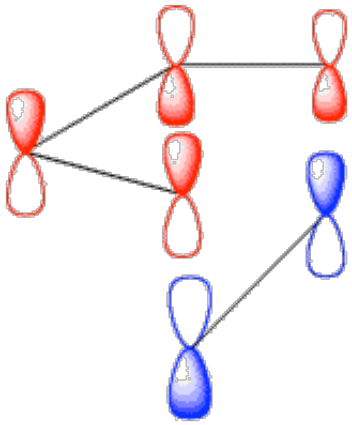
Chem 221b

Problem Set 2

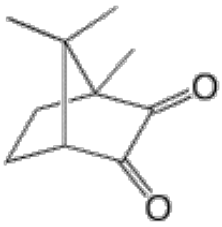
Chapter 15

Due: Monday, January 31, 2005



See Pericyclic Reactions in the StudyAids for a review on conjugation, cycloadditions, and electrocyclic reactions. Electrocyclic reactions are not covered in the text.

1.



1

Camphorquinone (**1**; CQ) is used as a photosenitizer by your dentist. CQ absorbs electromagnetic radiation and causes polymerization of a monomer, bis-GMA. These composites have mostly replaced silver amalgams. At the right is a spectrum of CQ.

a) What kind of spectrum is it?

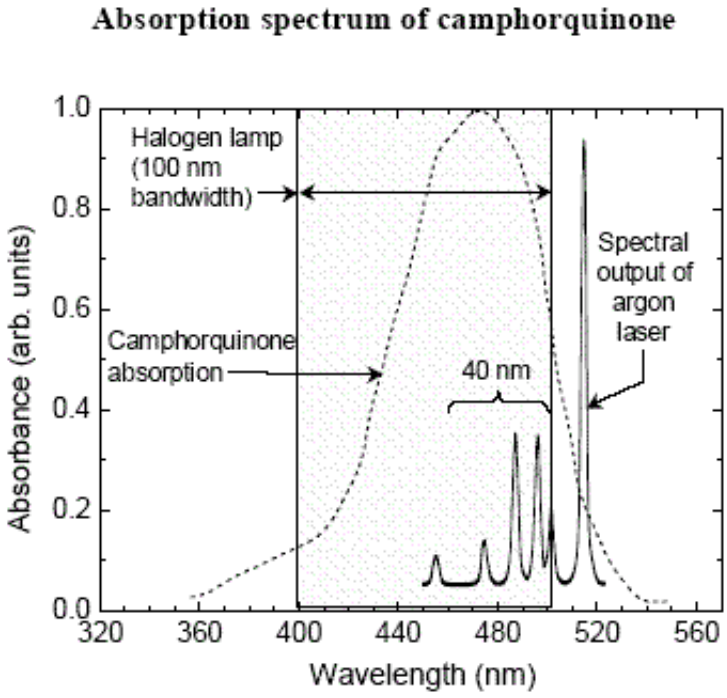
b) What is the λ_{max} of CQ?

c) What concentration (mg/mL) of CQ is required to produce this spectrum [ε_{log}=1.49 at λ_{max}]? [Assume a 1 cm cell.]

d) What color light does CQ absorb?

e) What color is CQ?

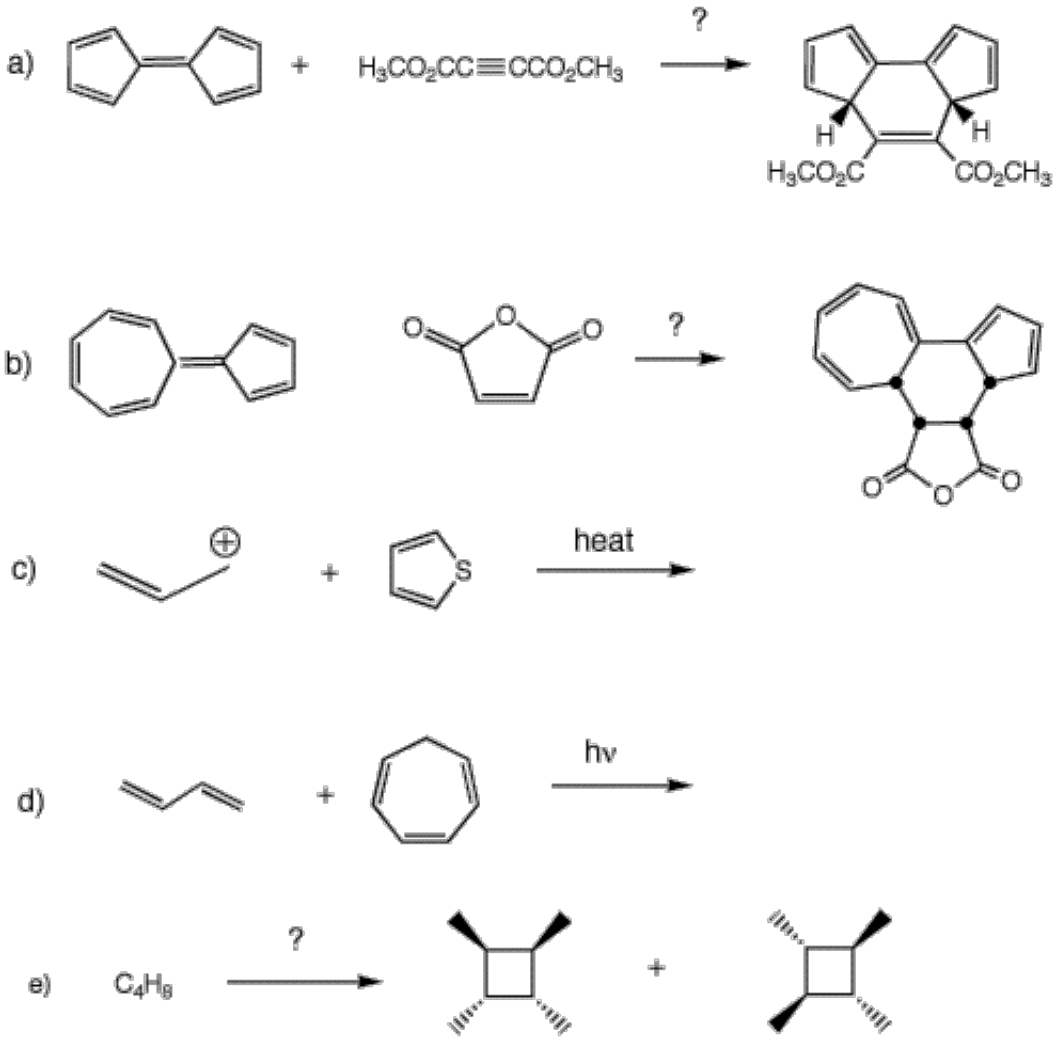
f) What color are the glasses that you wear when the dentist zaps you with the "light gun"? Why are they that color?



2. Draw the structures of the Diels-Alder adducts arising from 1,3-pentadiene and $CH_3CH{=}CHCO_2CH_3$ under the conditions described in the Table. Provide a transition state model for example 2. Which Examples give the same racemic product? Explain.

Example	Diene	Dienophile	Transition State
1	E	E	endo
2	E	Z	endo
3	Z	E	endo
4	Z	Z	endo
5	Z	E	exo

3. In each of the problems below, provide the missing information, i.e., conditions, product, reactant, etc. Also, explain the reason for your choice.

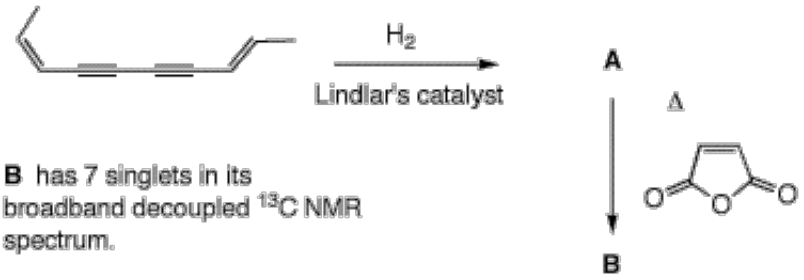


4. Compound **A** is colorless an it is devoid of absorption in the range 200-800 nm. Thermolysis of **A** affords **B**, which absorbs at 227 nm. When **B** is heated with maleic anhydride, compound **C** is formed, which has five singlets in its broadband decoupled ^{13}C NMR spectrum. Compound **C** displays vinyl hydrogens in its ^{1}H NMR spectrum. What are the structures **A-C**? Explain and illustrate.

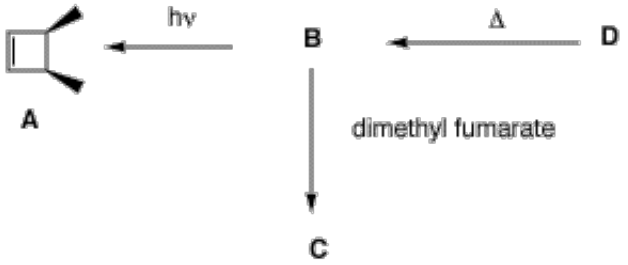
5. An optically active monoterpene **A** has λ_{max} = 265 nm (calc. 263 nm). Oxidation of **A** with warm $KMnO_4$ leads to the isolation of (*R*)-isopropyl succinic acid. Hydrogenation of **A** affords **B** and **C**. **C** is less stable than **B**. Both **B** and **C** have 7 singlets in their respective broadband decoupled ^{13}C NMR spectra. Treatment of **A** with methyl acrylate leads to the formation of an endo Diels-Alder adduct **D**. What are the structures of **A-D**. Explain and illustrate.

6. Complete the following problems. Be sure to explain the role of orbital symmetry.

a)



b)



i) What wavelength light (in nm) is required for **B** ---> **A**?
ii) Why is **B** ---> **D** unfavorable thermally?
iii) How many singlets in the ^{13}C spectrum of **C**?

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7. Explain and illustrate in terms of HOMOs and LUMOs why 1,3-butadiene and allyl cation undergo concerted, thermal cycloaddition but the allyl anion does not.