Your name: ______________________

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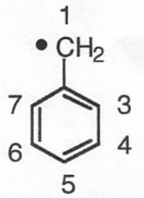
Chem 131(231)A; exam 2

1. The NBMO that is "home" to the odd electron of the benzyl radical is shown below as its LCAO-MO expansion, Ψ.
[a] Use it to determine the hyperfine coupling constant a_H at C_3. Assume that Q = 21 Gauss. Show your work.
[b] How does this value compare with a_H at C_7?
[c] Indicate how one could prepare the radical in one step from $PhCH_2X$ (you determine "X").



$$\Psi = (7)^{-1/2}(2\chi_1 + \chi_3 + \chi_5 + \chi_7)$$

(a) $a_H^3 = 21\left(\frac{1}{\sqrt{7}}\right)^2 = 3$ Gauss

(b) Same @ C_7

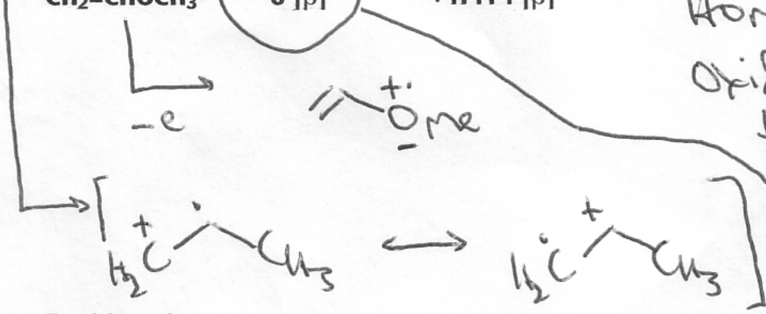
(c) $PhCH_2Br \xrightarrow[AIBN,\ h\nu]{n\text{-}Bu_3SnH} \phi\dot{C}H_2$ ("X" = Br)

2. Use the information provided to respond to the following query.
[a] Which is easier to oxidize, propene or methyl vinyl ether? Indicate how you used the information to arrive at your conclusion.
[b] In each case, illustrate the product of a one electron oxidation.

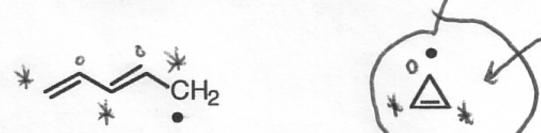
Compound	E(HOMO)	E(LUMO)
$CH_2{=}CHCH_3$	−1 |β|	+1 |β|
$CH_2{=}CHOCH_3$	0 |β|	+1.414 |β|

(a) The system w/ the higher energy HOMO will be easiest to oxidize. In this case, that's obviously //OMe (cf.)

(b)



Problem 3
(a) Which of the following molecules is not an alternate hydrocarbon?
(b) Determine which **one** has a NBMO. How does the pairing theorem allow you to make your assessment? Please be **brief.**



∃ 2 atoms of same parity adjacent to one another ⇒ not an AH.

– has a NBMO

Reasoning: (a) is an AH
(b) is an odd AH
(c) has 5 AO centers
∴ 5 MO's

→ 2 BMO's paired w/ 2 ABMO's
... leaves an "left over" ... the NBMO.

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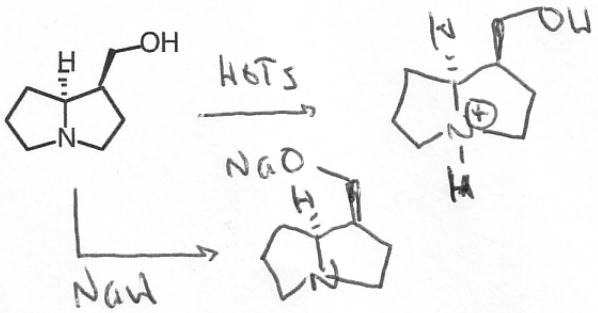
problem 4

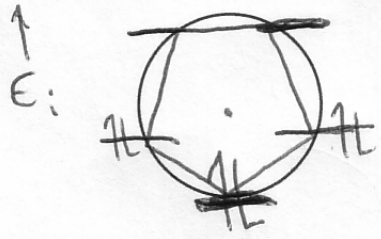
What would you expect to be the site of selective (a) protonation, and (b) deprotonation when the compound shown is treated with TsOH? with NaH? Illustrate the product in each instance.



problem 5

[a] Use the circle mnemonic to determine the relative energies of the pi MO's of the cyclopentadienyl anion.

[b] If the pKa of CpH is 15 and that of MeOH is 15, determine the equilibrium constant for the reaction of CpH with NaOMe. Show your work (be brief).



$CpH + NaOMe \rightleftharpoons^{Keq} CpNa + HOMe$

$Keq = 10^{-15}/10^{-15} = 1$

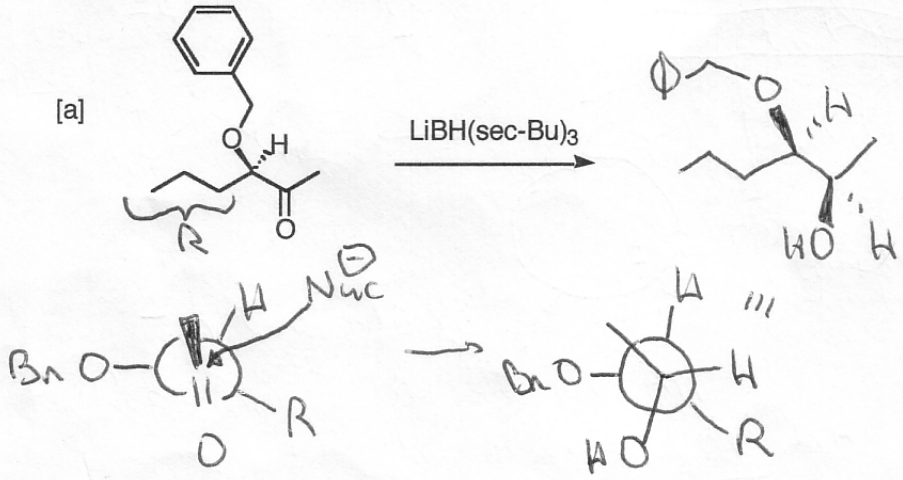
Problem 6.

Part I: In each instance, determine the product. Assume that an appropriate workup has been conducted. Of course, the stereochemical outcome of these reactions is of the utmost importance.

Part II: Provide a detailed analysis in each case. When appropriate, state which of the descriptors is appropriate. Choose from amongst these: Felkin-Anh, chelation control, Zimmerman-Traxler model, Houk model, Henbest epoxidation.

NOTE: You may use molecular models if you wish.

[a]



Felkin-Anh

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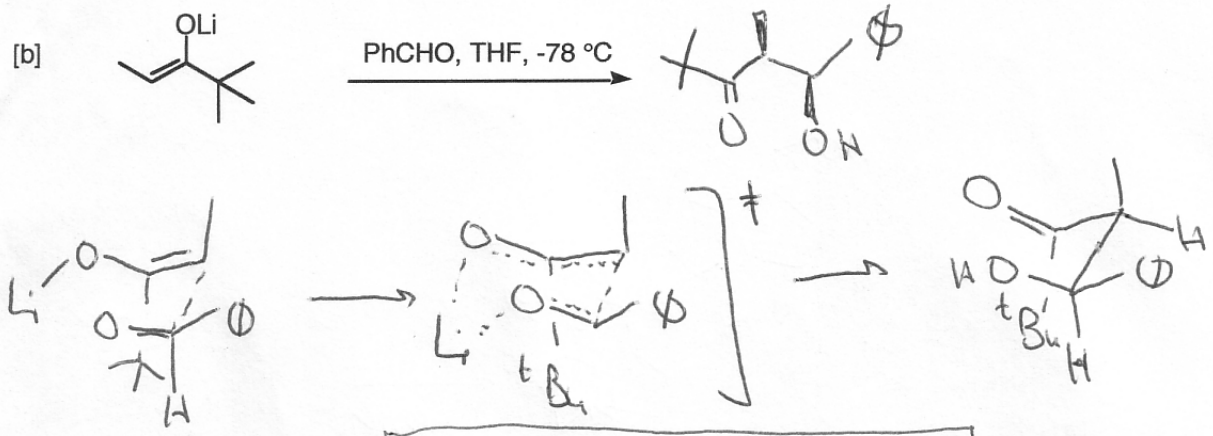
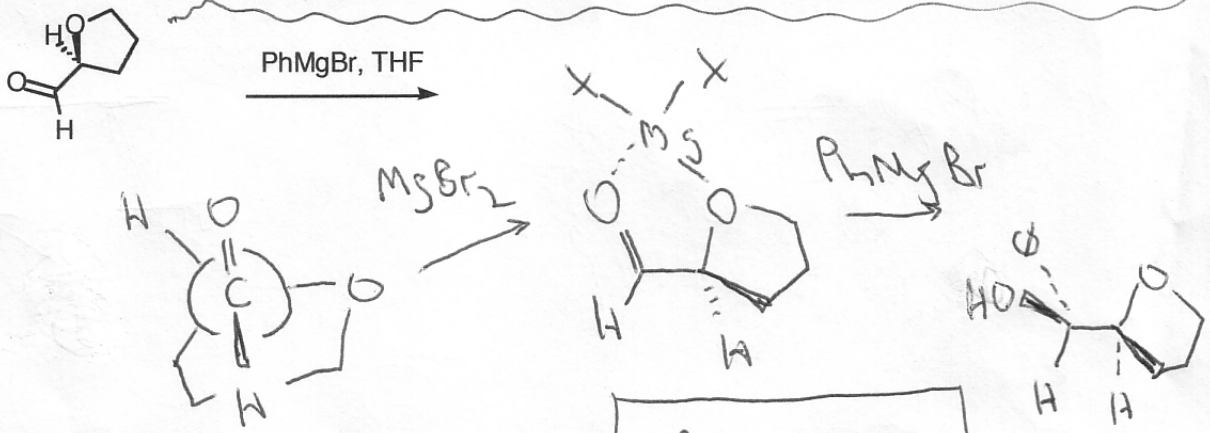
[b]



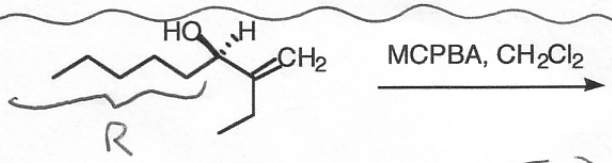
Zimmerman-Traxler model

[c]

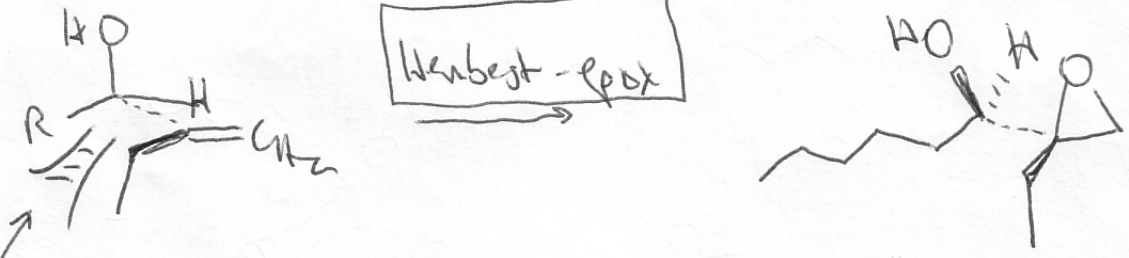


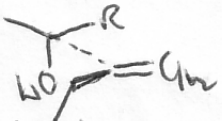
Chelation Control

[d]



Henbest-epox



Note $A^{1,2}$ interactions. To the extent they are significant,  might be preferred. If so, then the stereo. opposite to that shown would be obtained. A better problem would have been one that also set up an $A^{1,3}$-intxn (as in prob set)

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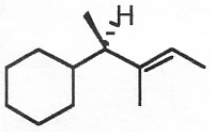
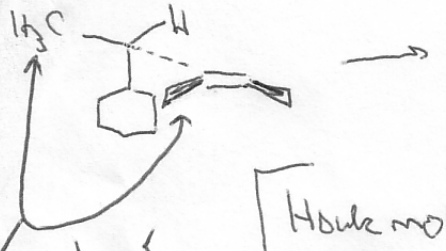
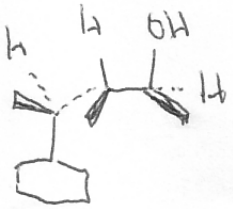
[e]  (a) BH_3-THF, (b) NaOH, H_2O_2



A'1,2 interactions. (see 6d comments)

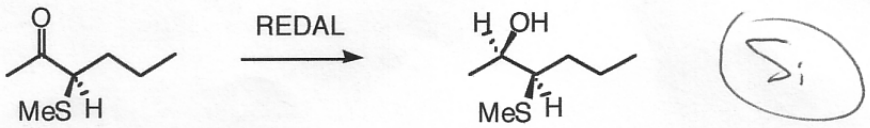
Houkmodel



- minimize A'1,3 strain
- place large Sp on side opposite to incoming reagent.

Problem 7

Has the reaction illustrated occurred via a 're' or a 'si face attack?



Si

problem 8

Diastereomers **A** and **B** are produced with a de of 65%. How much of each diastereomer is present? Show your work.

$A+B=100$

$A-B=65 \Rightarrow A=65+B$

$65+2B=100$

$2B=35$

$B=17.5$

$A=82.5$

Problem 9

Given that log A = 15 and k = 10^6 s^{-1}, determine E_a. Merely set up the equation, don't solve it.

$$k = Ae^{-E_a/RT}$$

$$-RT\ln\frac{k}{A} = E_a$$

$$= -RT(\ln k - \ln A)$$

$$= -2.303RT(\log k - \log A)$$

$$= -2.303RT(6-15) = -2.303(-9)RT \cong 21RT$$

Chem 131(231)A
Exam 1

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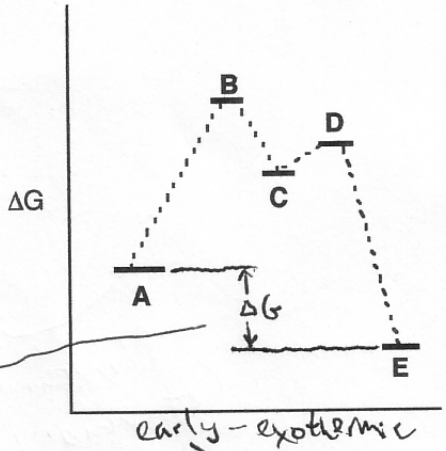
Chem 131(231) A; exam 1

Direct your attention to the potential energy diagram. Suppose that it refers to a reaction where **A** and **E** are neutral substances (i.e., they are not charged), while **C** is charged. The overall transformation converts **A** to **E**.



early - exothermic

[a] Label the rate determining step. It's A → C

[b] Suppose one switches from a nonpolar to a polar solvent. How would the rate of the reaction be effected? Explain. It would increase. Both B & C would be stabilized. This would decrease $\Delta G^{\ddagger}$ & lead to a rate increase.

[c] Which step is faster – the conversion of **A** to **C**, or **C** to **E**? Explain. $\Delta G^{\ddagger}_{C\text{-}E} < \Delta G^{\ddagger}_{A\text{-}C}$

[d] Does the first transition state come late or early? How about the second? In each instance, what is the basis for your answer? What is the name of the postulate that deals with these topics?

Hammond

because the transform. is endothermic

[e] Illustrate on the diagram, the quantity that determines how much of **A** and **E** will be present, assuming equilibrium has been reached.

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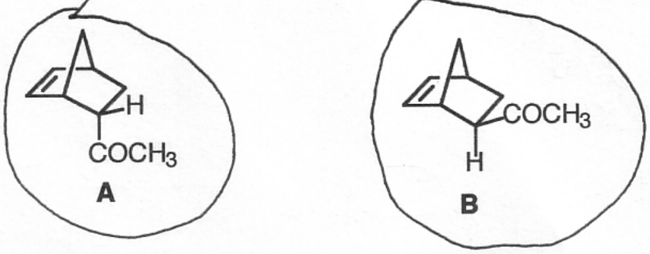
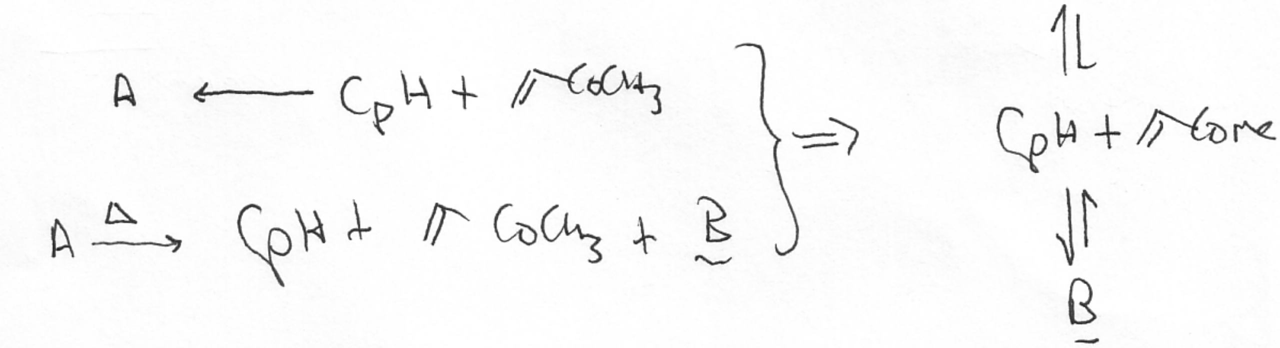
2.

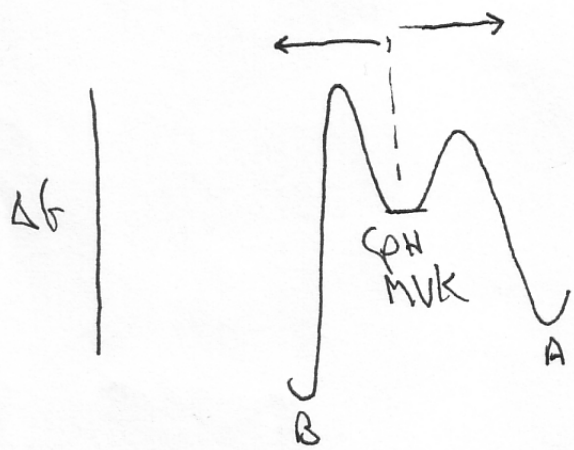
When cyclopentadiene is allowed to react with methyl vinyl ketone, the bicyclic ketone **A** is produced. When **A** is heated, it reverts to cyclopentadiene, methyl vinyl ketone, and a mixture of the bicyclic ketones **A** and **B**, with **B** dominant when ⇌'s been reached.

[a] Draw a potential energy surface that illustrates these observations.

[b] Which product is kinetically preferred? ... thermodynamically preferred? In each instance, explain.







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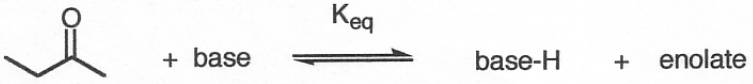
3. Focus your attention upon the following reaction.

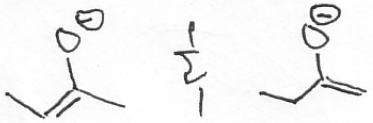


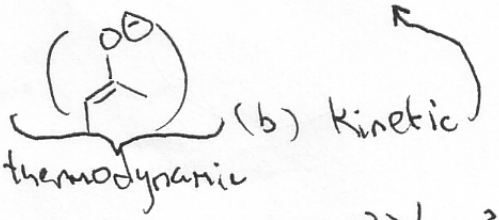
[a] Draw the structure of the two enolates that can be formed.

[b] Specify which enolate is expected to dominate under thermodynamic control. Do the same for kinetic control.

[c] Determine K_{eq} when LDA is used as the base. Do the same for sodium methoxide.

(a)





(c) $K_{eq}(LDA) = 10^{-20}/10^{-35} = 10^{15}$

w/ NaOMe, $K_{eq} = 10^{-20}/10^{-16} = 10^{-4}$

4. [a] Specify the general equation that relates K_{eq} to the thermodynamic free energy change.

[b] Suppose that a ketone is in equilibrium with its enolate and that the ratio of the two substances is 80/20 at 25 °C. Set up the equation that would allow you to determine the free energy difference between the two substances.

(a) $\Delta G = -RT \ln K_{eq}$

(b) $\Delta G = -1.987(298) \ln \frac{1}{4}$

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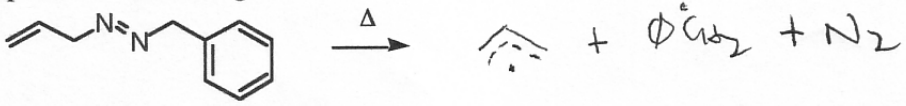
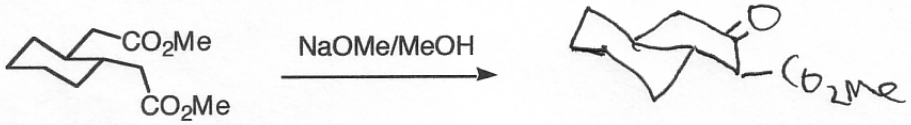
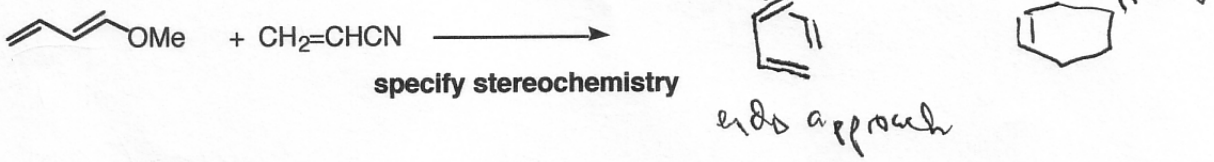
5. Complete the following.

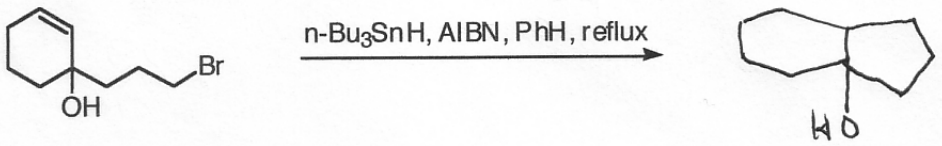
[a] 

[b] 

[c] 

specify stereochemistry

endo approach

[d] 

6. Formulate a mechanism for the acid catalyzed conversion of acetone dimethyl ketal to acetone.