\CEM 852 Exam-2

March 28, 2022

Please put away all notes and phones. *Use of cell phones for any reason is prohibited*. This exam consists of 5 pages. Make certain that your exam has all five necessary pages. Total points possible for this exam are 100. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

I. Illustrate the following "name" reactions (15 pts)

See: https://www.organic-chemistry.org/namedreactions/

1. Nozaki-Hiyama-Kishi reaction.

2. Peterson olefination.

3. Shapiro reaction.

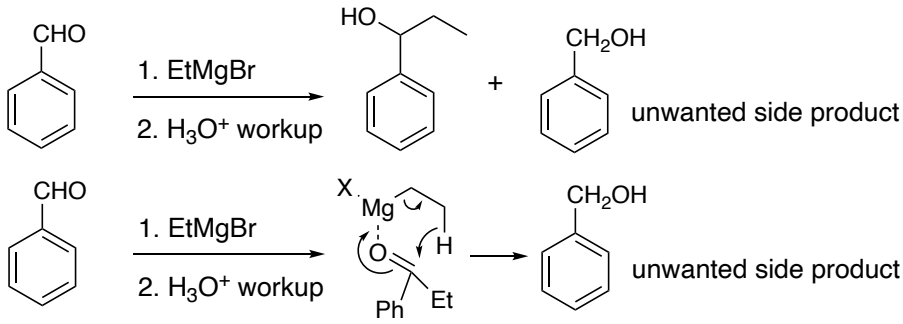
4. enyne metathesis.

5. Type III crotylation.

II. Wittig olefinations of esters are problematic. Why? **Because of the leaving group**. (2 pts)

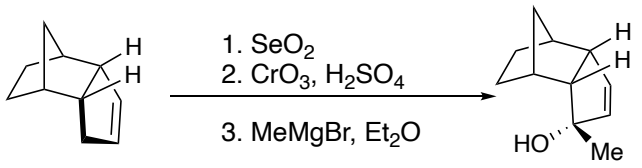
III. Allylic oxidations with oxygen require the presence of light and a sensitizer. Why? **To convert the ground state triplet O_2 to the excited state singlet O_2** (2 pts).

IV. Grignard reactions can give unwanted side products. Illustrate the β-hydride elimination mechanism by which the Grignard reaction shown below could afford benzyl alcohol as a side product. (2 pts)



V. Provide the product or products of the reactions below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, indicate the major and minor species. (27 pts)

1.



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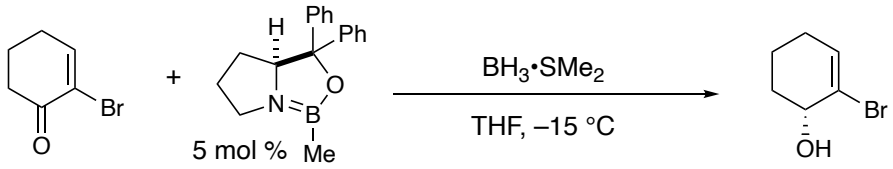

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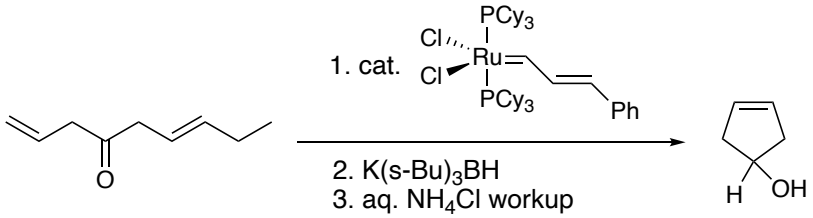

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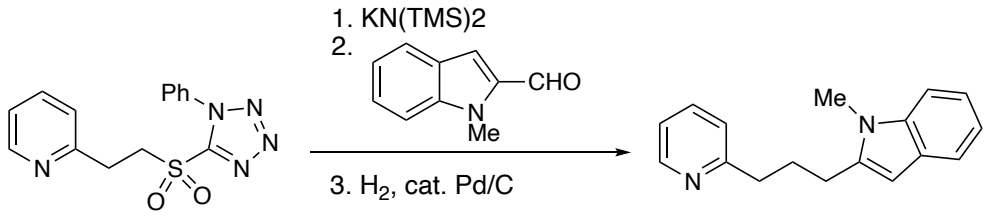

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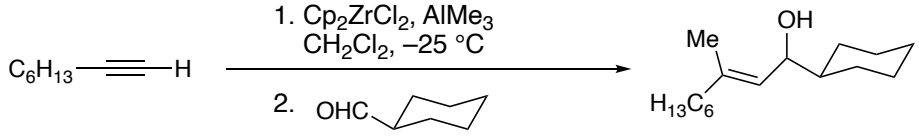

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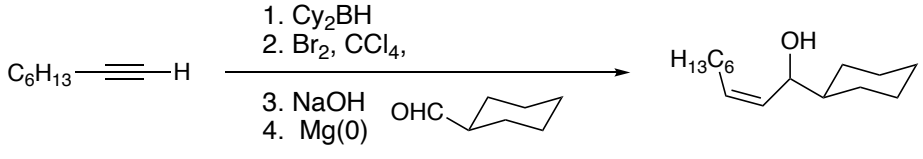

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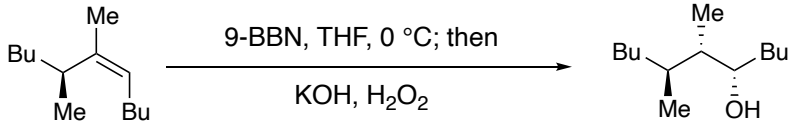

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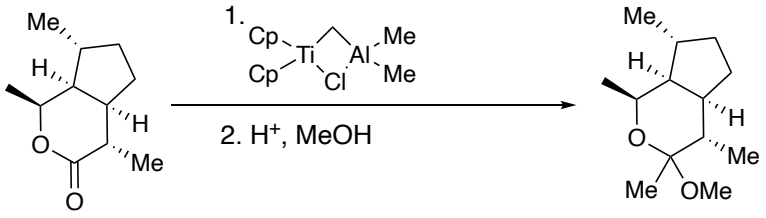

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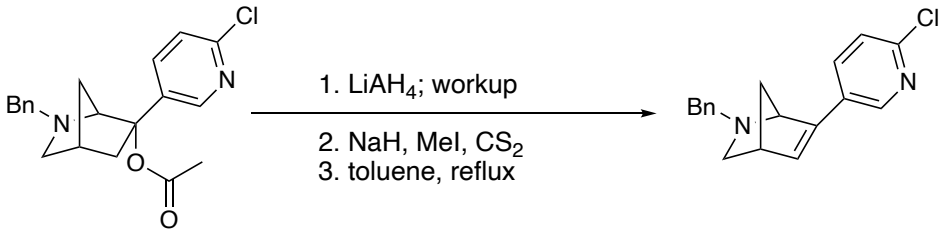
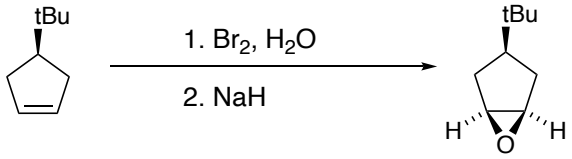


VI. Provide conditions that will affect the transformations outlined below. Some of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (15 pts)

1.



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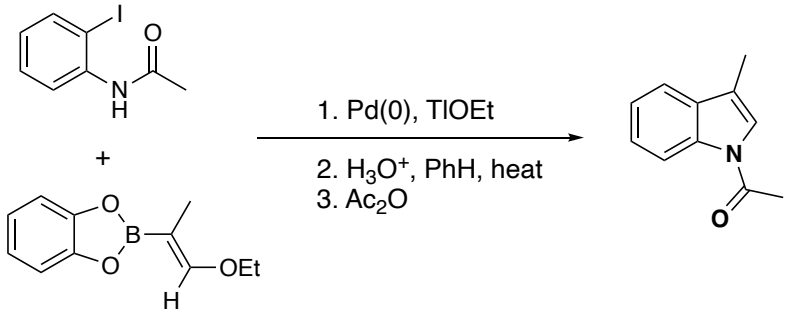

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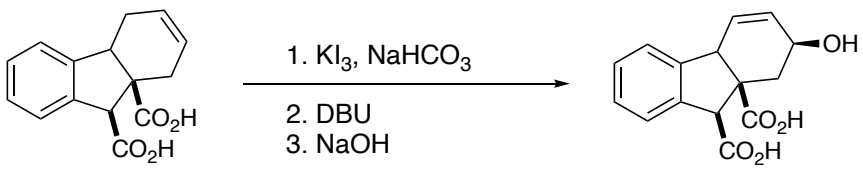

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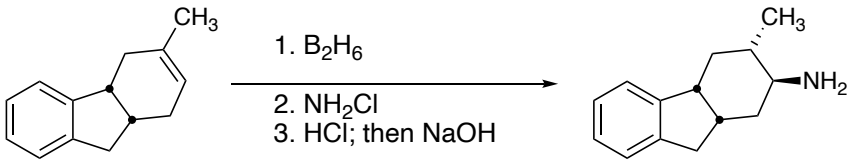

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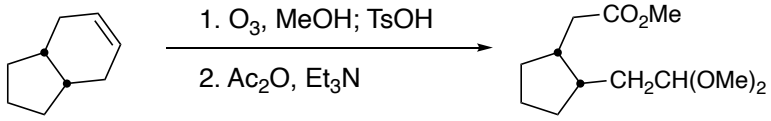
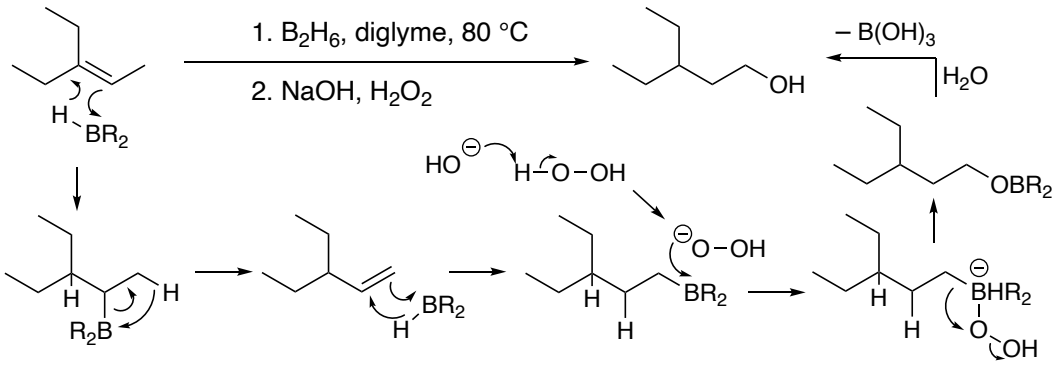
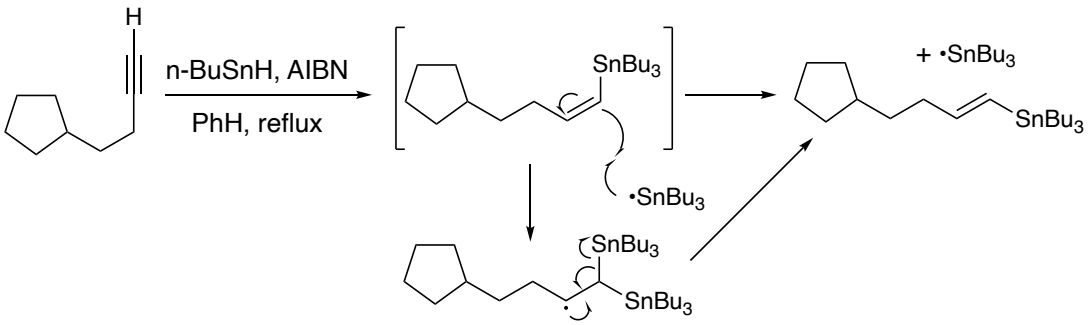


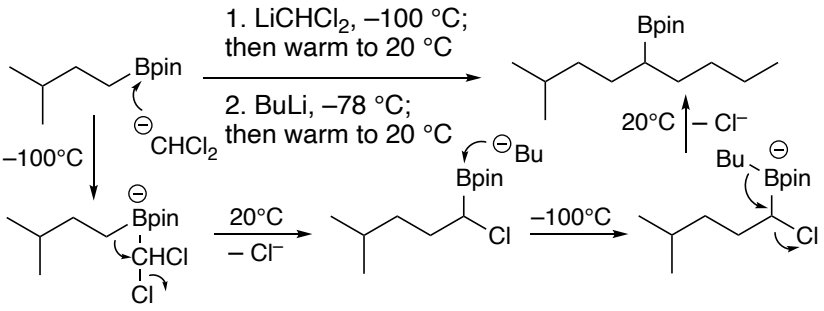
VII. Provide a detailed arrow (electron) pushing mechanism for the reaction shown below. (5 pts)



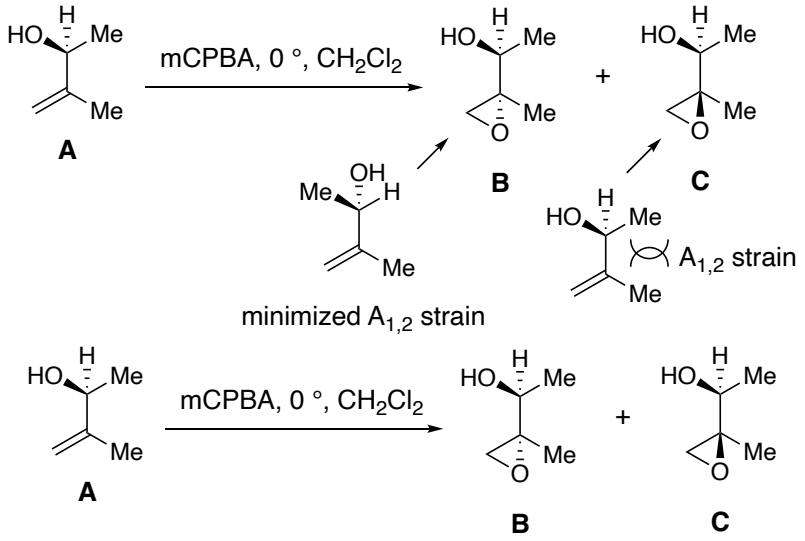
VIII. In class, we learned that free radical hydrostanations of alkyne afford the Z-alkene as the kinetic product and the E-alkene as the thermodynamic product. Provide a detailed arrow (electron) pushing mechanism for the conversion of the Z-alkene as the kinetic product into the thermodynamic product. Note: You do not need to show the initiation step with AIBN, i.e. you may simply start with $Bu_3Sn\bullet$ (5 pts)



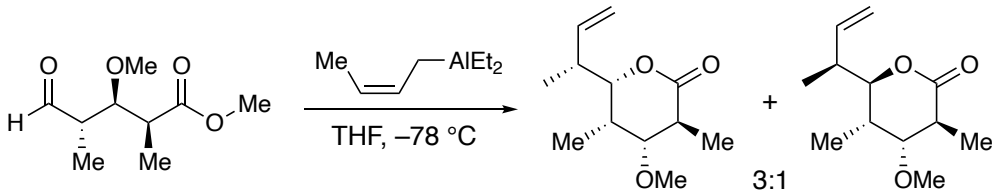
IX. Provide a detailed arrow (electron) pushing mechanism for the Matteson boronic ester homologation shown below. (8 pts)

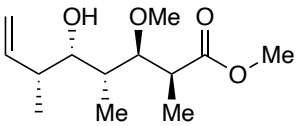


X. Using Newman projections, explain why the epoxidation of **A** favors **B** over **C**. Note: The olefin-hydroxy-bite angle for mCPBA allylic epoxidations is 120°. (5 pts)



XI. Explain the stereochemical outcome of the reaction below. (8 pts)



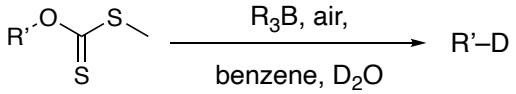


major product before lactonization

major product via Type I crotylation (closed Zimmerman-Traxler transition structure) and Felkin-Ahn model; followed by lactonization.

minor product via Type I crotylation (closed Zimmerman-Traxler transition structure) and anti-Felkin-Ahn model; followed by lactonization.

XII. In the course of a total synthesis, John Wood and co-workers discovered a method for the deoxygenation of alcohols employing water as the hydrogen atom source.



On the basis of calculations, along with experimental observations, they concluded that the process begins with air oxidation of the trialkylborane (R_3B) to liberate an alkyl radical (R•). This reacts with the xanthate to provide intermediate **D**, which rapidly decomposes to S-alkyl-S-methyl dithiocarbonate and the substrate-derived alkyl radical R'•. This species is then reduced by R_3B–OD_2 to provide the observed product R'–D, dialkyl borinic acid **E**, and an equivalent of alkyl radical (R•) capable of propagating the radical chain. Illustrate Woods proposed mechanism. (6 pts) **See: *J. Am. Chem. Soc.* 2005, *127* , 12513–12515.**

Bonus Question: In 1912, Victor Grignard was awarded the 1912 Nobel Prize in Chemistry (shared with Paul Sabatier) for the reaction that bears his name. When World War I broke out, Grignard was drafted into the French Army. At what rank did the French Army induct Nobel Laureate Victor Grignard? (2 pts)

(a) Corporal

(b) Chevalier

(c) Commander

(d) Généraux

(e) Marshal