## Homework for Chapter 17 Chem 2320

Name\_\_\_\_\_

## I. Cumulated, isolated, and conjugated dienes

1. Draw structures which fit the following descriptions. Use correct geometry!

a) a conjugated diene with the formula  $C_6H_{10}$ :

b) an isolated diene with the formula  $C_6H_{10}$ :

c) a cumulated diene with the formula  $C_6H_{10}$ :

d) two chiral, cumulated dienes with the formula  $C_7H_{12}$ :

e) two achiral, cumulated dienes with the formula  $C_7H_{12}$ :

f) two conjugated, cyclic dienes with the formula  $C_7H_{10}$  which are locked into an *s*-*cis* conformation:

g) e) two conjugated, cyclic dienes with the formula  $C_7H_{10}$  which cannot achieve an *s*-*cis* conformation:

2. Draw the following dienes using the correct geometry. Then rank them from highest energy (1) to lowest energy (3).

trans-1,4-hexadiene

1,2-hexadiene

 $(2\underline{E},4\underline{E})$ -2,4-hexadiene

- 3. Fill in the following about Diels-Alder reactions.
  - a) The two starting materials needed are:
  - b) The diene must have a conformation of:
  - c) The dienophile needs substituents that are:
  - d) The diene may have substituents like:
  - e) Two constitutional isomers can form if:
  - f) A fused bicyclic ring will result if:
  - g) A bridged bicyclic ring will result if:
  - h) If the dienophile is trans, in the prodcut its substituents will be:
  - i) If the diene has two substituents on the outside, in the product these substituents will be:

4. Give the product(s) of the following reactions, <u>without</u> showing stereochemistry. Draw arrows to show how the product(s) were formed.



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5. What diene and dienophile would be necessary to form the following products?



6. Give the products of the following reactions by first, writing the products without stereochemistry and labeling the stereocenters. Then write out all stereoisomers (write small!). Hint: the correct number of isomers is given in (). Label the relationships between the products.











## **II. Reactions involving allylic intermediates**

7. Answer the following questions about <u>trans</u>-1,3,5-hexatriene.



- b) How many pi orbitals will be formed?
- c) How many of the pi orbitals will be bonding orbitals?
- d) How many of the pi orbitals will be antibonding orbitals?
- e) How many of the pi orbitals will be occupied by electrons?
- f) How many nodes will each of the pi orbitals have?

g) Will this compound be more stable, less stable, or the same energy as 1,3-butadiene?

h) Draw a figure showing the energy of the p orbitals and the pi orbitals.

i) Sketch what the three lowest orbitals would look like.

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8. Draw in double bonds and poitive charges to make a different allylic carbocation on each structure below.



9. Draw the other resonance structure for each of the intermediates below. Draw arrows to indicate how the second resonance structure is generated. Circle any structures which are greater resonance contributors.









11. Rank the following radicals in order of stability (1 = most stable, some may have the same number). Only one resonance structure is shown!



12. Answer the following questions about the carbocation shown below.



How many resonance structures are there? Draw in the resonance structures. Over how many carbons is the positive charge spread? How many p orbitals are involved? How many pi orbitals are formed? Draw a diagram of the energy of the p orbitals and the pi orbitals, showing where the electrons are.

How many bonding, nonbonding, and antibonding orbitals are there?

How many nodes will the nonbonding orbital have?

What will the nonbonding orbital look like?

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13. Show the mechanism by which the given products may be formed, giving all steps, and showing the resonance structures of the intermediate.





14. Give the products of the following reactions, taking into consideration the resonance structures of the intermediates involved. The number of products you should obtain is given in ( ).





15. Would the following reactions give a different ratio of products at a cold temperature vs. a warm temperature? Why or why not?



16. Explain in your own words why NBS is used instead of  $Br_2$  in allylic bromination reactions.

17. Rank the following alkyl halides according to their rate of reaction with a strong nucleophile (1 = fastest).



18. Give the products of the following reactions.



19. Synthesize the following alkenes from an allylic halide and an organometallic reagent.

