Chemistry 116 Sec. A (8:00-8:50)
Exam No. 3
"Reactivity of Alkynes, Arenes, Polyalkenes, and Free Radicals"
November 10, 2000

Instructions: You have until 8:55 a.m. to complete the exam. At that time, I will request that all remaining test takers cease writing, turn their exams over, and pass them to their rightmost isle. If you finish before 8:50 a.m. you may turn in the exam at the front of the room prior to leaving. If you finish within the final 5 min. of class, please turn your exam over and remain seated until I call for the remaining exams to be turned in. *In fairness to all, anyone still working on the exam after "time" is called will receive a grade of zero!*

Be sure to read the instructions for each question. It may be helpful to skim the entire exam and solve the easier questions first.

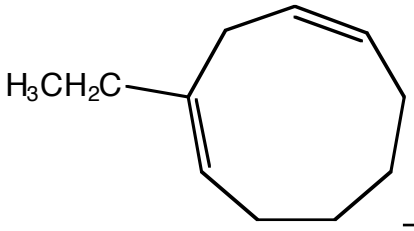
Exam Agreement: I, _____, have read and agree to
(Please print)
abide by the instructions above. On my honor, I have neither given nor accepted any help during this exam.

Signature: _____

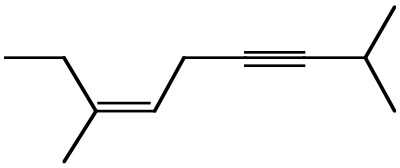
College: _____

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO

1. Provide an unambiguous name (IUPAC or common) for each of the following molecules. (6 points each)

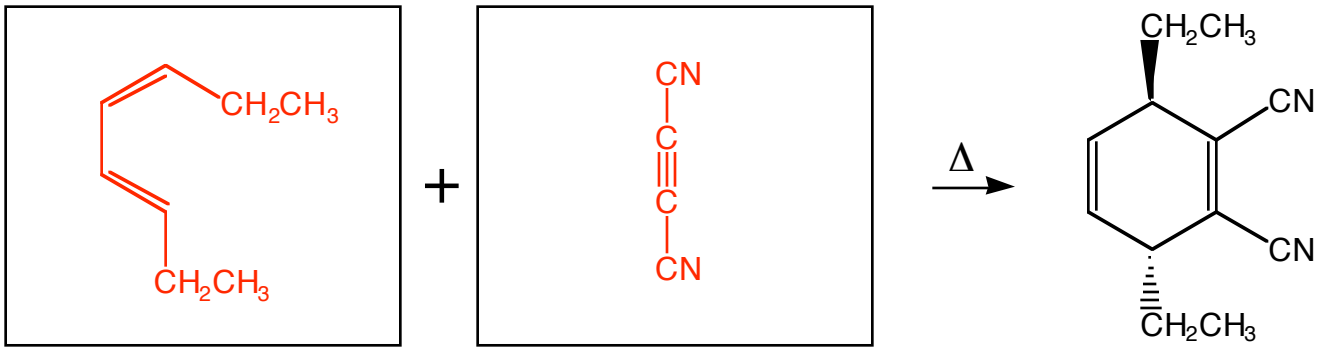


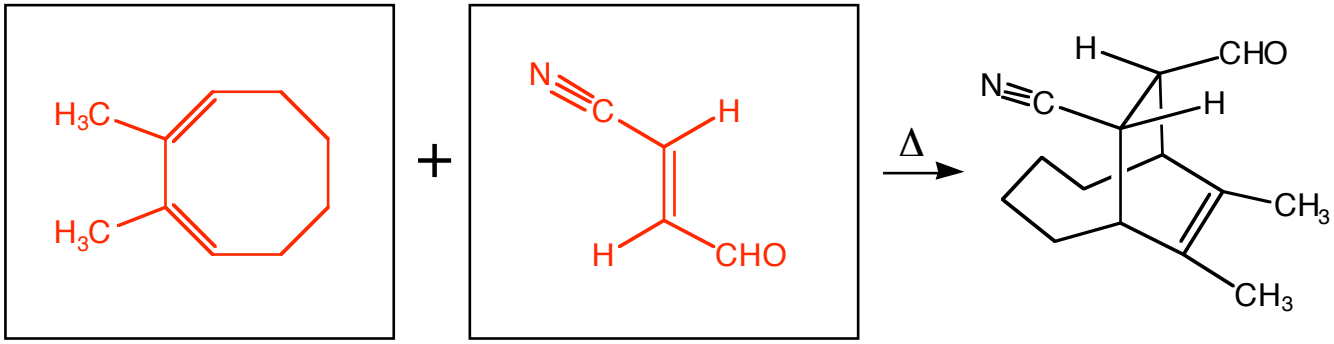
2-ethylcyclonona-1,4-diene
or
2-ethyl-1,4-cyclononadiene



(*Z*)-3,8-Dimethyl-non-3-en-6-yne

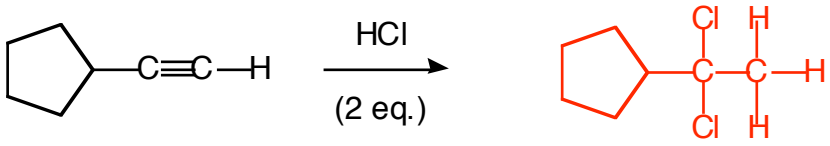
2. The following compounds can each be made from a Diels-Alder reaction. Show the starting material(s) necessary to achieve the reaction. (6 points each)



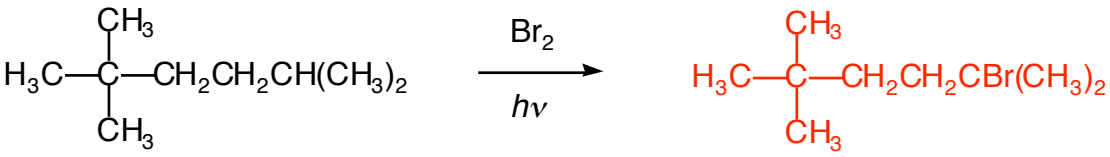


3. Predict the *major* product(s) for each of the following reactions and circle your final answer. Be sure to consider regiochemistry and stereochemistry in your answers. For problems where two or more products are formed in equal amounts, draw *all* of the products and circle each one. (6 points each)

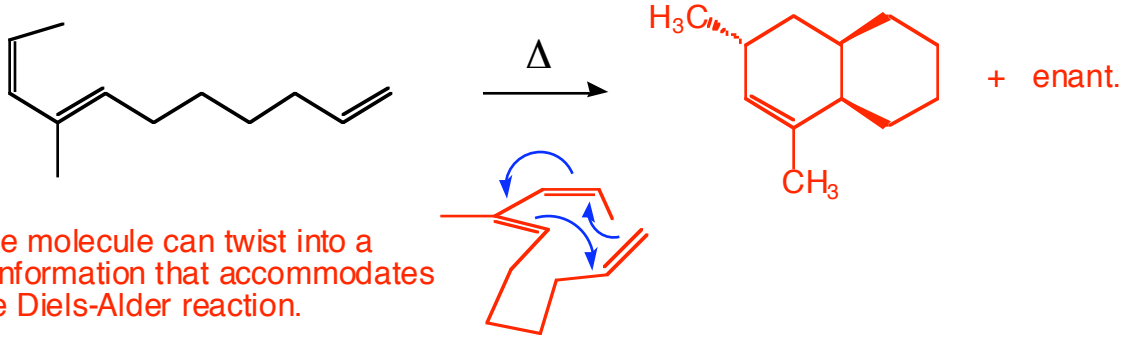
(a)



(b)

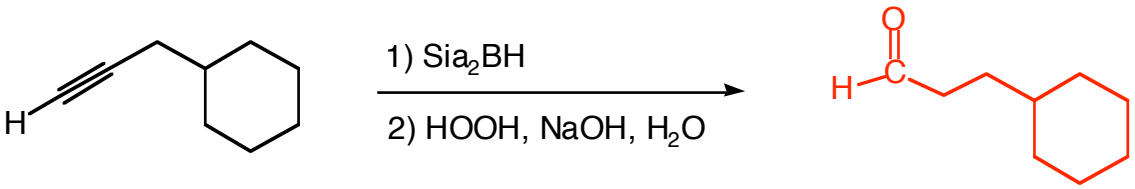


(c)

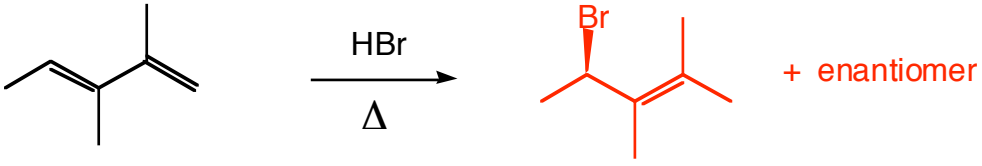


The molecule can twist into a conformation that accommodates the Diels-Alder reaction.

(d)

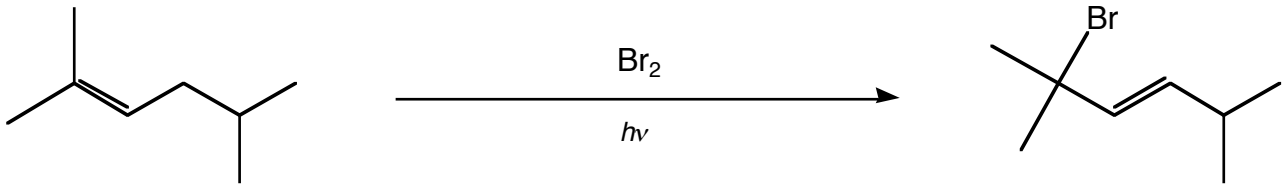


(e)

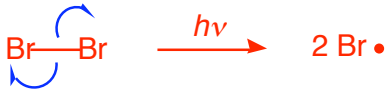


4. *Read these instructions carefully before proceeding*. Provide a mechanism for the following radical substitution reaction, paying close attention to the following details:

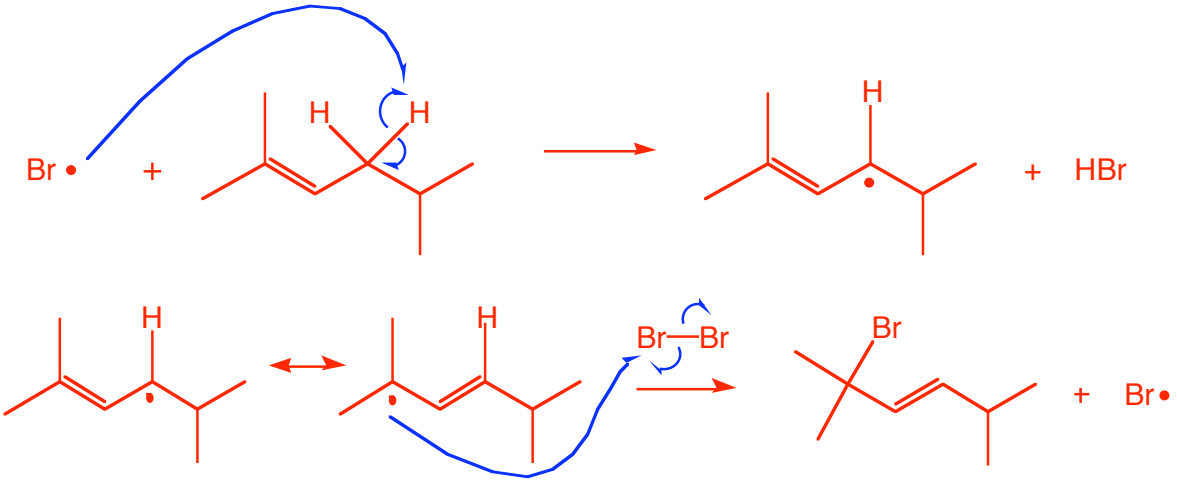
a) label the three major steps of the reaction,
b) include any intermediates *and* their resonance structures in your mechanism,
c) provide **at least 2** plausible termination steps
d) explain why the product shown is favored over any other possibilities. (16 points)



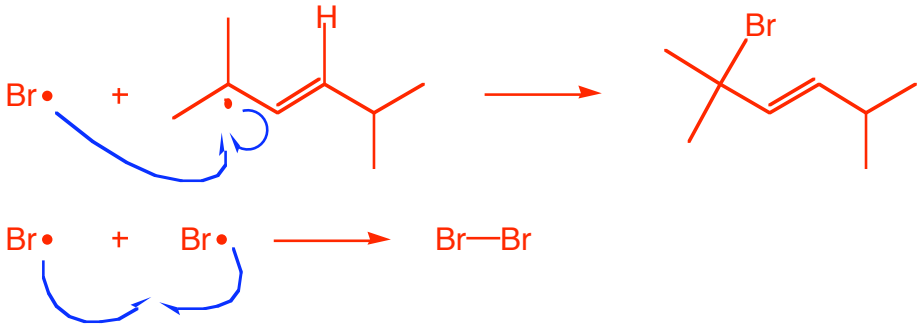
Initiation



Propagation



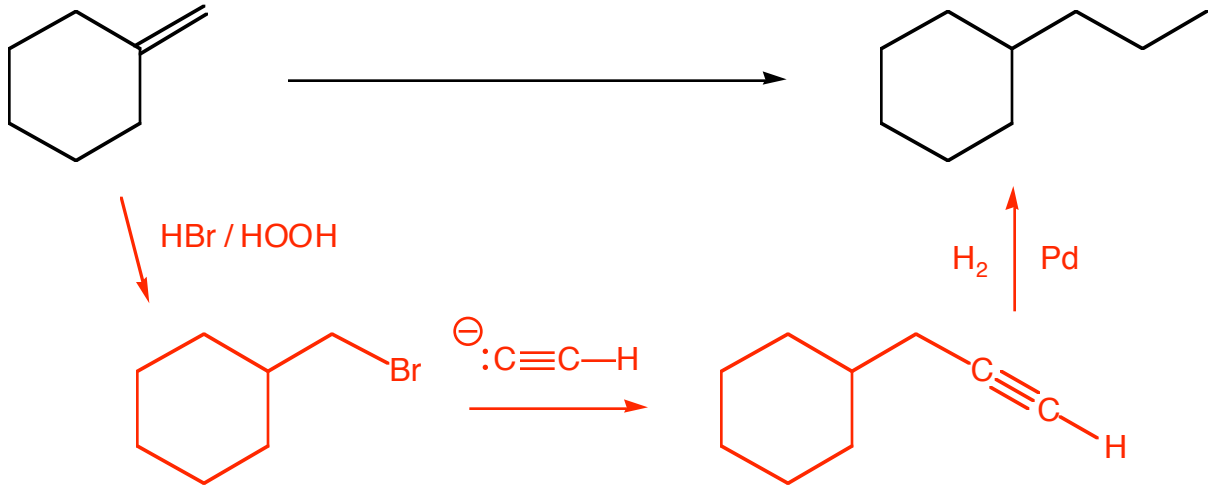
Termination (2 possibilities shown)



Of the two resonance contributors, the one with the radical at the tertiary position will contribute the most to the resonance hybrid because 3° radicals offer more electron delocalization through induction than 2° radicals. Since the 3° radical is the major contributor, the hybrid will have the most radical character at that position. Therefore the bromine radical will most likely "see" the radical at that position and react there preferentially, giving the product shown.

5. CHOOSE ONLY ONE OF THE FOLLOWING SYNTHESES. Circle the one you want me to grade. If you provide answers for both and do not indicate which one I should grade, I will grade the first one. (12 points)

Propose a synthesis (sequence of reactions) that will accomplish the following transformation. *Be sure to include the products of each step for full credit.*



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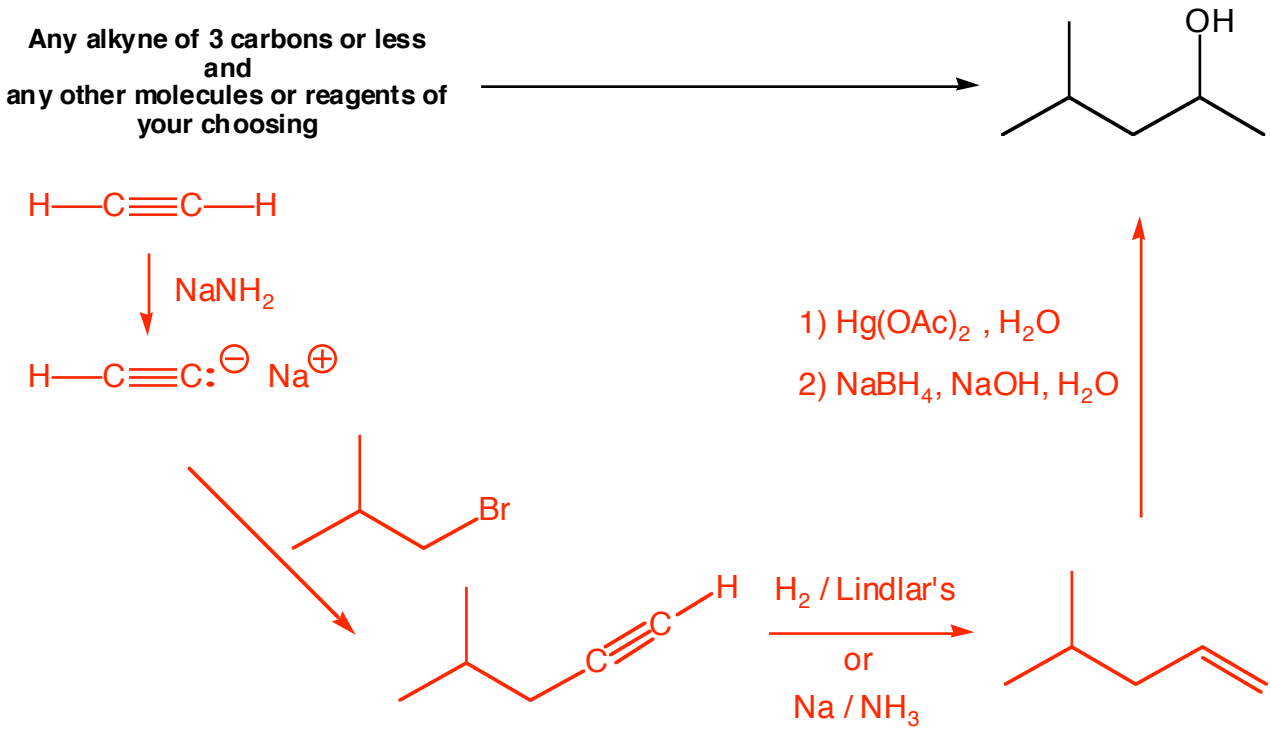
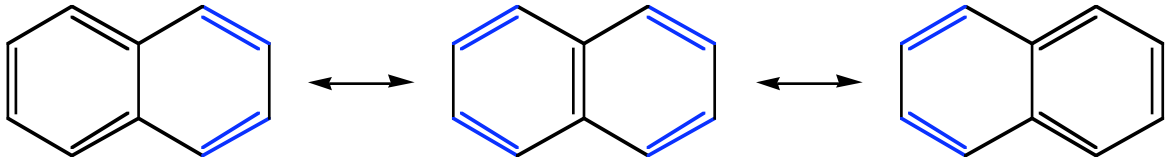


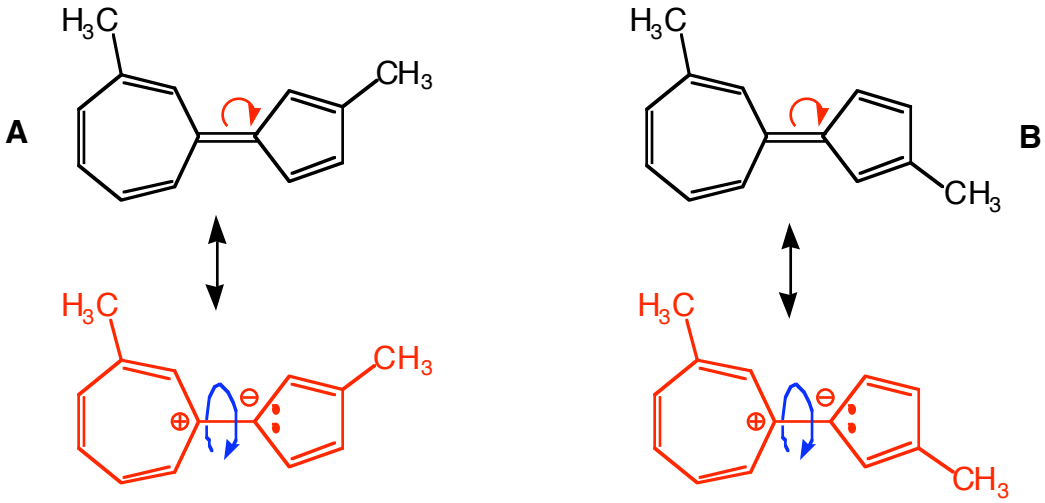
6. As you know, all the carbon-carbon bonds in benzene have the same bond length. In stark contrast to benzene, researchers have found that naphthalene *does not* possess equivalent carbon-carbon bond lengths! Use pictures *and* words to explain this phenomenon. (10 points)



Naphthalene

The bonds highlighted in blue represent carbon-carbon bonds that are doubly bonded in *at least two* of the resonance structures. All of the other carbon-carbon bonds are doubly bonded just once! Therefore we would expect the blue-colored C-C bonds to have more double bond character than the other bonds. This would have a significant effect on the bond-lengths in naphthalene.

7. A researcher on the East coast synthesizes **A** while a researcher on the West coast synthesizes **B**. Both researchers post the physical properties of their molecules on their web pages. To their surprise, **A** and **B** have exactly the same melting point, boiling point, refractive index, density, and dipole moment. Provide an explanation for these results using pictures & words. (8 points)



The major resonance contributors for each molecule are shown. These are the major contributors because placing a positive charge in the seven-carbon ring and a negative charge in the five-carbon ring allows both rings to become aromatic. Aromaticity is a huge stabilizing factor so the resonance hybrid will mostly assume the characteristics of the charged structure. In this structure, a single bond connects the two rings and as we know, single bonds allow for free rotation about the bond. If we rotate the central bond in **A** 180°, we obtain **B**. Thus, this creates a situation where **A** and **B** are conformers! As we know, conformers are really the same molecule; which explains why they have the same properties.