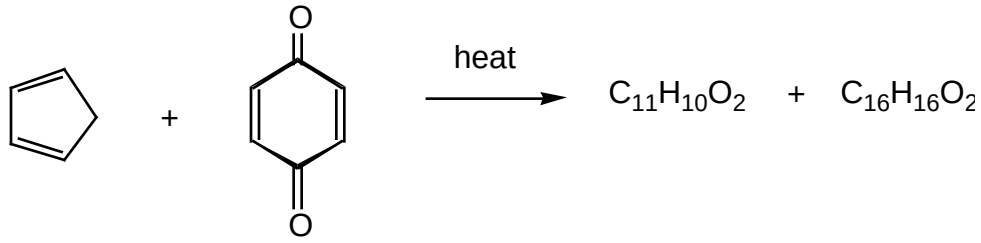
Hour Examination #1, Chemistry 302-302A, March 1, 2004, 7:30-10:00

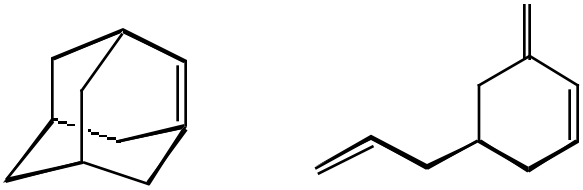
"Obscurity... is painful to the mind...."
David Hume

thanks to Susan M. Neider, former orgostudent

1 (16 points). Write arrow formalisms and provide detailed structures for the two unknown products. Be careful!

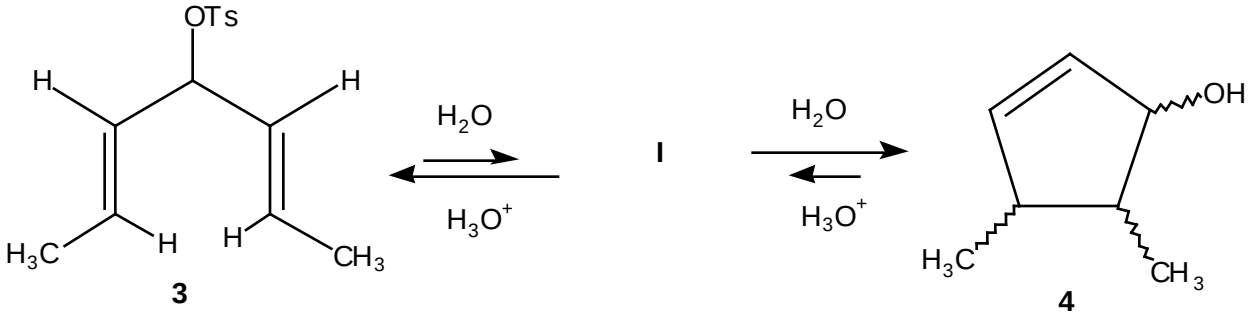


2 (10 points). Many, many attempts have been made to make adamantene, **1**. It is clear from the lack of success of most of these attempts that **1** is most unstable. *Briefly* show why. One attempt at making **1**, carried out in a small college town in New Jersey, involved a high-temperature elimination reaction and led not to **1** but to **2.** Nonetheless, those who did the work were overjoyed by this result, as they thought it meant that their suggested route did indeed work. Explain.



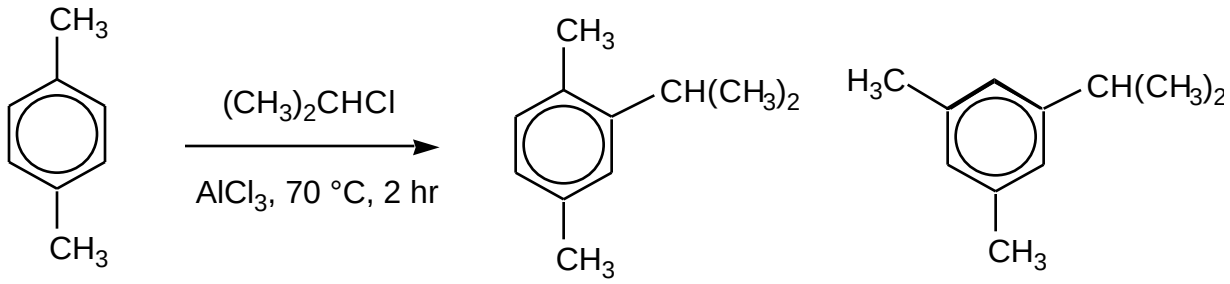
1 **2**

3 (16 points). When tosylate **3** is treated with warm H_2O/H_3O^+ in the dark, many acyclic alcohols are formed. However, in addition there are cyclic products of the general structure **4**. Your job is to show the structure of the intermediate **I**, and predict and explain the stereochemistry of the methyl groups in **4**. You do **not** have to worry about the stereochemistry of the OH group. A perfect answer analyzes the molecular orbitals of **I**, but the problem can be done reasonably well even if you can't derive the MOs of **I**.



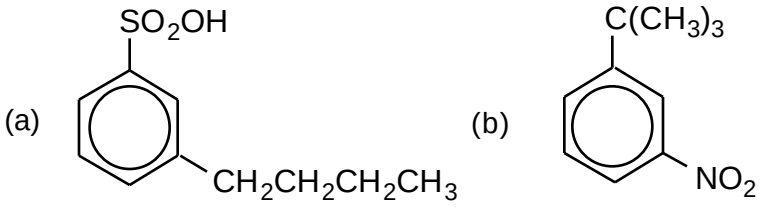
3 **4**

4 (16 points) . At low temperature, only a single product (**A**) is formed from the treatment of *p*-xylene with isopropyl chloride and $AlCl_3$. That is surely no surprise, as there is only one position open on the ring. However, at higher temperature some sort of rearrangement occurs, as two products are formed in roughly equal amounts. First, write a mechanism for formation of both products. Hint: Notice that HCl is a product of the first reaction to give **A**. Second, explain why product **A** rearranges to product **B**. What is the thermodynamic driving force for this reaction?

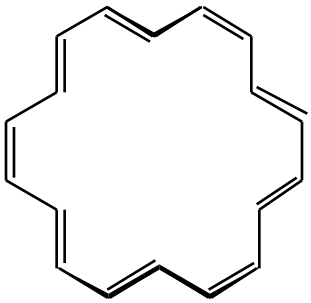


p-xylene **A**, 48% **B**, 52%

5 (16 points). Devise syntheses for the following two compounds. Hint. Part (b) is harder. Remember - it is possible to remove some groups from benzene rings. You may start from benzene, alcohols (R-OH) and carboxylic acids (R-COOH) containing no more than four carbons, and inorganic reagents of your choice.



6 (10 points) . [18]Annulene (**3**) shows a ^{1}H NMR spectrum featuring signals at δ 9.3 (2H) and – (minus) 3.0 (1H). By contrast, the spectrum of [16]annulene (**4**) reveals only a multiplet at δ 5.5. Explain.



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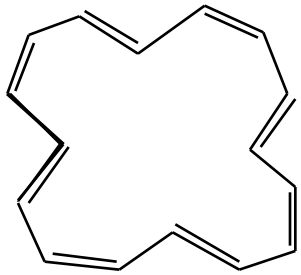
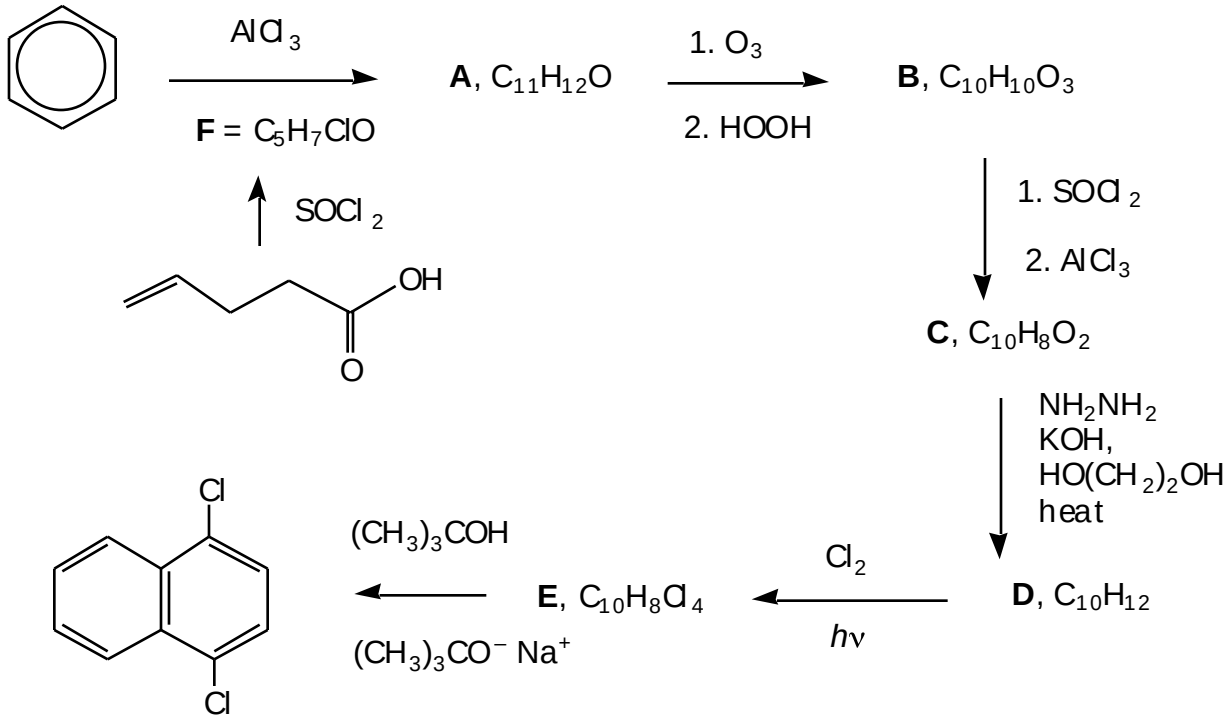


4

7 (16 points). Provide structures for compounds **A** - **F**. Mechanisms are not necessary but may well help you figure things out.



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