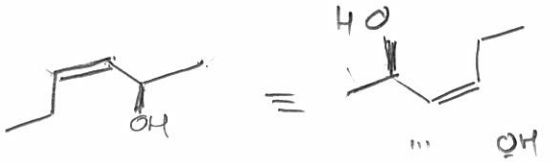
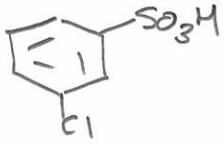
1. Provide structures for the following compounds (don't forget stereochemistry!). (20 points)

a. (2*R*,4*Z*)-hex-3-en-2-ol

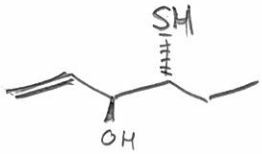
Should be 3Z



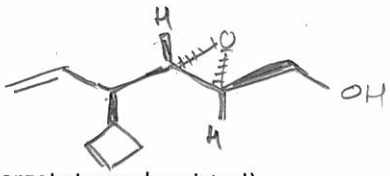
b. 3-chlorobenzenesulfonic acid



c. (3*S*,4*R*)-4-mercaptopent-1-en-3-ol

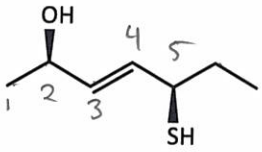


d. (2*S*,3*S*,4*R*)-4-cyclobutyl-2,3-epoxyshex-5-en-1-ol



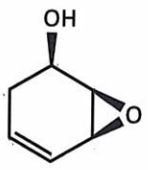
2. Provide IUPAC names for the following structures (don't forget stereochemistry!). (15 points)

a.



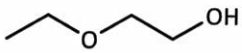
(1*R*,3*E*,5*R*)-5-mercaptohept-3-en-2-ol
or
(1*R*,3*E*,5*R*)-5-sulfanylhept-3-en-2-ol

b.



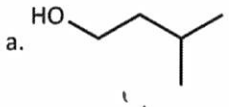
(1*R*,5*S*,6*R*)-5,6-epoxycyclohex-3-enol

c.



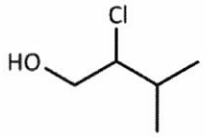
2-ethoxyethanol

3. For the series of alcohols below, indicate which one has the *highest* pK_a value and which has the *lowest*. Explain the reasoning for your choices. (20 points)

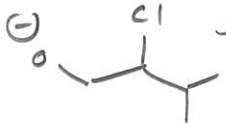
a. 

highest

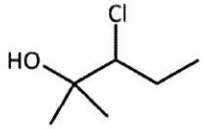
1° $pK_a \sim 16$

b. 

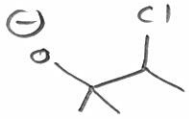
lowest



inductive Stability of conj base

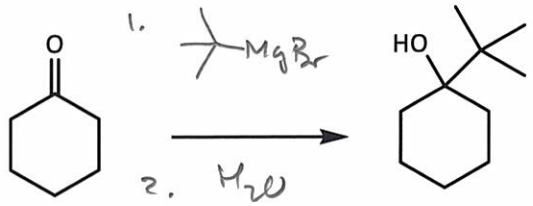
c. 

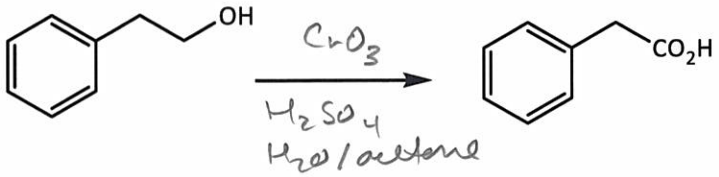
also inductive Stability, but

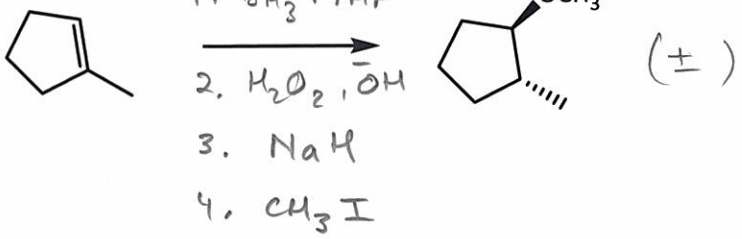


more hindered conj. base has less solvation Stability

4. Show the reagents and conditions to accomplish the following (more than one step may be necessary). (15 points)

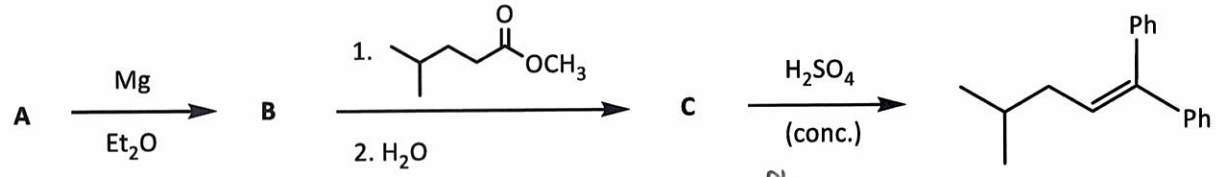
a. 

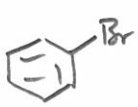
b. 

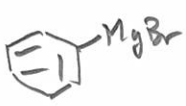
c. 

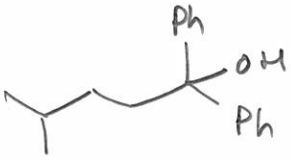
(±)

5. Show the structure of **A**, **B** and **C** in the following synthesis. (15 points)

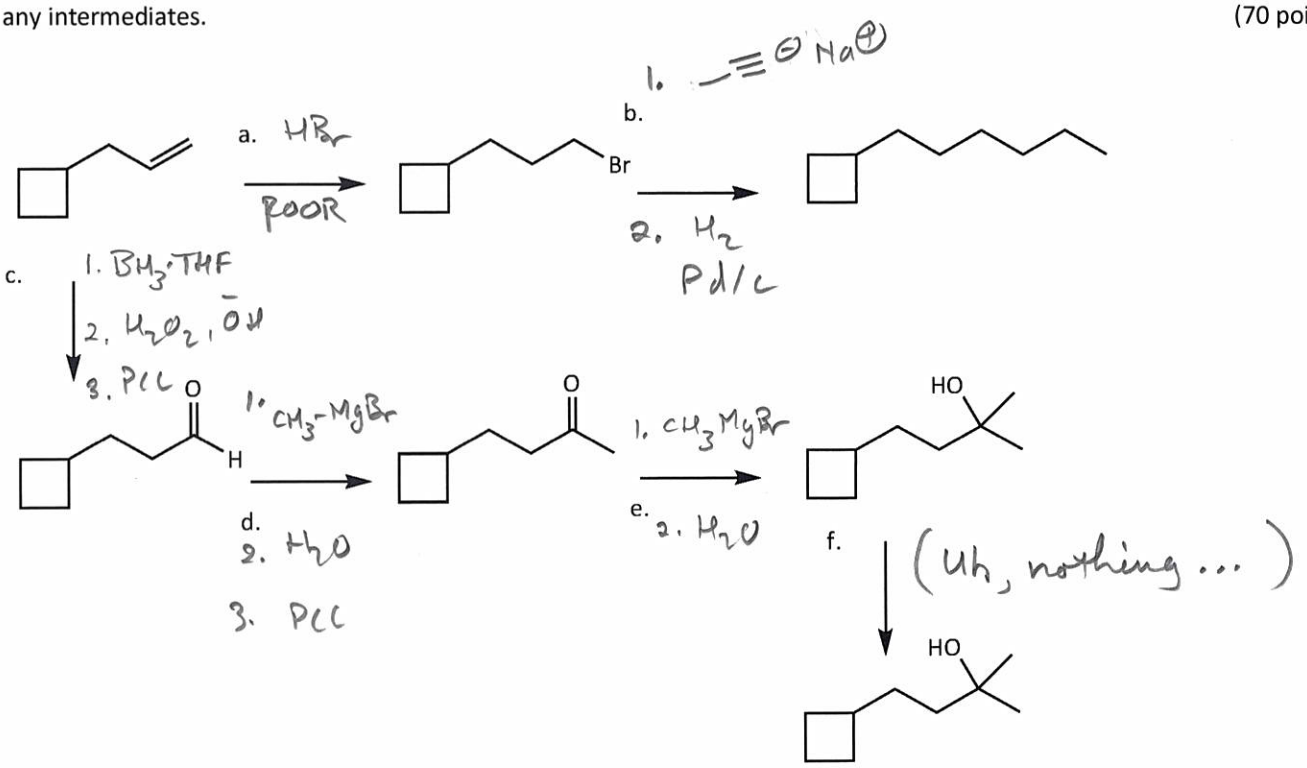








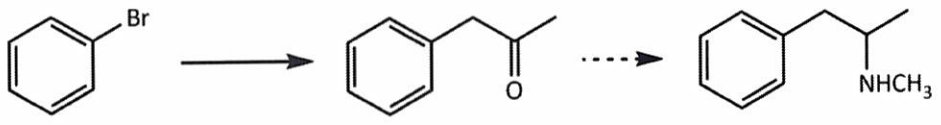
6. For the following series of reactions, fill in the reagents necessary to accomplish each transformation (some of them require more than one step – be sure to use numbers (1., 2., etc) to show separate steps when necessary. You do not need to show any intermediates. (70 points)



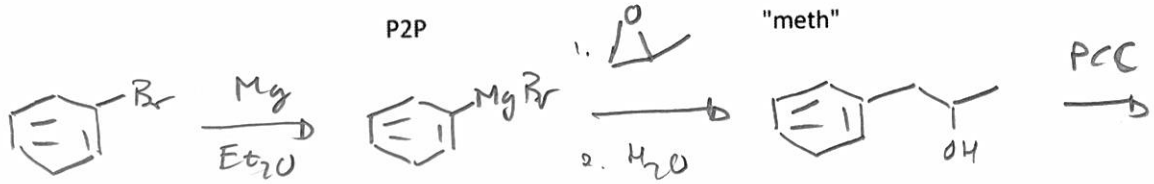
7. Explain why ether solvents, such as Et_2O and THF, are used for preparing and using Grignard reagents (R-MgBr), instead of solvents like methanol, ethanol (5 points)

In ethers, the oxygen lone pairs help stabilize the organometallic reagent, AND they don't have protic -OH group that would rapidly deprotonate under the strongly basic presence of Grignard.

8. The ketone shown below, P2P, is an infamous starting material for the street drug methylamphetamine ("meth"). Show how to convert bromobenzene into this ketone using any reagents that you want, but the synthesis must include an *epoxide* at some point. Show all intermediates. (Don't try to synthesize "meth" – that's illegal!) (20 points)

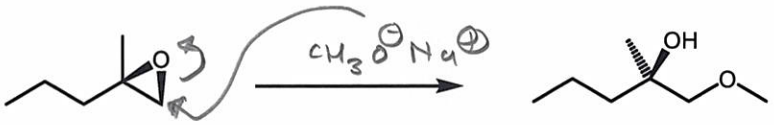


P2P "meth"

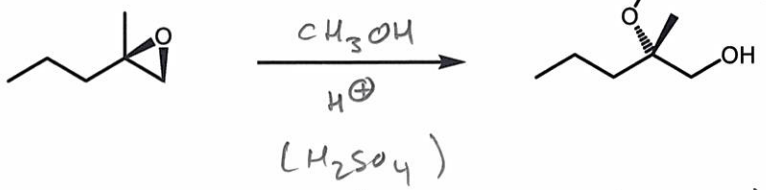


9. Show the reagents necessary to accomplish the two transformations. Explain your reasoning behind the choice of reagents, i.e., why they give the different products (20 points)

Extra Credit: Provide IUPAC names for the products (including stereochemistry) (10 EC points)

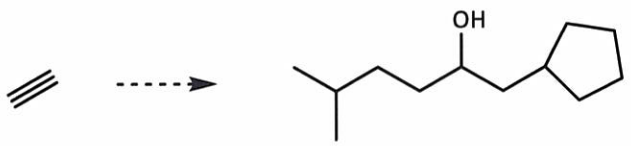


– strong Nu add to the least hindered site of the epoxide

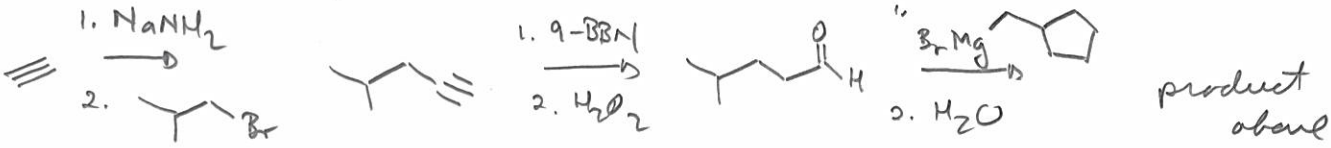


– weak nucleophiles require activation of oxygen w/ a proton

10. Starting from acetylene, show a synthesis of the following product. You can choose any reagents and other intermediates that you like, but the synthesis *must* start with acetylene. (50 points)



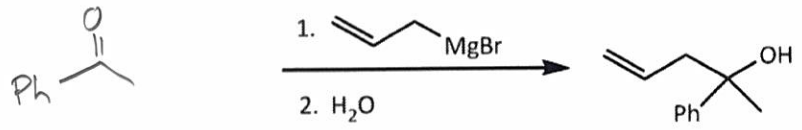
The challenge is that acetylides are too basic to alkylate them w/ 2° alkyl halides!



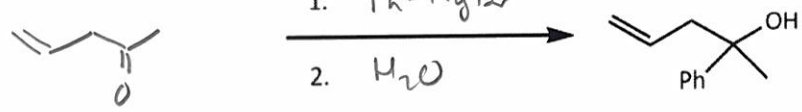
product above

11. Show all three possible methods to prepare the product alcohol using the using a Grignard reaction (a hint is given for the first case. (25 points)

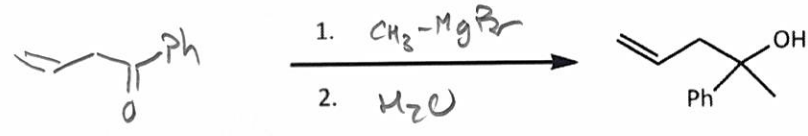
a.



b.

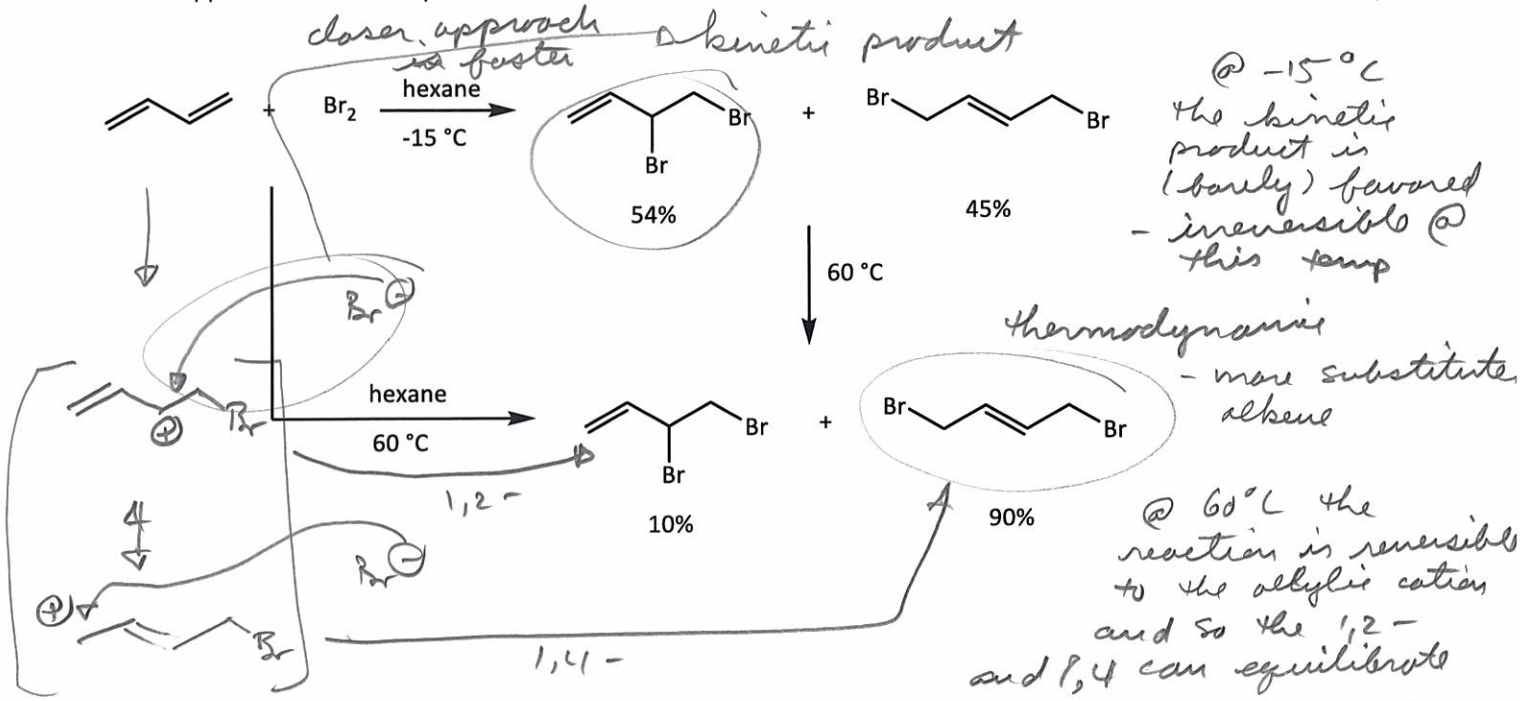


c.

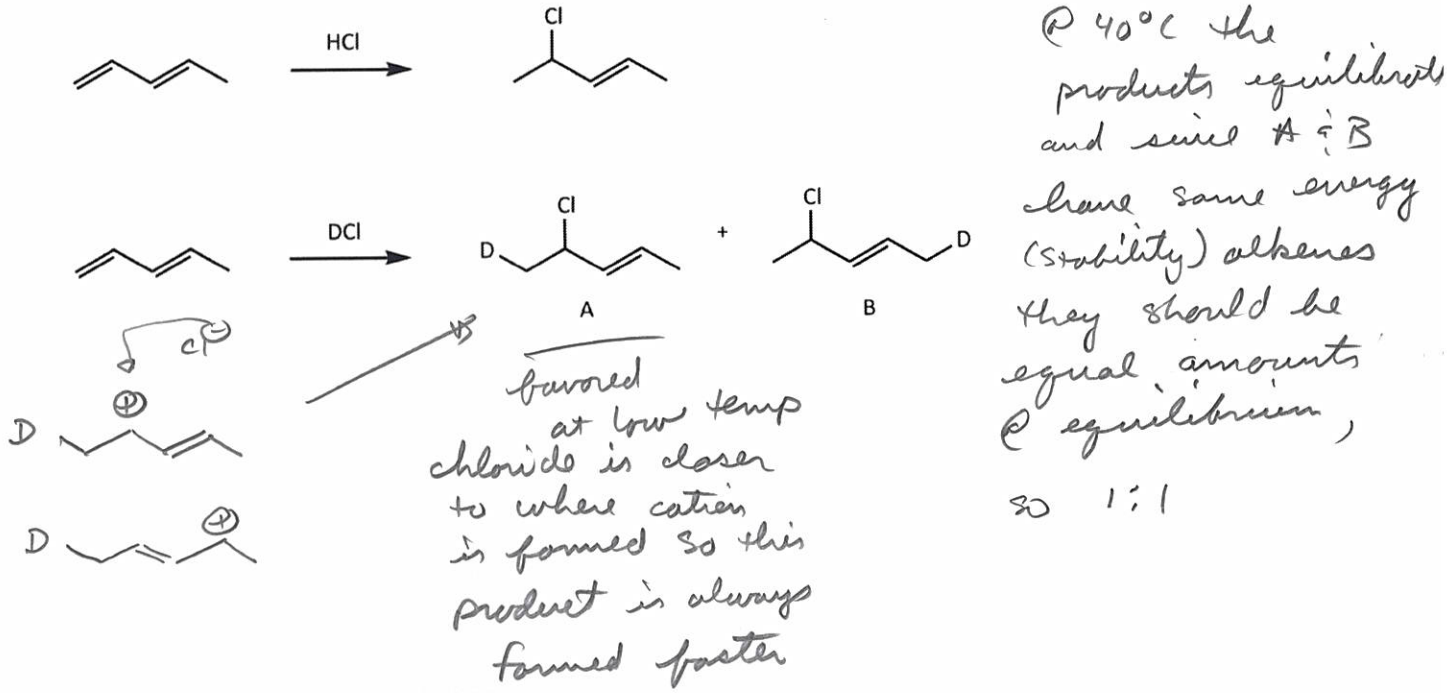


12. Consider the reaction shown below. In terms of the mechanism, clearly account for the formation of the two products and in the observed ratios at the different temperatures. Note that if the reaction is run at the colder temperature and then the mixture is warmed to 60 °C, the ratio of products is the same as if run only at the higher temperature. (20 points)

What happens to the ratio of products if the warmed mixture is then re-cooled back to -15 °C? (5 points)

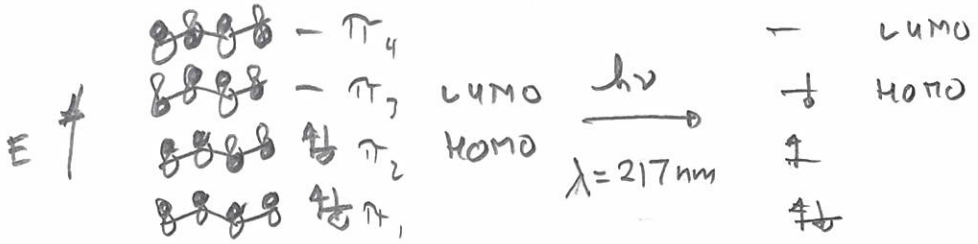


13. The reaction of 1,3-pentadiene with hydrogren chloride (HCl) gives only one product (shown as a *racemate*). However, the reaction with deuterium chloride (DCl) produces two products, A and B (also as *racemates*), and the ratio of these is temperature dependent. Which product, A or B is favored at low temperatures (0°C) and what happens to the ratio at higher temperatures (40°C)? Explain in terms of *kinetic* vs *thermodynamic* control. (20 points)



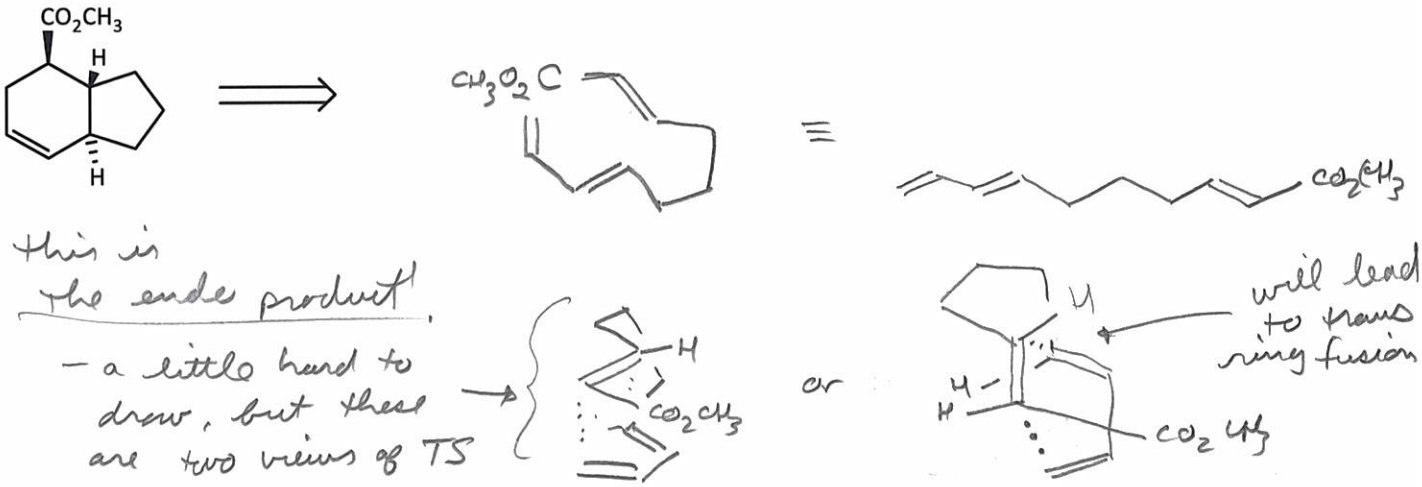
has 4 π electrons

14. Draw the pi molecular orbitals of 1,3-butadiene and their relative energy levels. Show how these orbitals are filled with electrons in the ground state. Indicate which orbital is the *Highest Occupied MO* (HOMO) and which is the *Lowest Unoccupied MO* (LUMO). Finally, describe what happens when 1,3-butadienene absorbs in the UV region at 258 nm. (40 points)



217 nm for butadiene

15. The compound below can be prepared using an *intramolecular* Diels-Alder reaction. What does the starting material look like? (5 points)

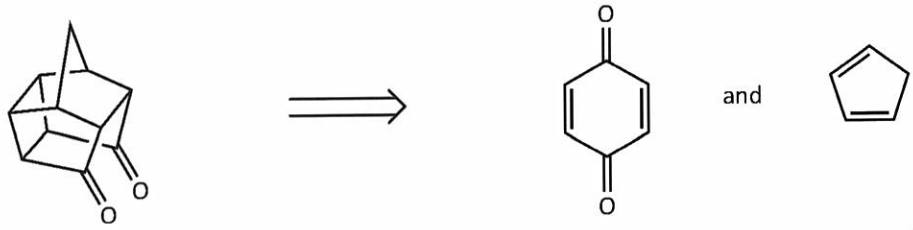


this is the endo product! – a little hard to draw, but these are two views of TS

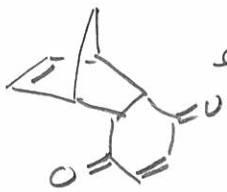
or

will lead to trans ring fusion

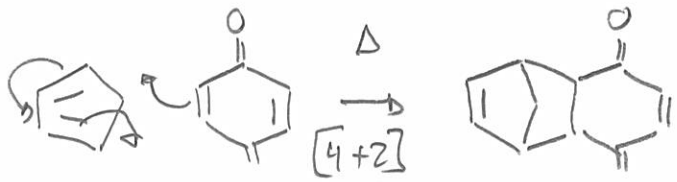
16. *Challenge problem.* The synthesis of the pentacyclic compound shown below is remarkably simple. Show how the following two compounds can be used to accomplish this.



Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]
-undecane-8,11-dione



endo product



Diels-Alder reaction

hν [2+2]