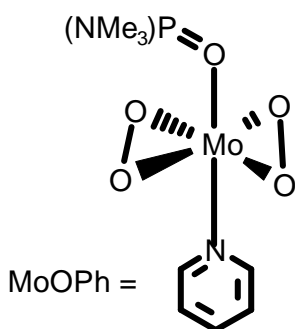
For trigonal substrates

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

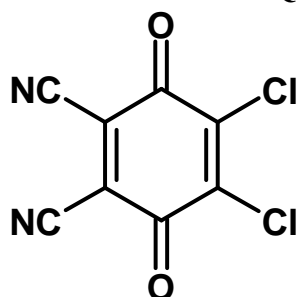
For digonal substrates

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

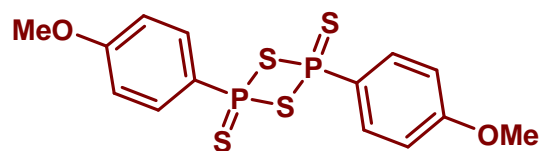
The structure of MoOPh is:



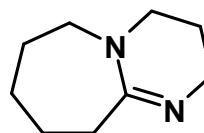
The structure of DDQ is



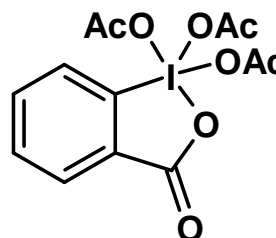
The structure of Lawesson's reagent is



DBU (diazabicycloundecane) is



DMP (Dess-Martin periodinane) is



The structure of xantphos is

