EXAMINATION 1
Chemistry 3B

Name: Key _____ **SID #:** _____

Print first name before second!
Use capital letters!

GSI (if you are taking Chem 3BL): _____

Peter Vollhardt
September 23, 2010

Please provide the following information if applicable.

Making up an I Grade _____
(If you are, please indicate the semester during which you took previous Chem 3B:

_____ _____
Semester Instructor

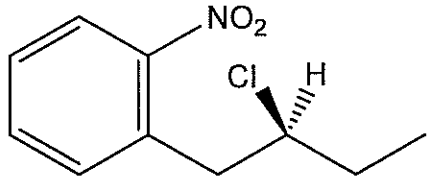
Please write the answer you wish to be graded in the spaces provided. ***Do scratch work on the back of the pages***. This test should have **15** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later!** ***Good Luck*****!**

DO NOT WRITE IN THIS SPACE

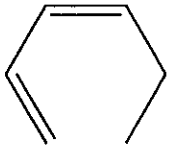
I.	_____	**(30)**
II.	_____	**(30)**
III.	_____	**(50)**
IV.	_____	**(40)**
V.	_____	**(40)**
VI.	_____	**(40)**
VII.	_____	**(20)**
Total:	_____	**(250)**

I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *E*, *Z*, *R*, or *S*).

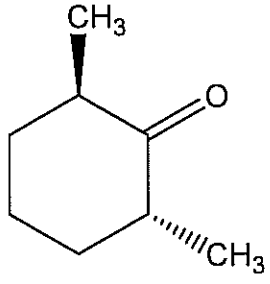
a. (*S*)-1-(2-Chlorobutyl)-2-nitrobenzene



b. cis-Hexa-1,3-diene



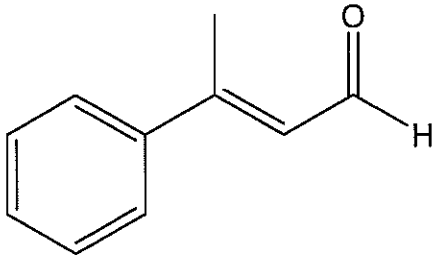
c.



Pure enantiomer

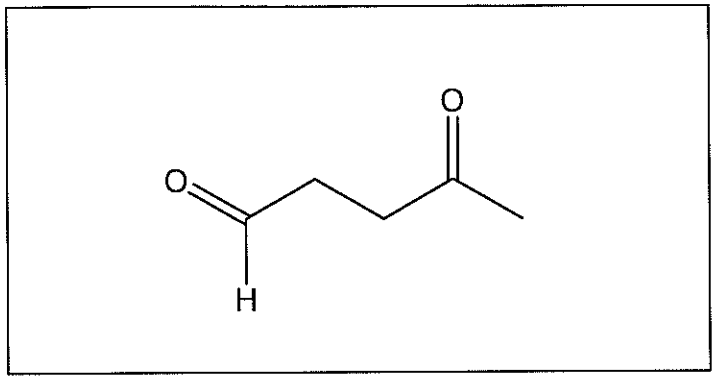
(2*R*,6*R*)-2,6-Dimethylcyclohexanone

d.

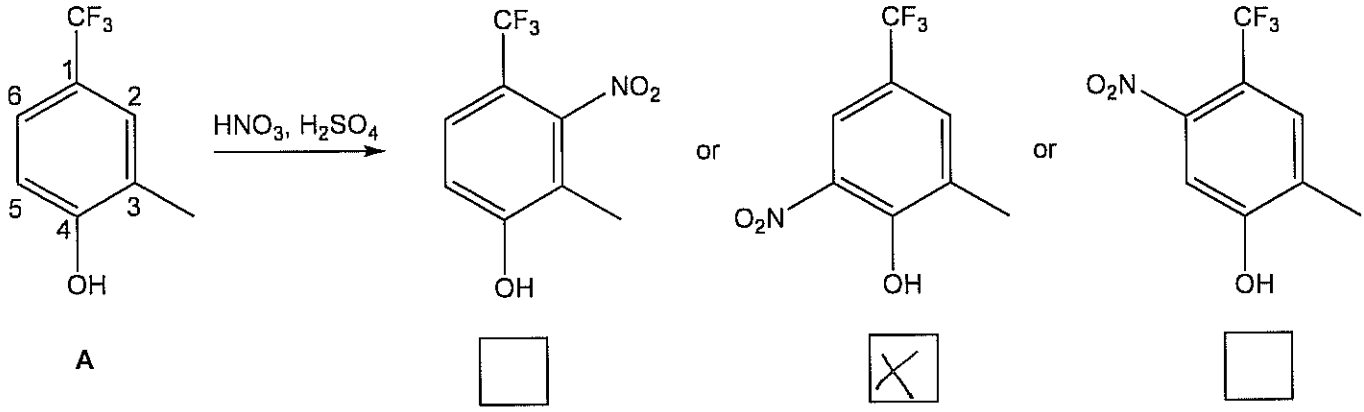


(*E*)-3-Phenylbut-2-enal

e. 4-Oxopentanal



II. [30 Points] Compound **A** undergoes preferential electrophilic nitration to give only one product.

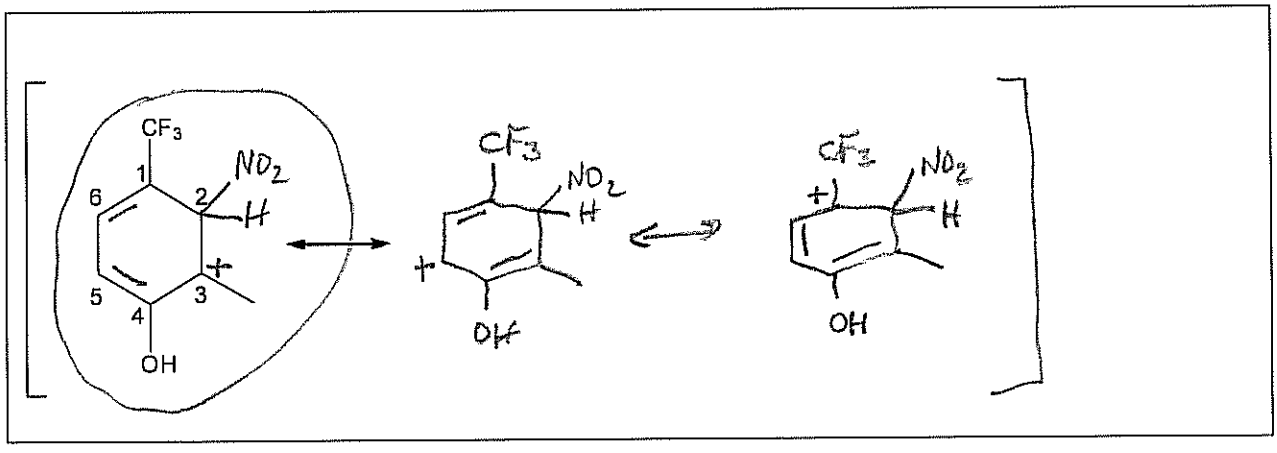


A

a. Which one? Mark the box below your choice with an X, **preferably after you have completed questions b.–d.**

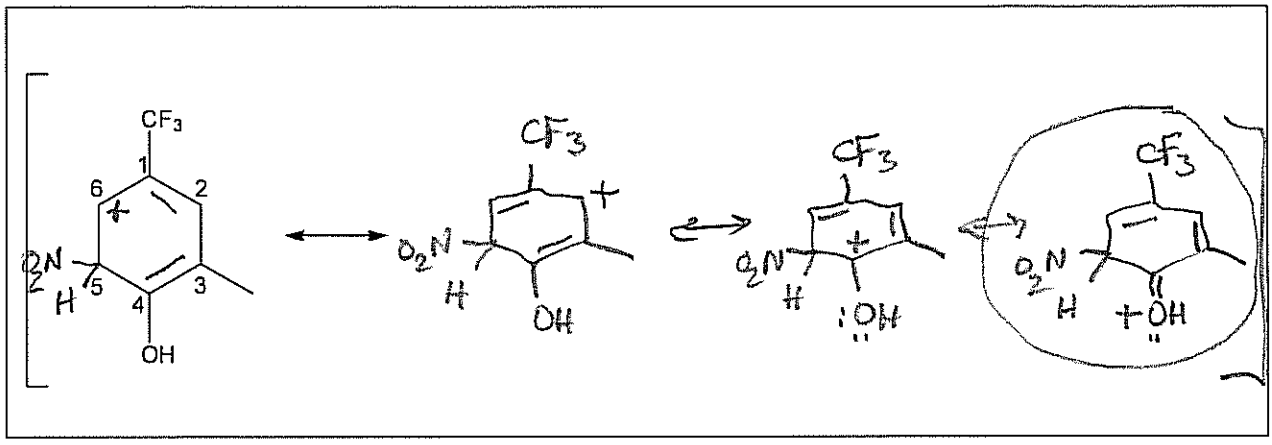
b. Write all the resonance forms of the intermediate formed by attack of NO_2^+ on **A** at:

C-2:



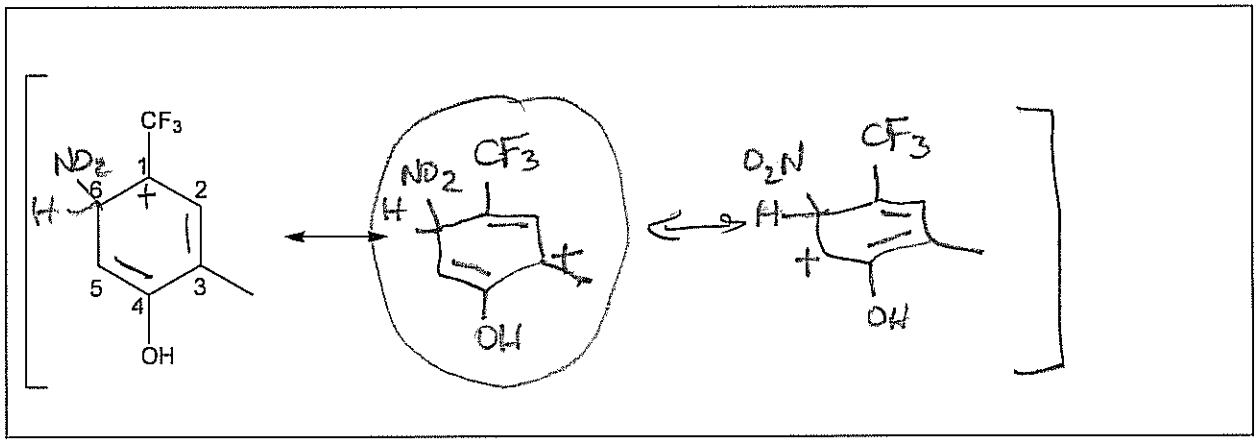
Note: A first stencil is provided for format. Leave out the numbering in any additional structures. Write the nitro group as "NO_2" (no need for the Lewis structure).

C-5:



Note: A first stencil is provided for format. Leave out the numbering in any additional structures. Write the nitro group as "NO_2" (no need for the Lewis structure).

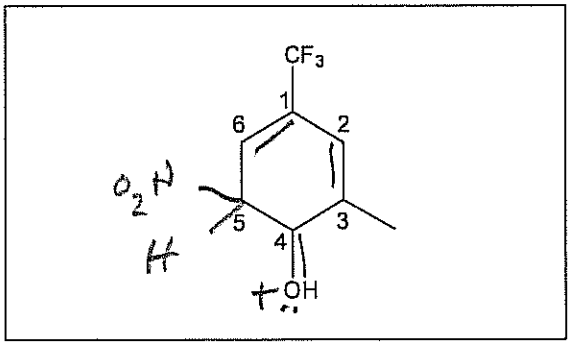
C-6:



Note: A first stencil is provided for format. Leave out the numbering in any additional structures. Write the nitro group as "NO_2" (no need for the Lewis structure).

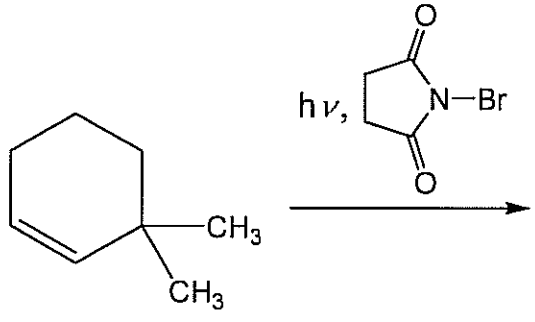
c. Circle (in your answers above) the **most strongly** contributing resonance forms of the attack at C-2, C-5, and C-6.

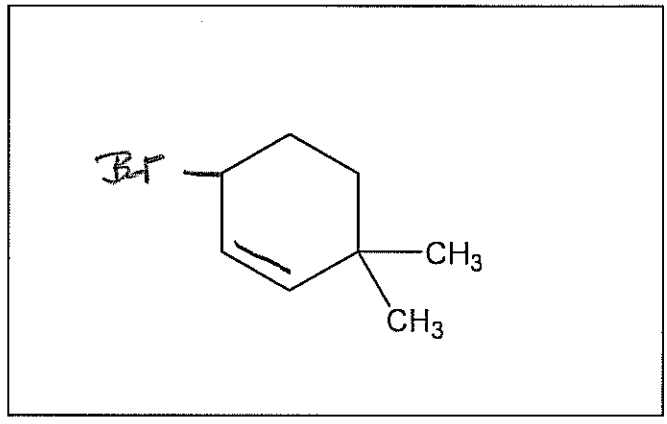
d. Considering all of the above **most strongly** contributing resonance forms, which one is the best overall? Redraw it in the box below.

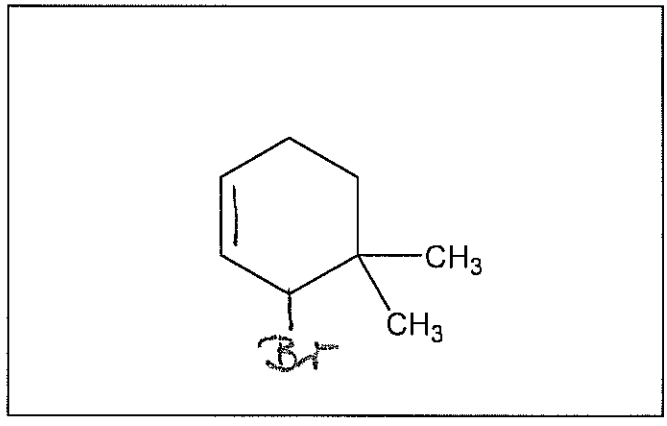


III. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Show stereochemistry when appropriate. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

a.

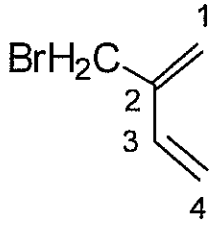


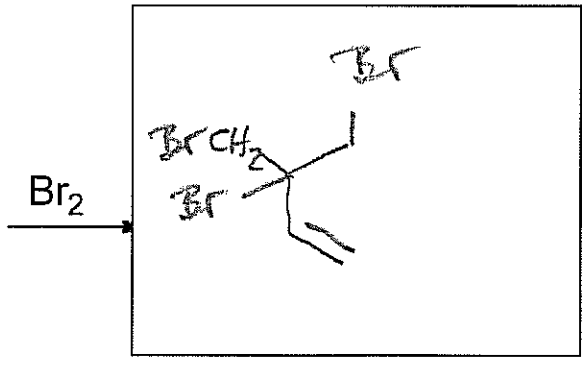




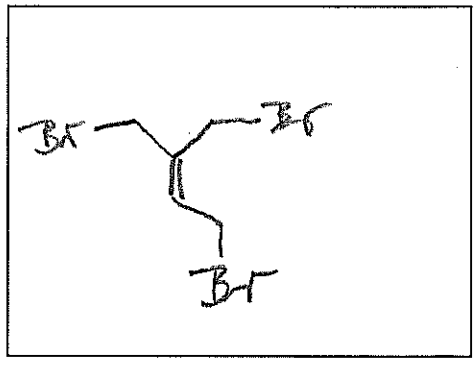
Two isomers. Add the missing pieces.

b.





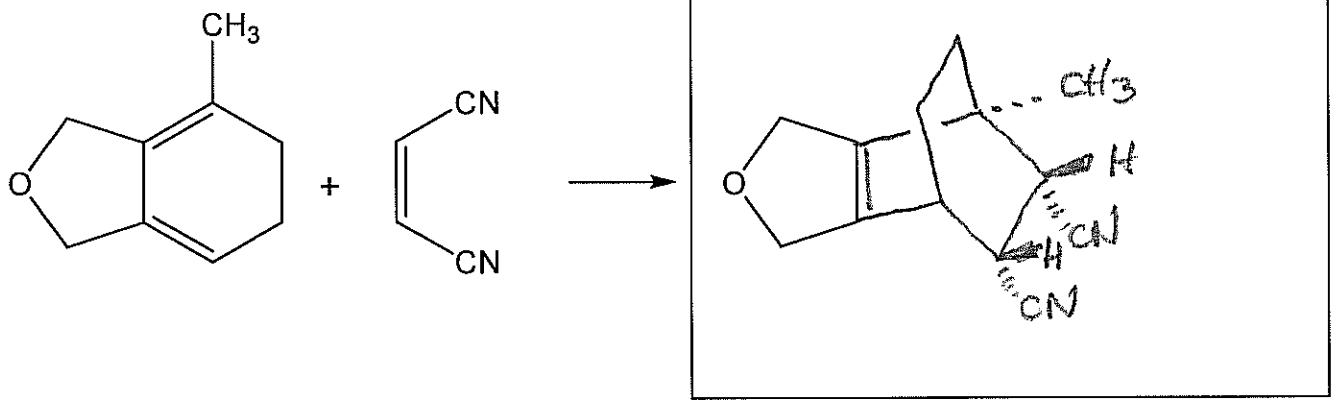
Kinetic product



Thermodynamic product

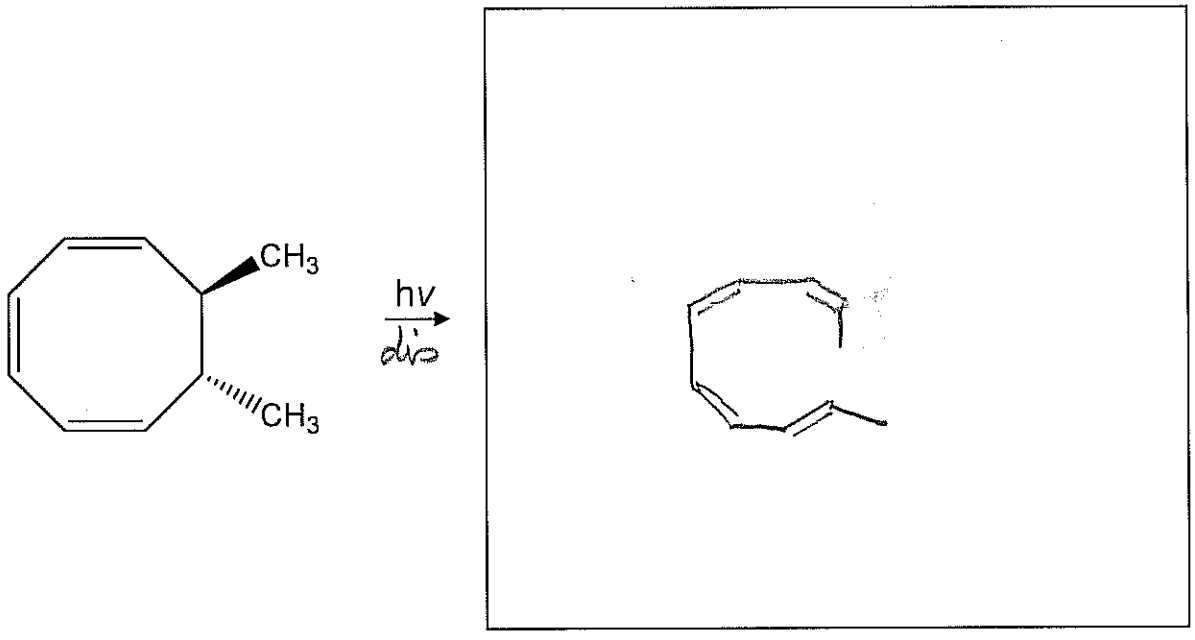
Hint: Electrophilic attack occurs preferentially at C-1.

c.



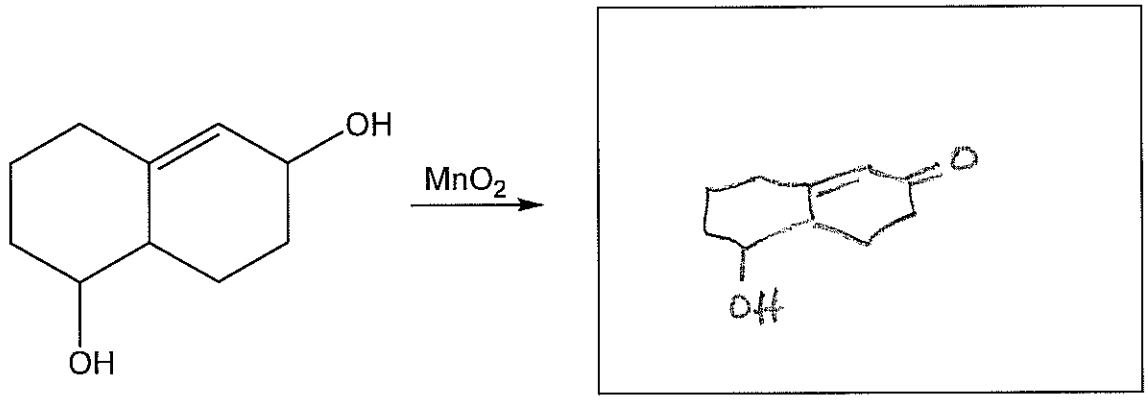
Complete the stencil above, showing clearly stereochemistry (hashed and wedged bonds).

d.

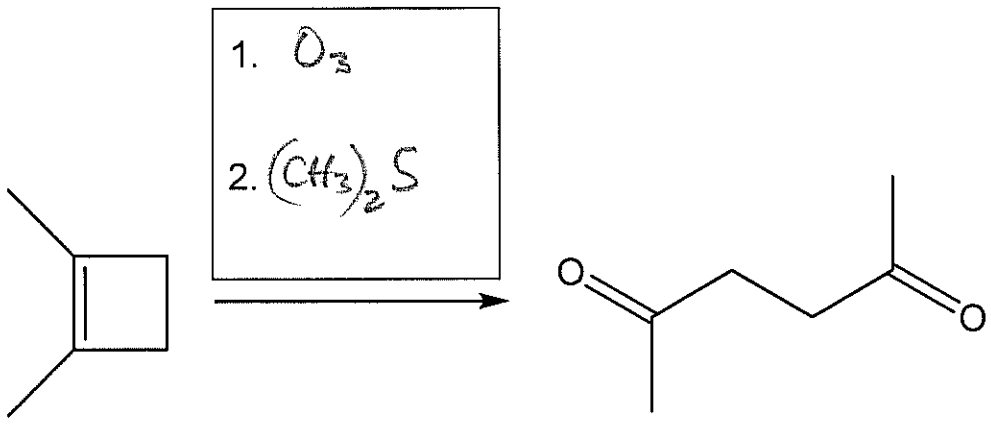


Product of ring **opening**

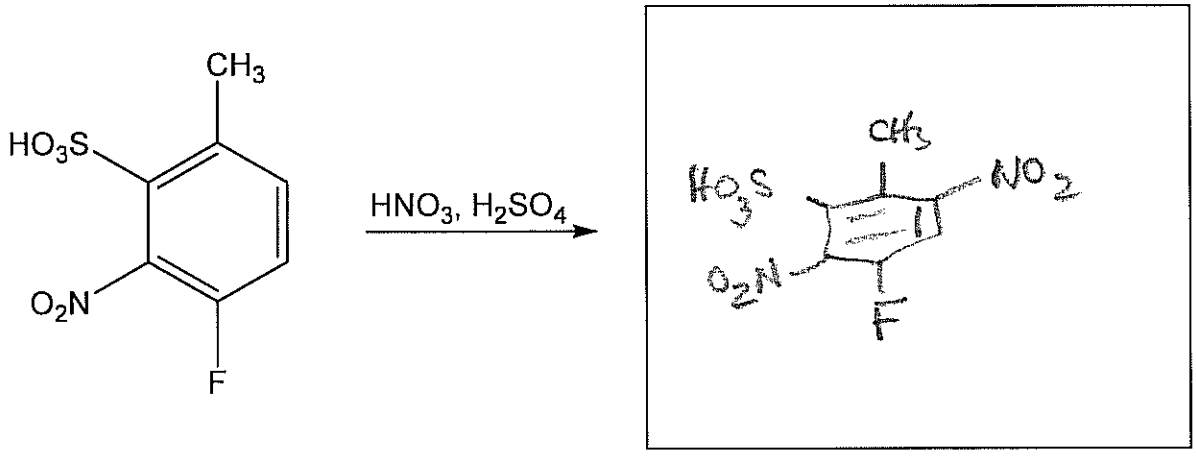
e.



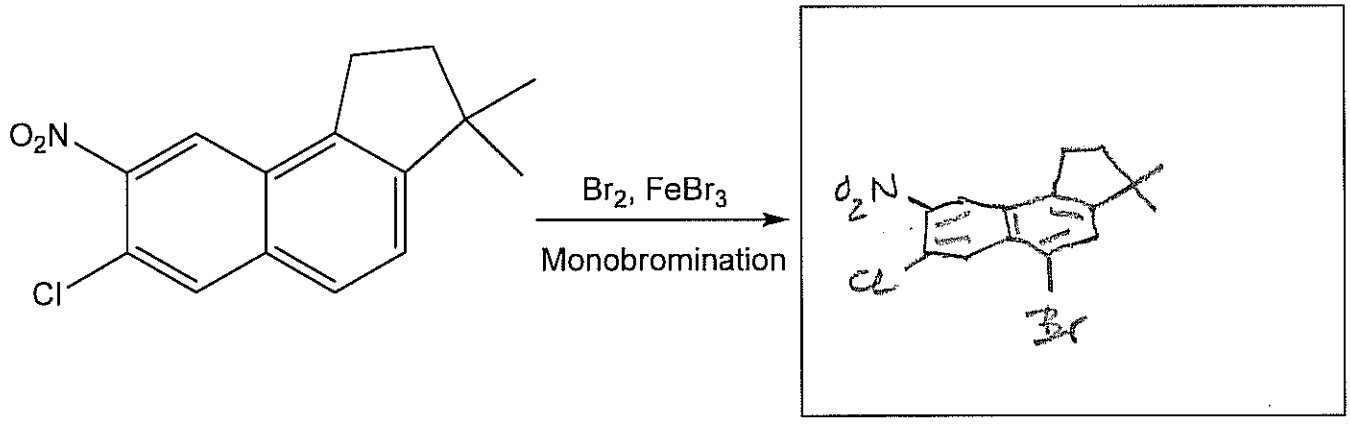
f.


1. O_3
2. $(CH_3)_2S$
O
O

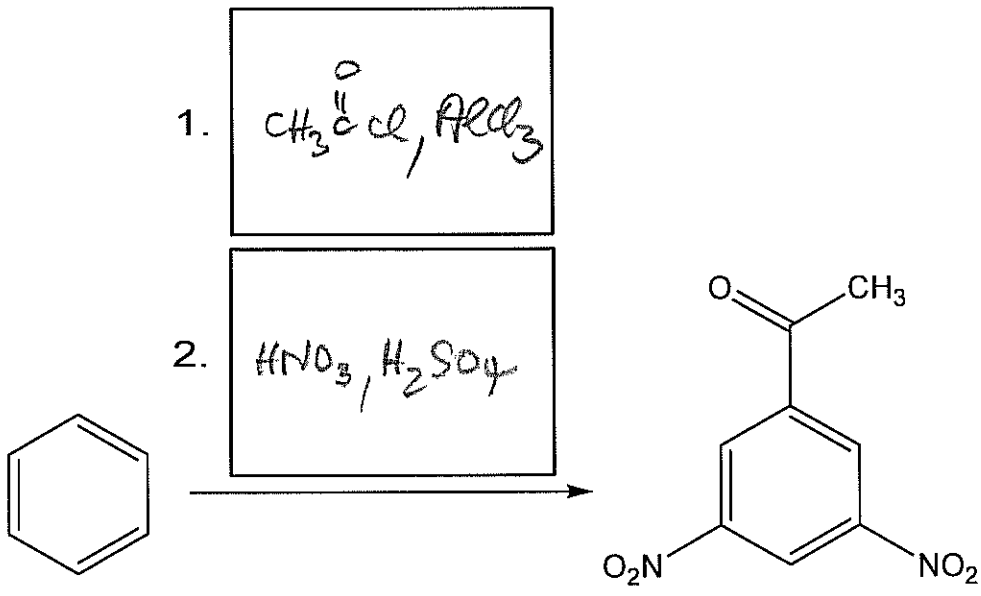
g.


CH_3
HO_3S
O_2N
F
HNO_3, H_2SO_4
CH_3
HO_3S
NO_2
O_2N
F

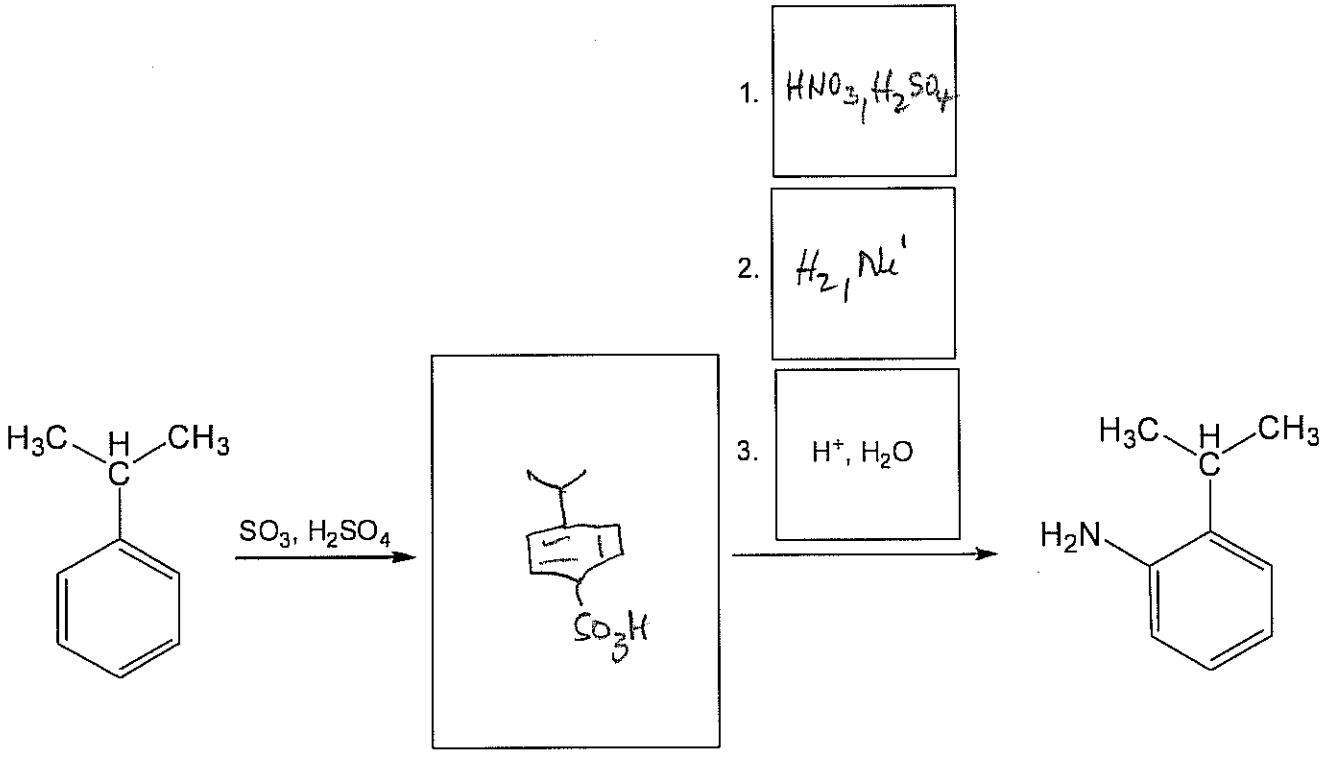
h.


O_2N
Cl
Br_2, $FeBr_3$
Monobromination
O_2N
Cl
Br

i.

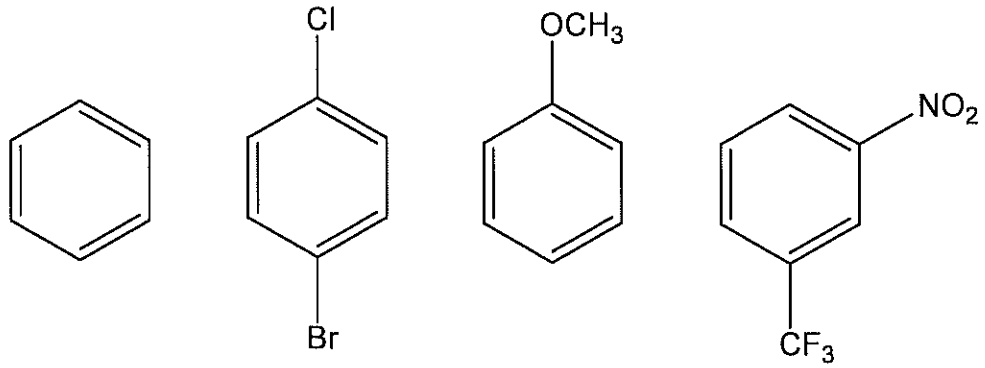

1.
$CH_3COCl, AlCl_3$
2.
HNO_3, H_2SO_4
O
CH_3
O_2N
NO_2

j.


1. HNO_3, H_2SO_4
2. H_2, Ni
3. H^+, H_2O
H_3C H CH_3
C
SO_3, H_2SO_4
SO_3H
H_2N

IV. [40 Points]

a. Rank the following arenes in order of reactivity (highest to lowest) toward electrophilic aromatic substitution. Mark the box next to the best answer below.



1 **2** **3** **4**

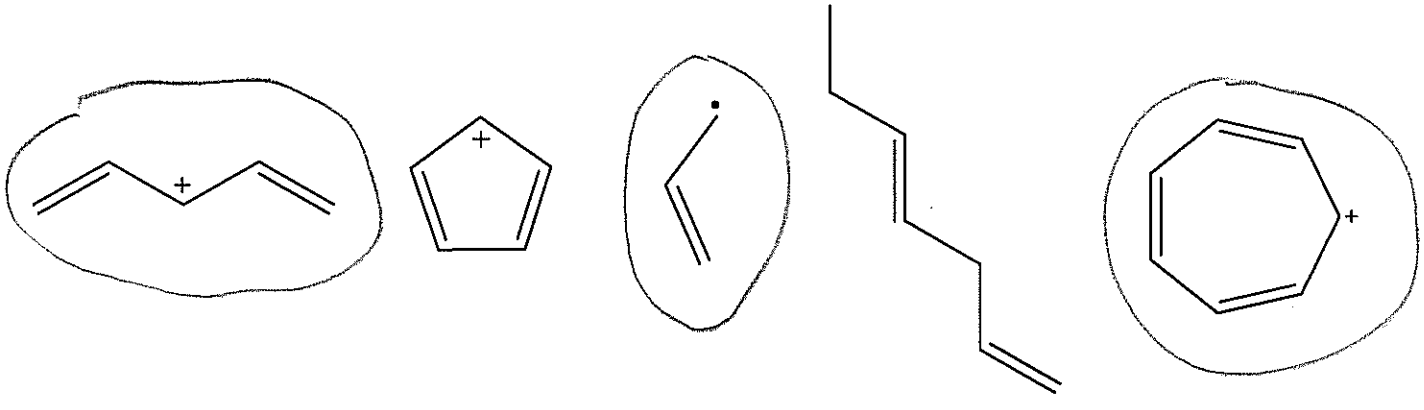
☐ **1, 2, 3, 4**

☒ **3, 1, 2, 4**

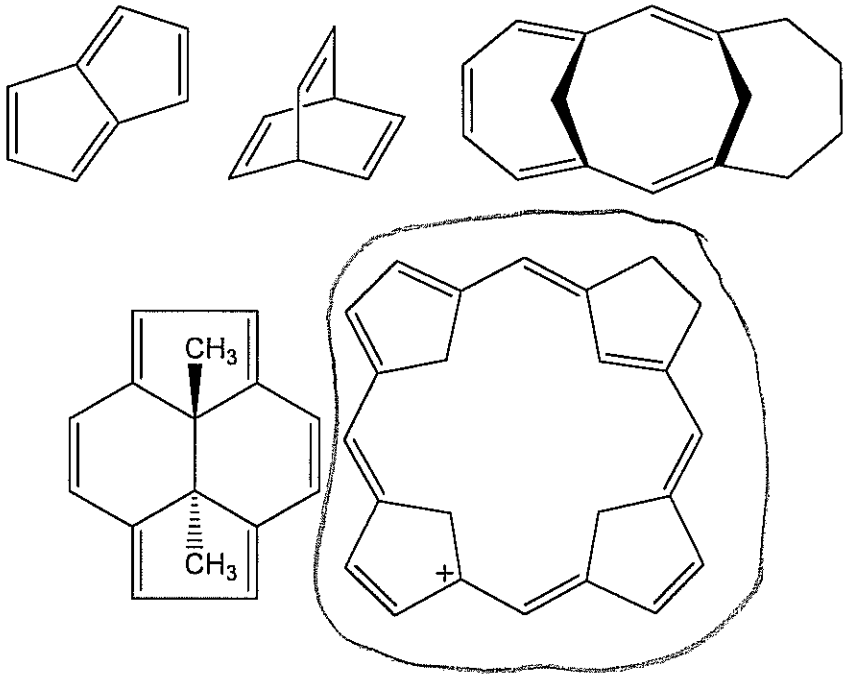
☐ **3, 2, 1, 4**

☐ **3, 1, 4, 2**

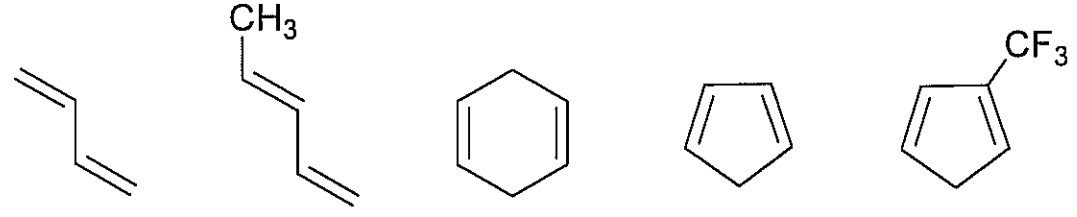
b. Among the compounds shown below, circle those that are **stabilized** by conjugation.



c. One of the compounds shown below is aromatic. Circle its structure.



d. Rank compounds **1–5** in order of **increasing** reactivity as dienes in the Diels-Alder reaction:



1 **2** **3** **4** **5**

☐ **1, 2, 3, 4, 5**

☐ **1, 4, 2, 3, 5**

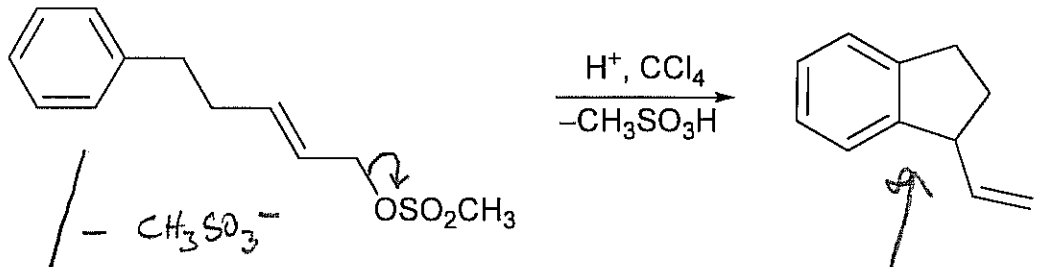
☐ **3, 1, 5, 4, 2**

☐ **5, 3, 1, 4, 2**

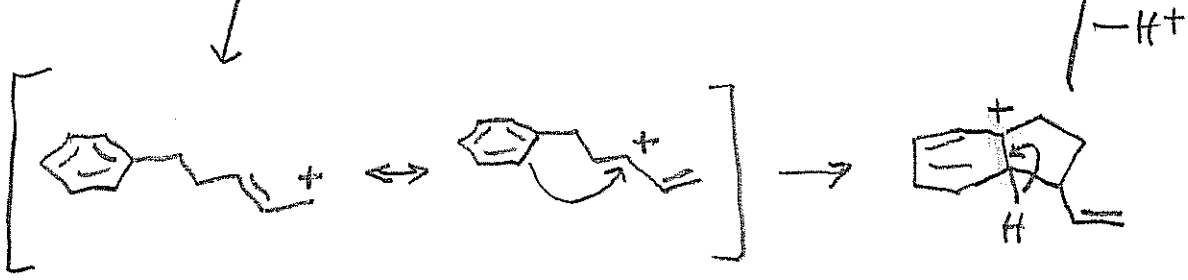
☒ **3, 5, 1, 2, 4**

V. [40 Points] Write detailed stepwise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are not synthetic problems. Do not add any reagents! What you see is what you have!

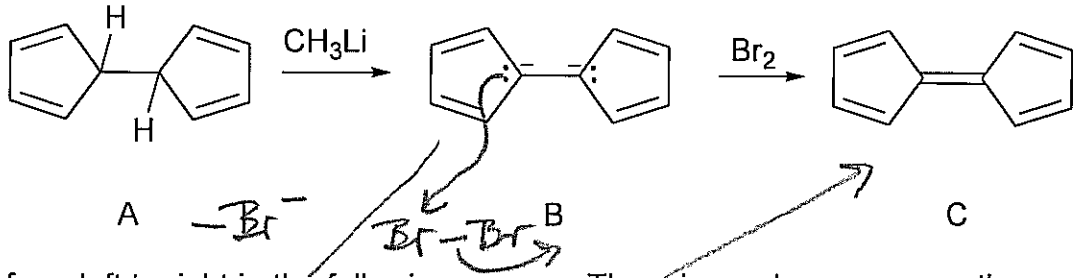
a.



Work from left to right in the following spaces. There is much more space than you will need.



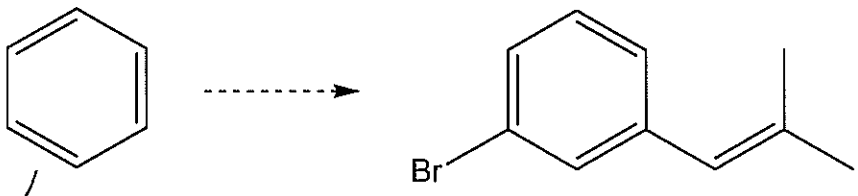
b. Hydrocarbon A is doubly deprotonated by methyllithium to give the aromatic dianion B. Treatment of B with bromine at low temperatures gave C. Write a plausible mechanism that leads from B to C.



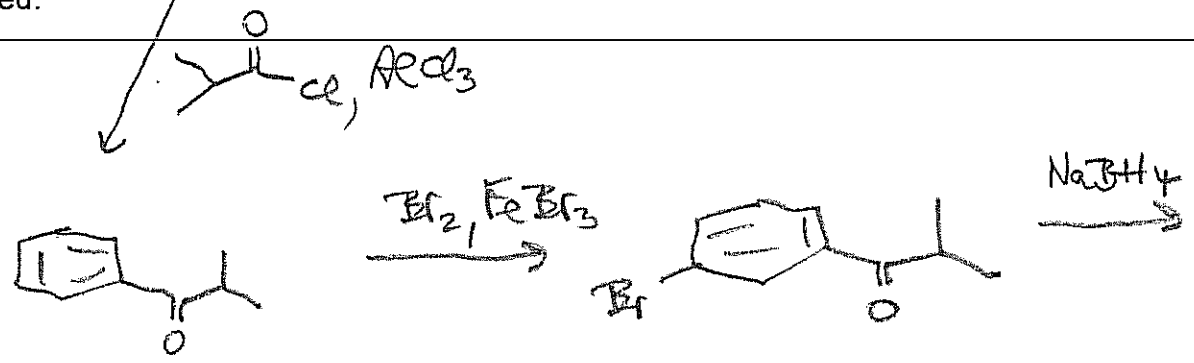
Work from left to right in the following spaces. There is much more space than you will need.

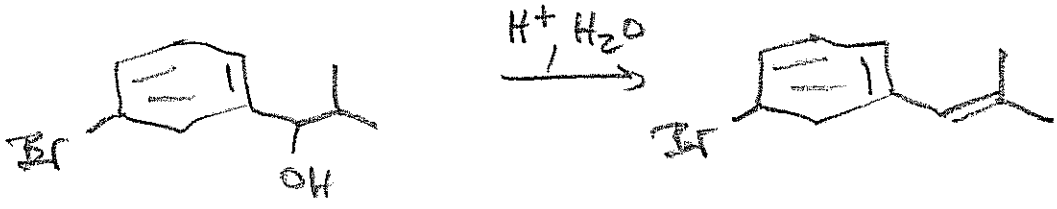
VI. [40 Points] Provide a reasonable synthetic route from starting material to product. Note: Several steps are required, and there may be more than one solution to the problem. Do not write mechanisms! Write out each step separately, including reagents and products.

a.

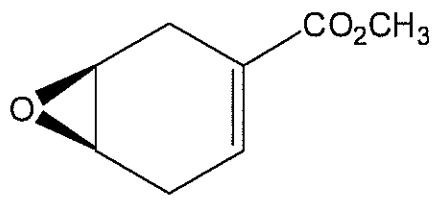


Work from left to right in the following spaces. There is much more space than you will need.



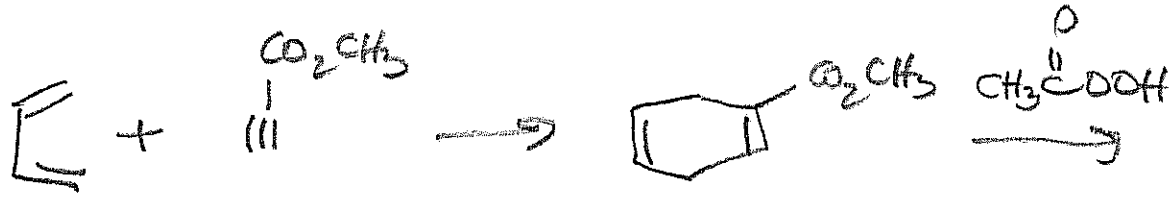


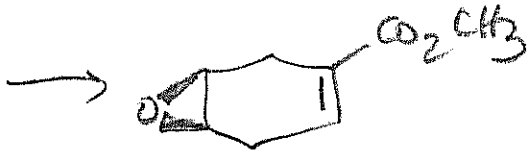
b. Synthesize compound A from any **acyclic** materials and any other reagent.
Hint: Think Diels-Alder reaction. **Caution:** Work backwards.



A (racemate)

Work from left to right in the following spaces. There is much more space than you will need.





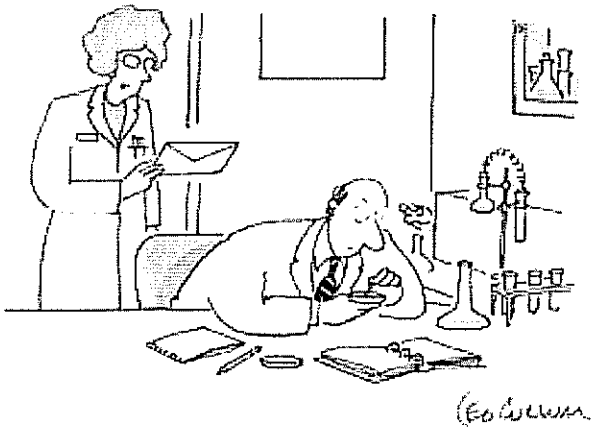
VII. [20 Points] Place an X mark in the box next to the most accurate statement.

a. The Diels-Alder reaction is made possible because

- [ ] a racemate is formed
- [ ] the (4*N*+2) rule overrides the Lewis octet rule
- [ ] of two isomeric products the less stable one is formed
- [ ] the reaction requires heat to go to completion
- [X] an aromatic transition state

b. The bromine substituent in bromobenzene directs electrophiles ortho/para because

- [ ] it is inductively donating
- [ ] it is inductively electron-withdrawing
- [X] it stabilizes the cationic intermediates by resonance
- [ ] it is sterically hindered
- [ ] it is an electron acceptor by resonance



"It says 'you may already be a Nobel Prize winner'."

♫ The End ♫