

# Organic Cumulative Exam

## December 6, 2003

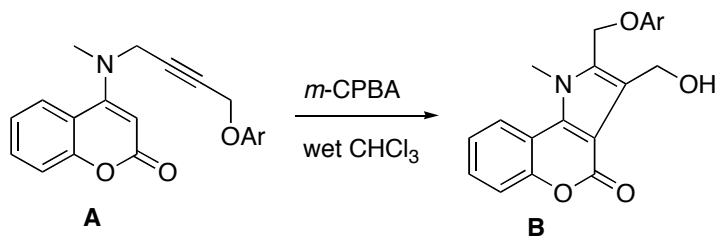
Your Identification Number: \_\_\_\_\_

Problem	Points	Score
1	20	
2	20	
3	20	
4	20	
5	20	
Total	100	

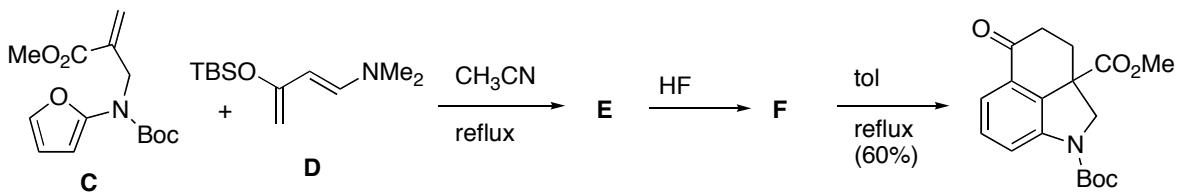
*Think pericyclic reactions!*

**Note: Please write down all of your final answers on this exam. Scratch paper will be provided as needed.**

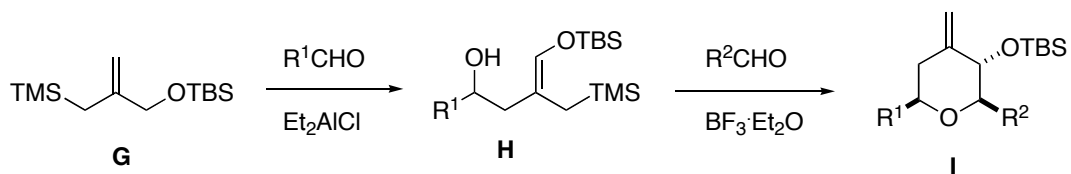
1. When compounds **A** were treated with one equivalent of *m*-CPBA at 0 ~ 5 °C for 10 min and stirred at rt for 10 h, pyrrolo[3,2-*c*]coumarin derivatives **B** were obtained. Propose a reasonable reaction mechanism. (*Tetrahedron Lett.* **2002**, *43*, 2119-2121.) Hint: Think oxidation, [2,3] and [3,3] sigmatropic rearrangement.



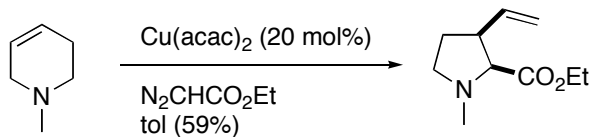
2. Heating a mixture of **C** and **D** in acetonitrile at reflux for 2 h furnished a 2:1 mixture of diastereomeric **E** that was immediately treated with HF at room temperature to provide **F**. The crude **F** was heated at reflux in toluene for 30 min to effect a cascade of processes to give the tricyclic product. Provide structures of intermediates **E** and **F**. A bonus 5 points will be given if an alternative substrate for **D** is correctly suggested. (*Org. Lett.* **2002**, *4*, 4135-4137.)



3. A reaction between an aldehyde and the allylsilane **G** promoted by  $\text{Et}_2\text{AlCl}$  leads to **H**. Subsequent condensation of **H** with another aldehyde affords the polysubstituted *exo*-methylene tetrahydropyran **I** in good yields and with total stereocontrol. Provide a rationale for the formation of **H** and **I**. (*Tetrahedron Lett.* **1999**, *40*, 5259-5262.)



4. Sweeney and his colleagues disclosed synthesis of proline derivatives using *N*-methyltetrahydropyridine, ethyl diazoacetate, and  $\text{Cu}(\text{acac})_2$ . Provide a reasonable mechanism for the step below and suggest an alternative catalyst containing a transition metal other than copper. Extra 5 points will be given if a correct rationale for the *cis*-stereoselectivity is proposed. (*J. Org. Chem.* **2003**, *68*, 4083-4086.)



5. In their biomimetic synthesis of litseaverticillols, Vassilikogiannakis and Stratakis applied the pioneering work of Foote for the photosensitized oxygenation of alkyl-substituted furans. Provide the structure of intermediate **J** and a reasonable mechanism for each of the three steps below. (*Angew. Chem. Int. Ed.* **2003**, *42*, 5465-5468.)

