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 22, 2011

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

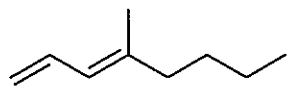
Please write the answer you wish to be graded in the spaces provided. ***Do scratch work on the back of the pages***. This test should have **14** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make 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

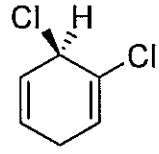
I.		**(30)**
II.		**(30)**
III.		**(50)**
IV.		**(40)**
V.		**(40)**
VI.		**(40)**
VII.		**(20)**
Total:		**(250)**

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. (*E*)-4-Methylocta-1,3-diene

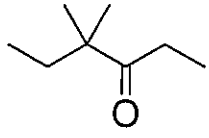


b. (*R*)-1,6-Dichlorocyclohexa-1,4-diene



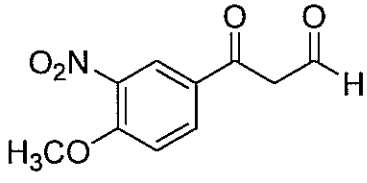
Use the stencil and its numbering.

c.



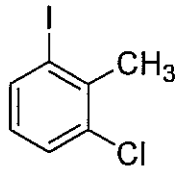
4,4-Dimethylhexan-3-one

d.



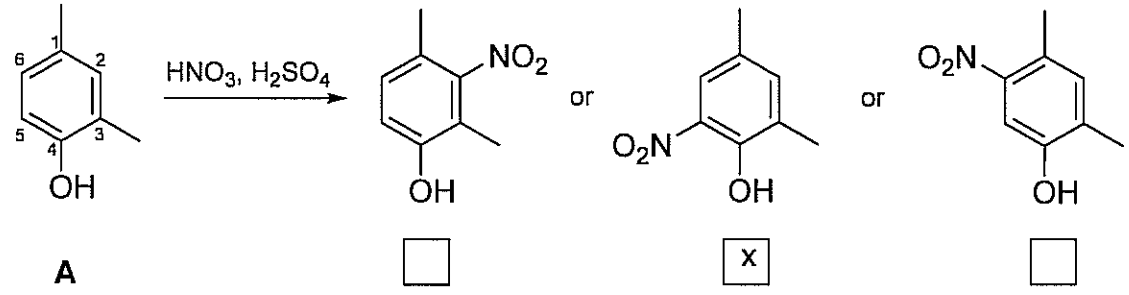
3-(4-Methoxy-3-nitrophenyl)-3-oxopropanal

e.



1-Chloro-3-iodo-2-methylbenzene

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



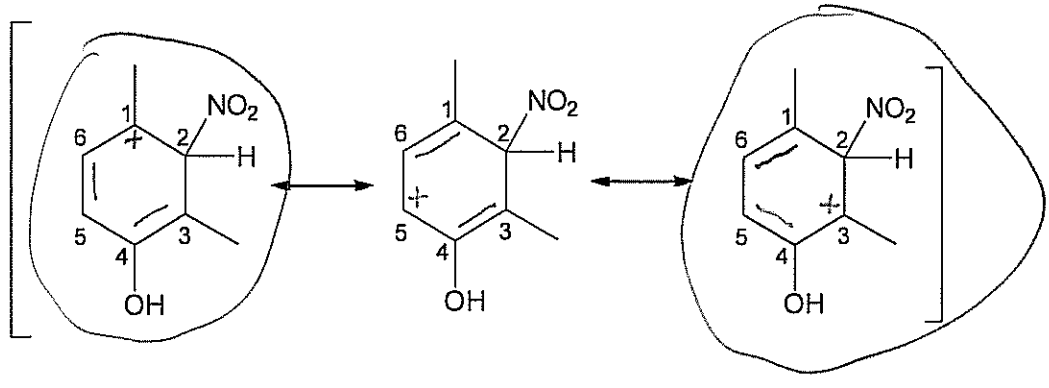
A

☐ ☒ ☐

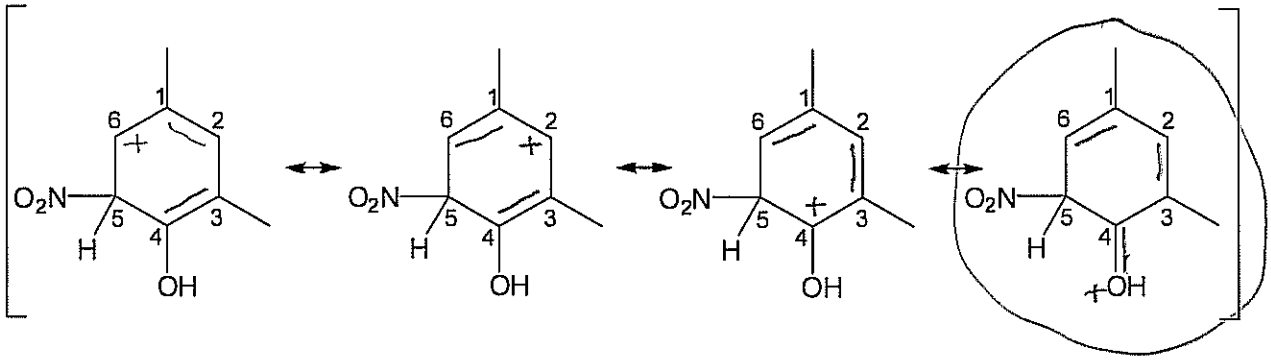
a. Which one? Mark the box below your choice with an X, **preferably after you have completed questions b.–d.**

b. Write all the resonance forms of the intermediate formed by attack of NO_2^+ on **A** at the positions indicated. A first stencil is provided for format. Leave out the numbering in any additional structures.

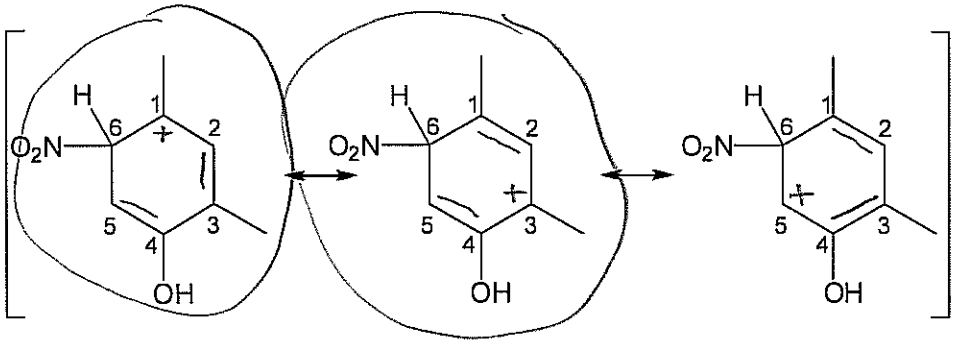
C-2:



C-5:

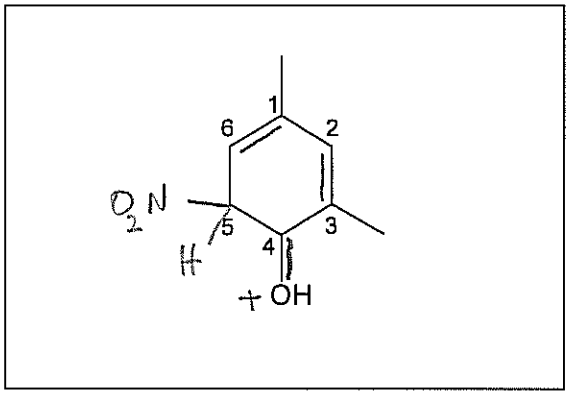


C-6:



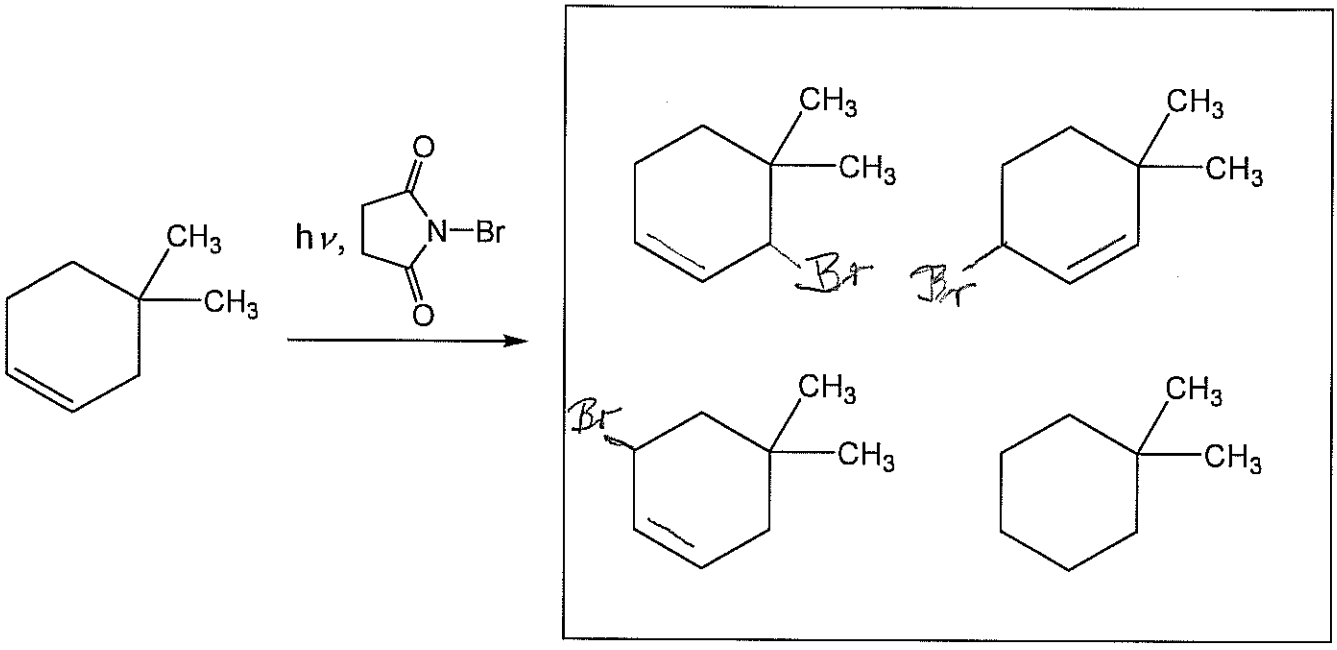
c. Circle (in your answers above) the **most strongly** contributing resonance forms of the attack at C-2, C-5, and C-6, respectively.

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



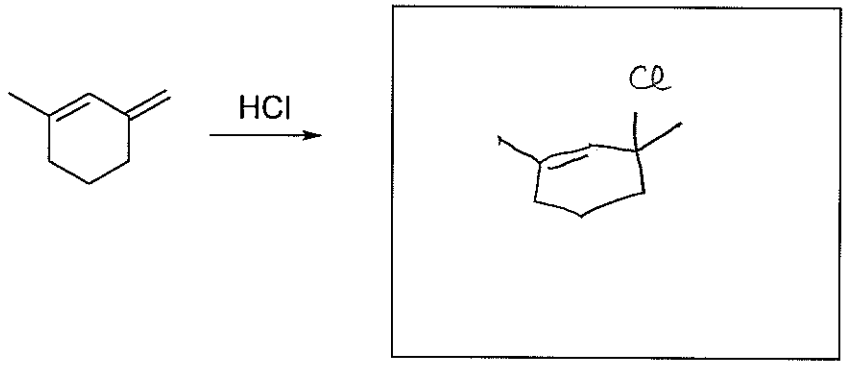
III. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Show **relative** stereochemistry when appropriate (**not enantiomers**). Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

a.

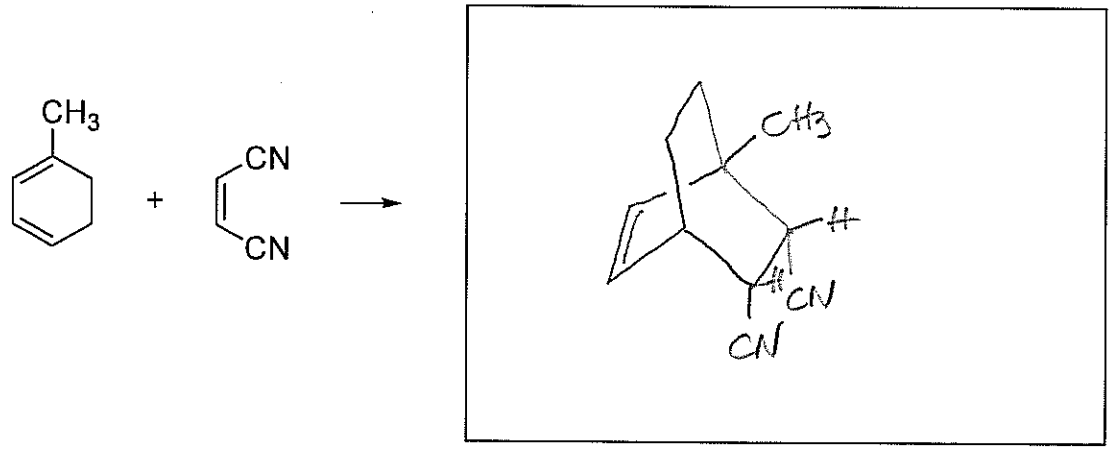


Several isomers (not enantiomers). Add the missing pieces.

b.

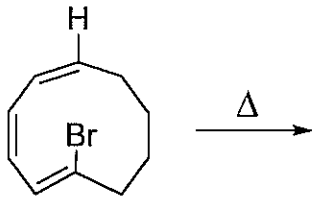


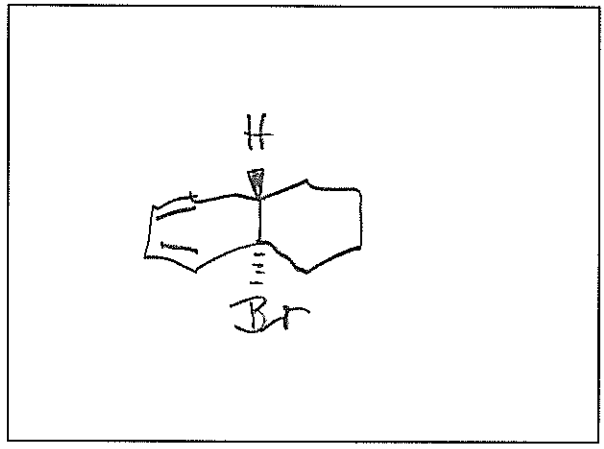
c.



Show stereochemistry (not enantiomers) clearly.

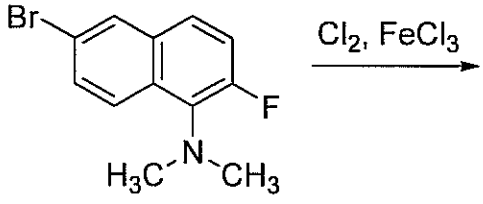
d.

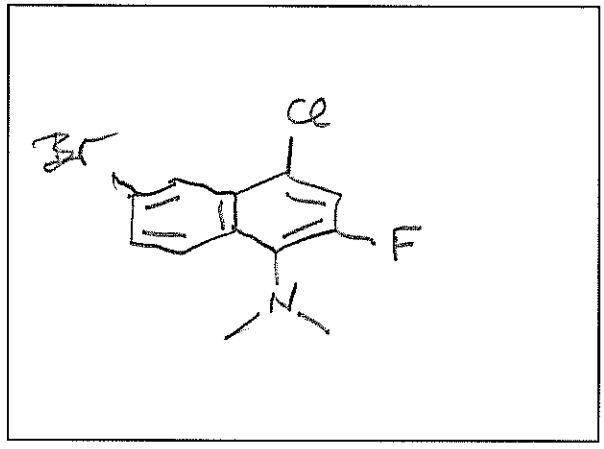




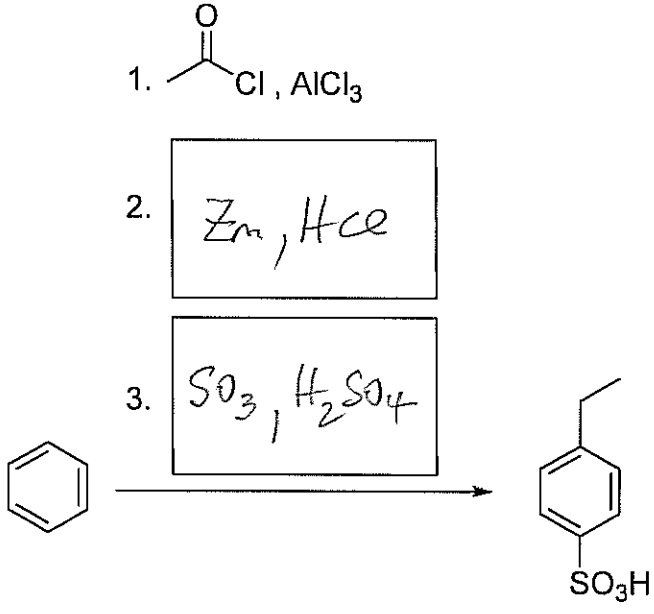
Product of ring ***closure***

e.

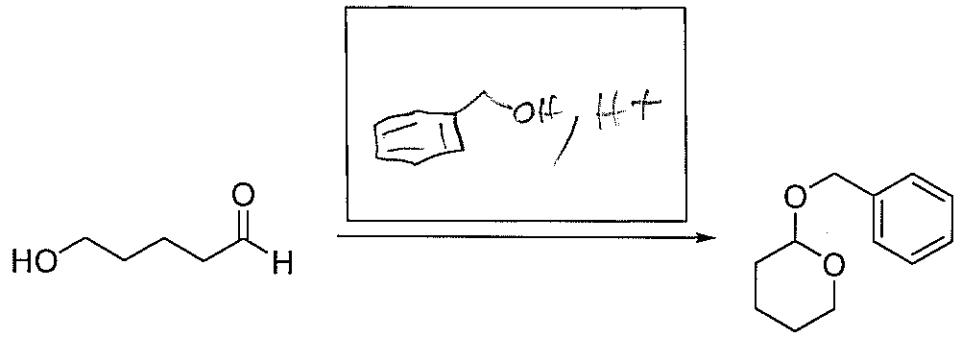




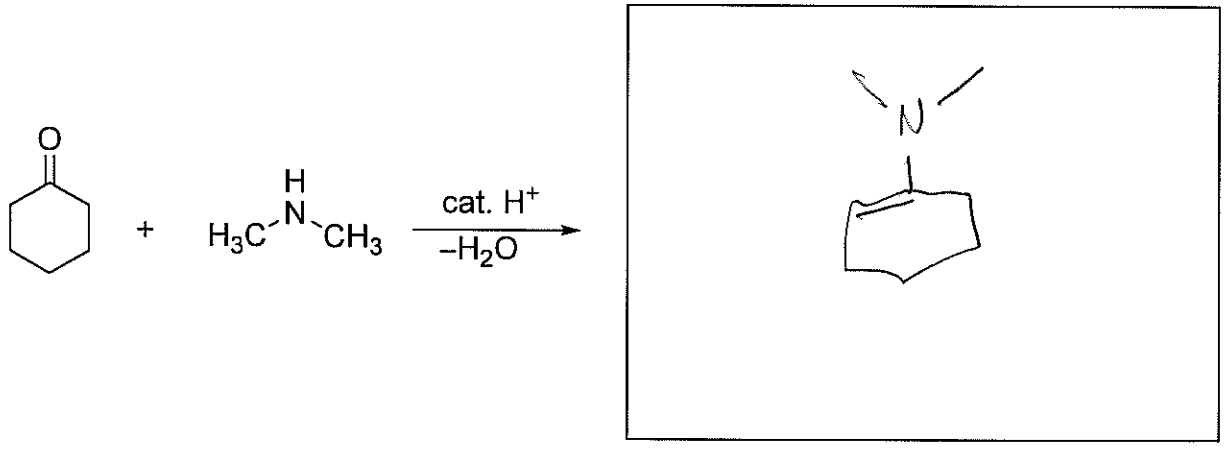
f.



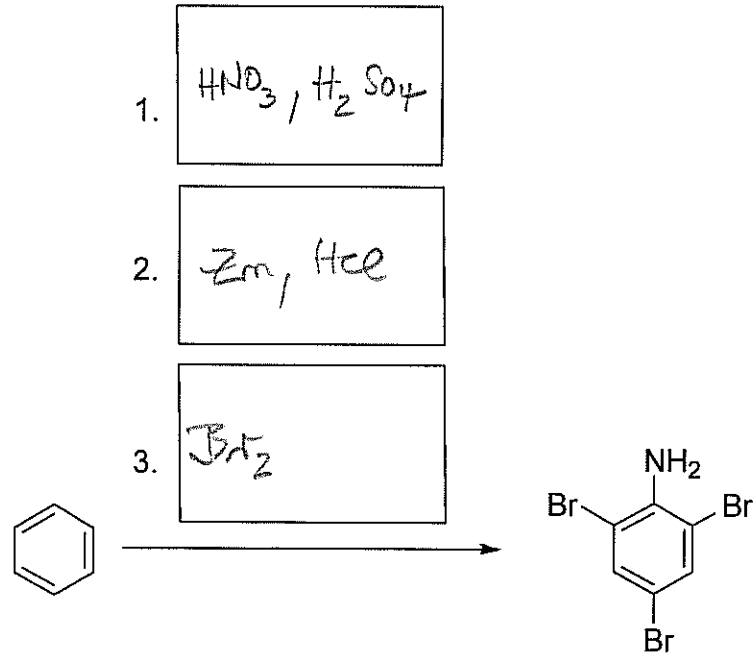
g.


OH, H+
HO
O
H
O
O

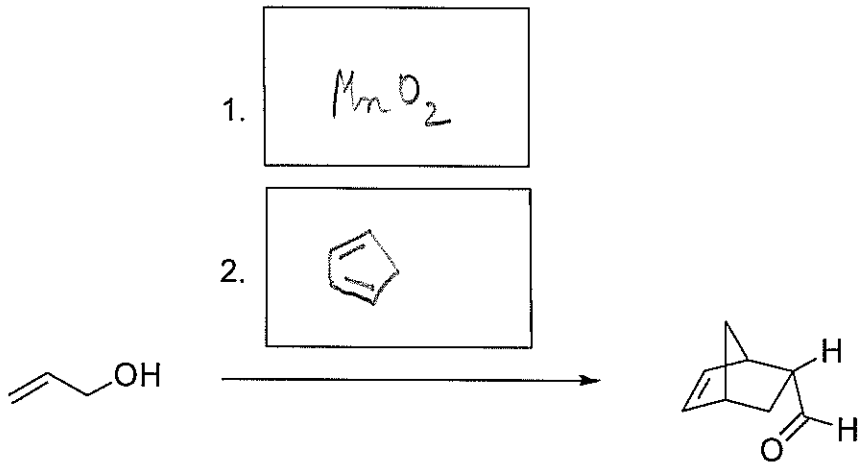
h.


O
+
H
N
H3C
CH3
cat. H+
–H2O
N

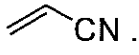
i.


1.
HNO3, H2SO4
2.
Zn, HCl
3.
Br2
NH2
Br
Br
Br

j.



IV. [40 Points]

a. Rank the following dienes in order of reactivity (**highest to lowest**) toward Diels-Alder reaction with 

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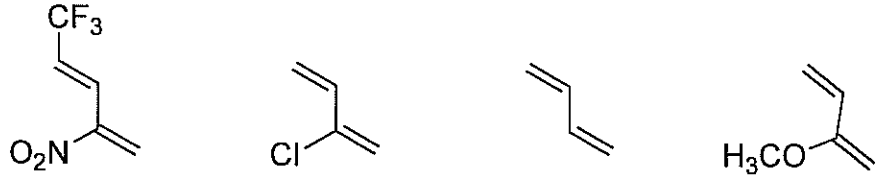
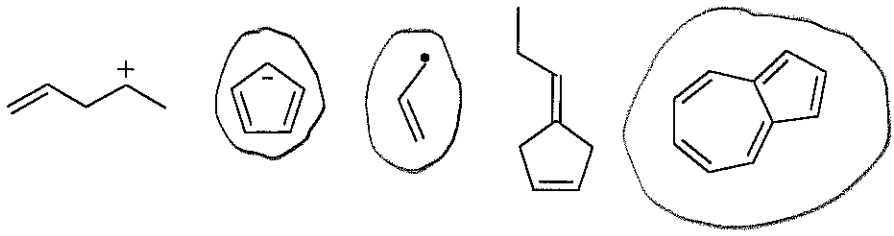
Mark the box next to the best answer below.



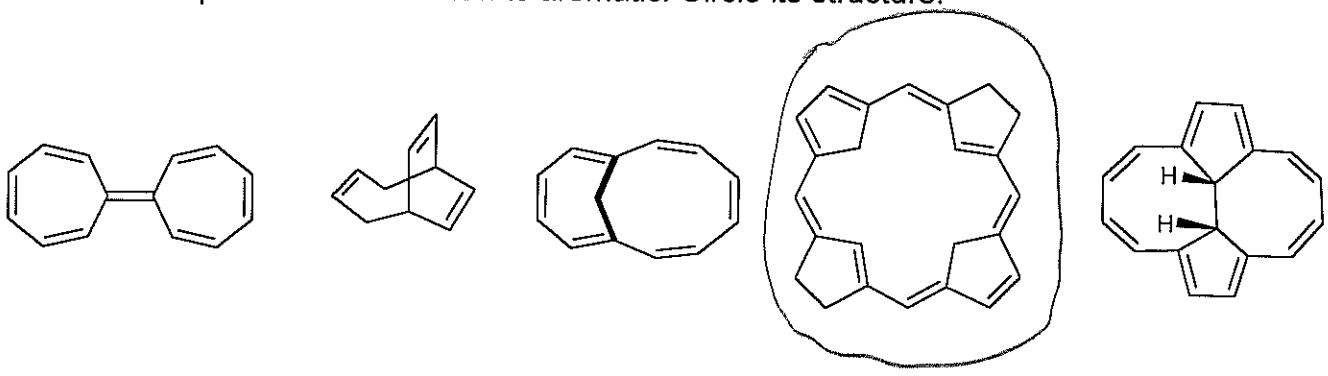
1 **2** **3** **4**

- [ ] **1, 2, 3, 4**
- [ ] **3, 1, 2, 4**
- [x] **4, 3, 2, 1**
- [ ] **3, 1, 4, 2**

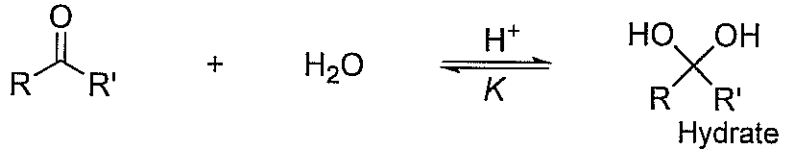
b. Among the compounds shown below, circle those that are ***stabilized*** by resonance.

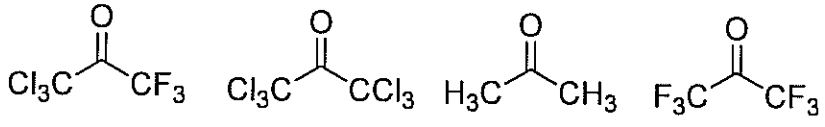


c. One of the compounds shown below is aromatic. Circle its structure.



d. Rank the carbonyl compounds **1–4** in order of ***increasing*** *K* of the equilibrium with their hydrates:



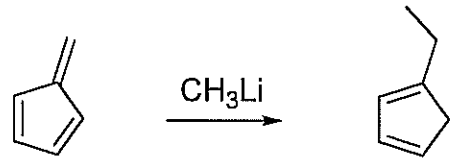


1 **2** **3** **4**

- [X] **3, 2, 1, 4**
- [ ] **1, 4, 2, 3**
- [ ] **3, 1, 4, 2**
- [ ] **2, 3, 4, 1**

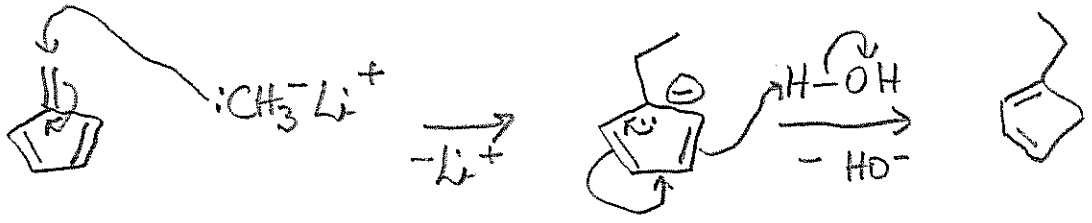
V. [40 Points] Write detailed stepwise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are not synthetic problems. Do not add any reagents! What you see is what you have!

a.

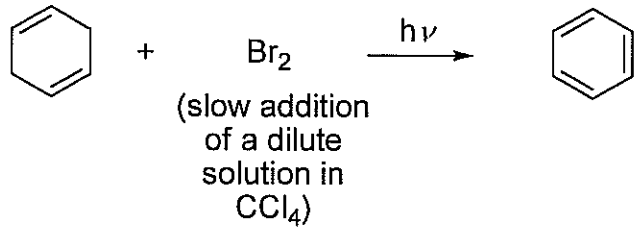


(After aqueous work-up)

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



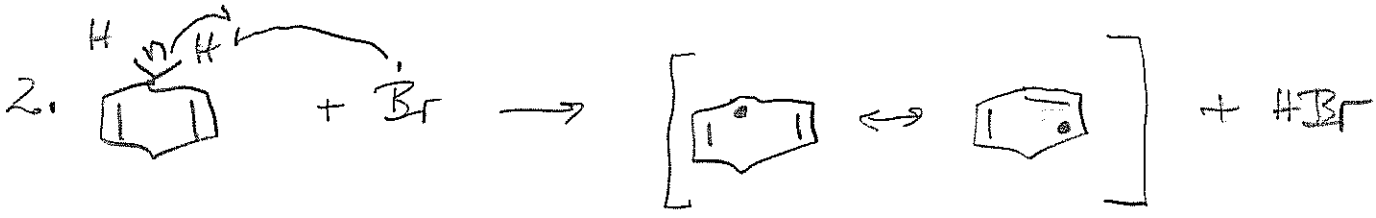
b.



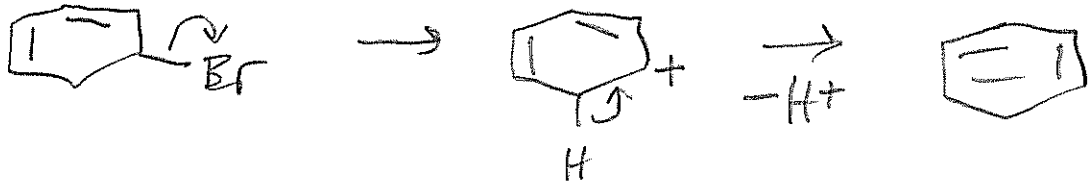
Work from left to right in the following spaces. There is much more space than you will need.

1.

2.

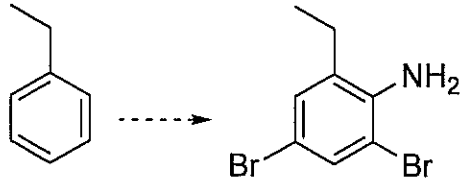


3.

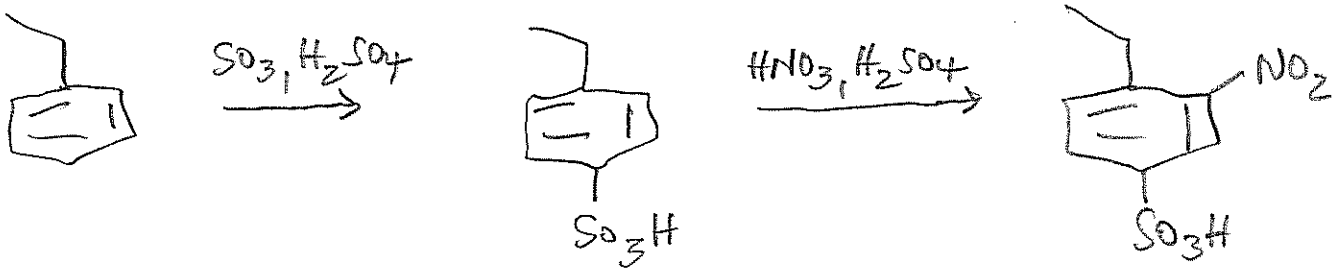


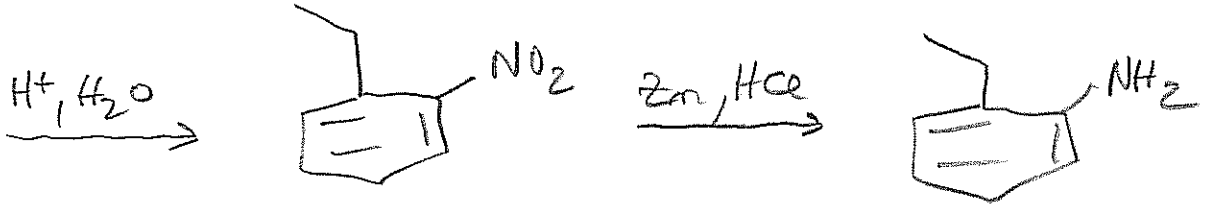
VI. [40 Points] Provide a reasonable synthetic route from starting material to product. Note: Several steps are required, and there may be more than one solution to the problem. Do not write mechanisms! Write out each step separately, including reagents and products. Work backwards.

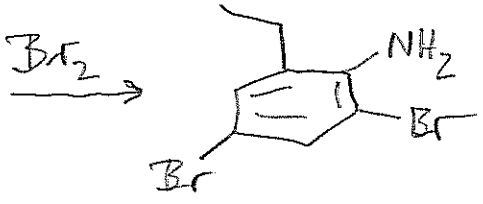
a.



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







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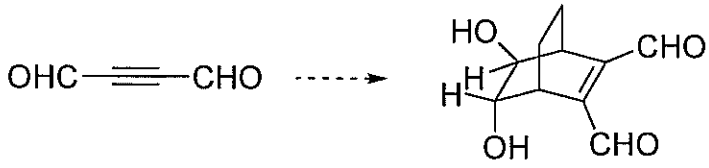
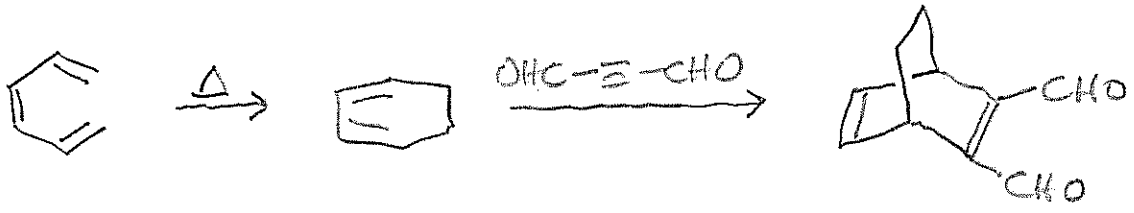
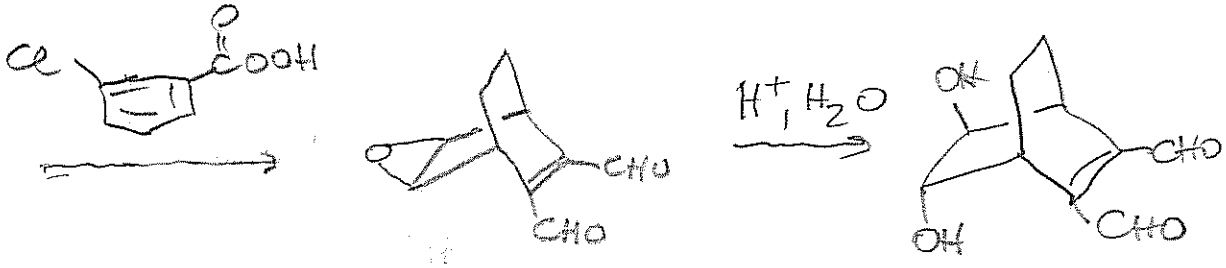
b. Synthesize compound **A** from any **acyclic** materials. **Hint:** Think Diels-Alder reaction. Work backwards.



A (racemate)

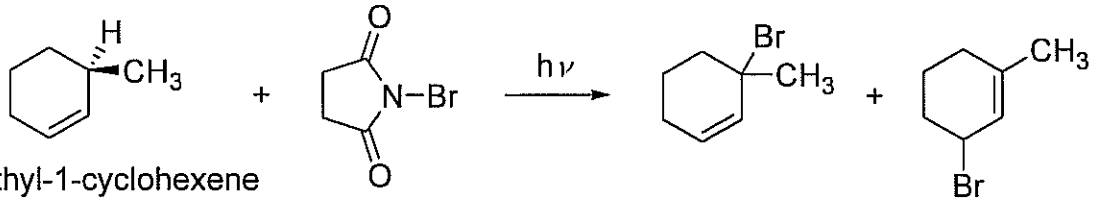
Work from left to right in the following spaces. There is much more space than you will need.





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

a. In the following reaction:



(*R*)-3-Methyl-1-cyclohexene

[X] the products are racemic

[ ] the two products are enantiomers

[ ] the reaction requires heat to allow complete conversion

[ ] the two products are diastereomers

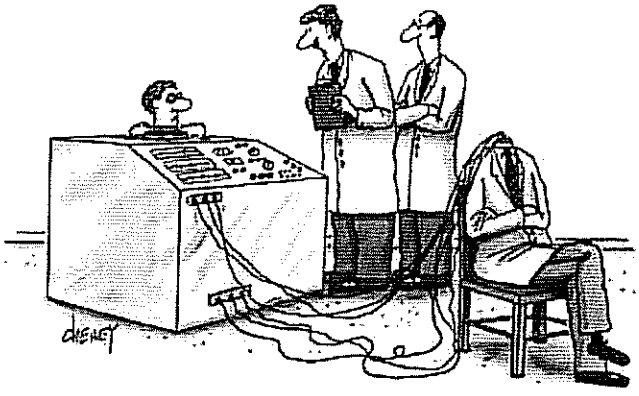
b. The nitro substituent in nitrobenzene directs electrophiles meta because

[ ] it is inductively donating

[X] it is electron-withdrawing by induction and resonance

[ ] it is sterically hindered

[ ] it has formal charges



"Bad news, Phil—due to federal funding cutbacks, we can't afford to put your head back on."

♫ The End ♫