Dr. Carl Wagner July 18th, 2006

Chemistry 3B

Midterm 1

Student Name: KEY

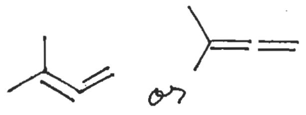
Student ID: ____________________

Write TA's full name (section number) or Lecture Only: ____________________

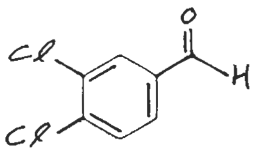
Problem 1		(28 pts)
Problem 2		(32 pts)
Problem 3		(24 pts)
Problem 4		(35 pts)
Problem 5		(20 pts)
Problem 6		(25 pts)
Problem 7		(30 pts)
Problem 8		(28 pts)
Problem 9		(18 pts)
Problem 10		(10 pts)
Total Points		(250 pts)

Calculators Not Needed
Be Sure Your Exam Has 13 Pages
Budget Your Time Carefully!
Be Sure to Try All Parts of Each Problem

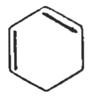
1. (a) (6 pts) Associating an image with a word is a vital skill in chemistry. Provide a structure for all compounds named within the boxes.



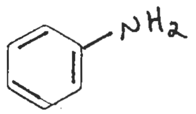
3-Methyl-1,2-butadiene



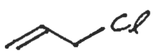
3,4-Dichlorobenzaldehyde



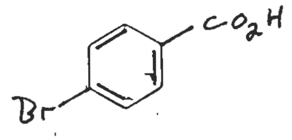
1,3-Cyclohexadiene



Aniline

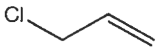


Allyl chloride



***p*-Bromobenzoic acid**

1. (b) (12 pts) Rank the chlorides that would undergo solvolysis most rapidly to least rapidly upon heating in H_2O [1 = **most rapidly**, 6 = **least rapidly**].



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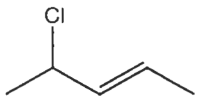

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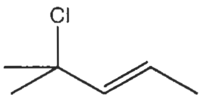

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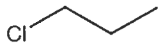
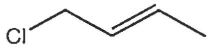


6



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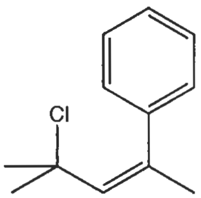
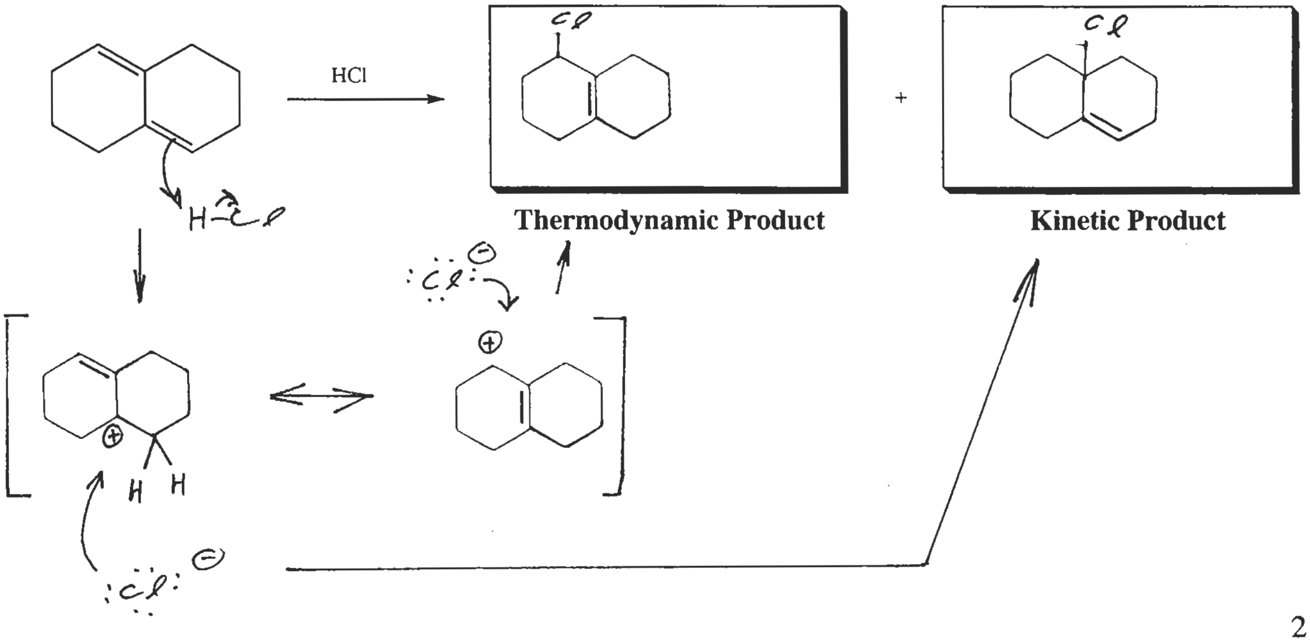
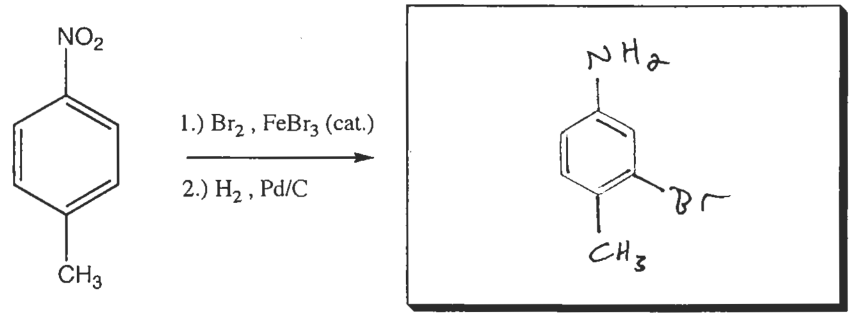


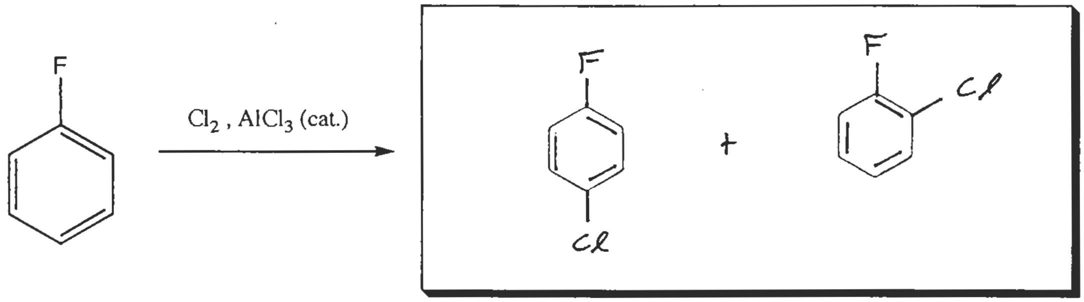
1

1. (c) (10 pts) Write a stepwise mechanism for the addition of HCl to the compound shown below. Include detailed structures of any intermediates and all applicable resonance forms. Write both the Kinetic and Thermodynamic products in the appropriate boxes.

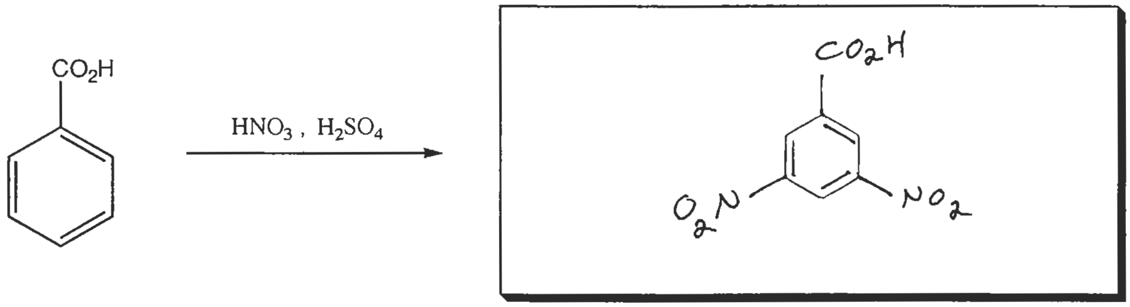


2. (32 pts) Write the structure of the expected product in the box provided. Be sure to indicate relative stereo- and regio-chemical specificity, if any.

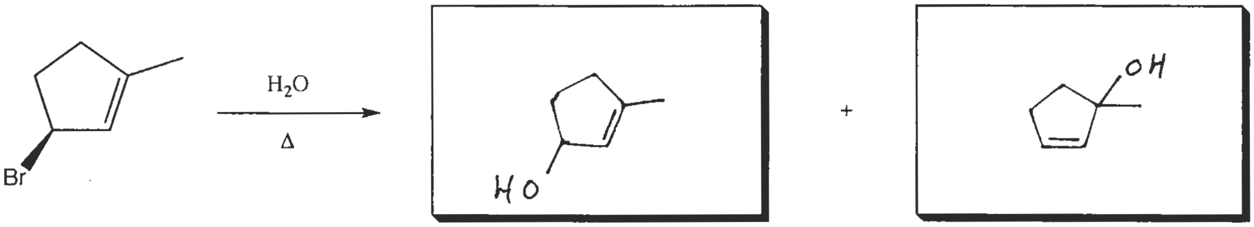




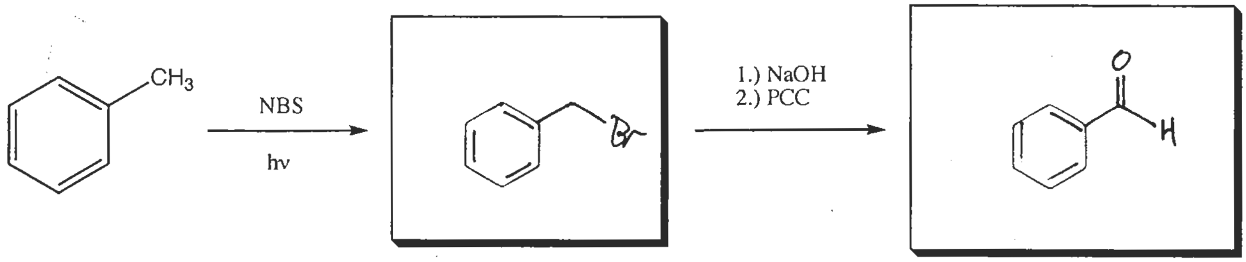
Favored Product(s)



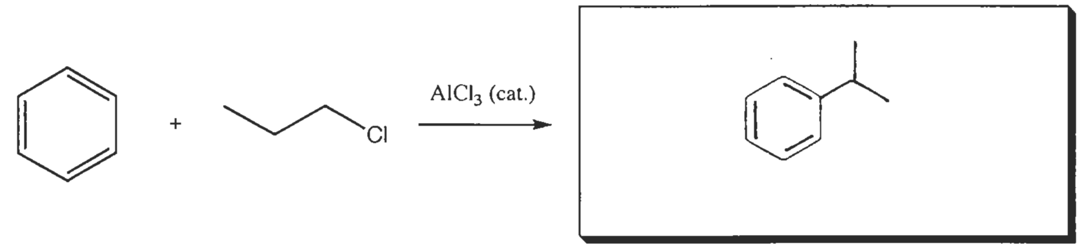
Product of Double Nitration



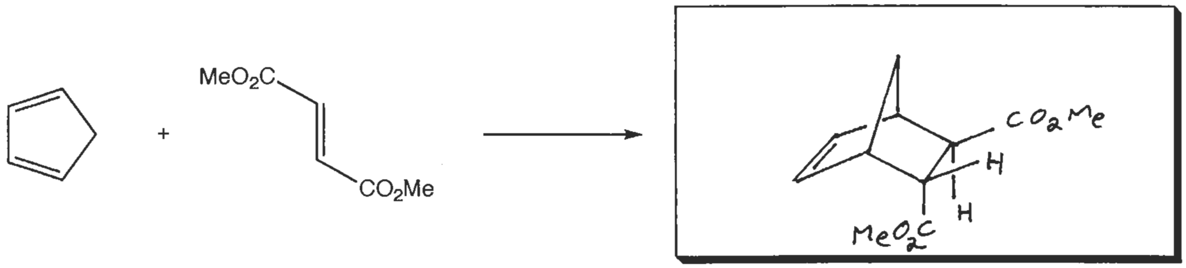
Thermodynamic Product **Kinetic Product**



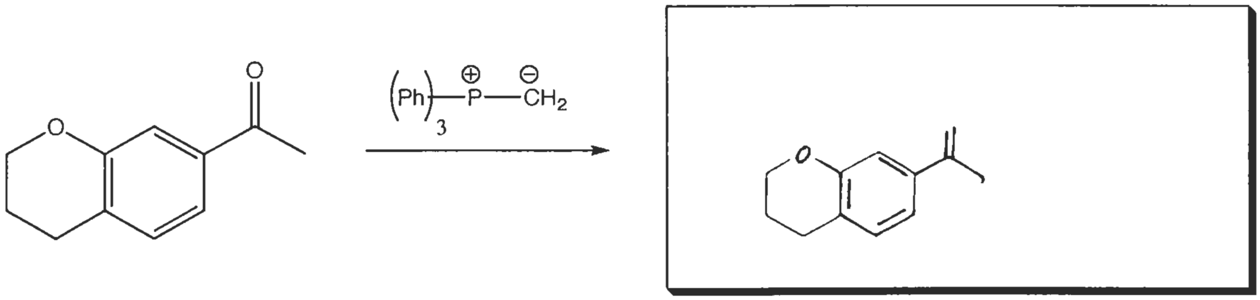
2. Continued. . .

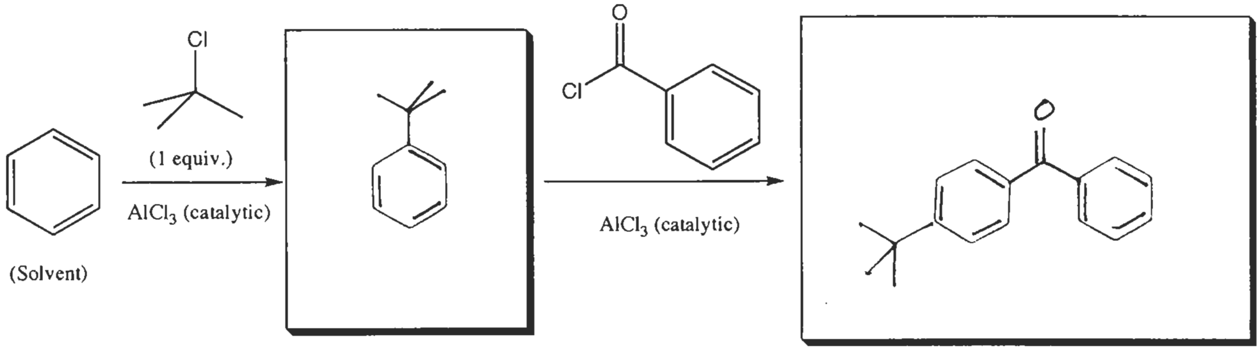


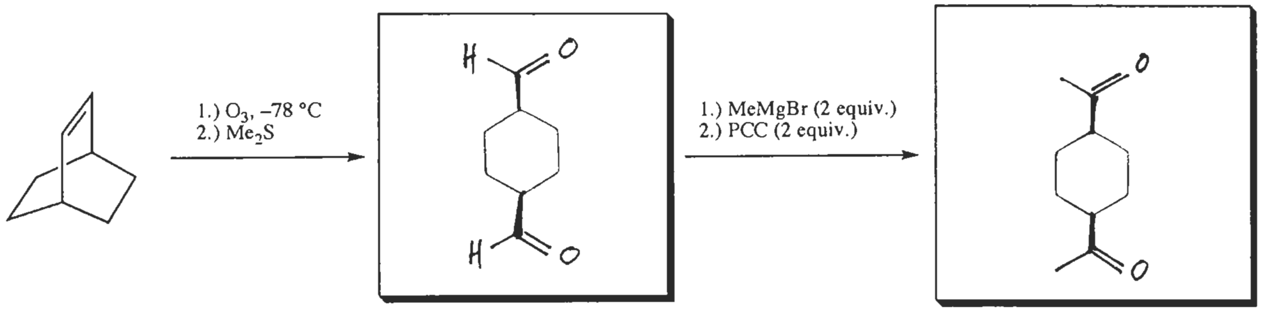
Major Mono-alkylation Product



[✓ Racemic] or a Single Isomer?

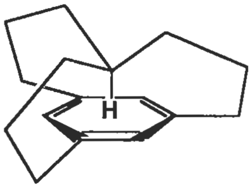




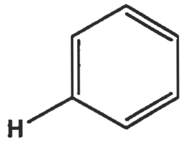


3. Answer the following questions, but be careful: every wrong answer cancels out a correct one.

(a). (6 pts) Rank the **bold** hydrogens that, in a ^{1}H-NMR spectrum, would be most **shielded** (*smallest* ppm) to most **deshielded** (*highest* ppm) using Roman numerals [i.e. 1 = most shielded, 4 = most deshielded].



1



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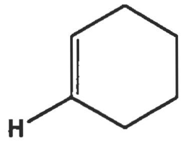

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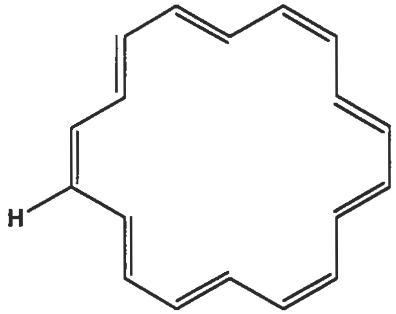
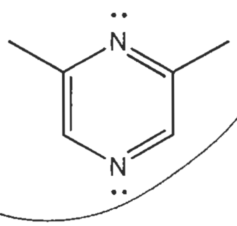
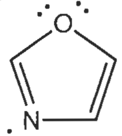
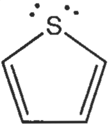


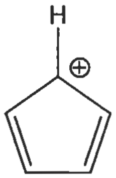
4

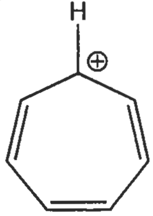
(b) (6 pts) Circle the compounds below that are aromatic.



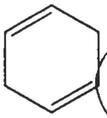


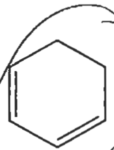


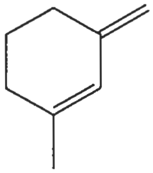


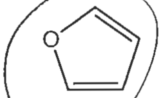


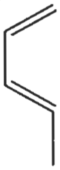
(c) (6 pts) Circle the compounds that will react with an alkene (dienophile) in a Diels-Alder [4+2] cycloaddition reaction.

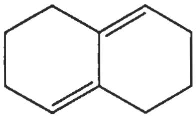




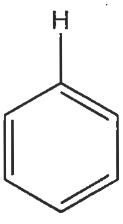








(d) (6 pts) Rank compounds below using Roman numerals to indicate the order of decreasing rate of reactivity toward Cl_2 and $AlCl_3$ [1 = highest rate, 5 = lowest rate].



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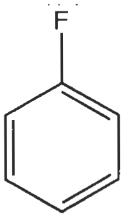

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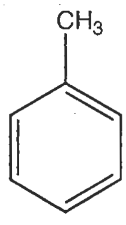

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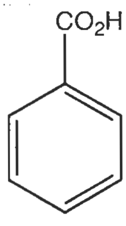

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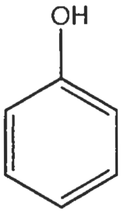
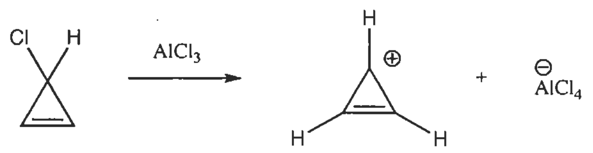
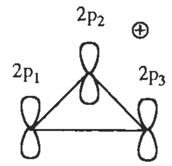


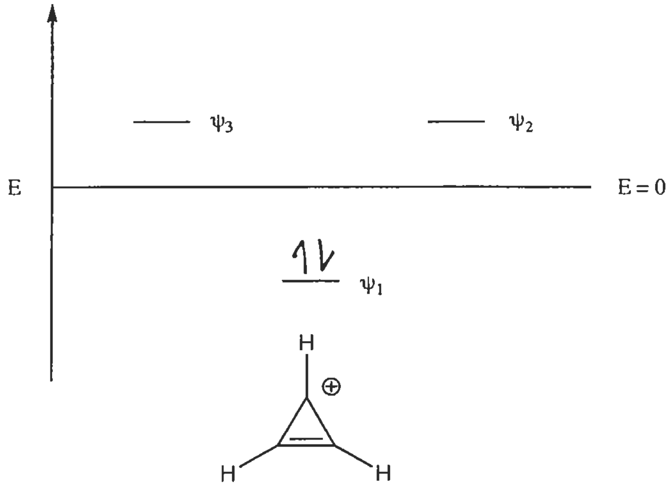
1

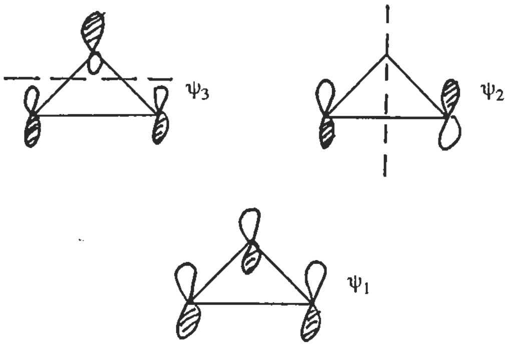
4. (a) (15 pts) The cyclopropenium cation can be readily formed from the reaction of 3-chlorocyclopropene with aluminum chloride. Since the cyclopropenium cation is planar, cyclic, and fully conjugated (with three adjacent 2p-orbitals) it can be classified as aromatic or anti-aromatic.





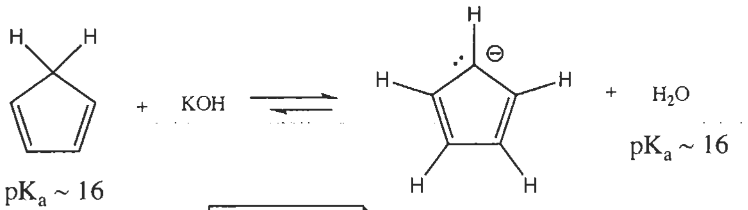
Using the Frost Diagram procedure, the following molecular orbital diagram was constructed for the cyclopropenium cation. Sketch the MO's (ψ_1, ψ_2, and ψ_3) on the rings provided, clearly showing the presence or absence of orbital lobes, their shading and all appropriate nodes.

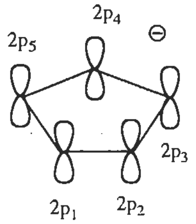




Fill the MO Diagram for the cyclopropenium cation with the appropriate number of electrons. Is the cycloproenium cation aromatic or anti-aromatic? $(4n + 2)e^-$ $n = 0$ aromatic

(b) (15) Similarly, cyclopentadiene has an unusually acidic saturated carbon that can be deprotonated with potassium hydroxide to form the cyclopentadienyl anion.



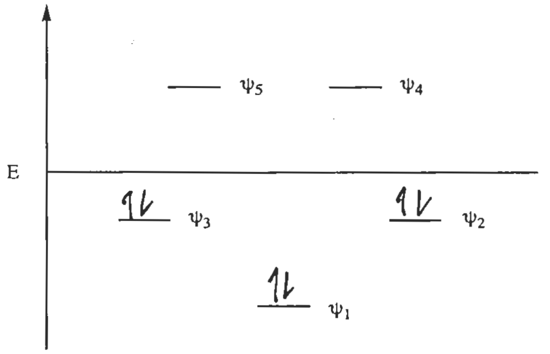


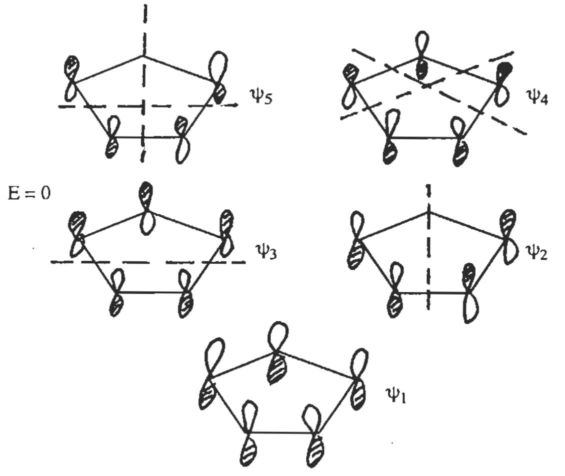
$\boxed{K_{eq} \sim 1}$

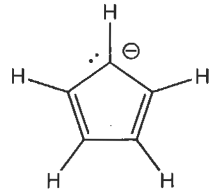
Calculate the K_{eq} for the reaction above.

$K_{eq} \sim 10^{16-16} = 10^0 = 1$

4. (b) Continued . . . Since the cyclopentadienyl anion is planar, cyclic and has 5 adjacent 2p-orbitals, it can also be classified as aromatic or anti-aromatic. Using the procedure for generating a Frost MO Diagram from the cyclopentadienyl anion, the following MO diagram was constructed.





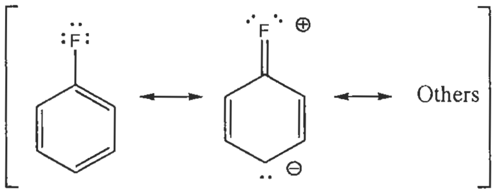


Sketch the MO's (ψ_1 , ψ_2 , ψ_3 , ψ_4 , and ψ_5) on the rings provided, clearly showing the presence or absence of orbital lobes, their shading and all appropriate nodes.

Fill the MO diagram for the cyclopentadienyl anion above with the appropriate number of electorons. Is the cyclopentadienyl anion aromatic or anti-aromatic? $(4n+2)e^-$ aromatic

$n = 1$

4. (c) (5 pts) Polar compounds exhibit "Dipole Moments" (μ) that are measured in Debyes (D). The greater the degree of polarity (and formal charge separation), the greater the μ. For example, fluorobenzene has μ 1.70 D and lithium fluoride has $\mu = 6.326$ D.

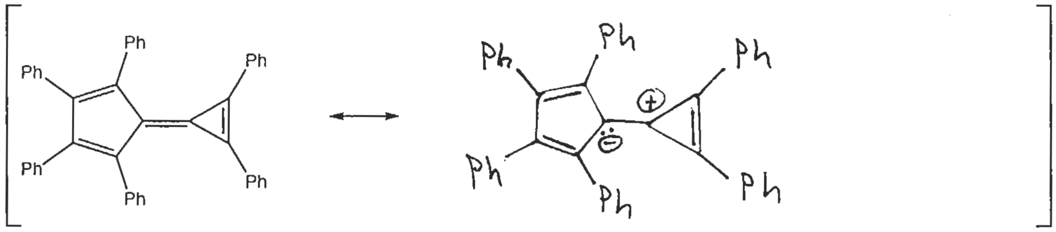


$\mu = 1.60$ D

$\mathrm{Li{-}F} \longleftrightarrow \mathrm{Li}^{\oplus}\ \mathrm{F}^{\ominus}$

$\mu = 6.326$ D

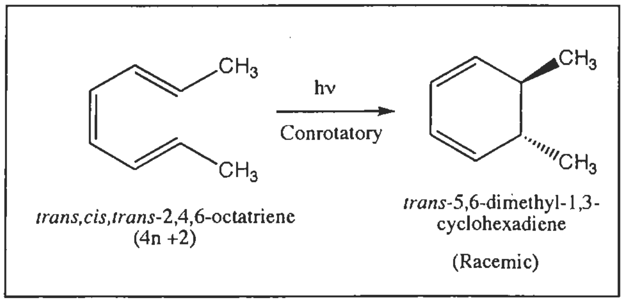
The organic molecule below has a large $\mu = 6.3$ D, characteristic of formal charge separation. Draw the major resonance isomer showing formal charge separation that accounts for this.

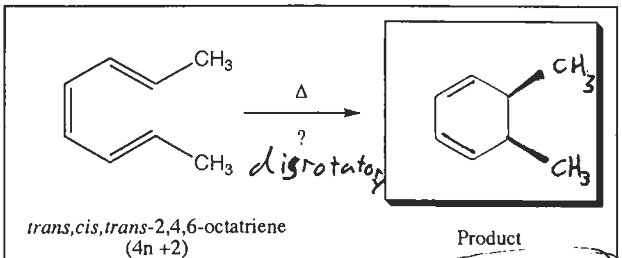


$\mu = 6.3$ D

or any resonance structure with a formal ⊖ in the 5-membered ring and a formal ⊕ in the 3-membered ring

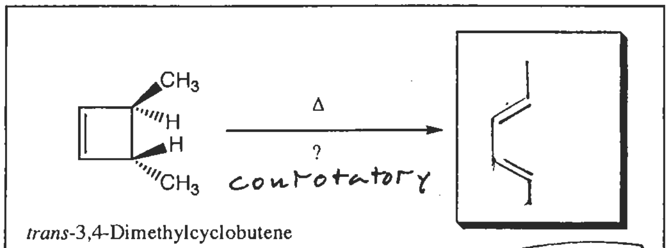
5. (a) (4 pts) Recall that the photochemical ring closure of *trans, cis, trans*-2,4,6-octatriene transpires through a conrotatory process. Draw the product of the thermal ring closure of *trans,cis,trans*-2,4,6-octatriene and describe the process as conrotatory or disrotatory.





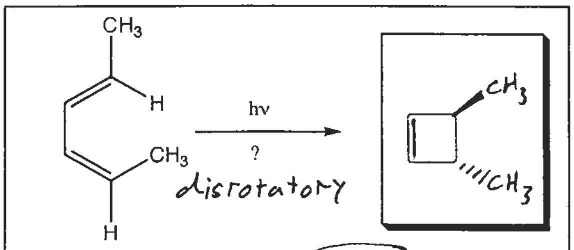
Racemic or [✓ Single Isomer?]

(b) (8 pts) Give the products of the thermal ring opening of *trans*-3,4-dimethylcyclobutene and the photochemical ring closing of *cis,trans*-2,4-hexadiene, and describe the processes as conrotatory or disrotatory. Hint: How many electrons are involved in these systems?



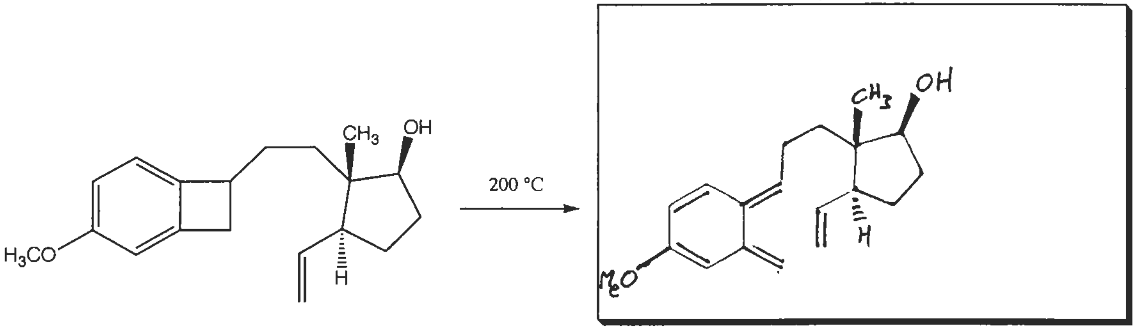
Racemic or [✓ Single Isomer?]

not really applicable...

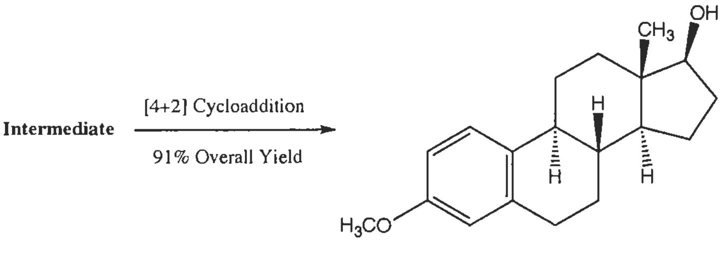


[✓ Racemic] or Single Isomer?

(c) (8 pts) When compound **1** is heated to 200 °C, a thermal electrocyclic reaction occurs to produce an **Intermediate** that proceeds to undergo a [4+2] intramolecular cycloaddition to give compound **2**. Draw a structure for the **Intermediate** in the box provided.

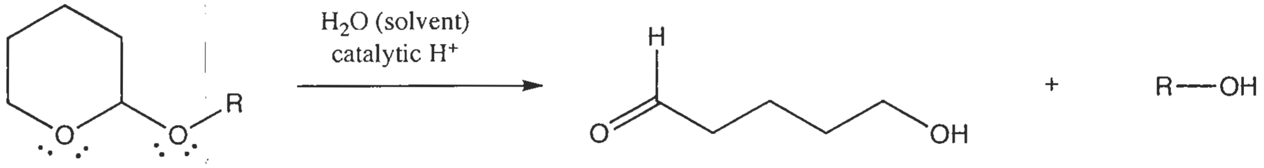


1 **Intermediate**

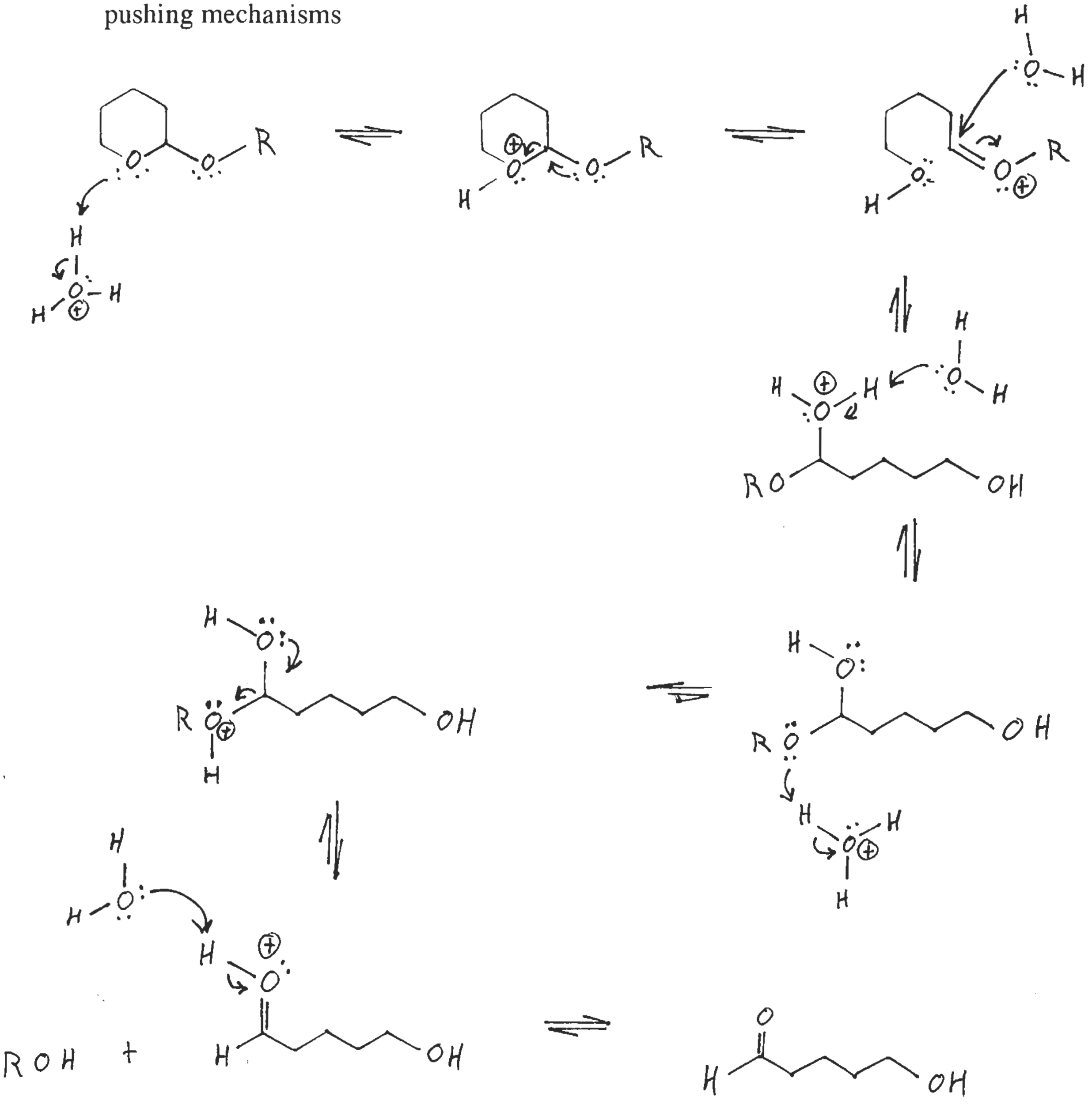


2

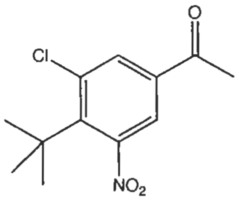
6. (25 pts) Provide a mechanism for the hydrolysis of the tetrahydropyranyl group.



Note: the tetrahydropyranyl group is commonly used to protect alcohols, and it is cleaved by acidic conditions. Hint: It's always good to make use of oxygen's lone pairs in step-wise, arrow-pushing mechanisms



7. (30 pts) Provide the most efficient synthesis for the aromatic compound shown below. You may employ reagents and conditions of your choice. Points will be assigned according to steps listed in the forward synthesis direction.



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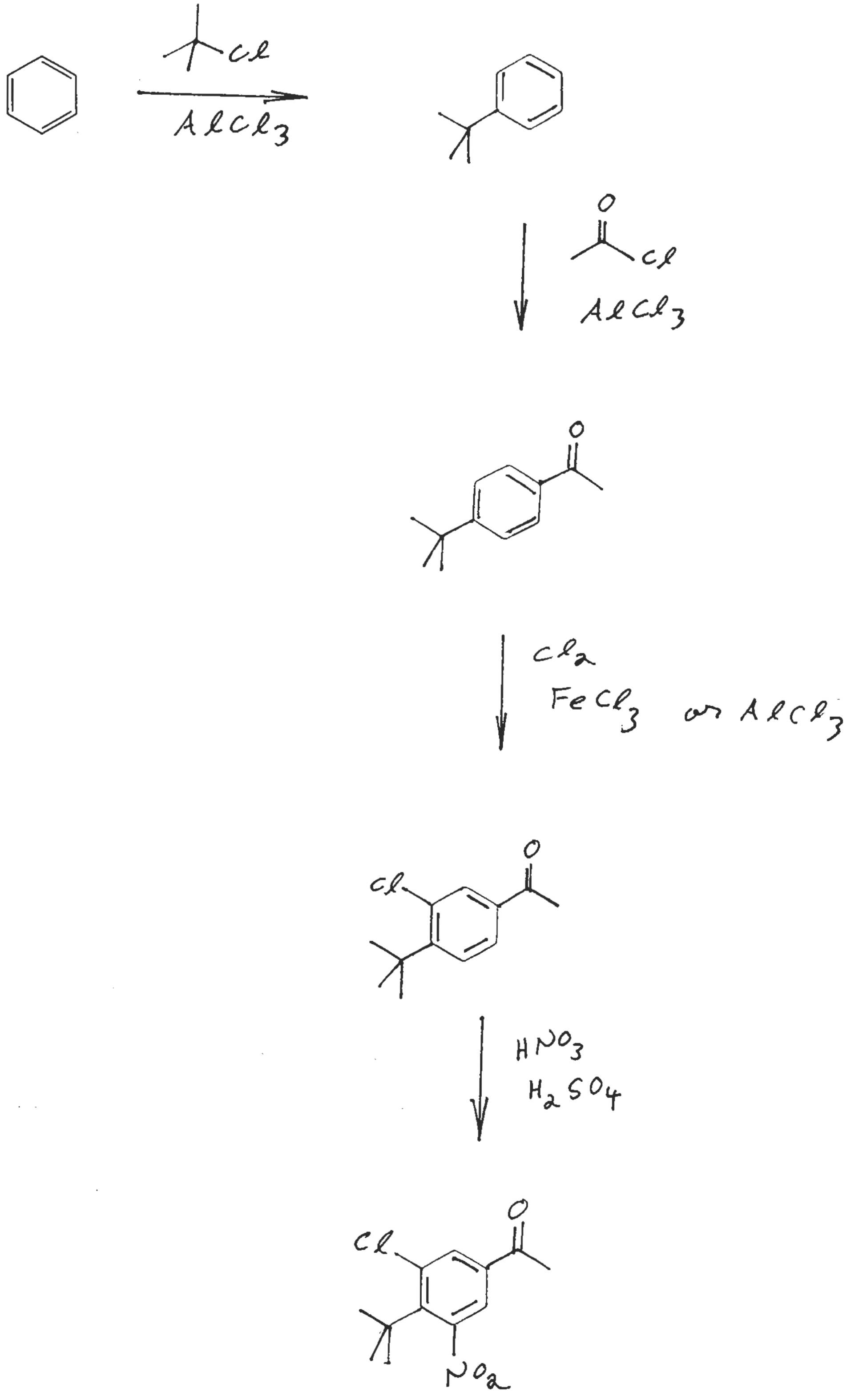
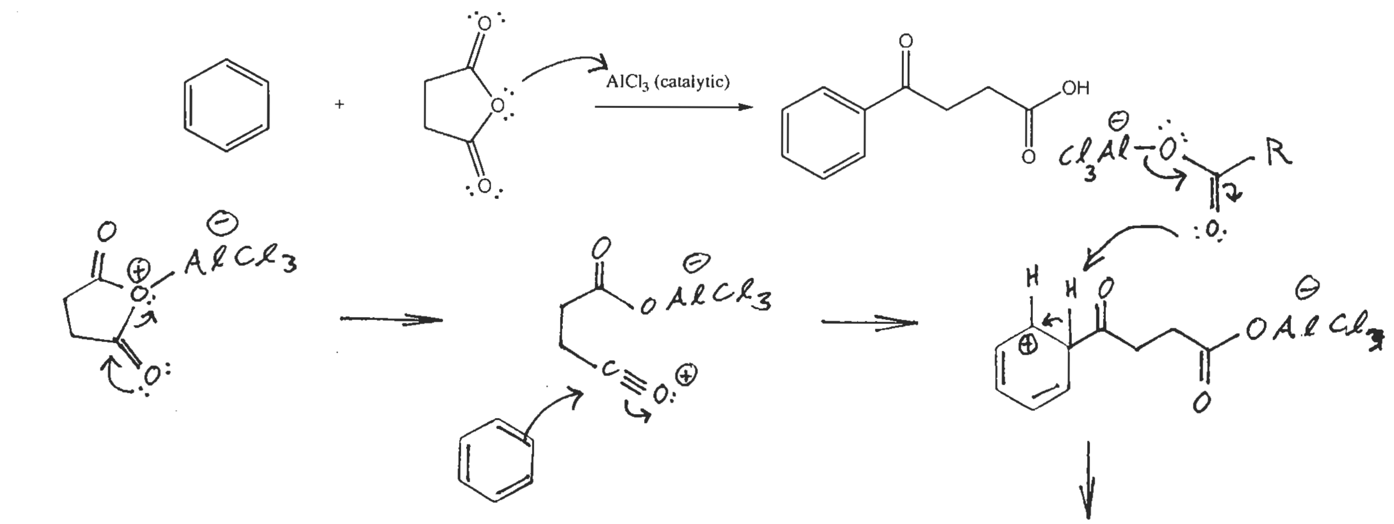
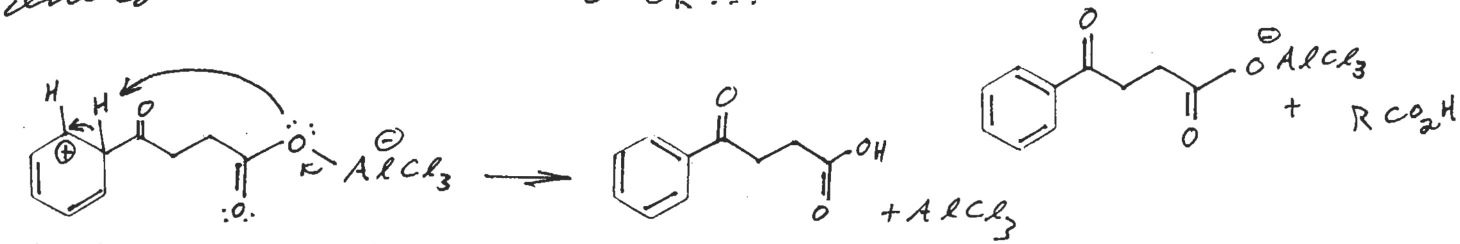


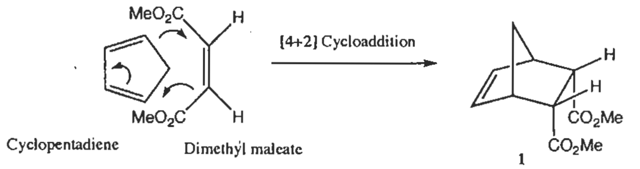
8. (a) (15 pts) Write a detailed, arrow-pushing mechanism for the following reaction.



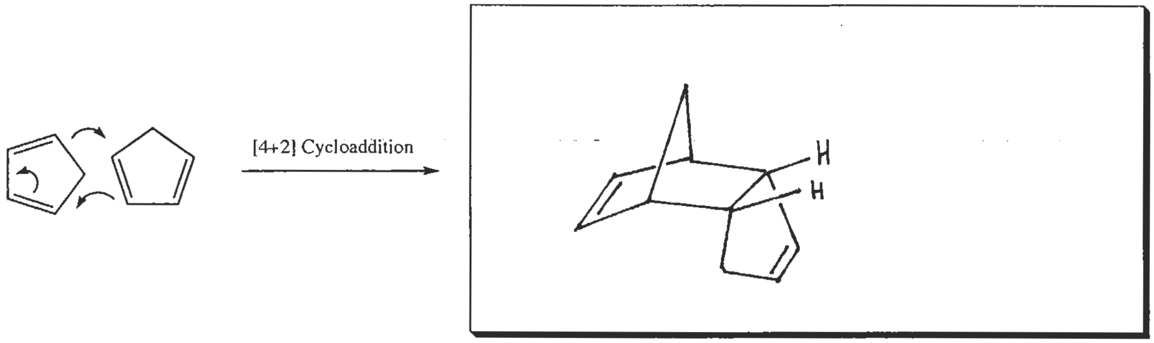
intramolecular also OK...



(b) (13 pts) Recall that cyclopentadiene reacts with dienophiles according to the "Endo-rule," as shown below in its reaction with dimethyl maleate to give cycloadduct (**1**).



Cyclopentadiene reacts with itself, slowly, through a [4+2] cycloaddition reaction to give dicyclopentadiene. Draw the structure of dicyclopentadiene in the box provided. Be sure to indicate stereospecificity, if any, associated with the reaction.

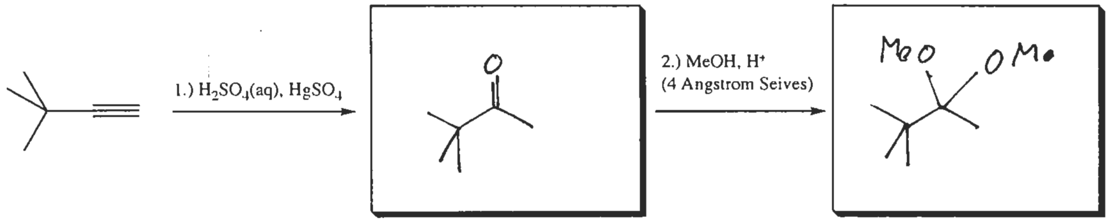


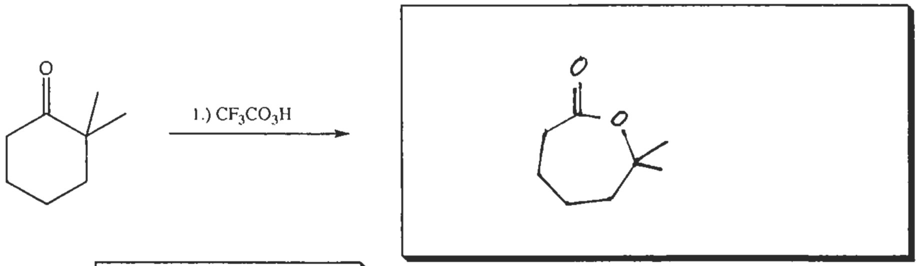
"Dicyclopentadiene"

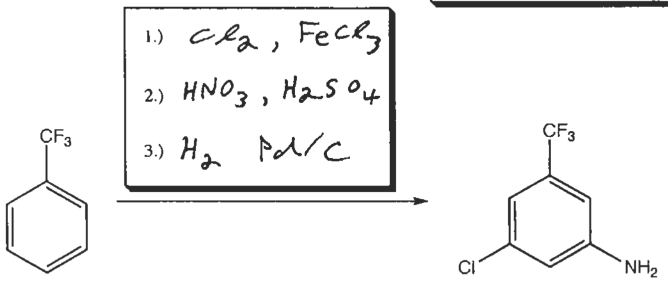
Is the product racemic or a single isomer?

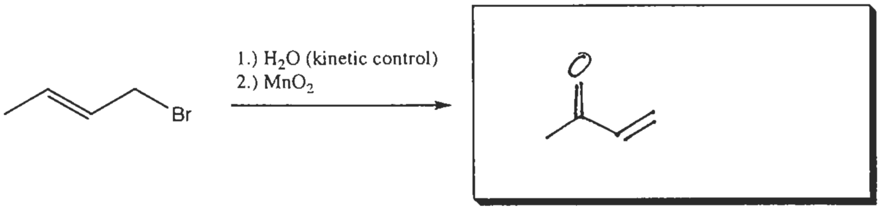
Racemic

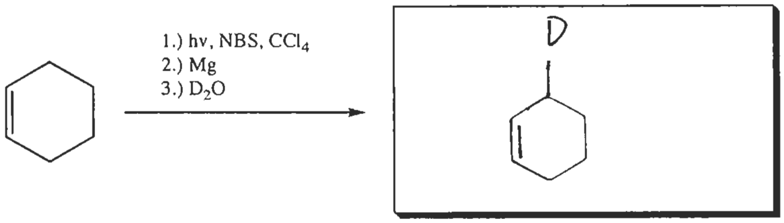
9. (18 pts) Fill in the products or the reagents in the boxes as indicated.

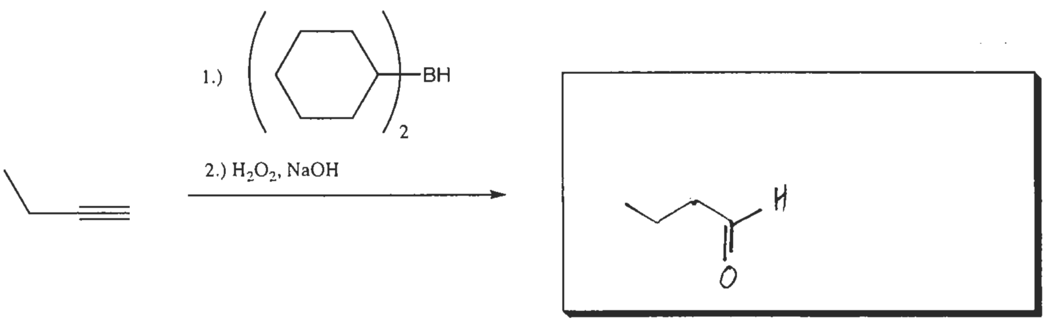




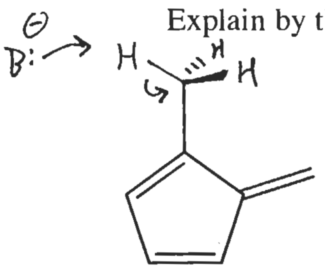








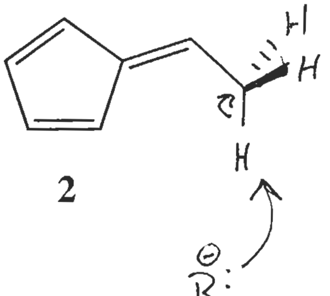
10. (10 pts) Predict which of the following hydrocarbons would be more acidic (i.e. lower pK_a). Explain by the proper use of resonance structures.



1

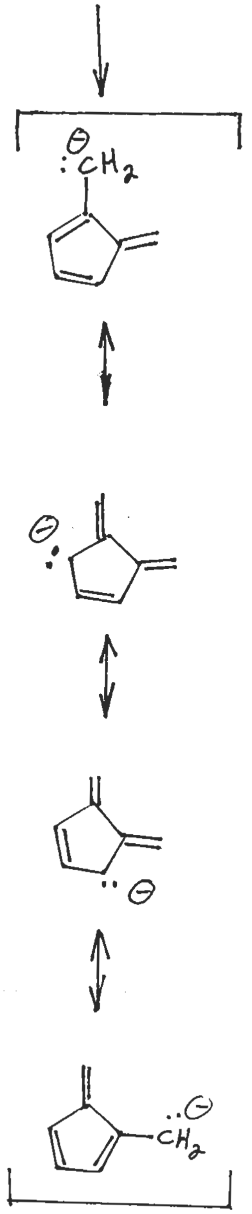
pK_a (**1**) $\boxed{>}$ pK_a (**2**)

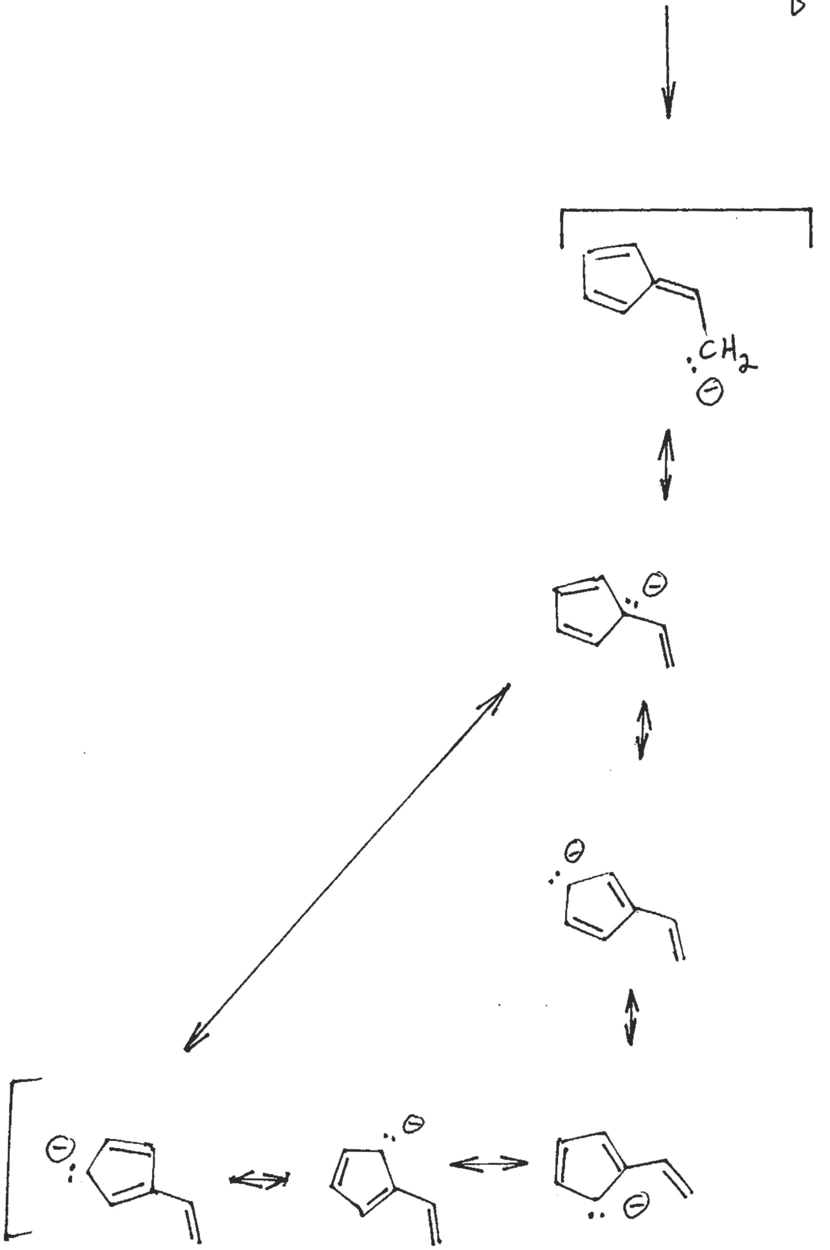
(< or >)



2

+ HB





Only 4 Resonance structures

6 unique resonance forms