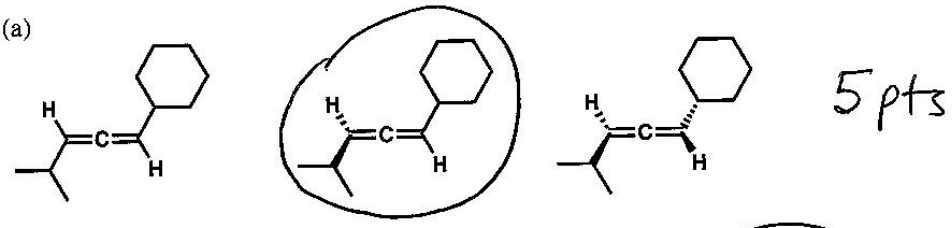
Question 1

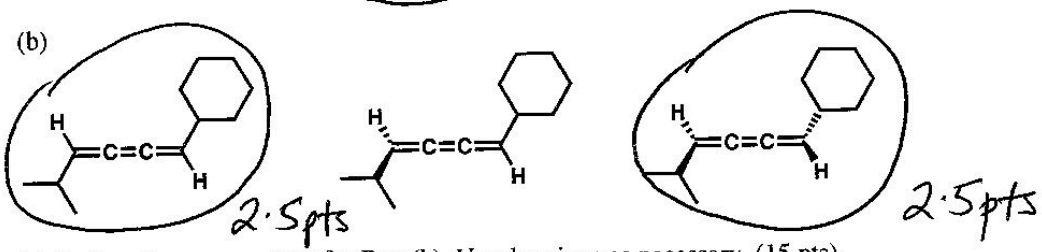
Circle the correct structural representations for the following cumulenes in Part (a) and Part (b) (5 pts each)

(a)



5 pts

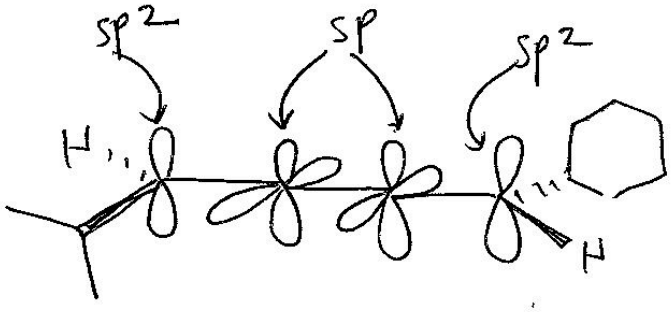
(b)



2.5 pts

2.5 pts

(c) Rationalize your answer for Part (b). Use drawings as necessary. (15 pts)



Drawing 10 pts

Mentioning hybridization 5 pts.

Question 2

(a) Provide a rationalization for why the equilibrium in the equation above lies toward **B** at relatively low temperature (e.g., 25 °C) (10 pts). $\Delta G = \Delta H - T\Delta S$

Explanation should be with regard to change in enthalpy dominating ΔG +5

+5 [i.e., cleave 2 π bonds (~66 kcal/mol) and make 2 C–C bonds (~90-100 kcal/mol)

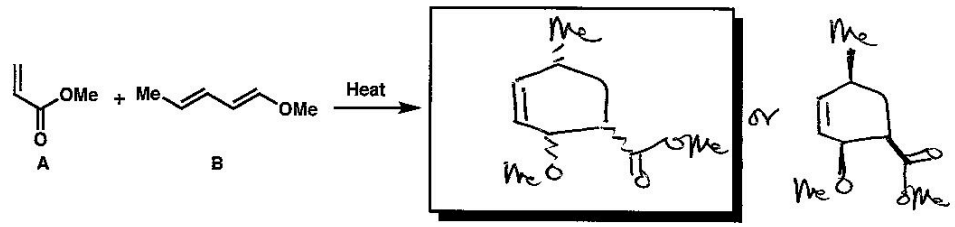
(b) Why does the equilibrium lie toward **A** at higher temperature (e.g., >150 C)? (10 pts)

+5 Entropy dominates ΔG, which means

+5 [equilibrium lies toward A because of increase in entropy

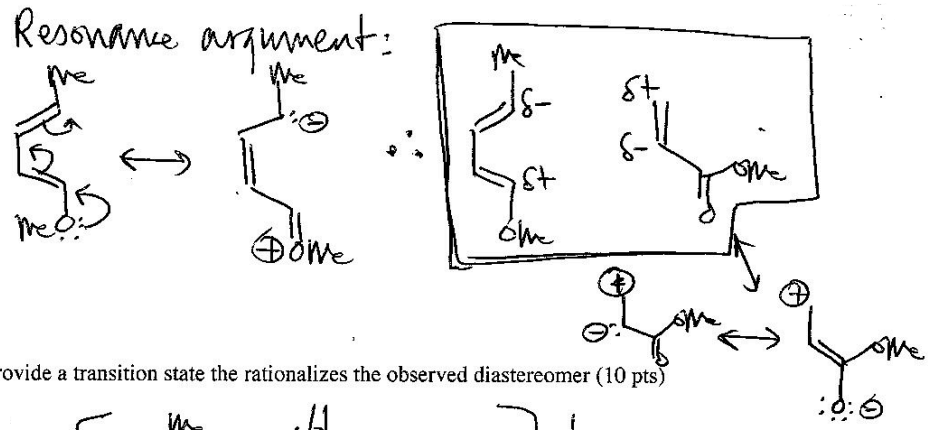
Question 3

(a) Predict the major product (with stereochemistry) of the following Diels-Alder reactio between **A** and **B** (Show only one enantiomer).

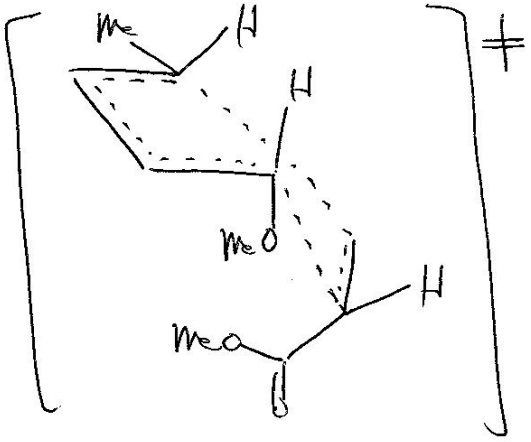


(5 pts)

(b) Provide rationalization for the observed regioisomer. (5 points)

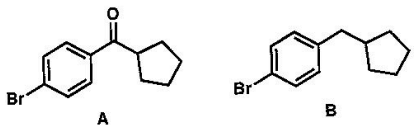


(c) Provide a transition state the rationalizes the observed diastereomer (10 pts)



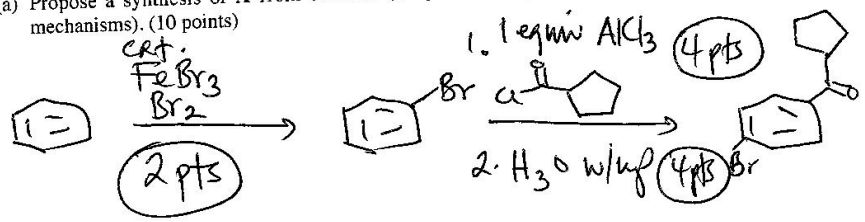
−2 for not showing partial bonds.

Question 4



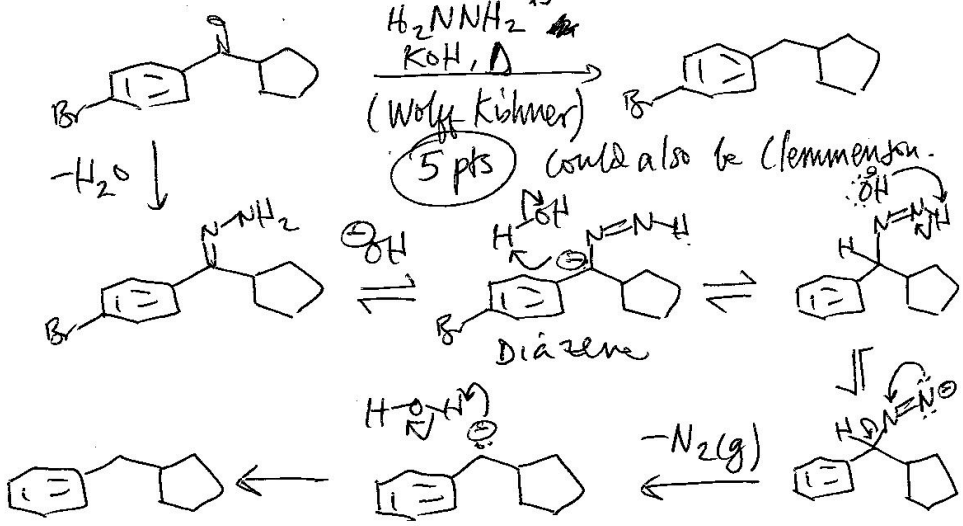
A B

(a) Propose a synthesis of **A** from benzene (Only show reagents. Do not show mechanisms). (10 points)



(b) Propose reagents and a mechanism of how **A** would be converted to **B** (15 points)

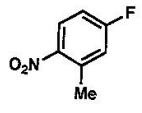
rxn arrows: +1/arrow



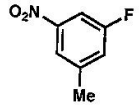
They may also show a concerted mechanism for loss of N_2 from diazene

Question 5

A reacts more than 10^3 times faster than **B** in a nucleophilic aromatic substitution reaction. Provide a rationalization for this observation (20 points).



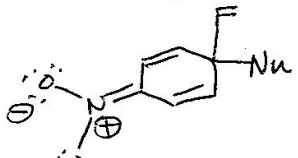
A



B

The rate limiting step is the formation of the Meisenheimer complex. Stabilization of the Meisenheimer complex is reflected in the transition state (Hammond postulate) (10 pts)

For A:

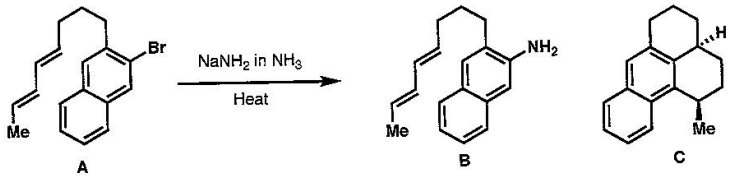


10 pts

This is a big resonance contributor that leads to stabilization. We do not have this for B.

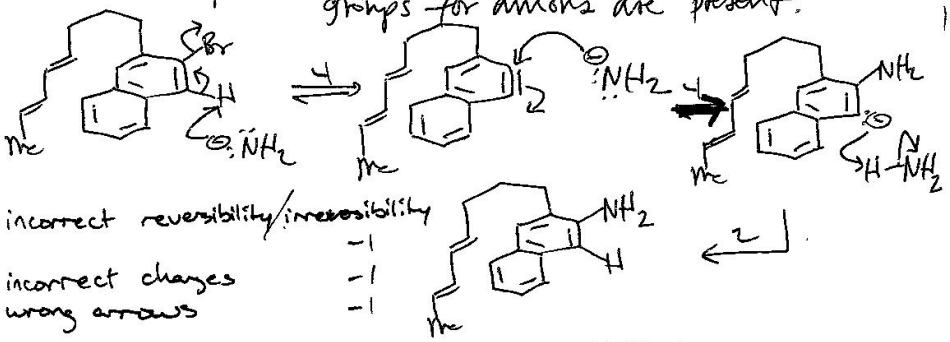
Question 6

A reacts with $NaNH_2$ in ammonia to give multiple products, which includes **B** and **C**.



(a) Provide a mechanistic rationalization for the formation of **B** (10 pts)

Benzyne-S; cannot be S_NAr b/c no stabilizing groups for anions are present.



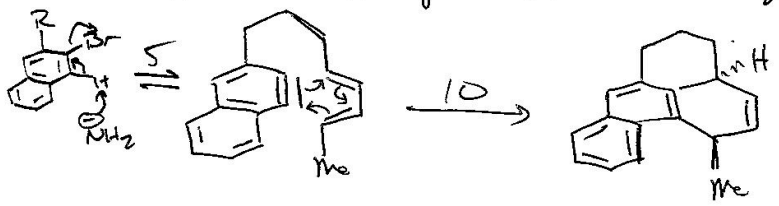
incorrect reversibility/irreversibility −1

incorrect charges −1

wrong arrows −1

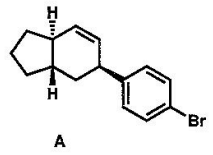
(b) Provide a mechanistic rationalization for the formation of **A** (15 pts)

Diels-Alder of intermediate benzyne



Question 7

Propose a synthesis that gives **A** as the major product starting from the Chem 112B stockroom chemicals indicated and any other reagents of your choice that is four carbons or less. It is important to show all reagents and conditions in your synthesis. Use the next page if necessary (Hint: A Sandmeyer reaction is involved) (40 pts)



A