

CONJUGATED PI SYSTEMS AND PERICYCLIC REACTIONS

A STUDENT SHOULD BE ABLE TO:

1. Recognize and give examples of conjugated, isolated, and cumulated dienes, and of allylic intermediates. Also, name given the structure, and draw the structure given the name, of polyenes (review). Distinguish conjugated dienes as *s-cis* or *s-trans*.
2. Distinguish resonance structures from other types, draw resonance structures of given species, and predict the relative stabilities of such structures (review).
3. Predict both the orders of diene and carbocation stabilities, and the relative reactivities of compounds in reactions proceeding by way of these intermediates.

Diene stabilities: conjugated > isolated > cumulated

Carbocations: allylic > 3° > allyl > 2° > 1° > CH₃⁺ > vinylic

4. Propose mechanisms for reactions involving conjugated systems, and explain and predict experimental results in such reactions from knowledge of the mechanisms involved.

Important reactions are:

Additions to conjugated dienes involving carbocations (Markovnikov) and free radicals (anti-Markovnikov addition of HBr). Factors contributing to the 1,2- vs. 1,4- addition conflict are important.

The Diels-Alder reaction. *Endo* product is favored over *exo*. The starting diene must be conjugated and in the *s-cis* conformation. These reactions are faster when: 1) The diene has electron-releasing (usually alkyl) groups attached to it, and the dienophile has electron-withdrawing groups attached to it, and 2) vice versa.

Other pericyclic reactions

5. Given the starting material and reaction conditions, predict the product(s) of reactions involving allylic intermediates and diene starting materials. Important reactions include:
 - Free radical substitution at allylic positions (review)
 - Addition reactions to dienes (1,2 and 1,4 additions)
 - The Diels-Alder reaction, and other pericyclic reactions
6. Devise syntheses of, or syntheses employing, dienes.
7. Identify and explain the processes involved in UV-Visible spectroscopy, including:
 - The importance of the Highest Occupied and Lowest Unoccupied Molecular Orbitals
 - The energy, frequency, and wavelength relationships between ultraviolet, visible, and other radiation.Alkenes and nonconjugated dienes have absorption maxima at wavelengths less than 200 nm, while conjugated systems have maxima at wavelengths greater than 200 nm. More conjugation gives absorption maxima at longer wavelengths.

To best prepare for this module, please work Chapter 17 Skill Builder problems in the textbook.

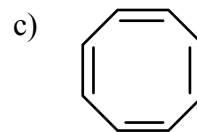
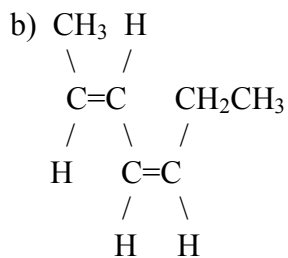
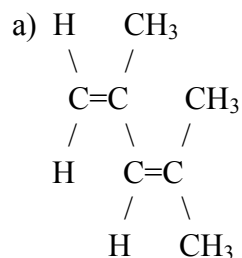
A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Draw an example of each of the following.

a) an allylic carbocation

b) a cumulated diene

1.2 Name each of the following.



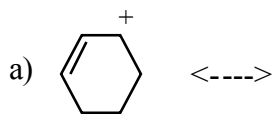
1.3 Draw each of the following.

a) 1,3-cyclohexadiene
Is this *s-cis* or *s-trans*?

b) allyl chloride

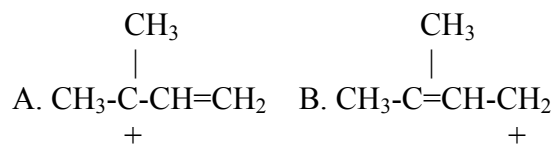
c) *trans*-1,3-pentadiene

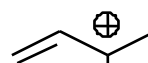
2.1 Draw resonance structures of the species indicated.

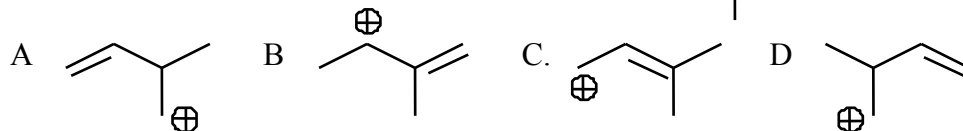


total:
five
forms

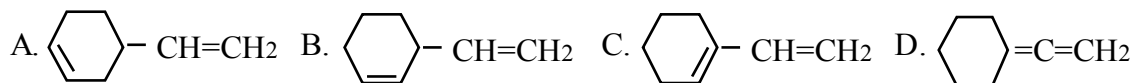
2.2 Which of the structures shown contributes more to the resonance hybrid?



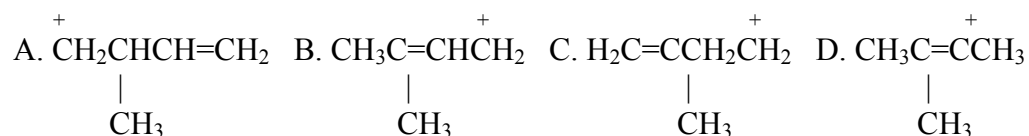
2.3 Which of these is a valid resonance structure of  ?



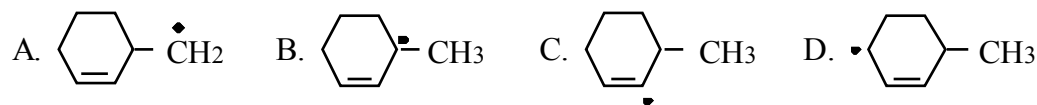
3.1 a) Which of the following dienes is the most stable? b) Which is the least stable?
c) Which one has an absorption maximum above 200 nm in its UV-Vis spectrum?



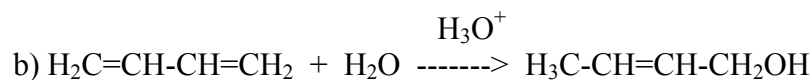
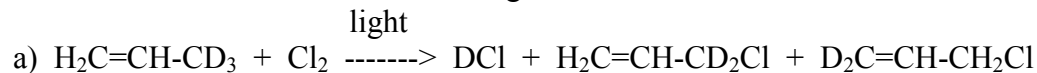
3.2 a) Which of the following carbocations is the most stable? b) Which is the least stable?



3.3 a) Which of the following free radicals is the most stable? b) Which is the least stable?



4.1 Propose a mechanism for each of the following reactions.



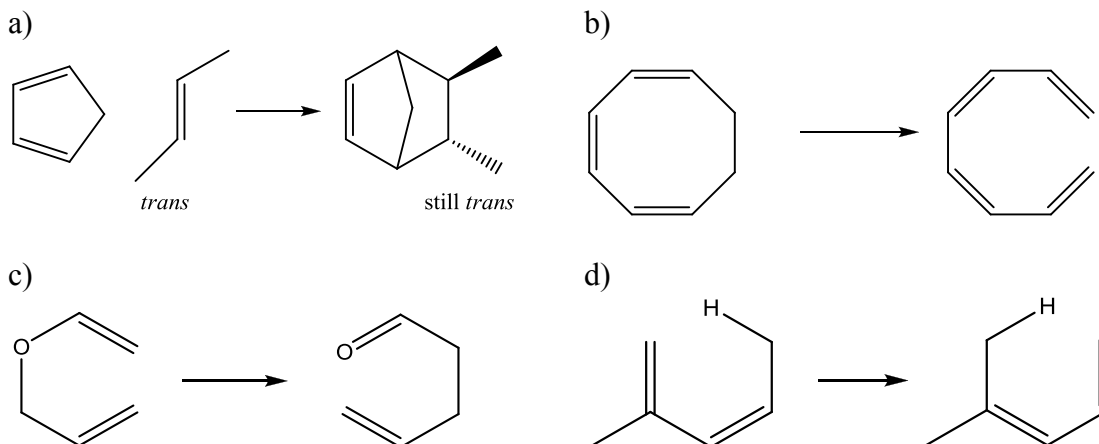
4.2 Arrange these dienes based on their reactivity as a Diels-Alder diene in a reaction with maleic anhydride, fastest first.



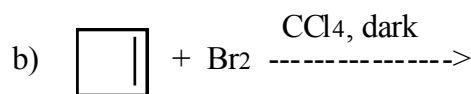
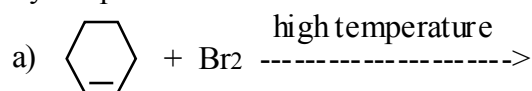
4.3 Arrange these dienophiles based on their reactivity as Diels-Alder dienophiles reacting with cyclopentadiene, fastest first.



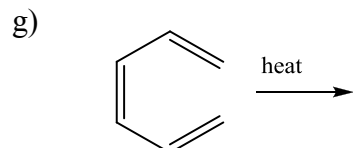
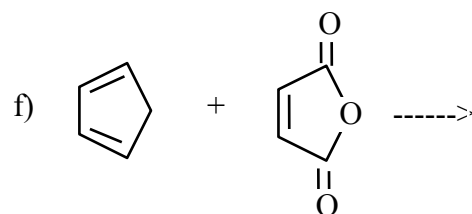
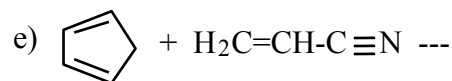
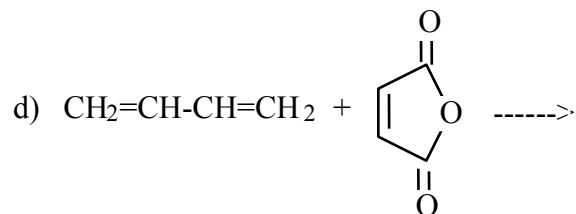
4.4 Draw mechanistic arrows for these pericyclic reactions.



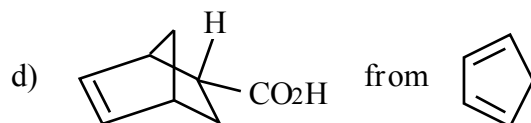
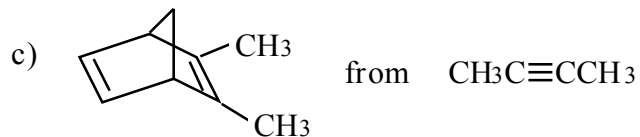
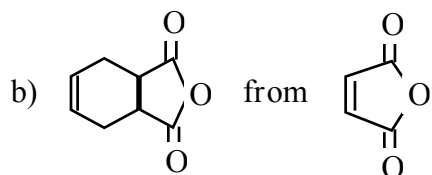
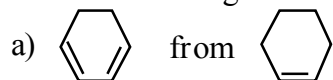
5. Predict the product or products of each of the following reactions. Indicate stereoisomers where they are produced.



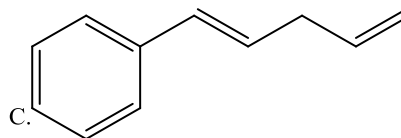
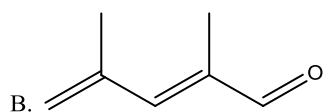
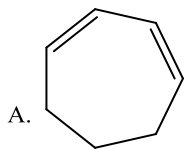
c) $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2 + \text{HI}(\text{one mole}) \rightarrow$
Which is major at low temperature? high temp?



6. Propose a synthesis of each of the compounds shown, from the given starting material and any other needed reagent.

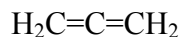
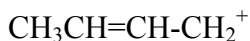


7. a) Circle the chromophore in each of these molecules.
b) Which has the largest difference in energy between the HOMO and LUMO?
c) Which has the largest λ_{max} in the UV/Vis range?



SOLUTIONS TO SAMPLE PROBLEMS:

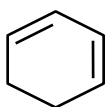
- 1.1 a) an allylic carbocation b) a cumulated diene



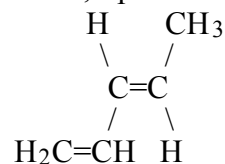
(There are many other possible examples here.)

- 1.2 a) 2,4-dimethyl-1,3-pentadiene
 b) *trans,cis*-2,4-heptadiene or (2*E*,4*Z*)-2,4-heptadiene
 c) 1,3,5,7-cyclooctatetraene

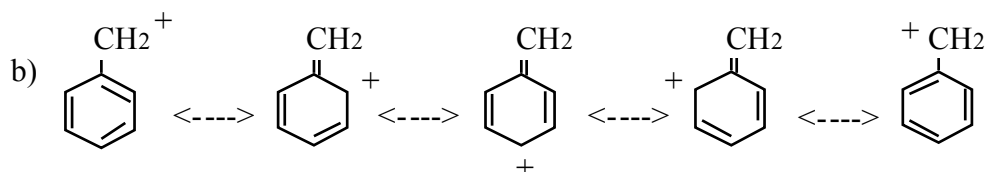
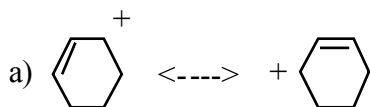
- 1.3 a) 1,3-cyclohexadiene (*s-cis*) b) allyl chloride



- c) *trans*-1,3-pentadiene



- 2.1 Resonance structures:



- 2.2 A: 3° allylic carbocation > 1° allylic. Carbocation stability is more important to factor in, vs alkene stability.

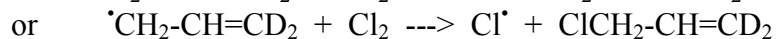
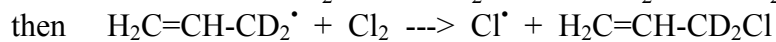
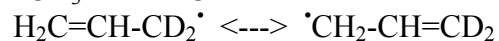
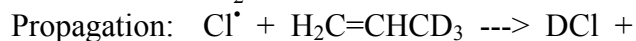
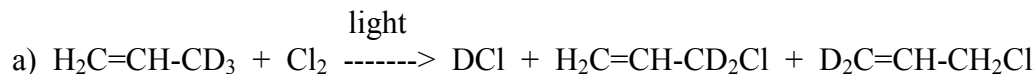
- 2.3 C

- 3.1 a) Most stable C; b) least stable D; c) absorption maximum above 200 nm, C.

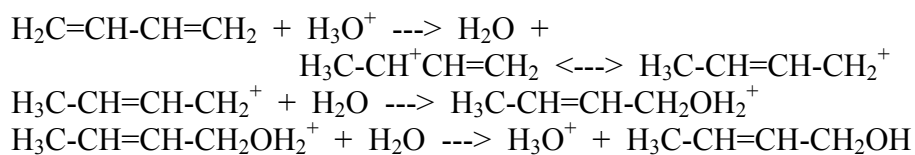
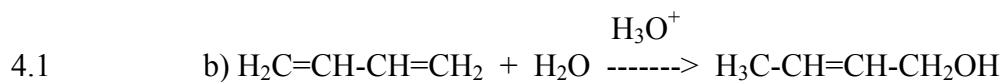
- 3.2 a) Most stable B (allylic); b) least stable D (vinylic)

- 3.3 a) Most stable B (allylic and 3°); b) least stable C (vinylic)

- 4.1



(The termination steps have been omitted).

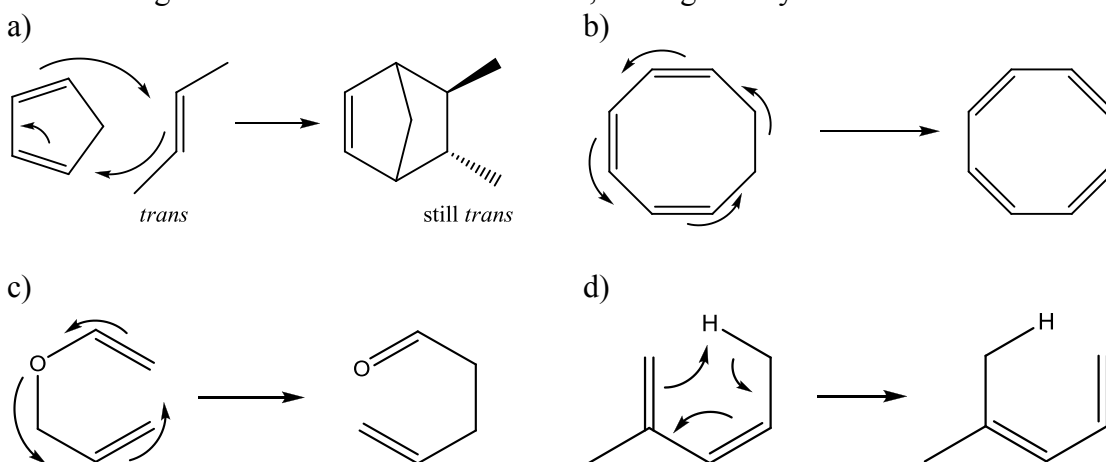


(Note: $\text{CH}_3\text{CHOHCH}=\text{CH}_2$ also forms)

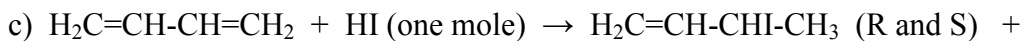
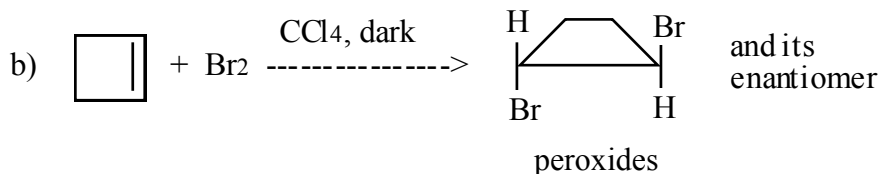
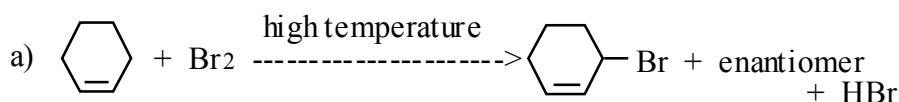
4.2 C

4.3 D

4.4 arrows can go clockwise or counterclockwise, as long as they're all in the same direction.

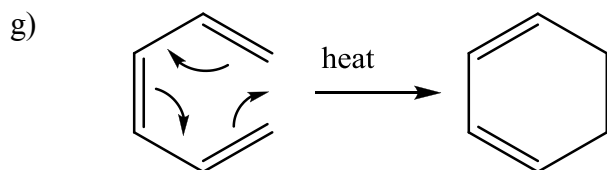
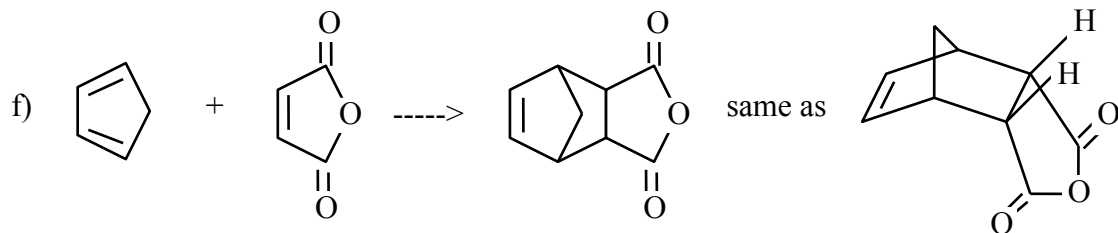
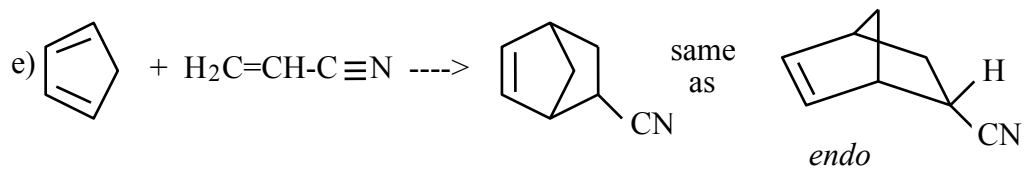
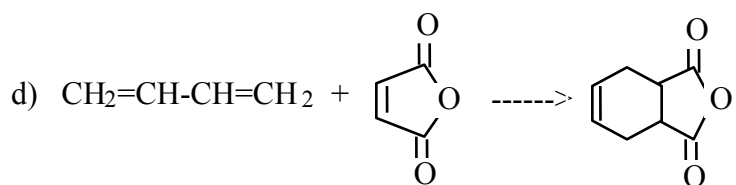


5. The product or products:

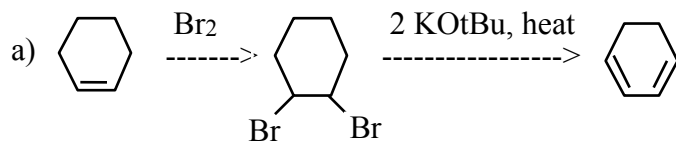


At low temp, $\text{H}_2\text{C}=\text{CH}-\text{CHI}-\text{CH}_3$ is major; 1,2 product forms fastest

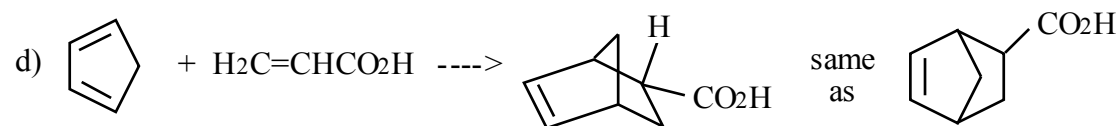
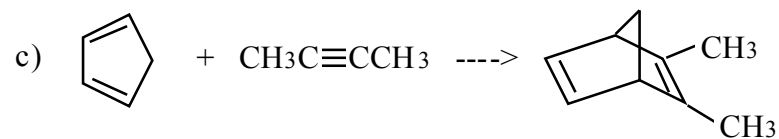
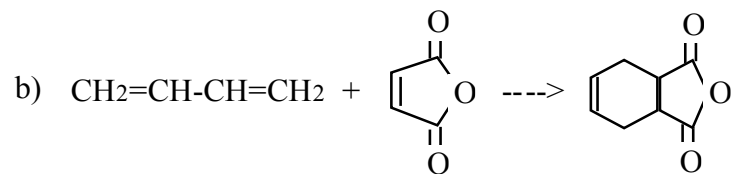
At high temp, $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{I}$ is major; this 1,4 product is more stable



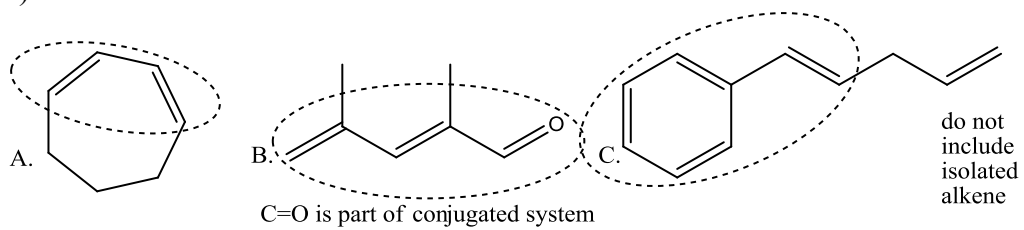
6. Synthesis problems:



Also OK: 1. NBS, ROOR (or Br_2 with heat or light), then KOtBu



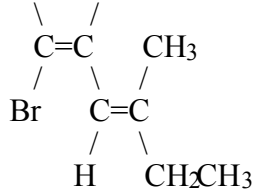
7. a)



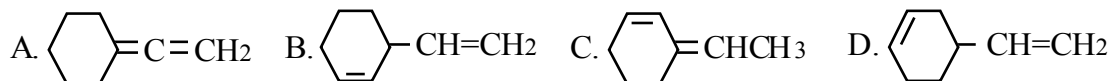
b) A: largest energy gap for least conjugation

c) C: λ_{\max} is inversely related to energy

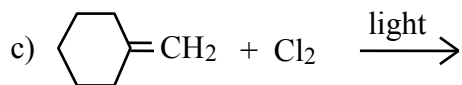
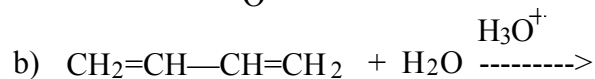
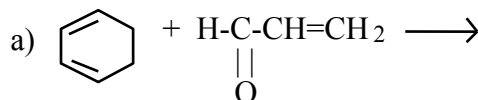
- 1) Name: CH_3CH_2 H 2) Draw 2-isopropyl-1,3-cycloheptadiene



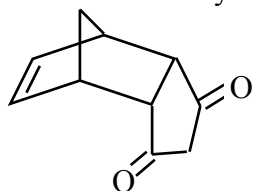
- 3) a) Which of the compounds shown is the MOST stable? _____
 b) Which one has an absorption maximum > 200 nm in its UV-visible spectrum? _____

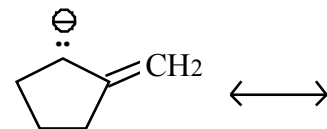


- 4) Predict the product or products (if any) of each of the following reactions.

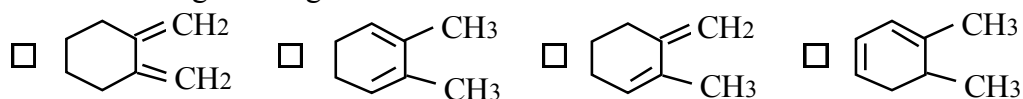


- 5) Propose a Diels-Alder synthesis of the compound shown.



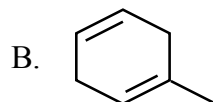
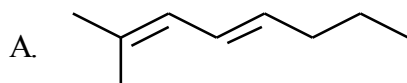
- 6) Draw a resonance structure for: 

- 7) Which of the following dienes gives the SLOWEST Diels-Alder reaction ?

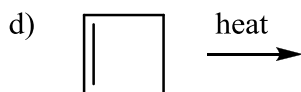
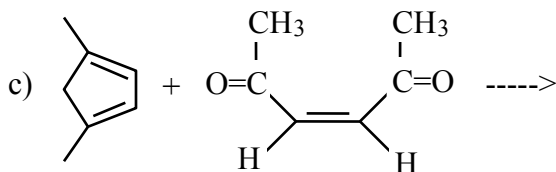
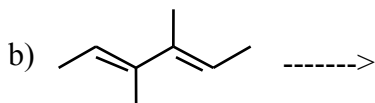
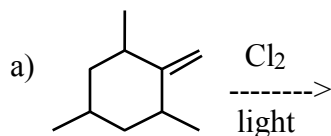


- 8) Propose a mechanism for: $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$

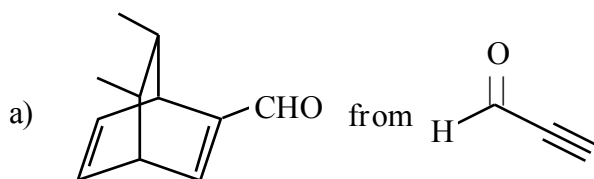
1. a) Give the complete IUPAC name of each compound. b) Classify each of the dienes as conjugated, cumulated, or isolated. c) Which of these absorbs UV-visible light at a longer wavelength? _____

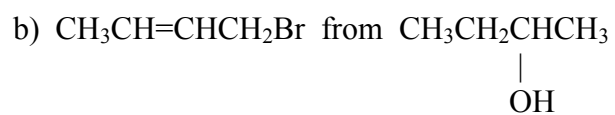


2. Draw the structure(s) of the organic product(s) of each of the following reactions.

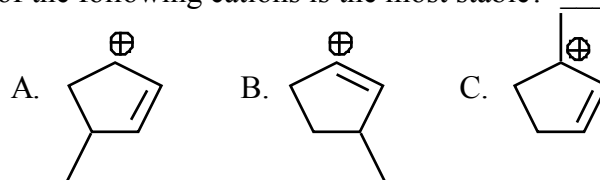


3. Propose a synthesis of each of the compounds shown from the indicated starting materials and any other needed reagents.

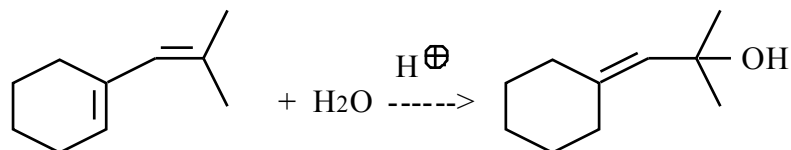




4. Which of the following cations is the most stable? _____ Which is least stable? _____



5. Propose a mechanism for the following reaction.



6. Draw a resonance structure of the one shown.

