

Chemistry 41c

FINAL EXAM

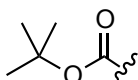
June 10, 2013

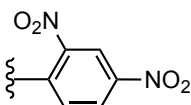
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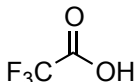
Note: You have four hours to work on the exam. Do not open the exam packet until you are ready to begin. This exercise must be completed in one sitting and is to be worked alone and is open book (Loudon's text & Loudon's Study Guide/ Solutions Manual), and open notes (restricted to 41a/41b/41c printed or electronically archived course material). You are not permitted to access the Internet or programs like ChemDraw during the examination period. Calculators and molecular models may be used. It is recommended to skim the entire exam and work more familiar problems first. Also, remember to show your reasoning whenever possible for partial credit.

Please do not discuss the contents of this exam with anyone else until after June 19, 2013.

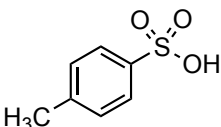
Some Useful Abbreviations and Symbols:

Boc = *tert*-butoxycarbonyl 

DNB = 2,4-dinitrobenzene 

TFA = trifluoroacetic acid 

TFE = trifluoroethanol 

TsOH = *para*-toluenesulfonic acid 

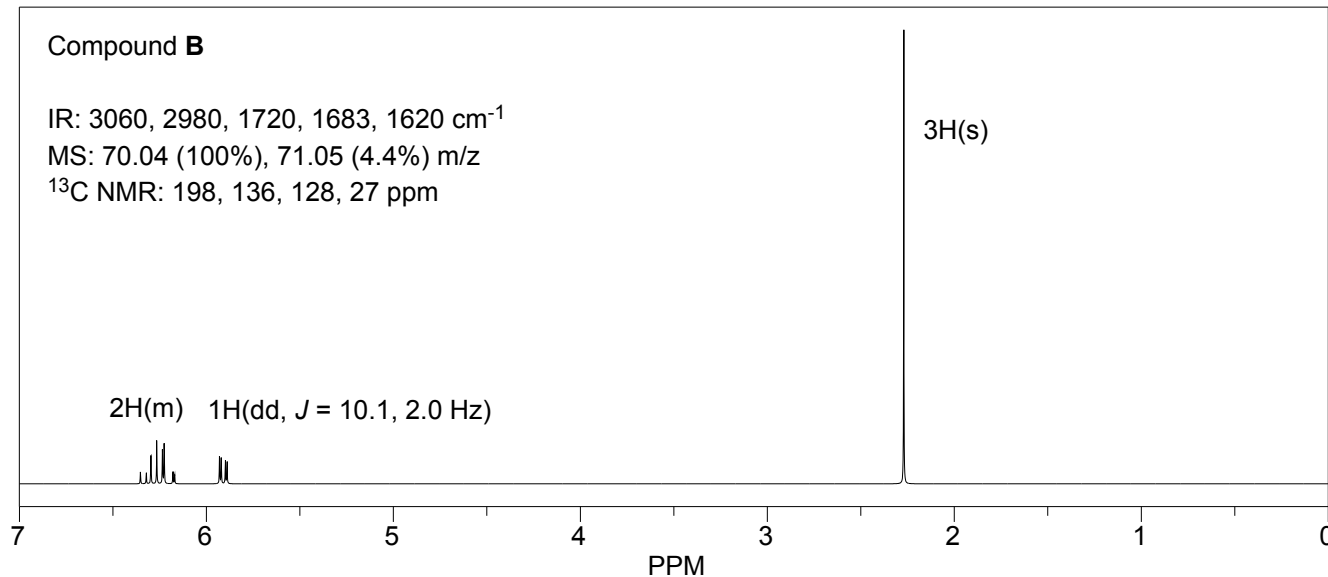
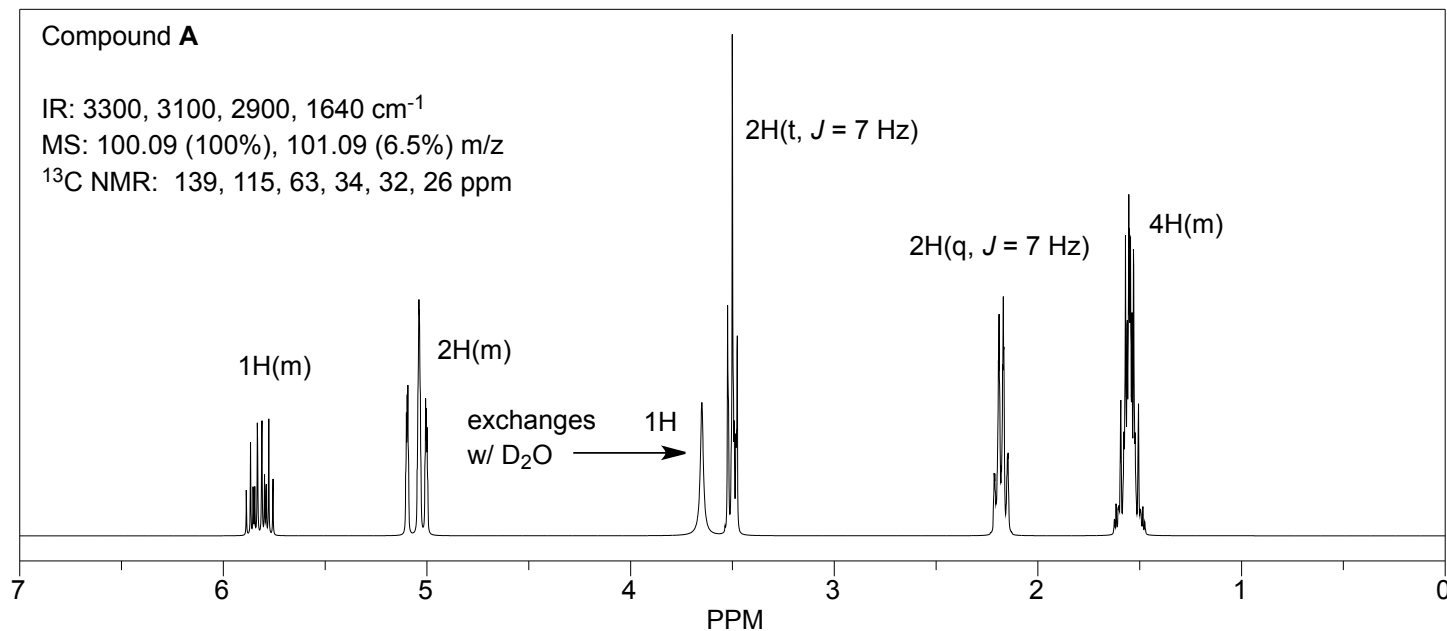
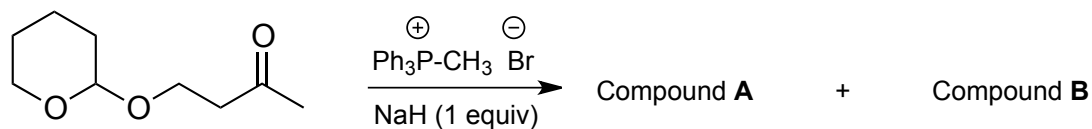
\Longrightarrow = retrosynthetic arrow

Submit your completed exam by **5:00 PM on Friday, June 14, 2013**, to the drop box in 357 Crellin. Late submissions will not be accepted without a Dean's note.

Good Luck!

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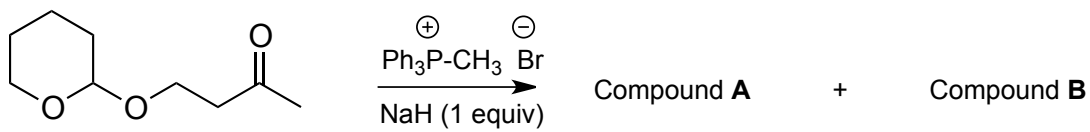
1a. Consider the reaction conditions and spectroscopic data and predict the structures of compounds **A** and **B**. (10 pts)



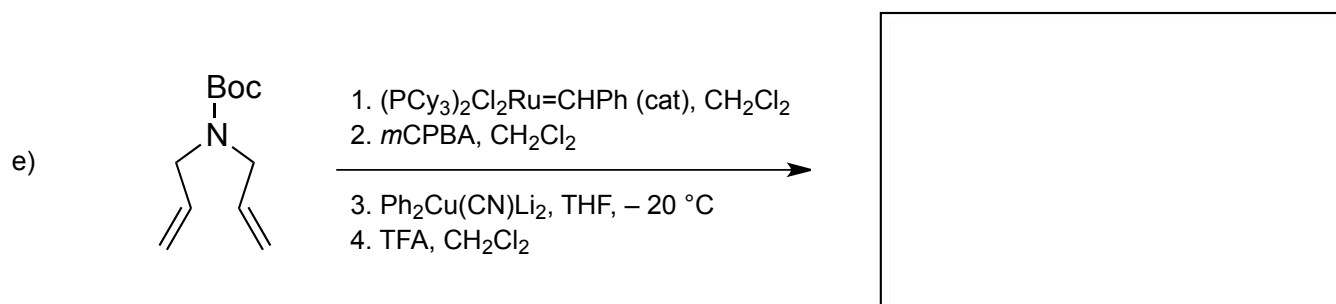
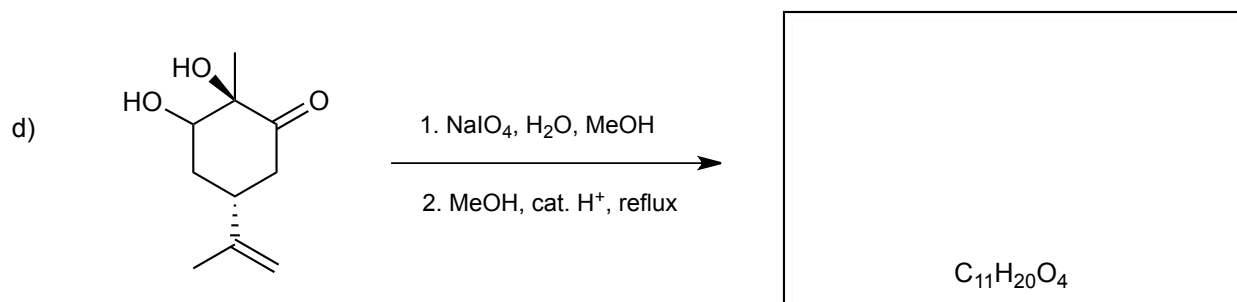
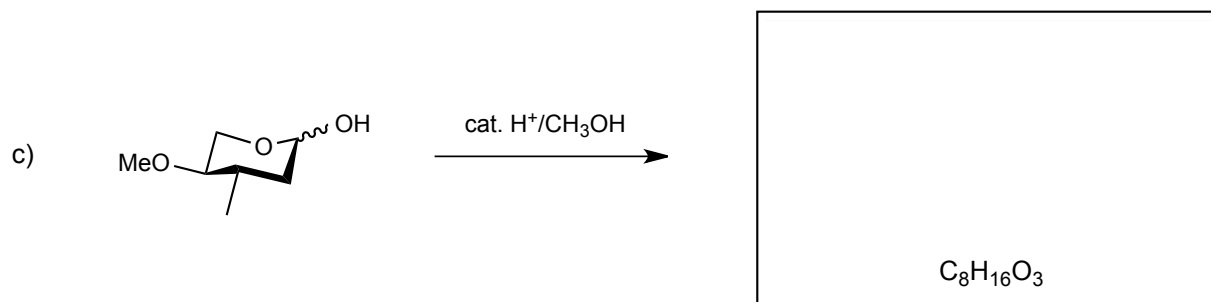
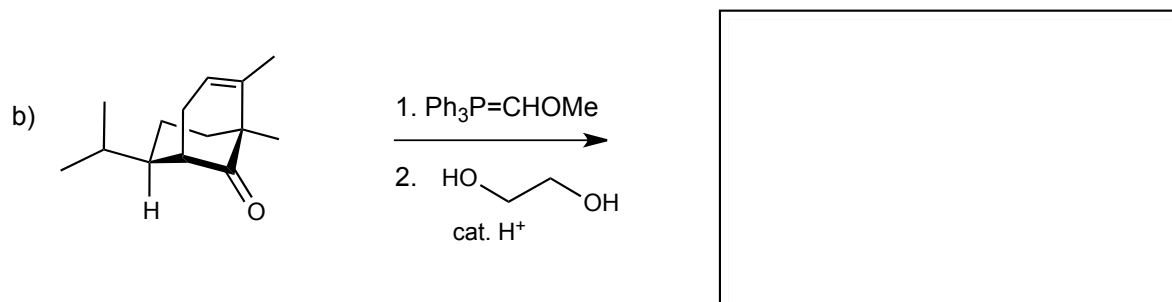
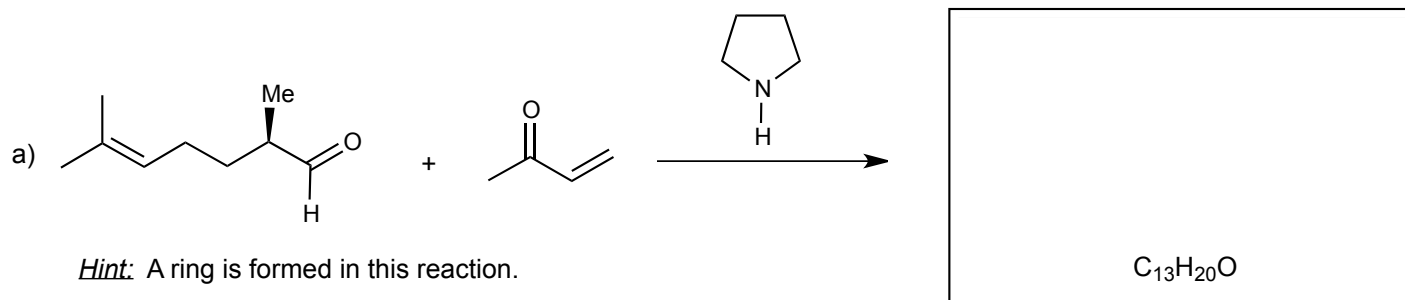
Compound **A**

Compound **B**

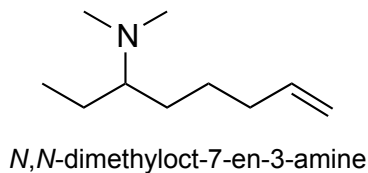
1b. In the space provided, write an arrow-pushing mechanism to account for the formation of compounds **A** and **B**. (8 pts)



2. Predict the principal products expected (if any) for the following reaction sequences. Provide accurate depictions of stereochemical outcomes. For each, draw the structure you want to be evaluated in the box provided. (6 pts each)

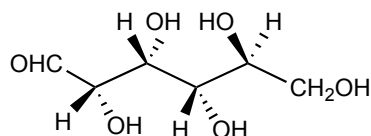


3. Compound **C** has the molecular formula $C_8H_{17}N$. Treatment of **C** with excess methyl iodide, followed by silver oxide and heating, gives the pure (*S*)-enantiomer of *N,N*-dimethyloct-7-ene-3-amine. Propose a stereochemically accurate structure for compound **C** and draw a curved arrow mechanism to show how this reaction gives observed product. (10 pts)

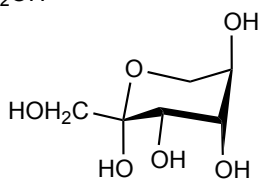


Compound **C** ($C_8H_{17}N$)

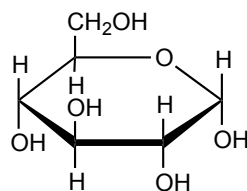
4. Redraw each of the following sugars in open-chain form as a Fischer projection, using the standard convention for depicting carbohydrates. Circle the letters associated with D sugars. (9 pts)



A



B



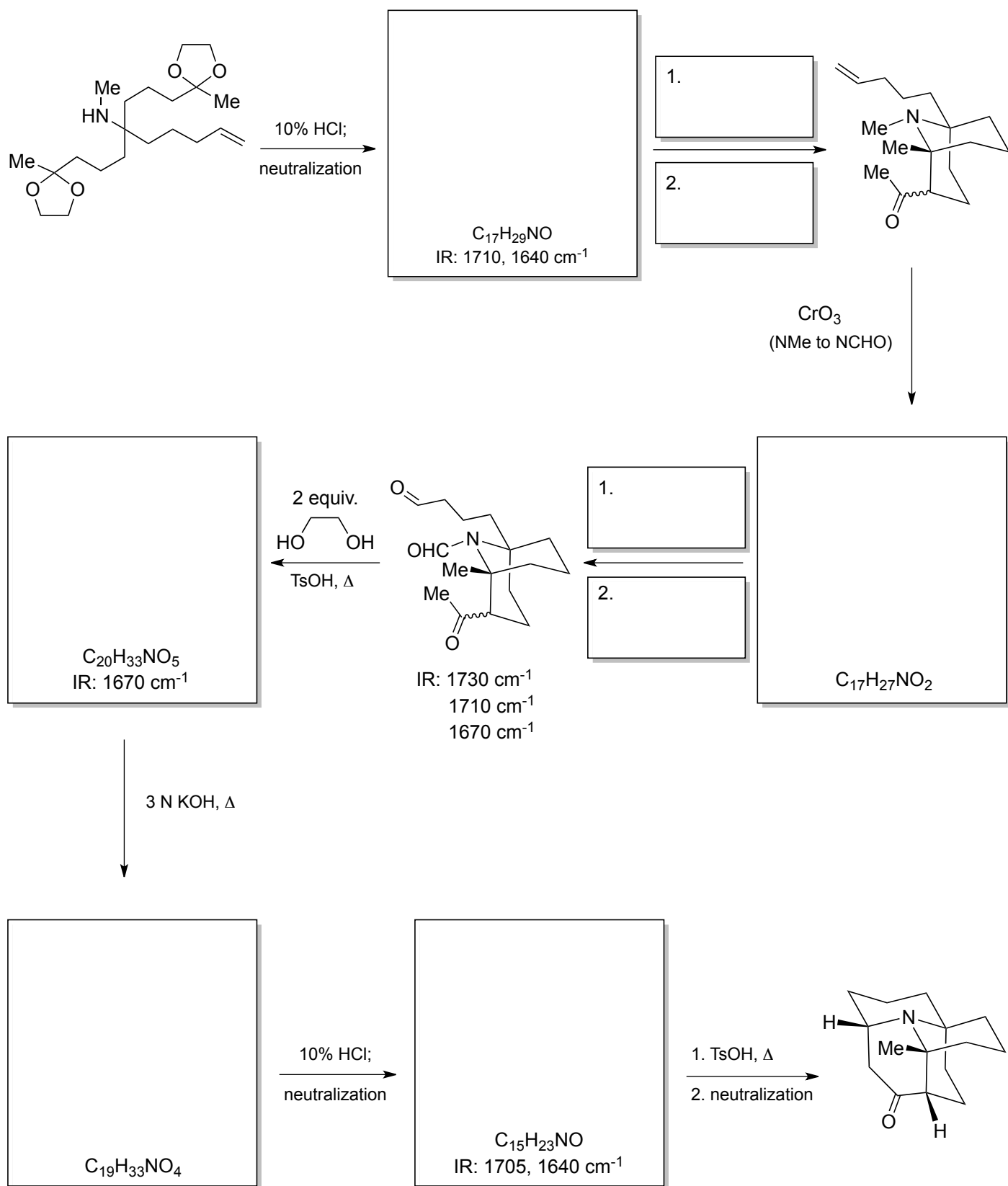
C

A

B

C

5. Predict the structure of the intermediates or provide the missing reagents in the following synthesis. (15 pts)



6. Crellinose is a reducing disaccharide which undergoes mutarotation. Hydrolysis by either aqueous acid or α -arabinosidases give L-arabinose and D-glucose. Oxidation of crellinose with bromine water followed by acid hydrolysis gives L-arabinose and D-gluconic acid. Methylation of the bromine-water oxidation product, followed by acid hydrolysis gives 2,3,4-tri-O-methyl-L-arabinose and 2,3,4,5-tetra-O-methyl-D-gluconic acid. Methylation and acid hydrolysis of crellinose gives 2,3,4-tri-O-methyl-L-arabinose and 2,3,4-tri-O-methyl-D-glucose. What is the structure of crellinose? Draw your representation using appropriate **Haworth** structures. Show your logic and explain the experimental data. (6 pts)

crellinose (Haworth representation)

7. The complete structure of **JZ**, a polypeptide with antibiotic properties, has been worked out as follows:

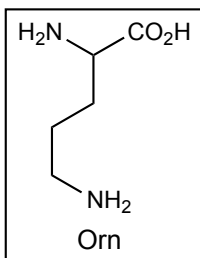
I) Analysis of the hydrolysis products gave equimolar amounts of Leu, Orn, Phe, Pro, Val. (Ornithine, Orn, is a rare amino acid whose formula is shown below.)

II) Measurement of the molecular weight gave an approximate value of 1250.

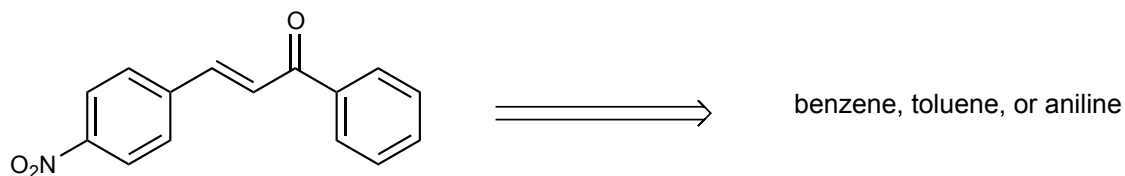
III) Sanger *N*-terminal residue analysis with 1-fluoro-2,4-dinitrobenzene gave only DNB-NHCH₂CH₂CH₂CH(NH₃⁺)CO₂⁻.

IV) Partial hydrolysis of **JZ** gave the following di- and tri-peptides: Leu-Phe, Orn-Leu, Phe-Pro, Val-Orn, Phe-Pro-Val, Pro-Val-Orn, Val-Orn-Leu.

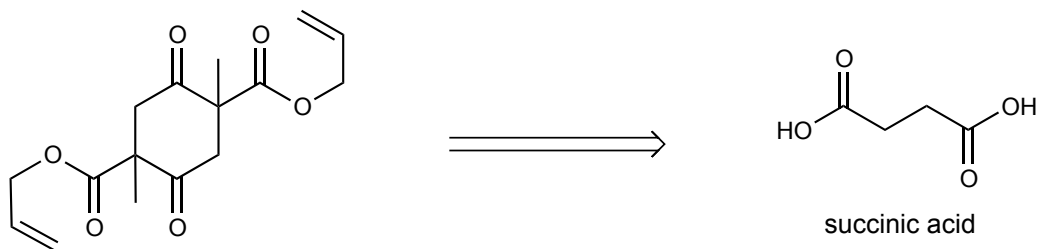
Explain the results of the Sanger experiment (statement III) and determine the structure of **JZ**. Write the structure using three-letter amino acid representations, and draw a box around it to indicate your proposed structure for evaluation. (6 pts)



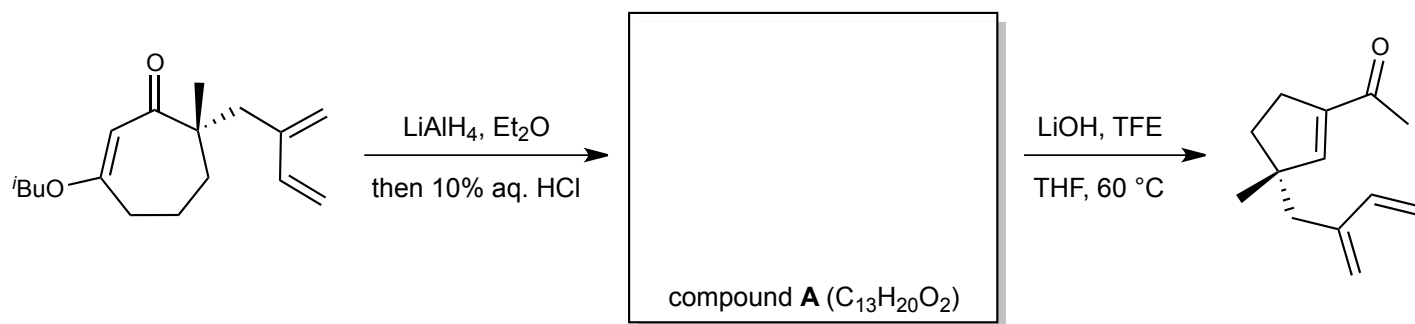
8. Outline a synthesis of the following compound starting from benzene, toluene, or aniline. You have at your disposal any reagents encountered in Ch 41a, b, or c, and may use any organic molecules containing four carbons or fewer. (8 pts)



9. Propose a synthesis of the following molecule from succinic acid. You have at your disposal any reagents encountered in Ch 41a, b, or c, and may use any organic molecules containing four carbons or fewer. (*Hint: A good synthetic route takes advantage of the symmetry present in the target molecule.*) (8 pts)



Bonus: Provide the structure of compound **A** and draw a reasonable arrow-pushing mechanism for the transformation of **A** into the final product shown. (10 pts)



Problem 1 (18 pts) _____

Problem 2 (30 pts) _____

Problem 3 (10 pts) _____

Problem 4 (9 pts) _____

Problem 5 (15 pts) _____

Problem 6 (6 pts) _____

Problem 7 (6 pts) _____

Problem 8 (8 pts) _____

Problem 9 (8 pts) _____

Bonus (10 pts) _____

TOTAL (110 pts) _____