

CEM 852 Final Exam

April 27, 2021

This exam consists of 5 pages. Please make certain that your exam has all of the necessary pages. Total points possible for this exam are 150. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

I. For the following compounds provide the pKa's within 2 pKa units of the compounds most acidic proton. (10 pts)

1. 1-hexyne

2. acetonitrile

3. $\text{CH}_2(\text{CN})_2$

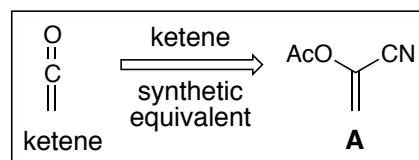
4. ethyl acetate

5. hexanoic acid

II. Provide examples of the following name reactions: (a) Buchwald-Hartwig amination, (b) Fisher indole synthesis, (c) Wittig olefination, and (d) a [2,3]-Wittig rearrangement. (12 pts)

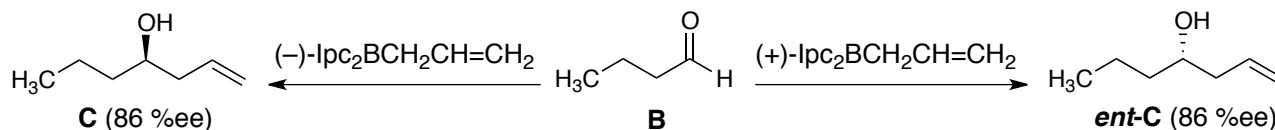
III. Provide chemical illustrations of the following terms: (a) A(1,2)-strain, (b) cine substitution, (c) umpolung, and (d) vinylogous. (12 pts)

IV. (a) Illustrate the use of compound **A** as a ketene equivalent in a [4+2]-cycloaddition. Be sure to provide detailed reaction conditions in your illustrations. (6 pts)

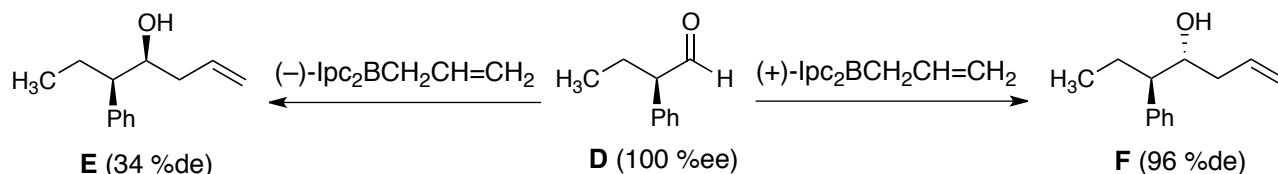


(b) Provide a detailed arrow pushing mechanism for the reaction you illustrated in part (a). (6 pts)

V. Depending on the chirality of the allyl borane used, compound **B** affords **C** or its enantiomer **both** in 86 %ee.



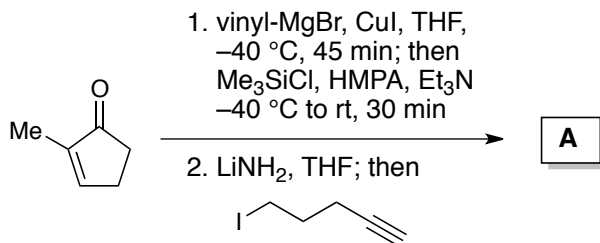
In contrast the asymmetric allyl borane of **D** affords **E** or its diastereomer **F** in very different %de's.



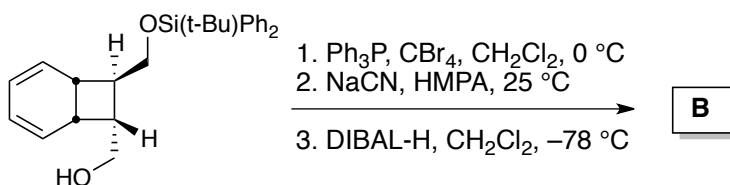
Provide an explanation for why the %de for **E** is lower than the %ee of **C**, while the %de for **F** is higher than the %ee of **ent-C**. (8 pts)

VI. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (18 pts)

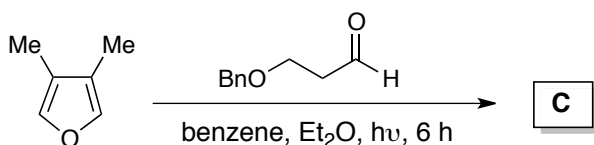
1.



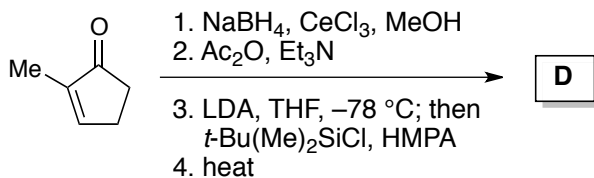
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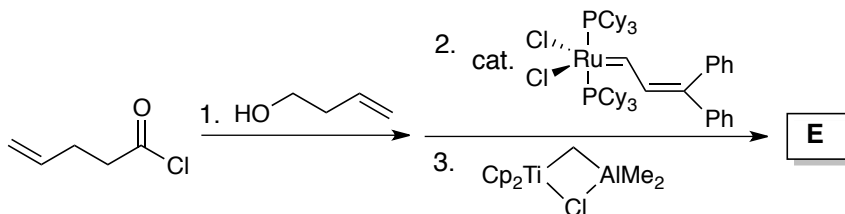
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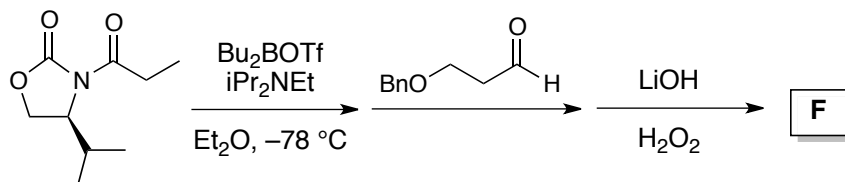
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5.

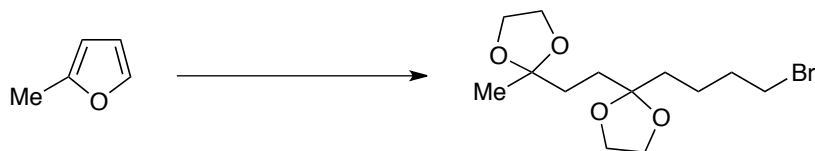


6.

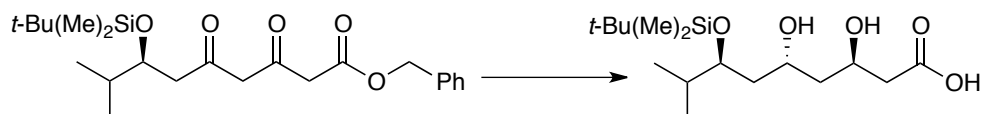


VII. Provide conditions that will afford the transformations outlined below. Some of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (18 pts)

1.



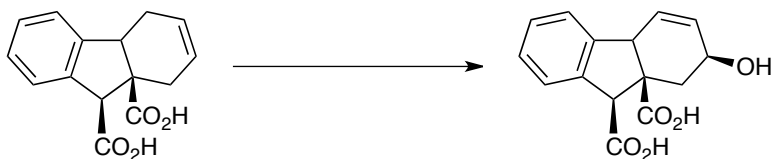
2.



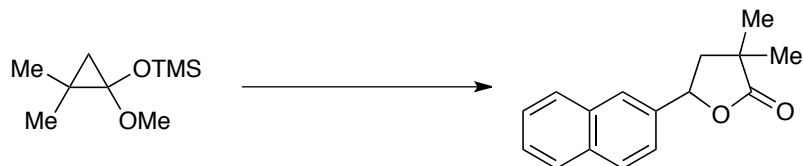
3.



4.



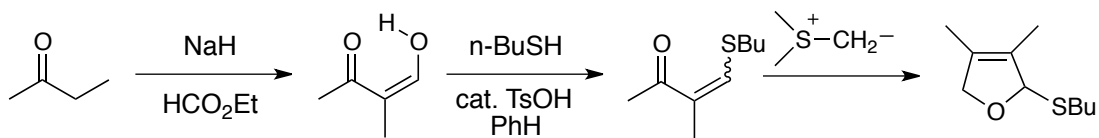
5.



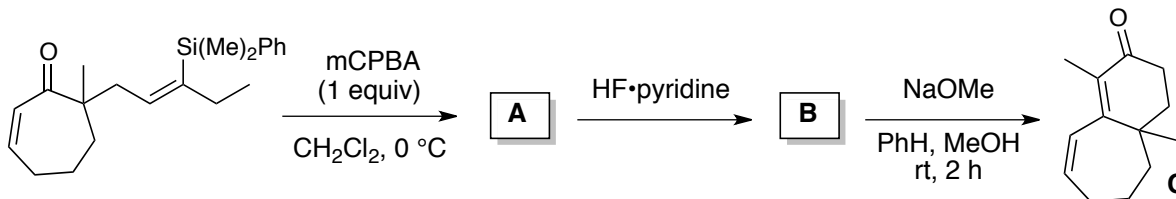
6.



VIII. Provide a detailed arrow pushing mechanism for the reaction shown below. (10 pts)



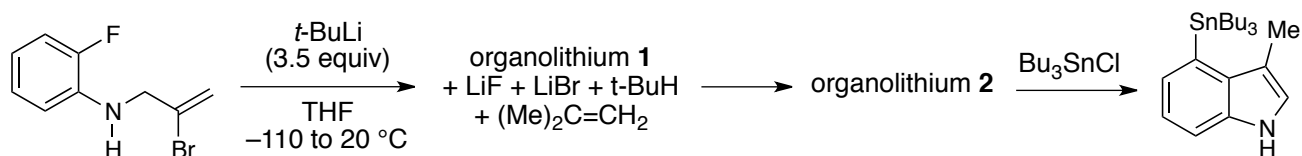
IX. (a) For the sequence below, provide the structures of intermediates **A** and **B**. (6 pts)



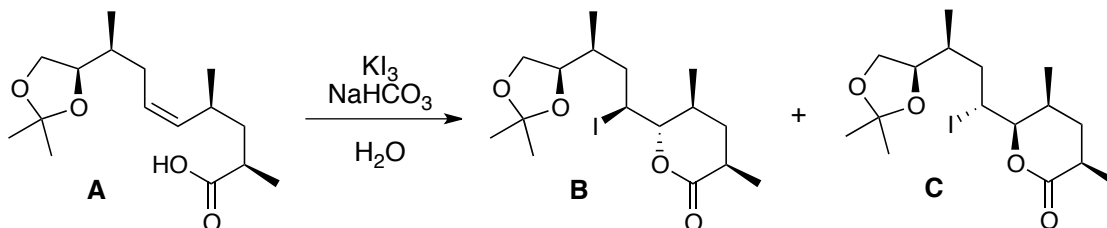
(b) Provide a detailed arrow pushing mechanism for the conversion of **B** to **C**. (6 pts)

(c) How might you make this process afford a single enantiomer of **C**? (2 pts)

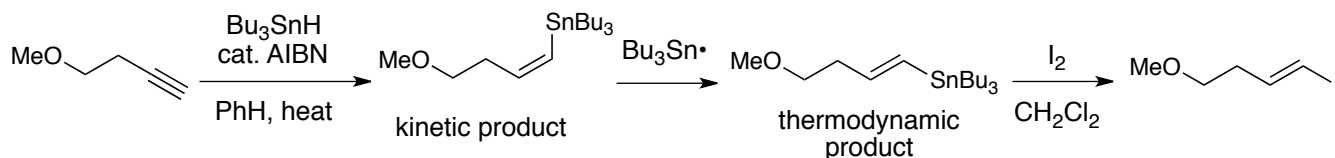
X. (a) For the sequence below, provide the structures of organolithium **1** and organolithium **2**. (8 pts)



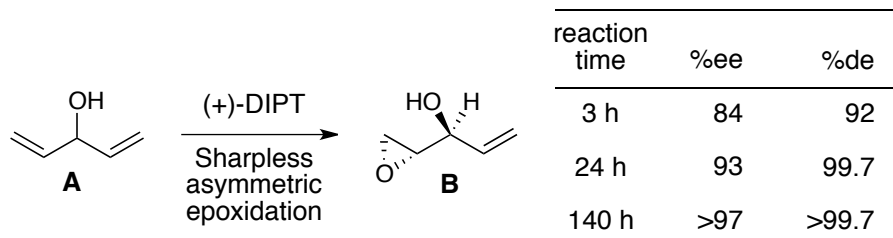
XI. Unsaturated carboxylic acid **A** possesses the requisite structural features for an iodolactonization reaction. A source of electrophilic iodine could conceivably engage either diastereotopic face of the double bond in **A**, leading to a mixture of **B** and **C**. However, this reaction only affords **B** in 87% yield. Minimization of A(1,3)-strain can explain why **C** is so disfavored relative to **B**. Illustrate this explanation. (8 pts)



XII. Radical hydrostannation of alkynes initially makes the Z-stannane which reacts with another $\text{Bu}_3\text{Sn}\cdot$ to give the E-stannane. The E-stannane can be titrated with I_2 to afford the E-vinyl iodide. Provide a detailed arrow pushing mechanism for the conversion of the Z-stannane to the E-stannane and then the E-stannane to the E-vinyl iodide, being sure to explain the alkene geometry of both the E-stannane and the E-vinyl iodide. (10 pts)



XIII. Subjecting symmetric compound **A** to Sharpless epoxidation conditions with (+)-DET affords **B**. Over time the %ee and the %de of **B** improves. Provide a hypothesis that would explain these observations. (10 pts)



Bonus Question: NASA's Perseverance Rover recently set down on Mars along with NASA's Martian helicopter Ingenuity. Prior to becoming an astronaut, what PhD chemist was a flavor chemist working for Mars (the candy company). (2 pts)

- (a) Mae Jemison
- (b) Sally Ride
- (c) Helen Sharman
- (d) Valentina Tereshkova
- (e) George Taylor