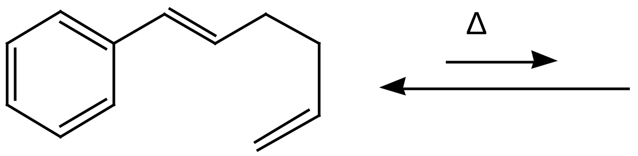
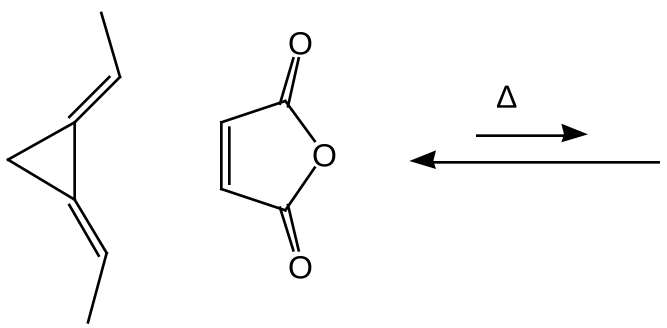
Hour Examination #1, Chemistry 302-302A, Feb. 28, 2005, 7:30-10:00

> "Scientists are a friendly, atheistic, hard-working, beer-drinking lot whose minds are preoccupied with sex, chess and baseball when they are not preoccupied with science."
>
> Yann Maitel, Life of Pi

1 (28 points). (a) Each of the following two reactions might be expected to yield a product, but neither does. It appears that the putative products are strongly disfavored at equilibrium. What are the products and why are they disfavored? In part (a) you may ignore stereochemical details of the putative products.



X



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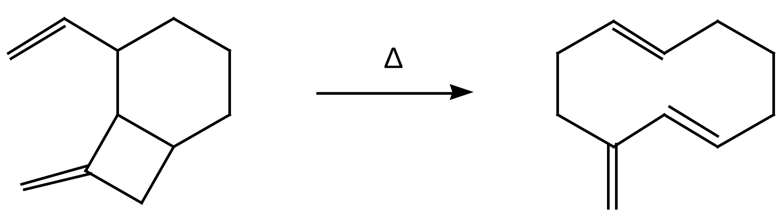
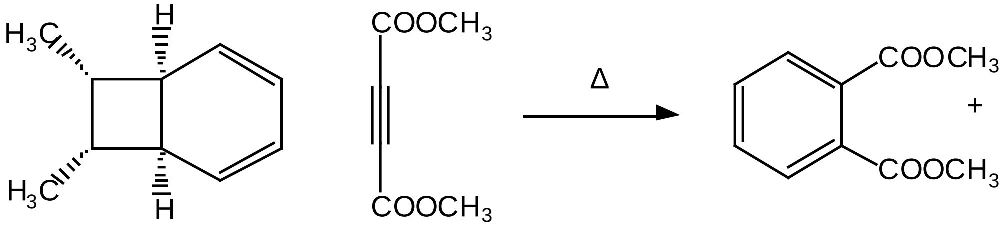
(b) Here are two thermal reactions that do succeed. Sketch arrow formalism mechanisms and identify **Z**. In part (b) please do pay attention to stereochemistry.

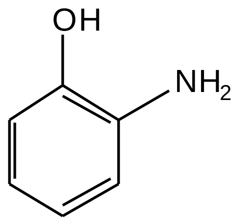




Z

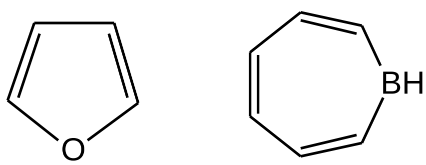
4H at δ ~5.5 in the ^{1}H NMR spectrum

2 (16 points). Devise a synthesis of the following molecule, starting from benzene and inorganic reagents of your choice. Mechanisms are *not* necessary.



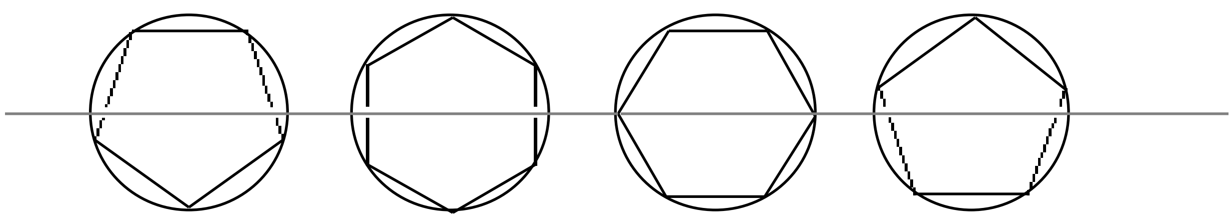
no para isomer!

3 (14 points). In the olden days, there was a frantic race to synthesize the molecule called "borepin," because it was thought that it might be aromatic.

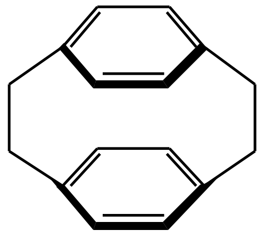


furan borepin benzene

First, explain to us why chemists thought borepin might be aromatic and then tell us whether you think furan is more or less aromatic than benzene. The following diagrams may, or may not be helpful.



4 (22 points). [2.2]Paracyclophane (**1**) undergoes electrophilic aromatic substutution as any sensible aromatic compound does.



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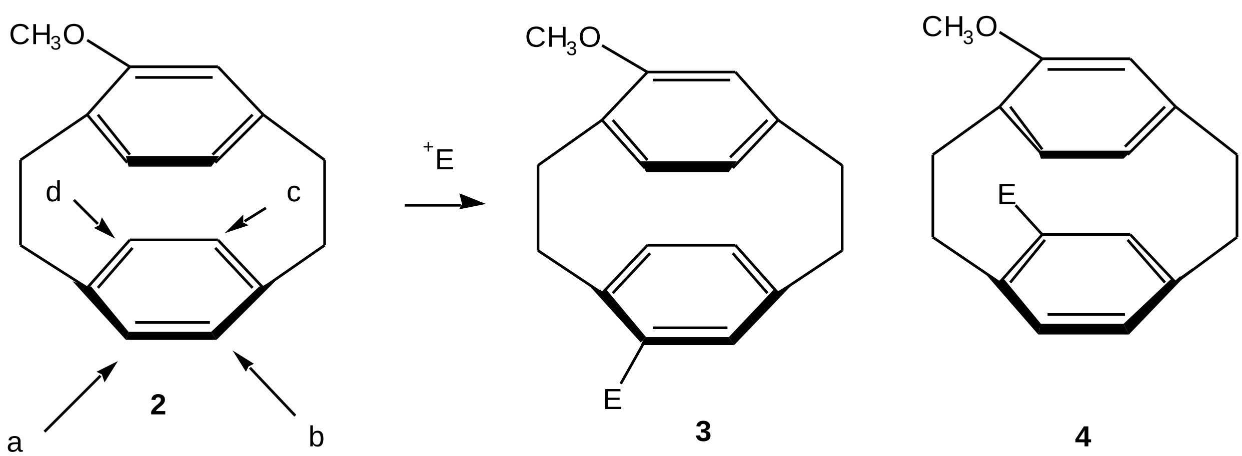
There are, however, some very interesting substituent effects. For example, cyclophane **2** substitutes in both rings.

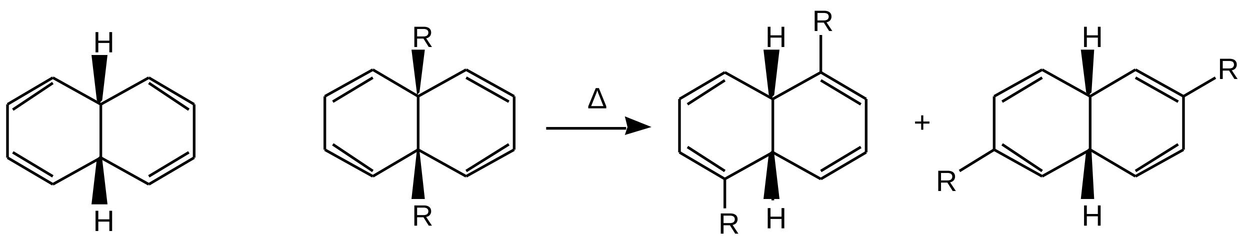
(a) The top ring undergoes further substitution at two of the available positions, but not at the third. Which positions in the top ring undergo substitution and why?

(b) Explain why the lower ring is substituted faster at positions a and d rather than at positions b and c.



2 **3** **4**

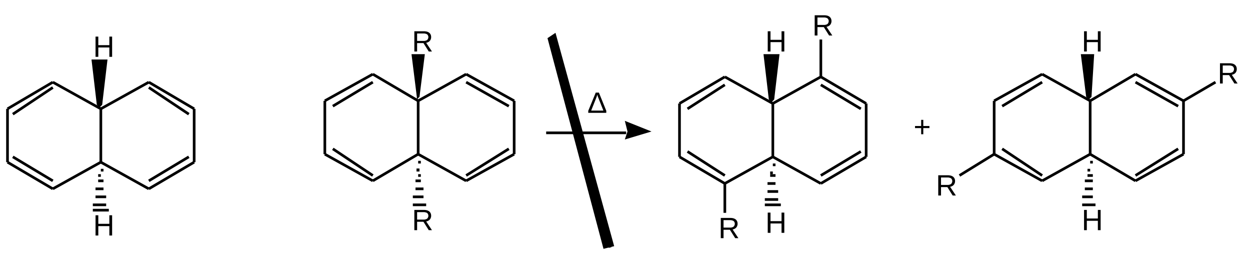
5 (20 points). When heated, *cis*-9,10-dihydronaphthalene (**5**) underges no obvious reaction - basically, it seems to just sit there. But a closer look reveals that much must be going on. For example, labeled **5-R2** rearranges on heating to two new labelled **5**'s.



5 **5-R$_2$**

(a) Your first job is to write a reasonable arrow formalism mechanism that explains what is going on. There is nothing new here, and you are not being asked to think up or use reactions that have not (yet) appeared. Specifically, there are no [1,5] (or other [1.n]) shifts involved. We are not asking for a detailed orbital analysis here, just arrow formalisms and a few words about what is happening.

(b) Next, explain why *trans*-9,10-dihydronaphthalene (**6**) does not show similar behavior.



6 **6-d$_2$**

"I pledge that I have not violated the Honour Code on this examination."