D	o	R	K

Final Exam
Chem 22
May 11, 2010

Name Gary Snyder

page **1** (30) _____
2 (40) _____
3 (40) _____
4 (35) _____
5 (35) _____
6 (30) _____
7 (25) _____
8 (35) _____
9 (40) _____

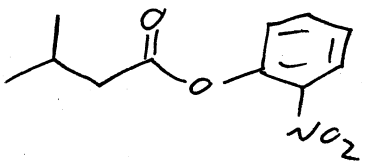
_____ total (300)

___ chk

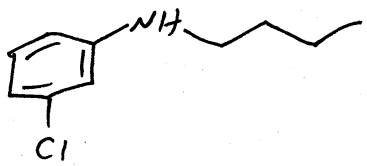
Go ahead and write in this space... NOT.

1. (30 points) Draw these. Show stereochem where relevant; don't abbreviate groups.
(a) *o*-nitrophenyl 3-methylbutanoate

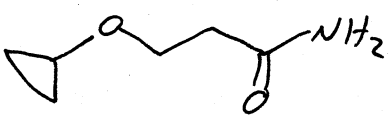
6 pts each



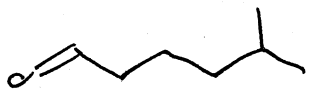
(b) N-butyl-*m*-chloroaniline



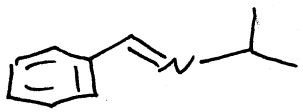
(c) 3-cyclopropoxypropanamide



(d) 5-methyl-5-hexenal



(e) The imine formed by acid-catalyzed reaction of benzaldehyde and isopropyl amine (aka 2-propanamine)



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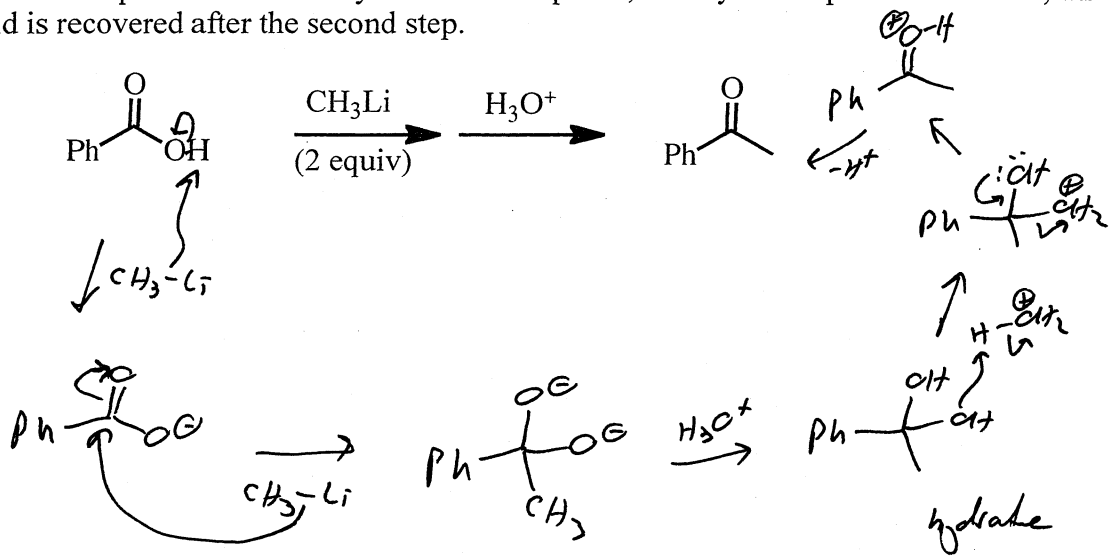
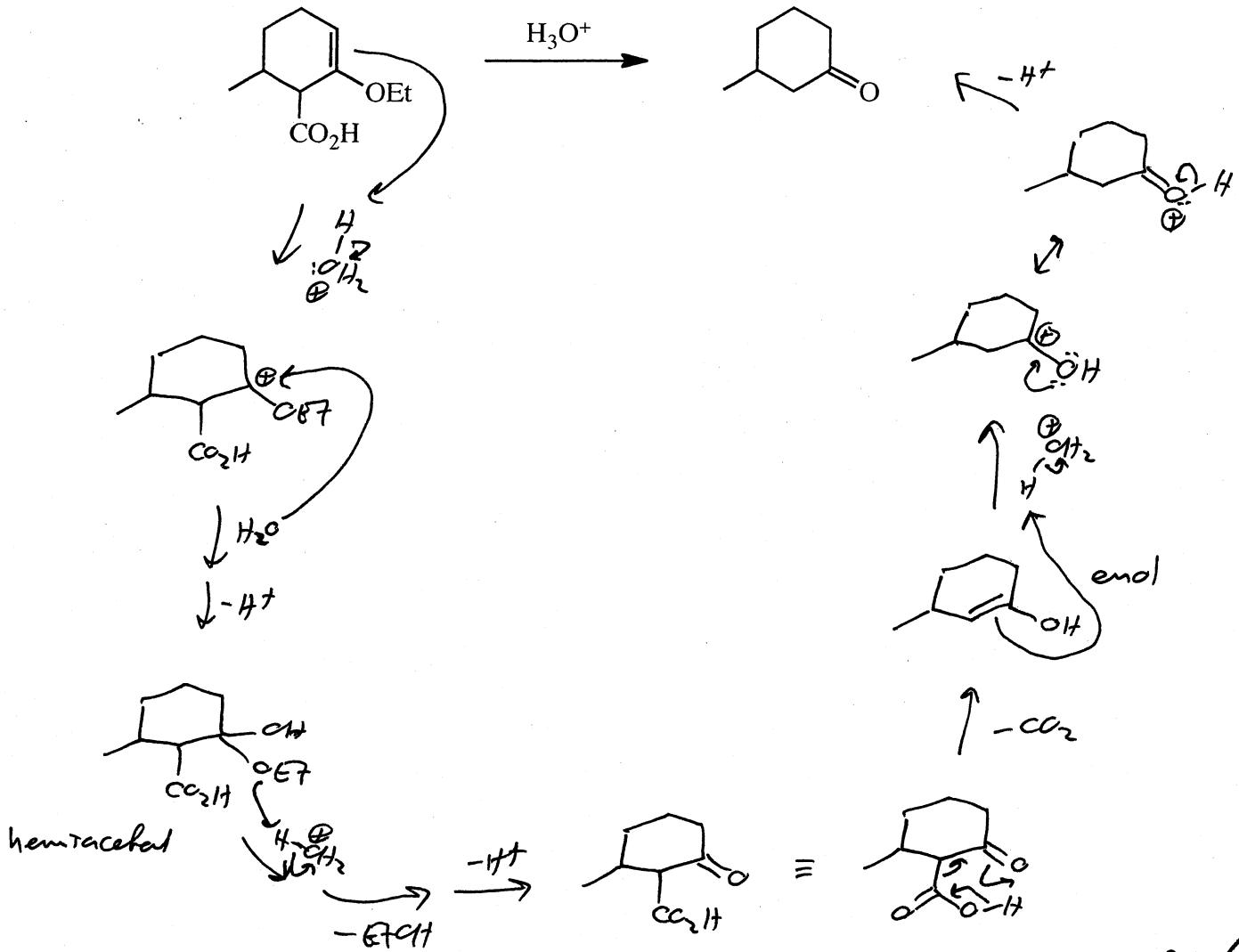
2. (13 points) Write a mechanism to explain the following reaction. Show every step clearly with curved arrows. Two equivalents of methyllithium is required; if only one equivalent is used, all the benzoic acid is recovered after the second step.



3. (27 points) Suggest a mechanism to explain the following reaction. You may abbreviate proton transfers as "$+H^+$" and "$-H^+$", as long as the sequence is clear and reasonable.



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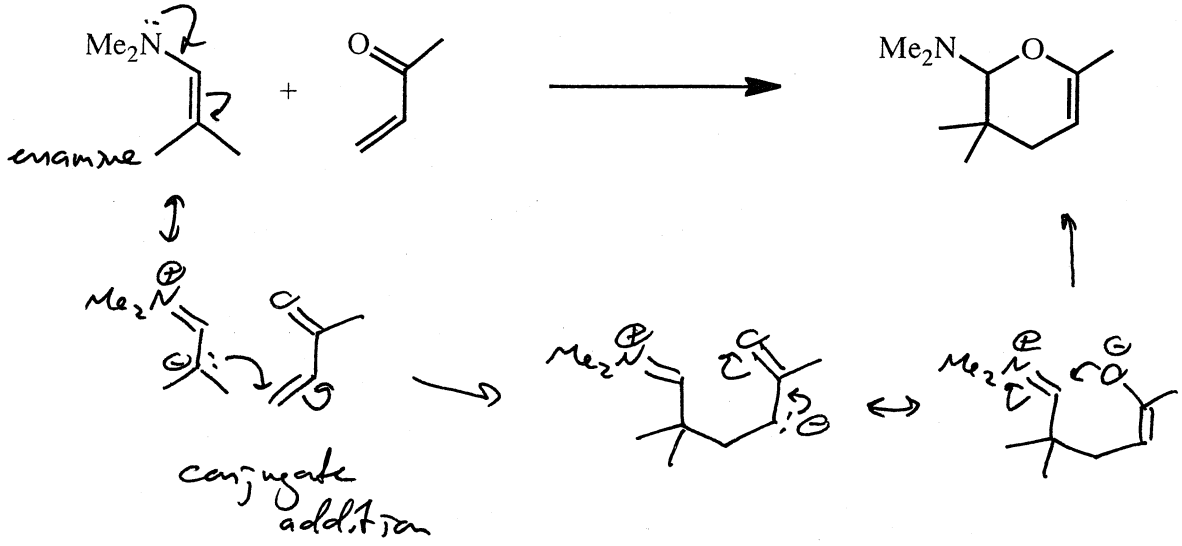
4. (15 points) This looks like a Diels-Alder reaction but it's not. The reaction does *not* involve any kind of concerted, pericyclic process. Suggest a mechanism.



5. (25 points) Suggest short syntheses of the compounds below from 1,5-hexanediol.

(a)

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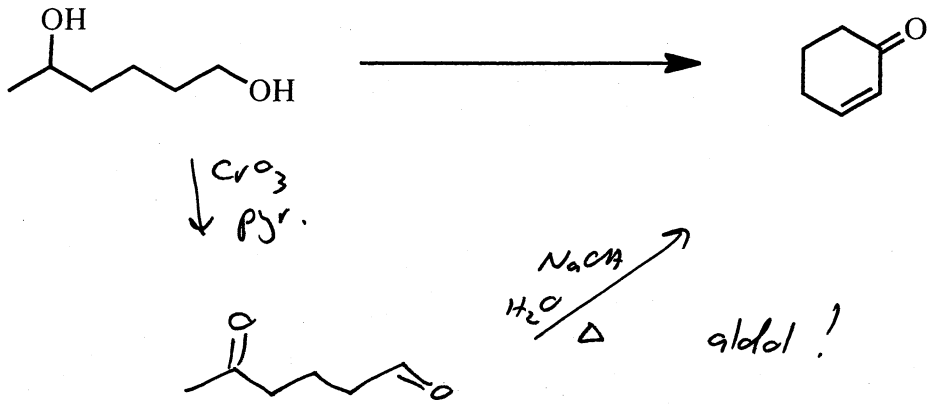
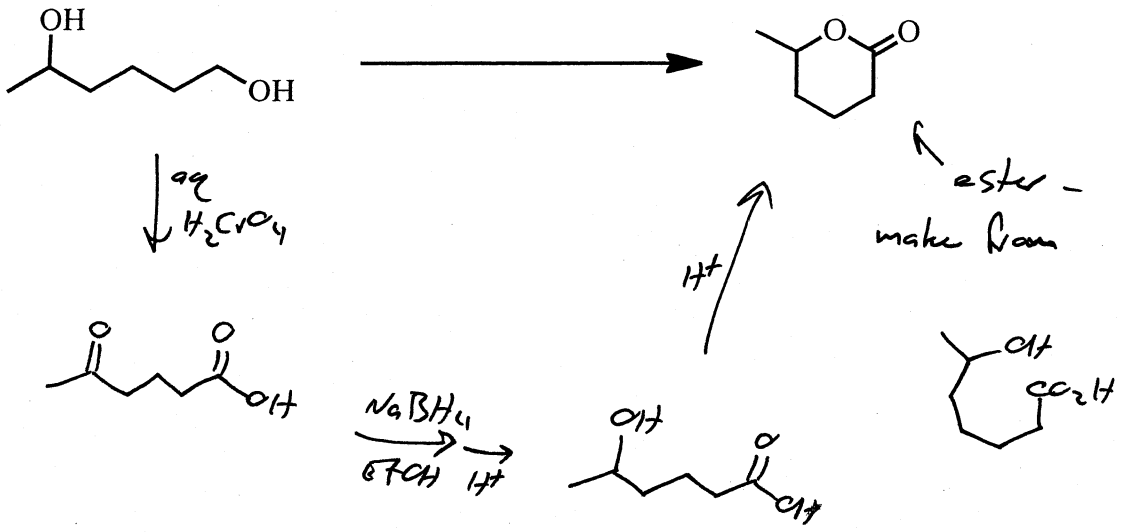


(b)

13



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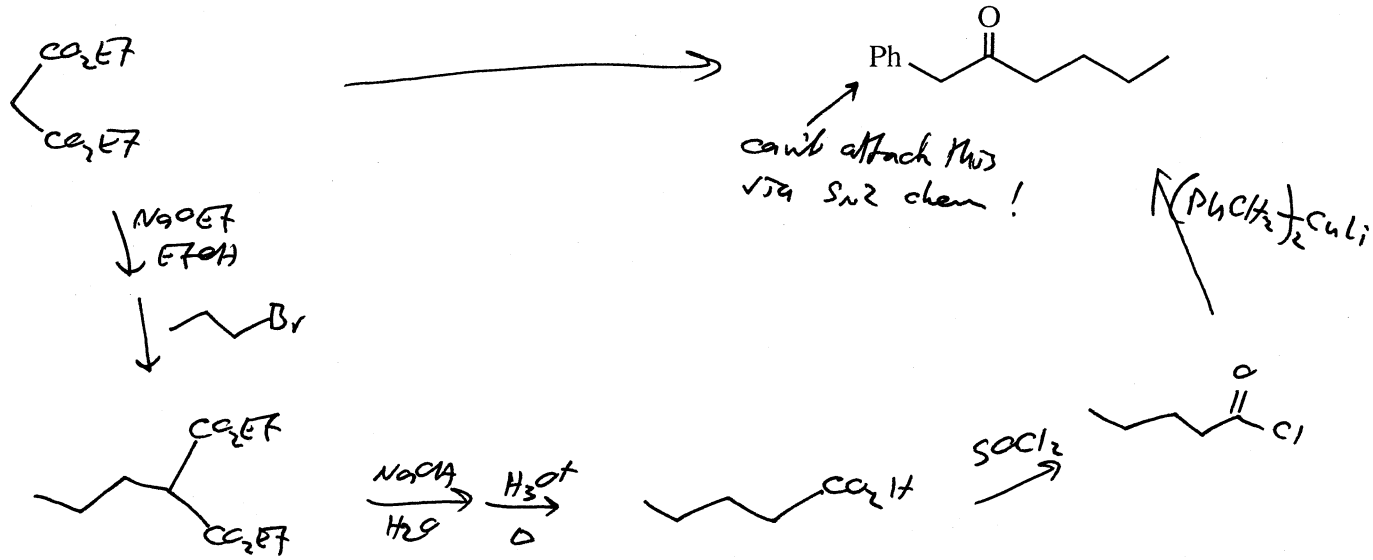
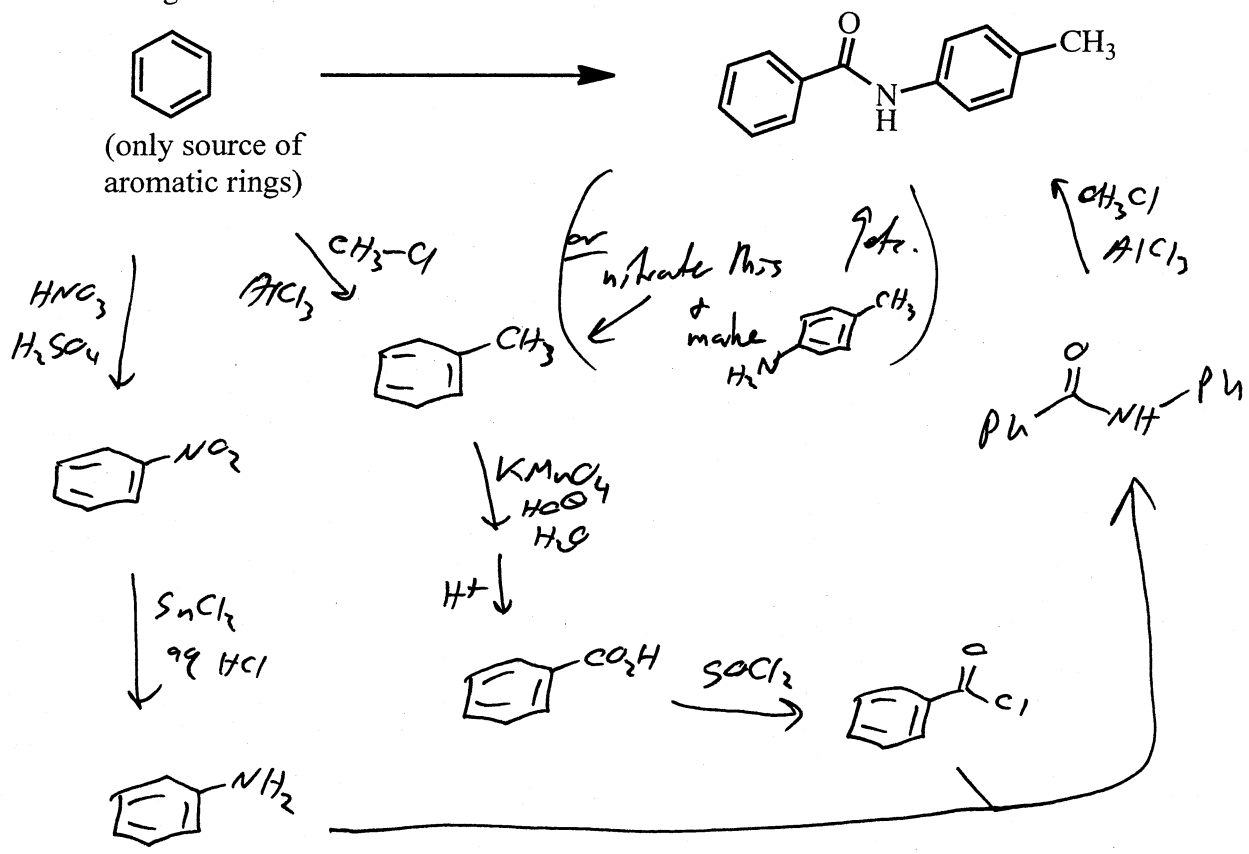
6. (17 points) Starting with either malonic ester or acetoacetic ester, suggest a synthesis of the ketone below. You may use only compounds available in the Chemical Store (catalog attached at the end of this exam).



7. (18 points) Suggest a synthesis of the amide below, using benzene as the only source of aromatic rings.



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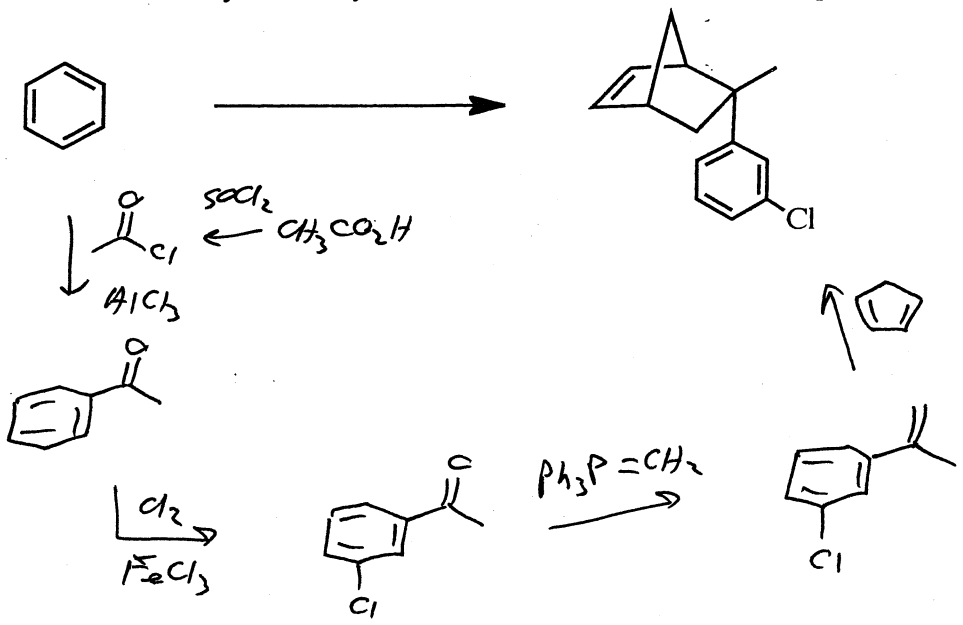
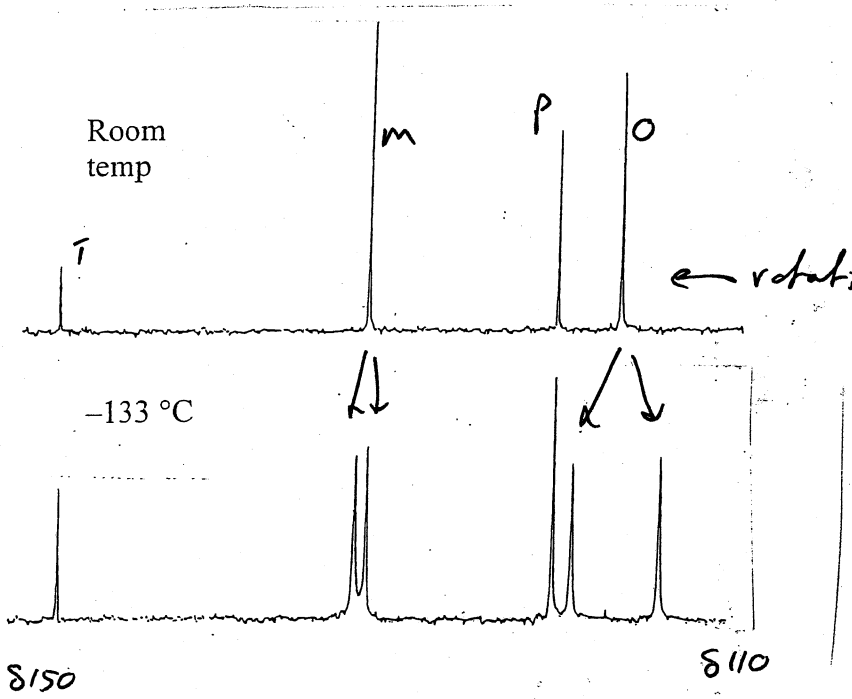
8. (18 points) Suggest a synthesis of the compound below from benzene. As long as you begin with benzene, you may use anything else in the Chemical Store (hint: Note that cyclopentadiene has been added to the inventory, in case you want to use a D-A rxn at some point.)



9. (17 points) N-methylaniline, Ph–$NHCH_3$, displays the following ^{1}H-decoupled ^{13}C NMR spectra at the temperatures indicated. Only the aromatic region is shown.

(a) Briefly explain the difference between the two spectra in terms of the structure of the compound. (b) Assign the peaks in the room temperature spectrum to the aromatic Cs.



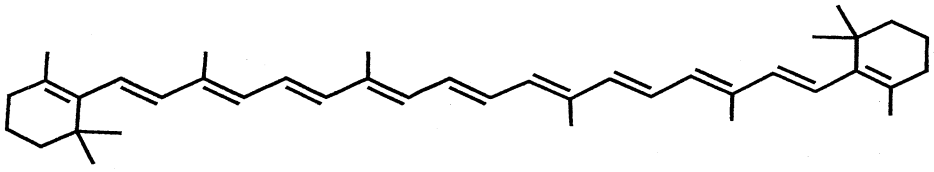
← rotation fast ⇒ rxn Cs became equiv on NMR timescale

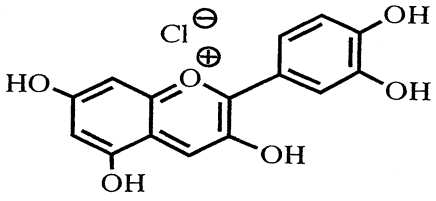
← rotation slow ortho Hs are very different; metas are not as different

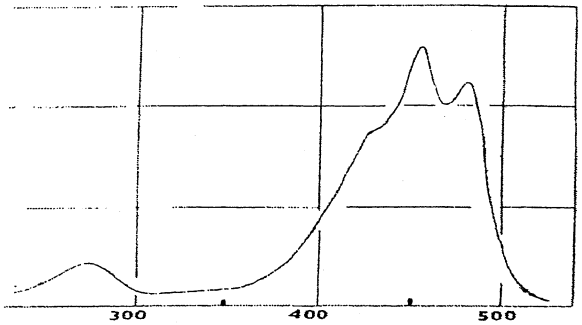
o & p upfield due to resonance e⁻-donation by N

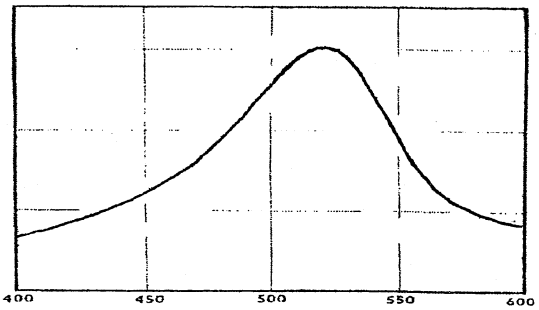
35

10. (15 points) The structures and UV-vis spectra of β-carotene and cyanidin chloride (an anthocyanine derivative), are shown below.









3 pts each

(a) Based on the spectra, what *color* light does each compound absorb most strongly?

β-carotene: blue (-purple) **cyanidin chloride**: green

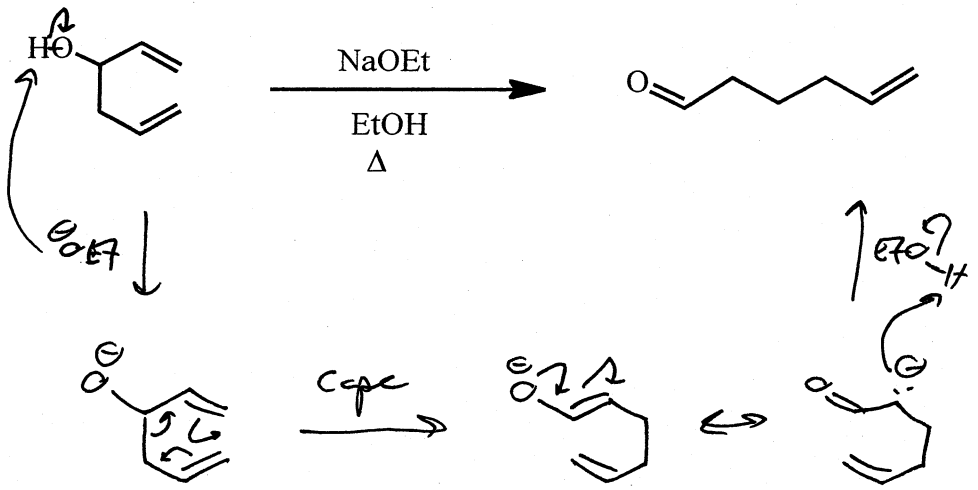
(b) Based on the colors absorbed, what colors do these compounds appear to be?

β-carotene: orange (-yellow) **cyanidin chloride**: red

(c) Which compound has the smaller HOMO-LUMO gap?

based on abs λs ! ⟹ cyanidin chloride

11. (15 points) The reaction below is an anionic oxy-Cope rearrangement. Write the mechanism. The first step is a proton transfer.



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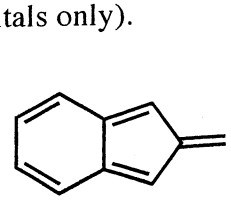
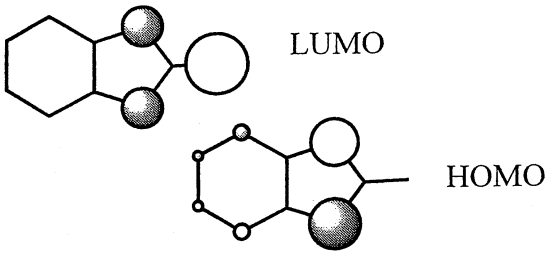
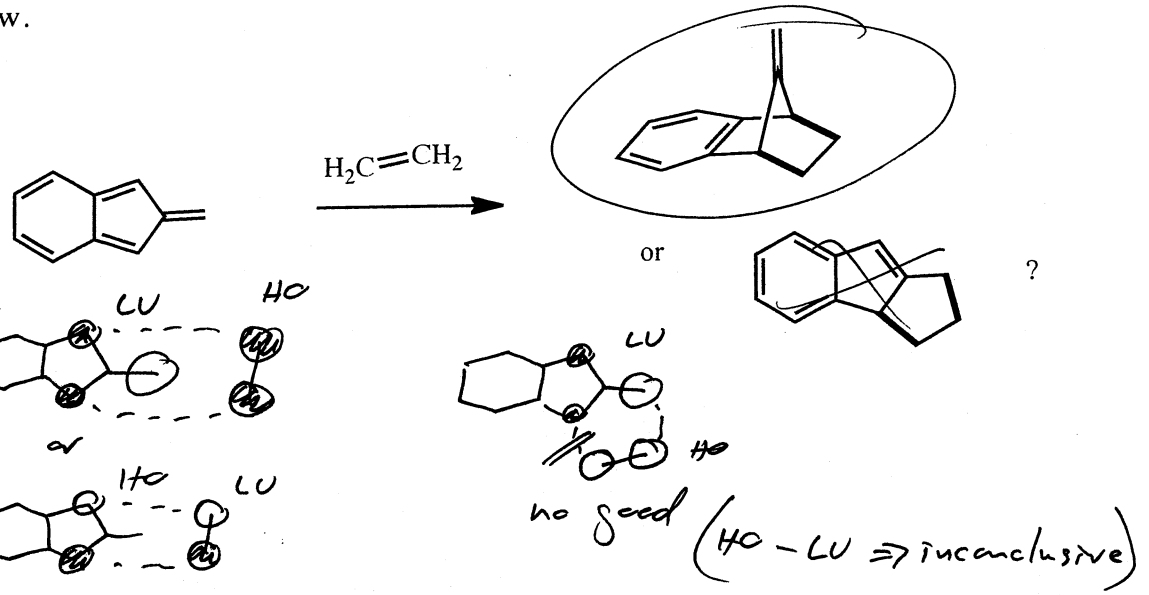
12. (25 points) Isobenzofulvene's HOMO and LUMO are shown below (top lobes of the p-orbitals only).

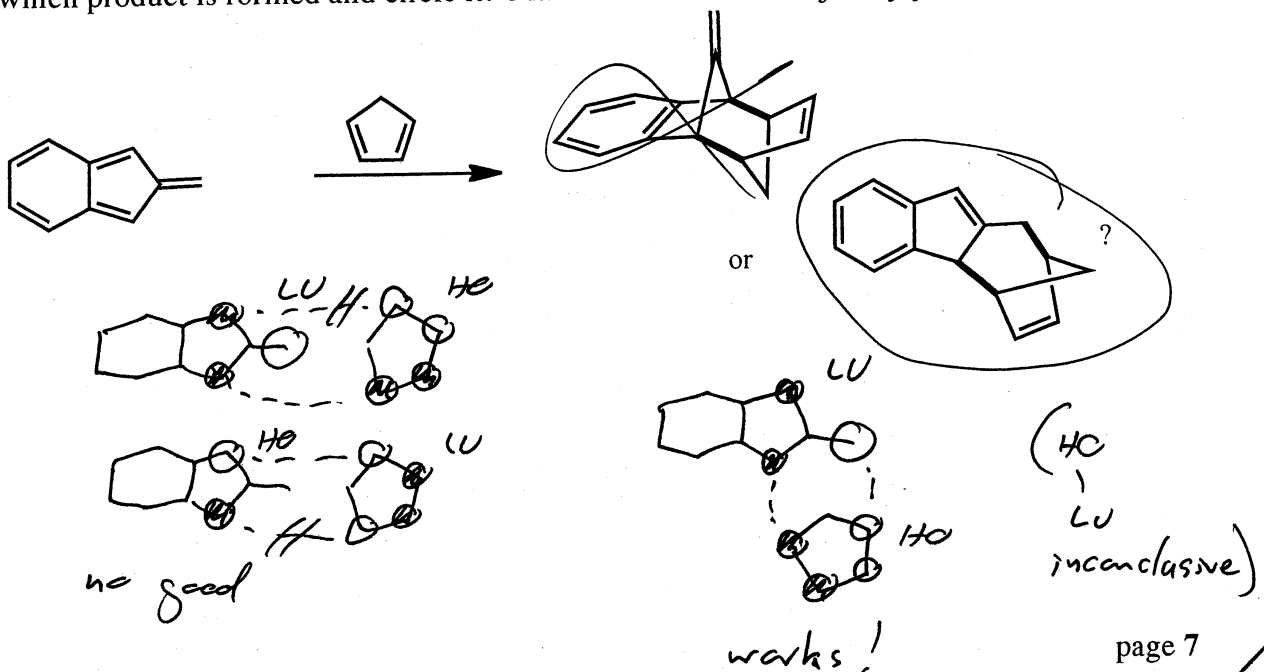




(a) When this compound reacts with a dienophile (we'll use ethylene for simplicity), one of the two products shown is formed. Use Frontier Orbital Theory (i.e. HOMO-LUMO interactions) to decide which product is formed, and circle it. Explain your choice by making some sketches in the space below.



(b) When the compound reacts with cyclopentadiene, one of the following two products is formed (ignore stereochemistry for this problem). As you did in part a, use frontier orbital theory to decide which product is formed and circle it. Make some sketches to justify your choice.



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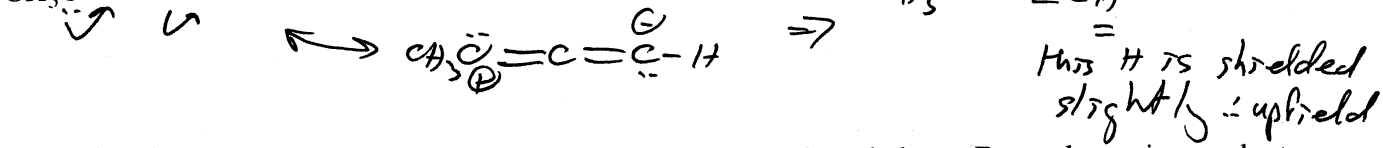
13. (15 points) (a) The ^{1}H NMR signals for acetylenic Hs (e.g. in propyne) typically appear at δ1.8. In contrast, the corresponding H of methoxyacetylene (marked with the arrow) is about half a ppm upfield of this, at **δ1.3**. Explain briefly by drawing a key structure or two.

5

$CH_3-C\equiv C-H$ **δ 1.8**

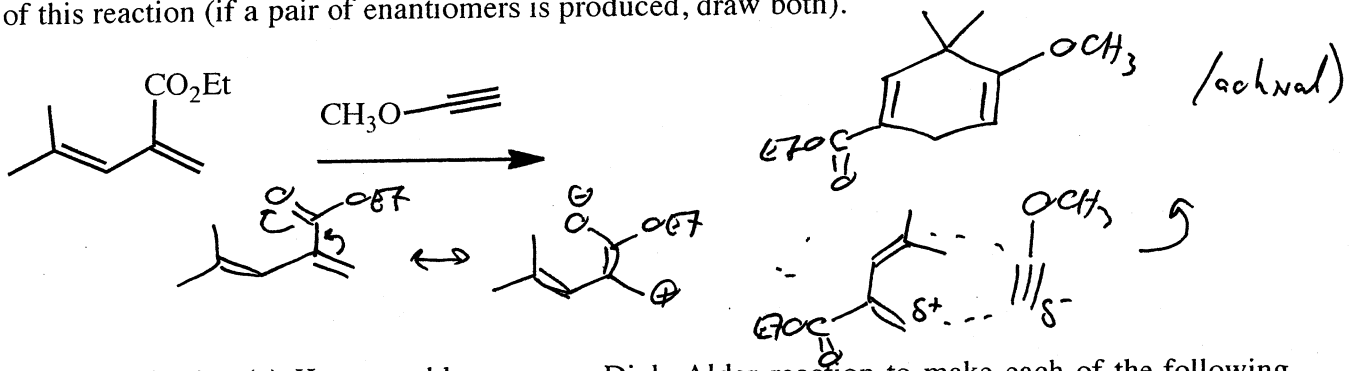
$CH_3\ddot{O}-C\equiv C-H$ **δ 1.3** ←



This H is shielded slightly ∴ upfield

(b) Methoxyacetylene does a Diels-Alder reaction with the diene below. Draw the major product of this reaction (if a pair of enantiomers is produced, draw both).

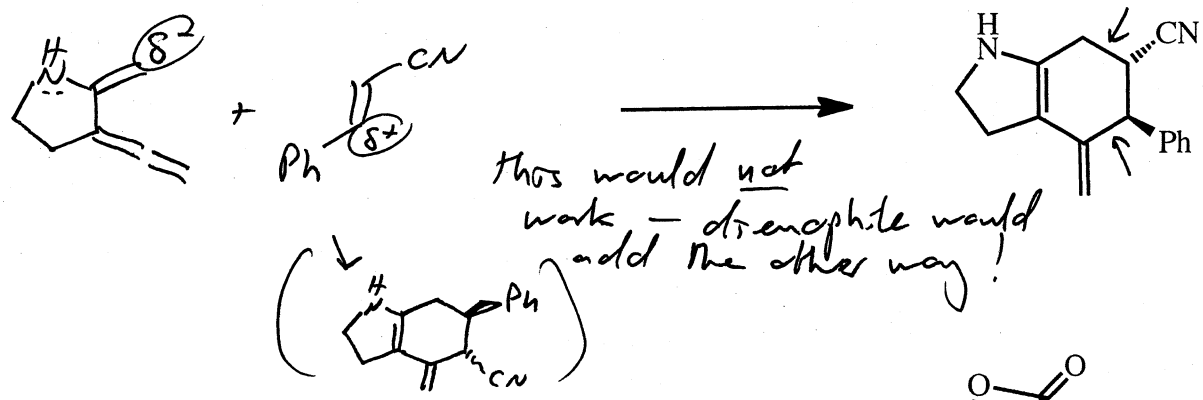
10



(achiral)

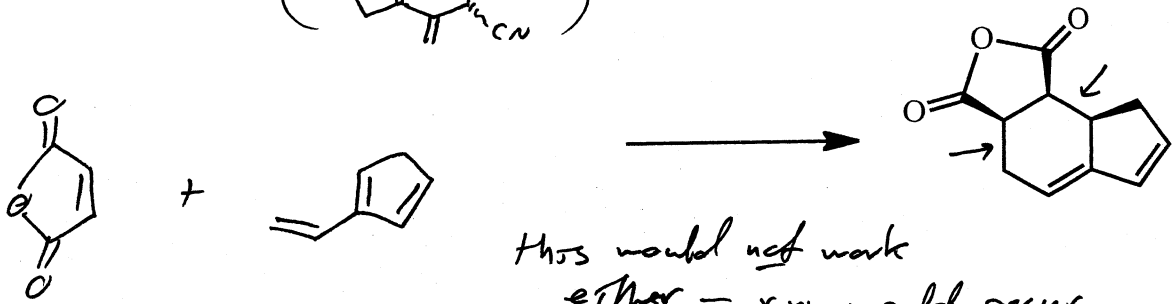
14. (20 points) (a) How would you use a Diels-Alder reaction to make each of the following (racemic) compounds? Draw the reactants that you would need to use. (b) In each case, would the D-A rxn be expected to produce the product shown in good yield? Explain briefly.

10



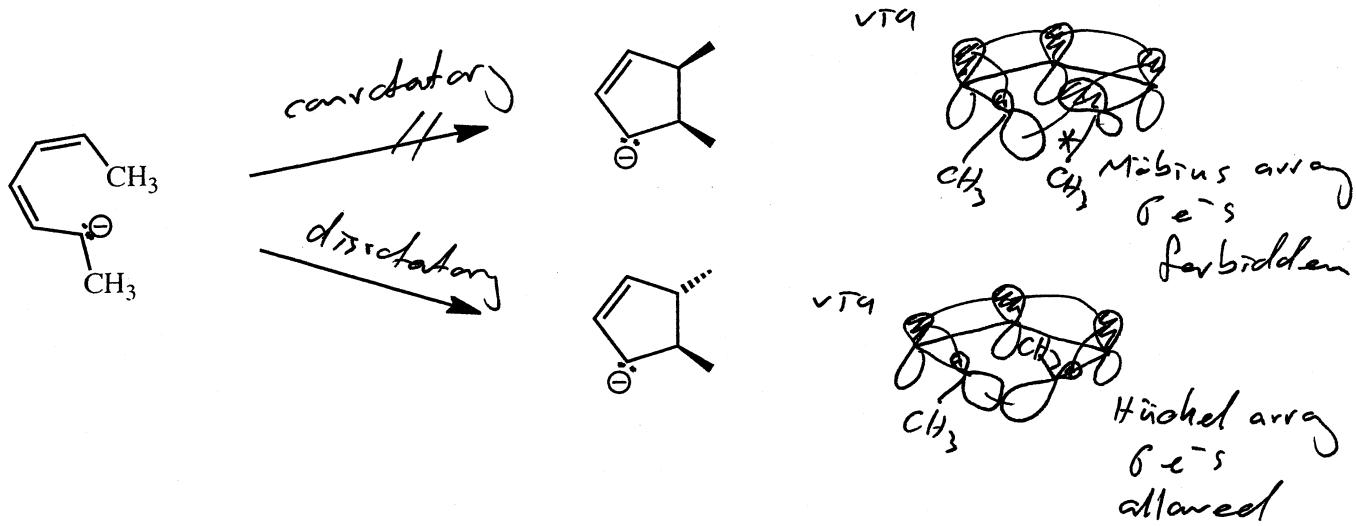
this would not work — dienophile would add the other way!

10



this would not work either — rxn would occur (mostly) on the cyclopentadiene rxn!

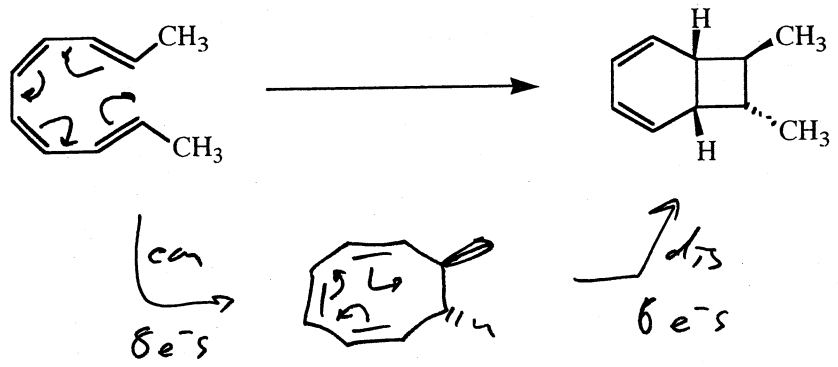
15. (15 points) Use aromatic transition state theory to decide whether each electrocyclic process shown below is allowed or forbidden thermally. Sketch the transition state orbital array for each process.



16. (25 points) Suggest a mechanism to account for each of the following thermal transformations. More than one step may be involved.

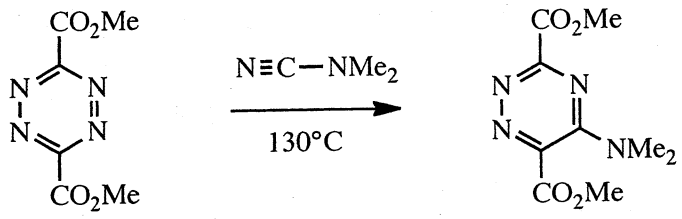
(a)

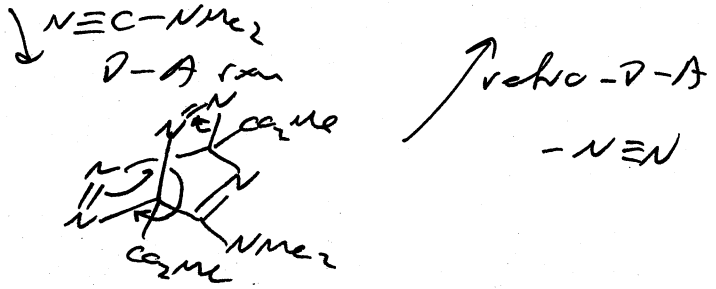
13



(b)

12





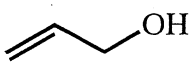
Chemical Store

In addition to the compounds below, you may use any inorganic reagents, aqueous acids, or bases, and common organic bases like NaOEt, nBuLi, LDA, $NaHCO_3$.

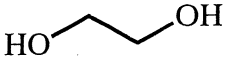
alcohols

Ph—OH

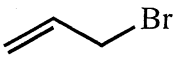
$Ph—CH_2OH$



and any R–OH where R is a saturated alkyl group with 4 Cs or fewer



organohalides



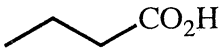
$Ph—CH_2Br$

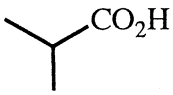
Ph—Br

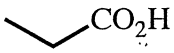
and any R–Br, RCl, or RI where R is a saturated alkyl group with 4 Cs or fewer

carboxylic acids

$Ph—CO_2H$





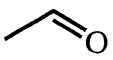


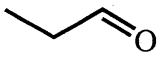
$CH_3—CO_2H$

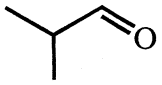
HCO_2H

aldehydes

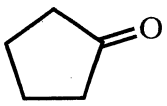
$H_2C=O$

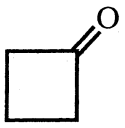


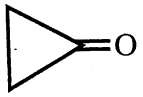


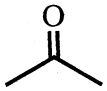


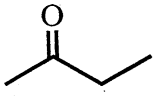
ketones







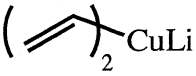




cuprates

Ph_2CuLi

$(PhCH_2)_2CuLi$



and any R_2CuLi where R is a saturated alkyl group with 4 Cs or fewer

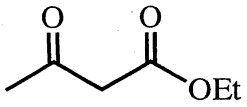
Wittig reagents

$Ph_3P=CH_2$

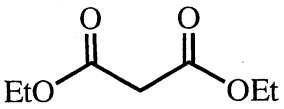
$Ph_3P=CHCH_3$

$Ph_3P=CHCH_2CH_3$

$Ph_3P=C(CH_3)_2$



acetoacetic ester



malonic ester