

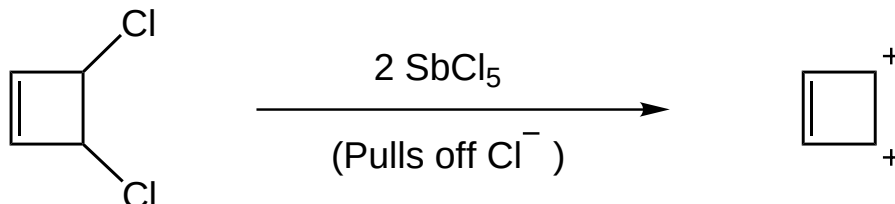
Organic Chemistry c3444y

Problem Set 2 - Aromaticity

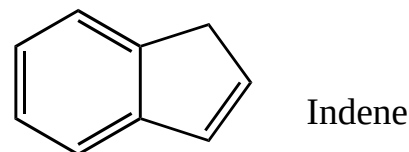
Due in class Wednesday Feb. 3

1. Here is a question from last year's final exam:

Recall that what we have called the "polygon" method can be used to arrive at an approximation of the relative energy levels of the molecular orbitals of a given cyclic π -system. Use the Frost method to decide whether the following hypothetical dication would be aromatic or not (be sure to clearly indicate the non-bonding level). What might be a more accurate representation of the structure of this dication?



2. Indicate which is(are) the most acidic proton(s) of indene:

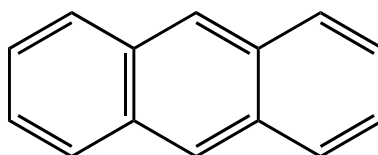


If you were to deprotonate indene at this site would there be any special stability associated with the anion you have left behind? Explain.

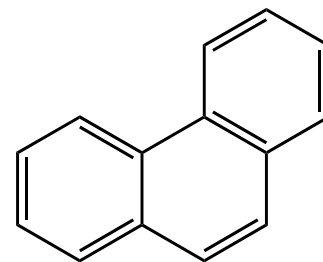
3. Recall our in class analysis of the structure of naphthalene and anthracene. Use resonance theory to explain the greater resonance energy of phenanthrene relative to anthracene. In other words why is phenanthrene "more aromatic" than anthracene?

Resonance Energy

Benzene	= 36 kcal/mol
Naphthalene	= 61 kcal/mol
Anthracene	= 84 kcal/mol
Phenanthrene	= 92 kcal/mol



Anthracene

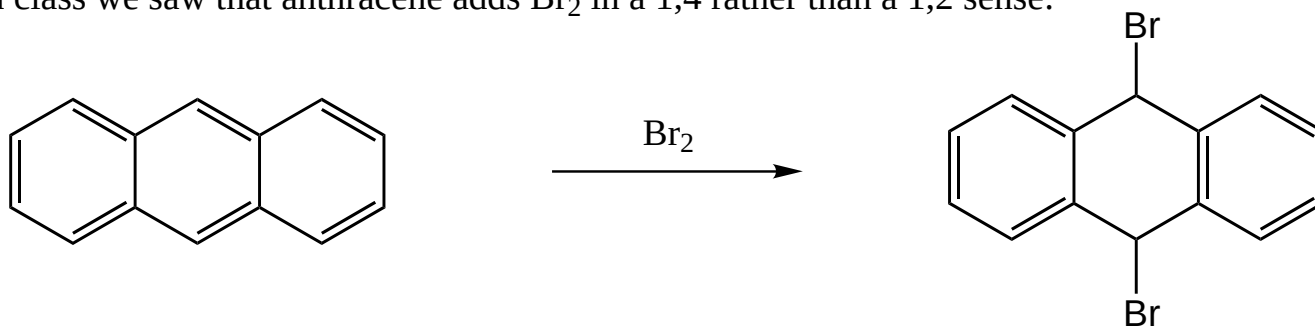


Phenanthrene

Begin by drawing all possible neutral resonance structures for phenanthrene. (Hint: phenanthrene and anthracene do not have the same number of possible neutral resonance structures.)

4. a. Like anthracene, phenanthrene will do many normal reactions of alkenes. For example, in the presence of an appropriate catalyst, H_2 will add to phenanthrene. Draw the product of this reaction and explain why this product is formed. How much resonance energy is lost in this transformation?

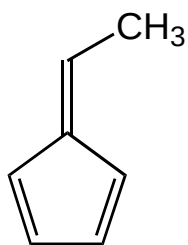
b. In class we saw that anthracene adds Br_2 in a 1,4 rather than a 1,2 sense:



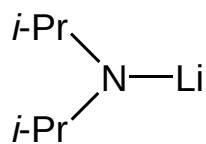
Starting from the illustrated resonance structure of anthracene, draw a mechanism for this transformation. (Hint: You are not limited to the formation of a symmetrical bromonium ion in the first step. You may form a carbocation instead.)

5. Here is a question from the first hour exam two years ago: 6-methylfulvene is unusually acidic, and can be cleanly deprotonated with lithium diisopropylamide (LDA). (By contrast, propene cannot be deprotonated with LDA.)

a. Indicate at which site you would expect 6-methylfulvene to be deprotonated upon treatment with LDA.



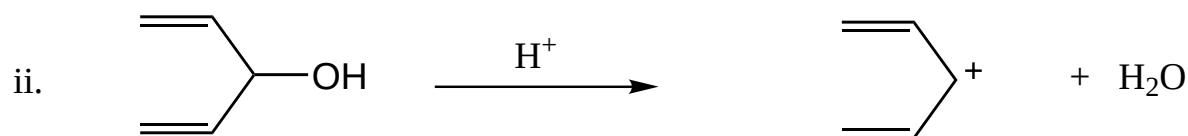
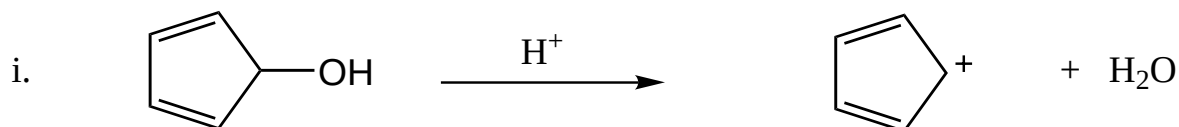
6-Methylfulvene



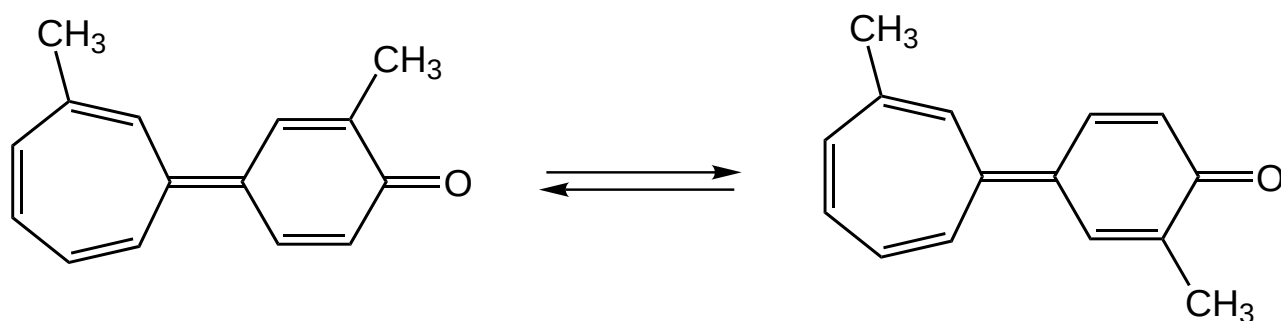
LDA - a strong base

b. Is there any special stability associated with the anion that is generated upon deprotonation of 6-methylfulvene? Explain concisely with clear drawings.

6. For the following pair of reactions, which one should be faster? Why?



7. It has been observed that the following molecule undergoes unusually facile rotation about the central double bond, whereas "normal" double bonds will not rotate in such a manner. Using resonance structures, provide a simple explanation for this phenomenon.



8. It has been shown (by our own Prof. Katz in 1964) that the following anion spontaneously rearranges to a *monocyclic* anion with unusual stability. What is this anion, how is it formed, and what is the reason for its stability?

