

## Chem 221b

### Problem Set 3

#### Chapter 16

Due: Monday, February 7, 2005



Styrox benzoin (Gum benzoin)

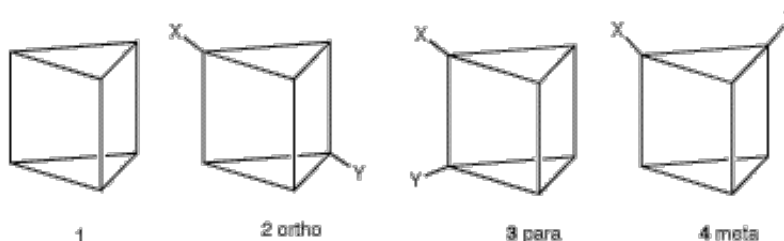
Gum benzoin is a balsamic extract of the Indonesian tropical tree *Styrox benzoin*. It has been used in both medicine and perfumery. Benzoic acid is a constituent of gum benzoin. Mitscherlich (1834) produced benzene from benzoic acid by heating it with CaO. Independently and earlier, a young [Michael Faraday](#) (1825), isolated benzene from coal tar residues and determined its composition,  $C_6H_6$ . Kekule proposed the correct structure of benzene in 1865. His "dream", related at the 25th anniversary celebration of his work, of visualizing the structure of benzene as a snake chasing its tail may well be hyperbole.



Friedrich August Kekule

(1829-1896)

1. During the mid-nineteenth century numerable structures had been proposed for benzene. One of Kekule's students, [Albert Ladenburg](#), proposed the prismane structure for benzene (1869), four years after Kekule's structure. Three sides of the prism are identical squares.



a) If an NMR had been available in 1869, how would the  $^1H$  and  $^{13}C$  spectra of the [prismane](#) structure **1-4** have compared with the Kekule formulation?

The prismane structures **2-4** were offered as the ortho, para, and meta isomers of a disubstituted benzene derivative where  $X=Y$  or  $X \neq Y$ . Although the correct number of isomers is predicted, van't Hoff noted that some of the prismane structures have a property that the aromatic compounds do not have.

b) What was van't Hoff's objection and what was the property? Illustrate and explain.

2. The  $^1\text{H}$  NMR of benzene displays a singlet at  $\delta$  7.3. Cyclopropenium cation has a singlet at  $\delta$  11.1 while [18]-annulene has a singlet at  $\delta$  9.3 and -3.0.

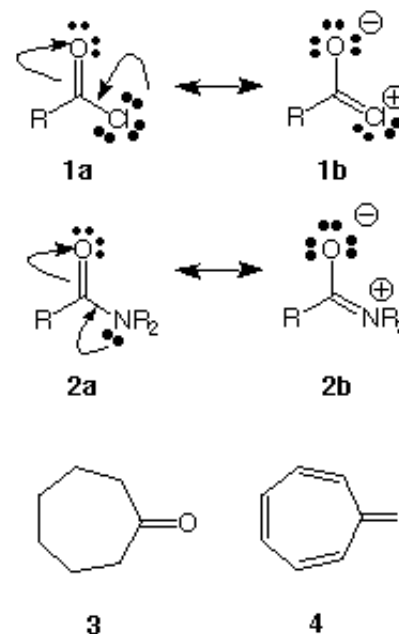
a) Why are the chemical shifts for the cyclopropenium cation and [18]-annulene what they are relative to benzene?

b) Why does the cyclopropenium cation absorb farther downfield than either benzene or [18]-annulene?

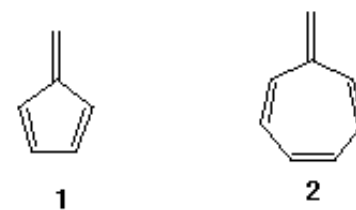
c) What are the relative areas in the NMR spectrum of [18]-annulene?

d) Assign the chemical shifts of [18]-annulene.

3. Resonance structure **1a** of an acyl halide is favored over **1b** because of the inability of electronegative chlorine to sustain a positive charge relative to nitrogen. On the other hand, resonance structure **2b** is a major contributor to the resonance stabilization of an amide. Because C=O bonds are stronger than C-O bonds, C=O bonds absorb at higher energy than C-O bonds (see pg. 509). Thus, acyl halides absorb at higher energy ( $\sim 1780\text{ cm}^{-1}$ ) while amides absorb at lower energy ( $\sim 1680\text{ cm}^{-1}$ ) in the IR. Based on this information, does the carbonyl group in cycloheptanone **3** absorb at higher or lower energy than the carbonyl group in tropone **4**?

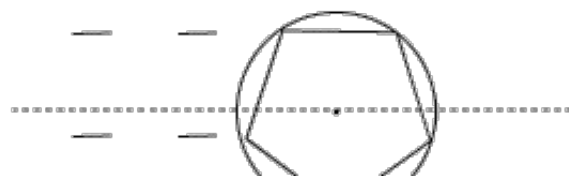


4. Methylene cyclopentadiene (fulvene) **1** is electrophilic while methylene cycloheptatriene **2** (heptafulvene) is nucleophilic. Explain. What is the site of bond formation? Explain and illustrate.



5. The Frost diagram is a convenient mnemonic device to determine rapidly the energy levels of conjugated systems. The figure on the right shows a regular pentagon simulating a cyclopentadienyl species. It is stood on a vertex and inscribed in a circle of radius  $r$ . The vertical height of each vertex gives the relative energy of each of the eight MOs.

a) If the dotted line is taken as zero energy (through the center of the circle) and the radius of the circle is 2, use geometry to demonstrate that the three energy levels of



the orbitals are: -2, -0.618 (degenerate), and 1.618 (degenerate). [What do the last two numbers have to do with the [DaVinci Code](#)? [Also see [From Baeyer to the Golden Section](#).]

b) Illustrate aromaticity/antiaromaticity for cyclopentadienyl cation and the anion. Which one is which. Explain.

6. [You should make a model of 1,6-methano-cyclodecapentaene **2**.]

a) Although the decapentaene **1** is a 10-electron system, it is not expected to have aromatic properties. Why?

b) In 1964, Vogel and Roth synthesized compound **2** from triene **3**. Explain the steps. [FYI: The tetrasubstituted double bond of **3** was found to be more reactive than the disubstituted double bonds.]

c) What is the structure of **A** and how do the rules of electrocyclicization govern its transformation into **2**?

d) Compound **2** displays a broad 8 hydrogen singlet at  $\sim\delta$  7.0 and a two hydrogen singlet at  $\delta$  -0.5 in its  $^1\text{H}$  NMR spectrum! Explain. [For help with the NMR spectrum, consult [PS3 #2](#) from Spring 2003. Also see pg. 549 in your text. All about ring currents.]

