EXAMINATION 1

Chemistry 3B
Professor K. Peter C. Vollhardt
February 21, 1995

Name:_____
[Print first name before second! Use capital letters!]

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

101	Paikoff, Sari	_____	311	Liu, Guangcheng	_____
102	Panomitros, Demetra	_____	312	Yang, Jerry	_____
111	Herrmann, Paul	_____	313	Gonazles, Hector	_____
112	Mayberry, Kit	_____	411	Yang, Kelly	_____
113	Bunin, Barry	_____	412	Panomitros, Demetra	_____
211	Herrmann, Paul	_____	413	Siesel, Brian	_____
212	Jalisatgi, Satish	_____	511	Fuller, Joannna	_____
213	Chen, Melissa	_____	512	Frost, Mareia	_____
301	Backes, Brad	_____	513	Tsai, Sheryl	_____
302	Gonzales, Hector	_____	601	Lecture Only	_____

Making up an I Grade _____

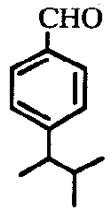
(If you are, please indicate the semester in which you took previous Chem 3B_____)

Please write the answer you wish to be graded in the spaces provided. Do scratch work on the back of the pages. This test should have 14 pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases, it is better to be pedantic in accuracy! Good Luck!**

I.	_____	**(30)**
II.	_____	**(50)**
III.	_____	**(60)**
IV.	_____	**(30)**
V.	_____	**(30)**
TOTAL		**(200)**

I. [30 Points] Name (IUPAC) or draw, as appropriate, the following molecules, including their stereochemistry.

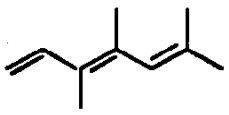
a.



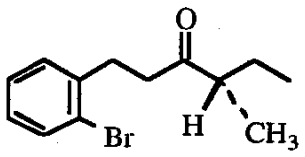
b.

cis-2-Ethenyl-3-methyl-cyclohexanone

c.



d.

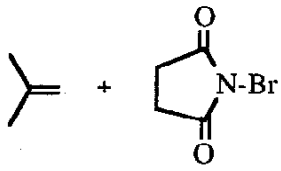


e.

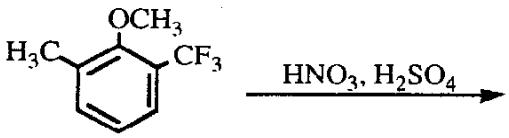
(R)-2-Chloro-2-phenylethanol

II. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

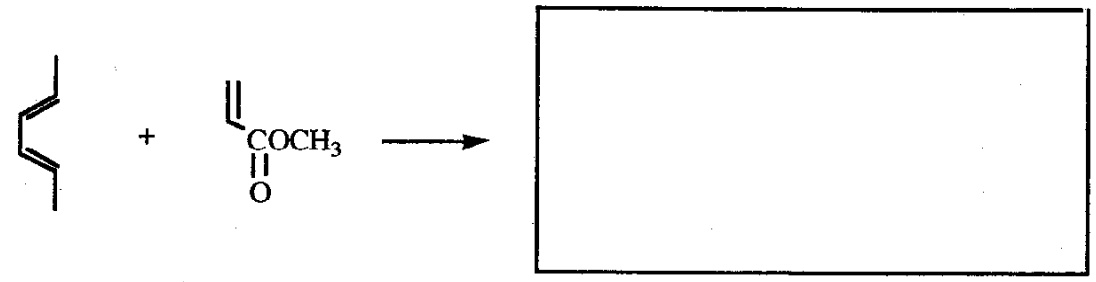
a.



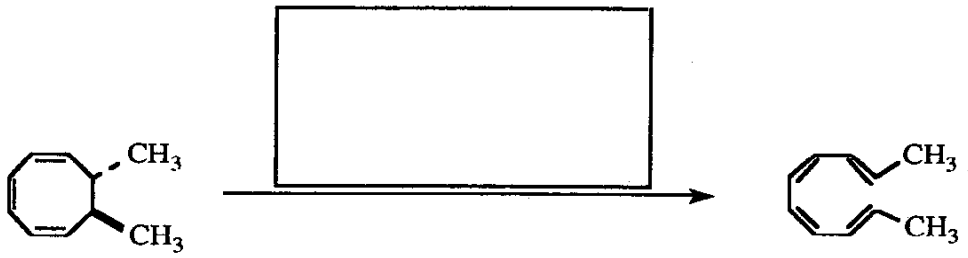
b.



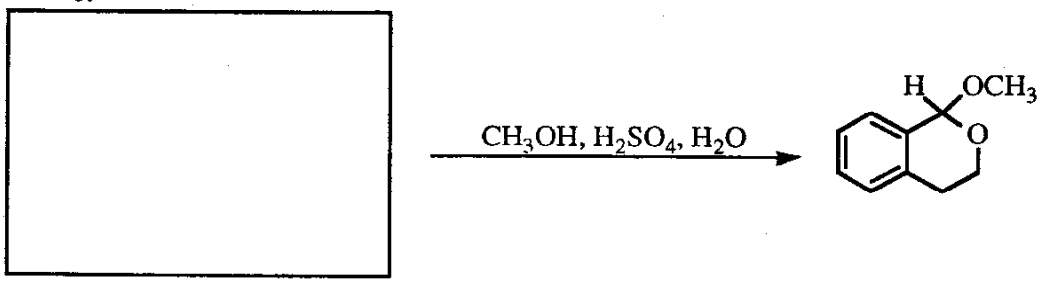
c.



d.

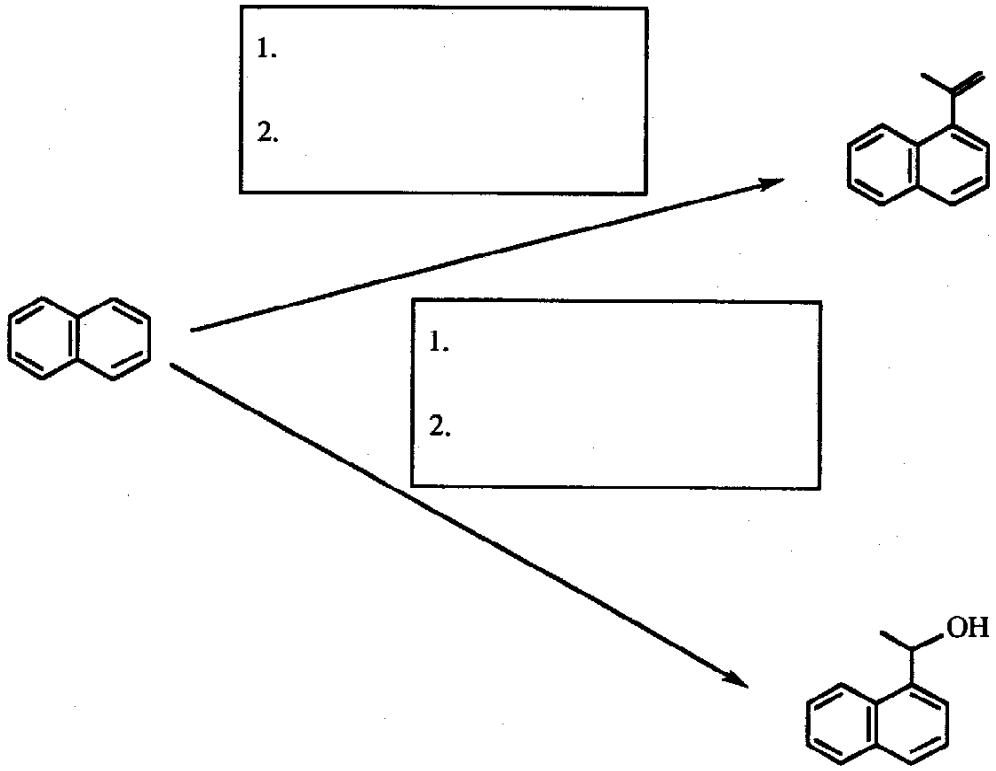


e.

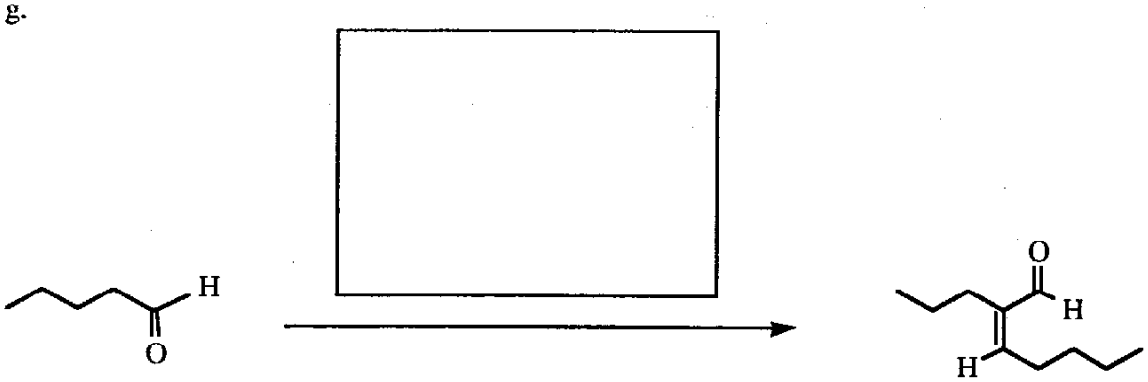


IR: $\nu = 3350, 1690\ cm^{-1}$

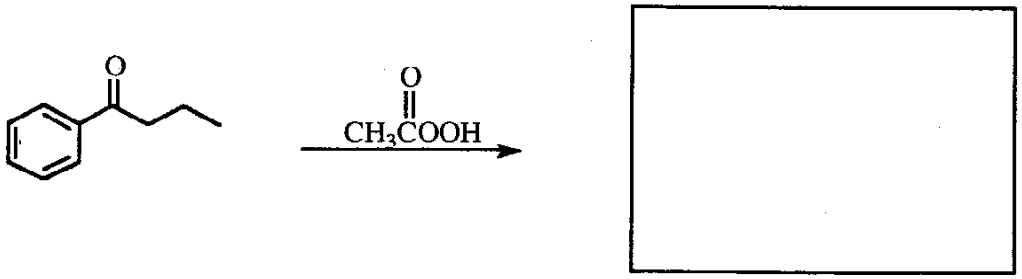
f.



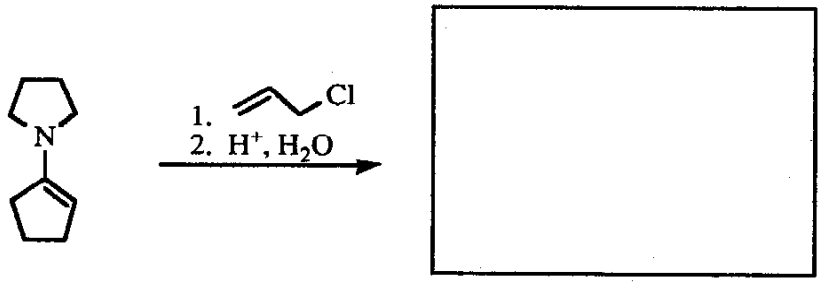
g.



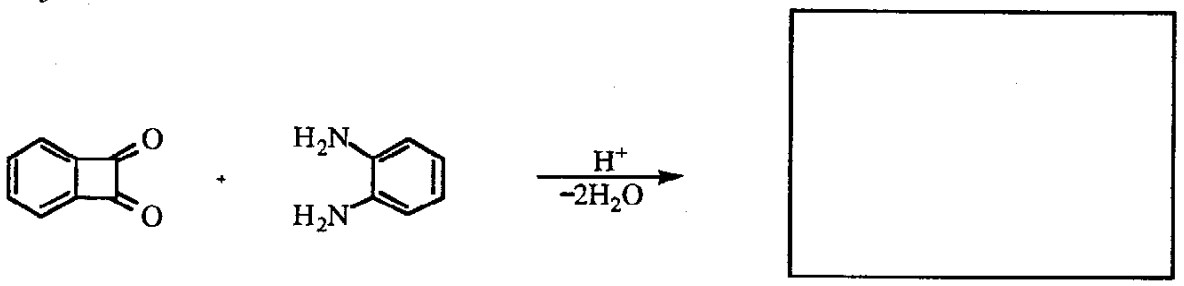
h.



i.

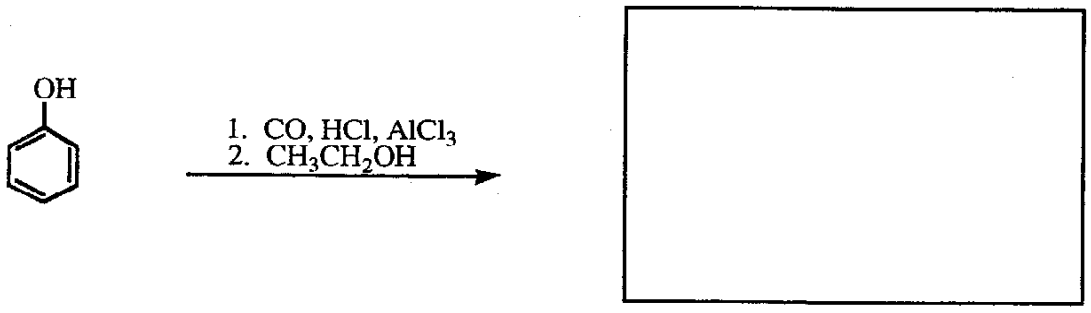


j.



$C_{14}H_8N_2$

III. [60 Points] Treatment of benzenol with CO and conc. HCl (a source of HCCl) in the presence of $AlCl_3$, followed by work-up with ethanol, gave compound **A**. Its IR and NMR spectra are depicted below; the UV spectrum shows a peak at λmax 290 nm.

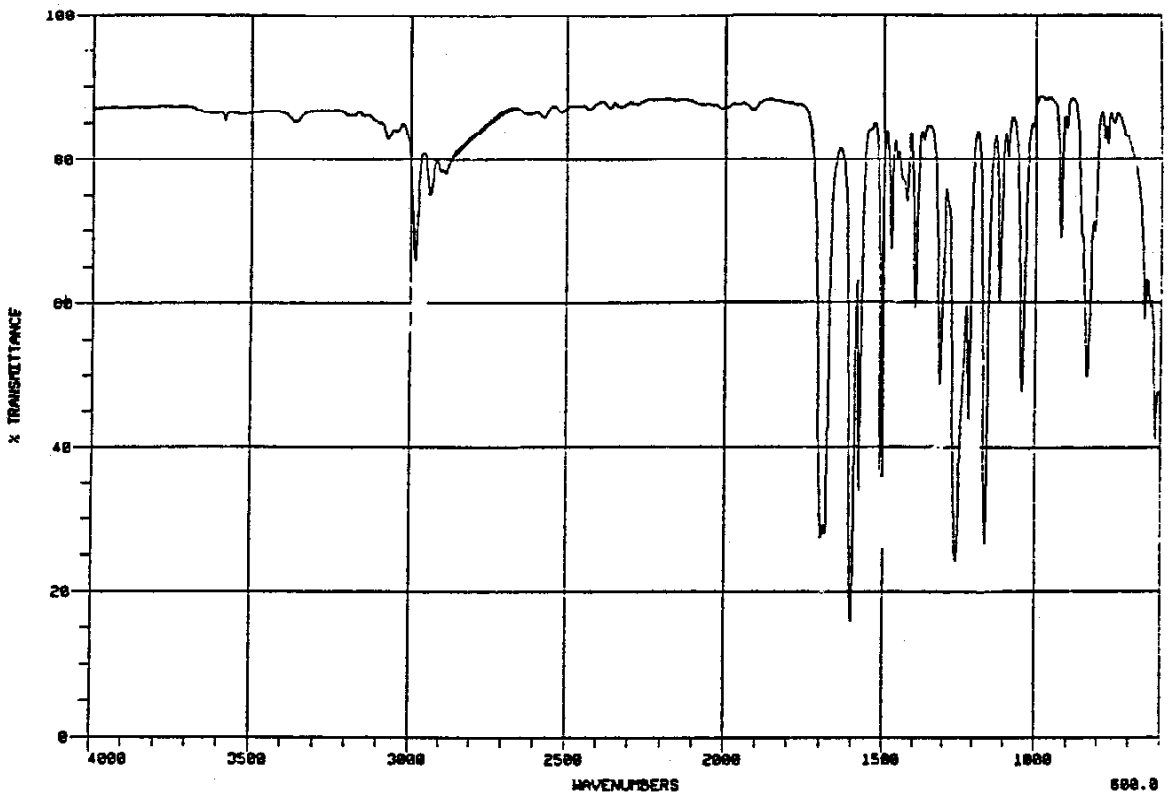


A

a. What is **A**? (Draw in the box provided.)

b. Interpret the spectral data as requested in the spaces provided.

1. IR Spectrum

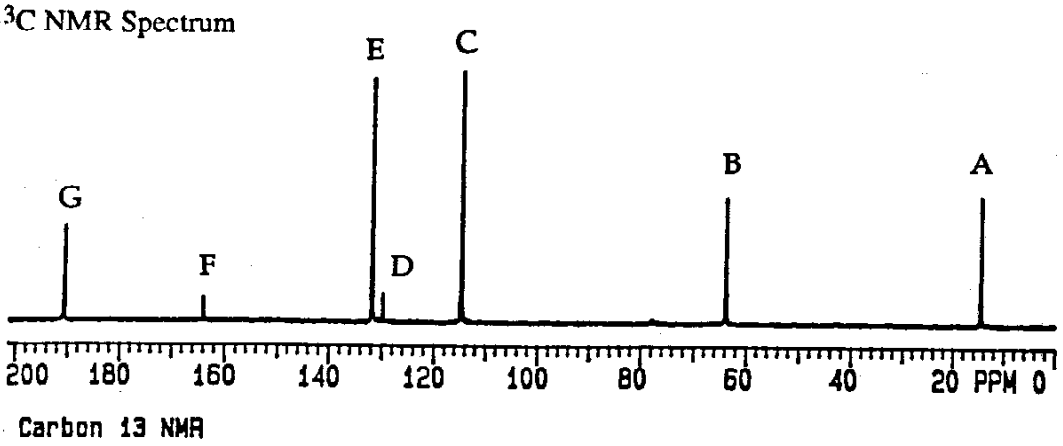


There is a characteristic peak present and (considering the starting material) a characteristic peak absent in the spectrum. Specify and assign to stretching frequencies:

Peak present at _____, due to _____.

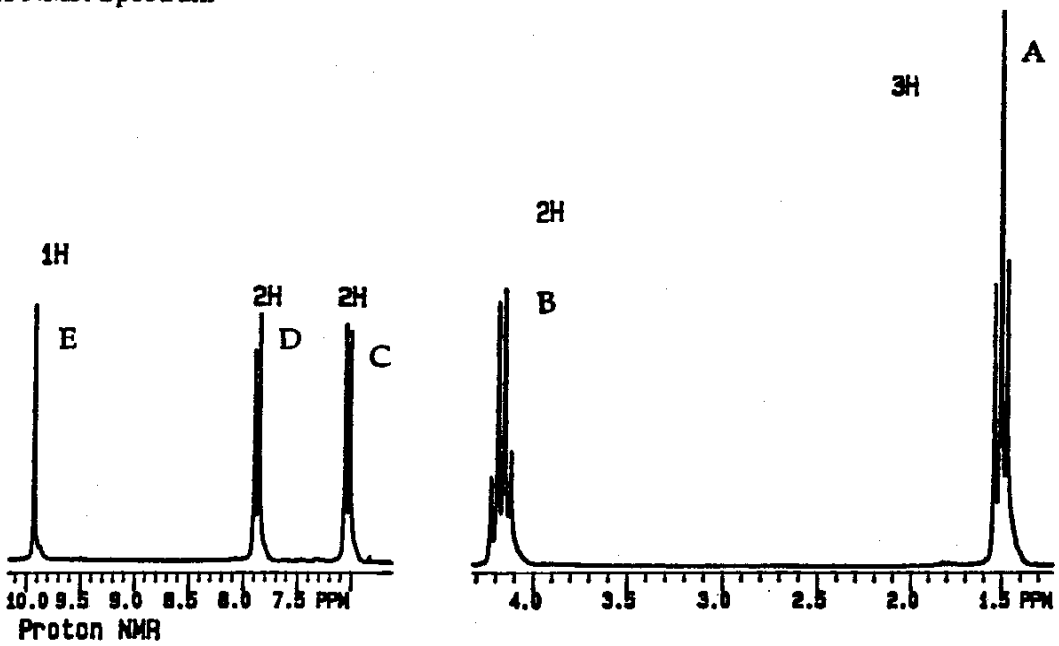
Peak absent at _____, due to _____.

2. ^{13}C NMR Spectrum



Note: in this spectrum, the relative peak heights can be used as a measure of relative abundance, with the exception of the small peaks at 129.5 and 164.0 which are due to two quaternary carbons.
Draw your suggestion for **A** and label the carbon atoms, A, B, C, etc., giving rise to the corresponding signals in the spectrum.

3. ^{1}H NMR Spectrum

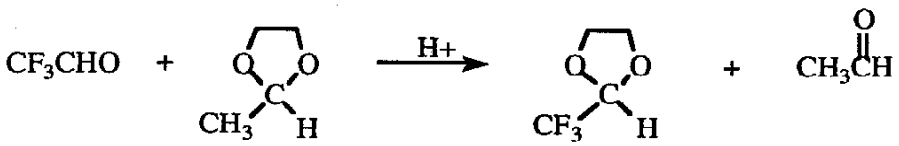


Note: the J values for the peaks at δ = 1.50 and 4.15 ppm are 8 Hz, for those at 7.05 and 7.90 they are 9 Hz. Draw your suggestion for **A** and label the hydrogens A, B, C, D, and E giving rise to the corresponding signals in the spectrum.

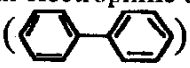
c. Suggest a plausible mechanism for the formation of **A**.

IV. [30 Points] Write detailed mechanisms to explain the following observations.

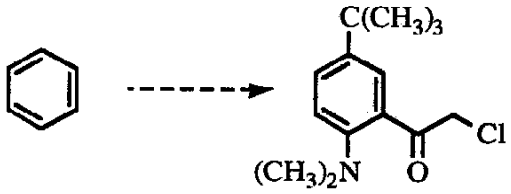
a.



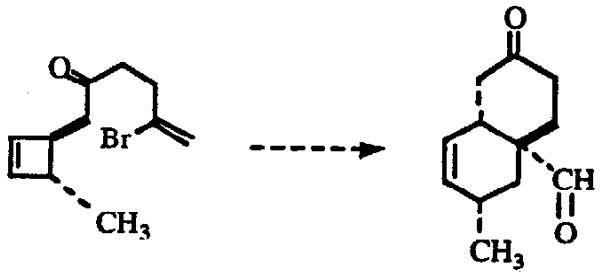
Why does the equilibrium lie to the right? Explain.

b. The phenyl substituent is an ortho-para director in electrophilic aromatic substitutions. Show why this is so for the monobromination of biphenyl ().

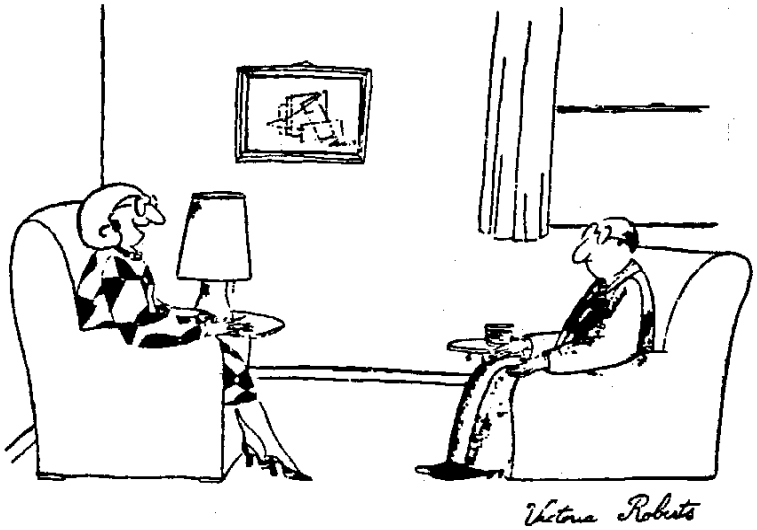
V. [30 Points] Provide a reasonable synthetic route from starting material to product. Note: several steps are required and there may be more than one solution to the problem. You may use any additional organic or organometallic reagents to effect your conversions.



b.



Hint: work backwards (reverse Diels-Alder reaction)! Work forwards (electrocyclic reaction)! Use a protecting group as part of your scheme.



"Don't worry, Howard. The big questions are multiple choice."