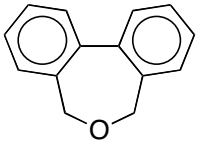
Chem 342 Organic Chem II

# Midterm Exam 02
14 March 2003

**NAME**_____

If you are not part of the solution, you are part of the precipitate!

 mercedes benzene



another micky mouse molecule

Please read through each problem carefully. Enter your answers in the spaces provided.

Problem 1 10 pts _____

Problem 2 9 pts _____

Problem 3 18 pts _____

Problem 4 5 pts _____

Problem 5 15 pts _____

Problem 6 27 pts_____

Problem 7 16 pts _____

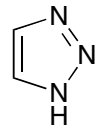
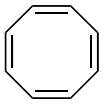
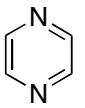
TOTAL 100 pts_____

A note about drawing structures: you should make your drawings as clear as possible to understand. Stereochemistry should be indicated unambiguously using conventional drawing techniques (eg. bold wedges and dashes).

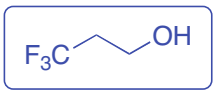
The most common mistake on an exam is not reading the question carefully. I suggest you go through the exam and answer the questions that come easily. Then go back and tackle the more challenging problems. Finally, check any work you have done, but remember, your first instinct is usually correct.

If you need scrap paper or more room, use the back of the test pages.

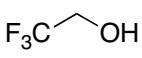
1. For each of the following molecules indicate the number of electrons in the delocalized pi-system and check the appropriate box for whether or not it is an aromatic molecule. (10 pts)

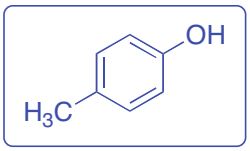
| | number of pi electrons | Aromatic | Not Aromatic |
|---|---|---|---|
|  | 6 | X | |
|  | 8 | | X |
|  | 4 | | X |
|  | 6 | | X |
|  | 6 | X | |

2. For each pair of alcohols below, circle the one that is least acidic (harder to deprotonate). (9 pts)

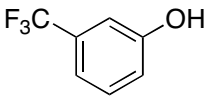
a) 

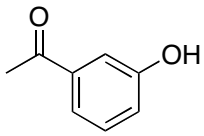
or



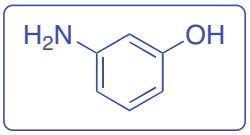
b) 

or

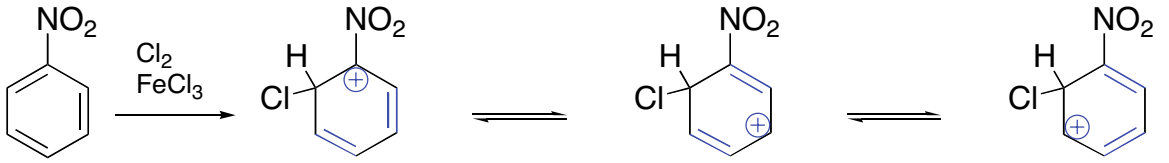


c) 

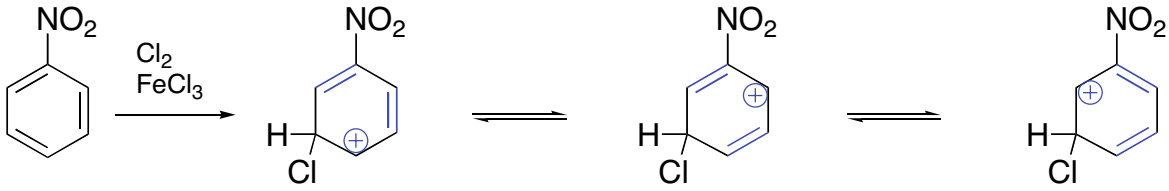
or



3. In the electrophilic chlorination of nitrobenzene, the electrophile could add ortho, meta, or para. Examples of addition of the electrophile to the ortho or meta position to form the carbocation intermediate are shown below. On the structures below, complete the drawings by filling in all the pi-bonds and formal charges. (12 pts)




**Especially unstable**
**UNFAVORED**

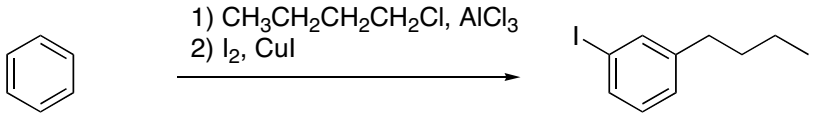



Is the product of this reaction more or less reactive than nitrobenzene? (2 pts) **Less Reactive**

Which of the pathways above, ortho or meta addition would be preferred for this example? Why? (4 pts)

**The reaction would prefer the meta-substitution pathway (the second one) because if the $Cl^+$ attaches ortho or para, this places the (+) right next to the eletron withdrawing nitro group.**

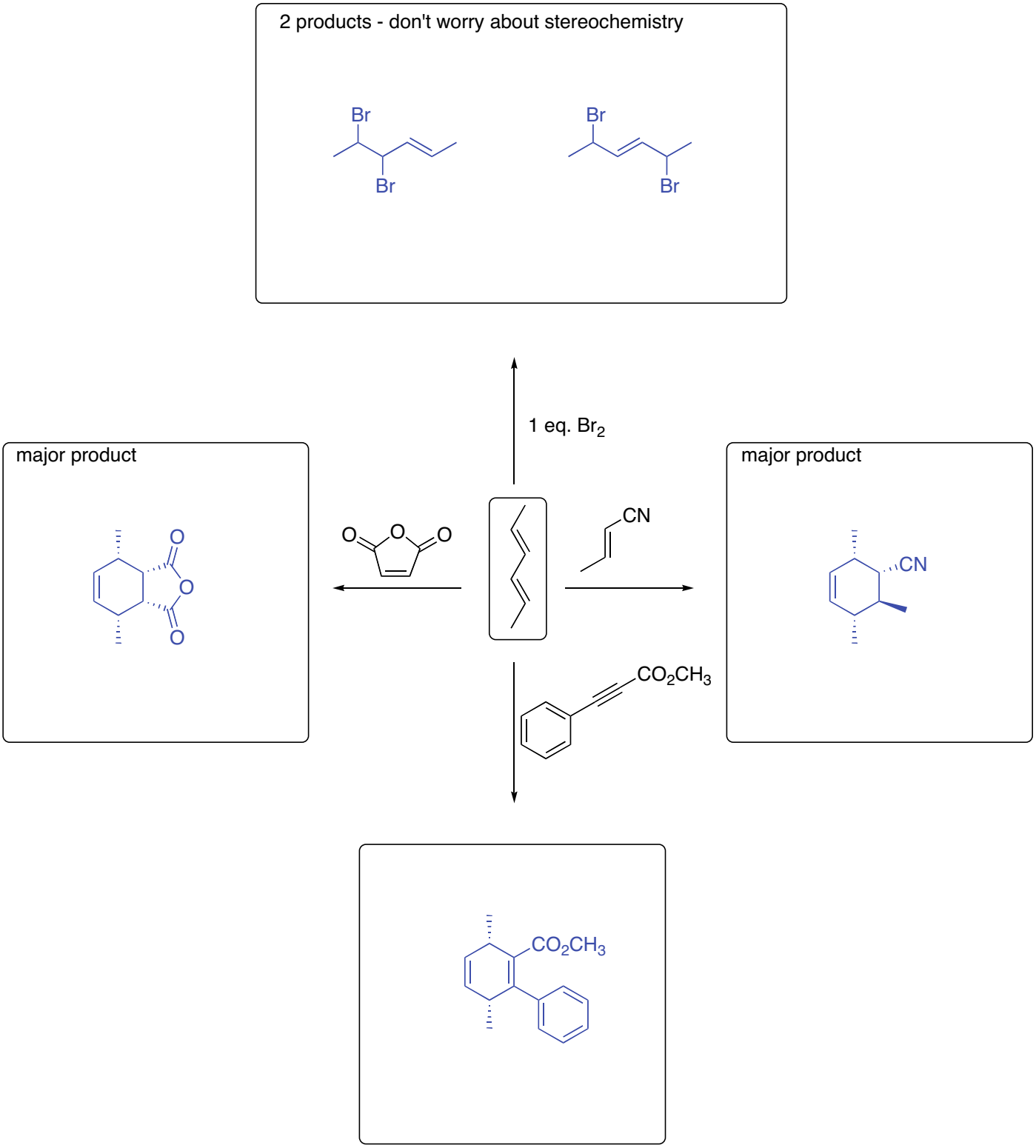
4. The following sequence of reactions will not work to provide the indicated product. Explain what is wrong with this synthesis. What would you do different? (5 points)




**In the first step, the alkylation reaction would not favor the linear butane product. There would be carbocation rearrangements. Also, an alkyl group is an o,p-director, and you need to place the I meta to it. The solution is to do a FC-acylation followed by $I_2$, then reduction of the ketone.**

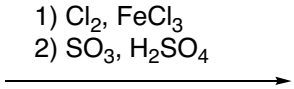
1) $CH_3CH_2CH_2COCl$, $AlCl_3$
2) $I_2$, CuI
3) $H_2$, Pd/C

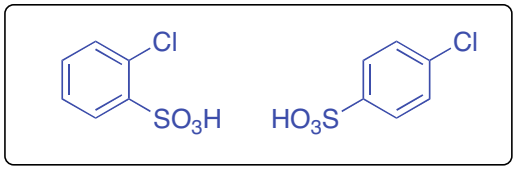
5. Provide the product or products for the following reactions. (15 pts)

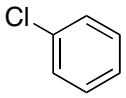


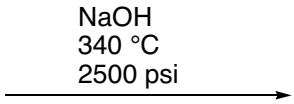
5. Draw the product or products for the following reactions. If there is more than one possible product (eg. o, p), draw both. Assume any of the reagents only react once. (27 pts)

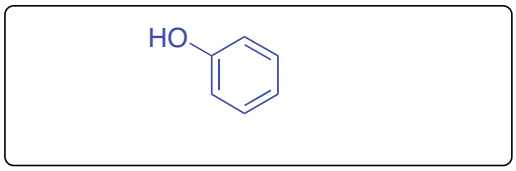
(a) 

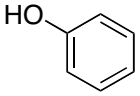


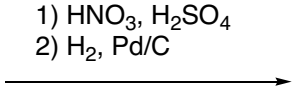



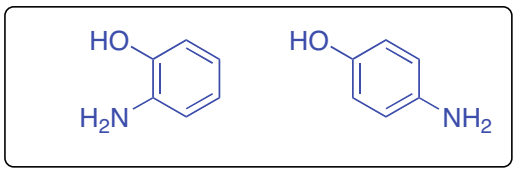

(b) 

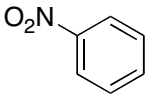



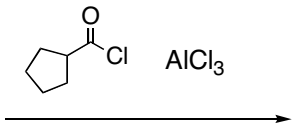



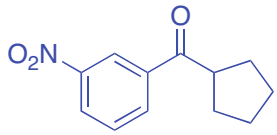

(c) 

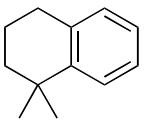



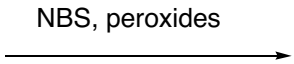



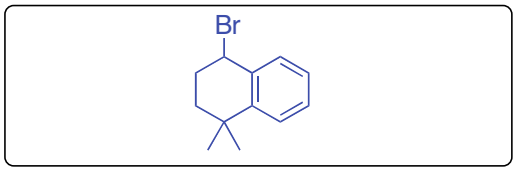

(d) 

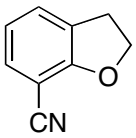



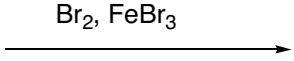



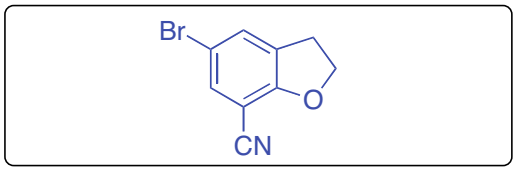

(e) 

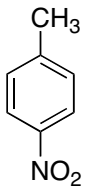


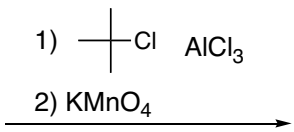



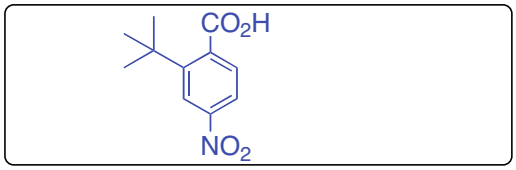

(f) 

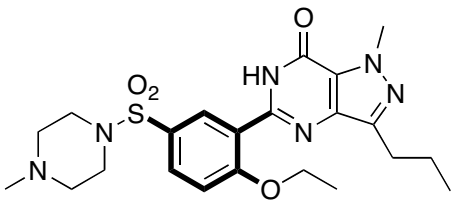




(g) 

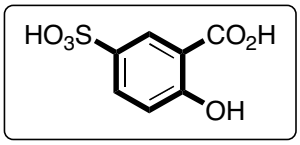



7. The structure of the pharmaceutical drug, viagra is shown below. At the core of viagra is a trisubstituted benzene ring. The structure on the right could be a potential intermediate for the preparation of viagra. Show how you would synthesis this trisubstituted derivative starting from benzene and any other reagents you need. Hint - you should be able to do this in five steps. Start by making phenol. (16 pts)



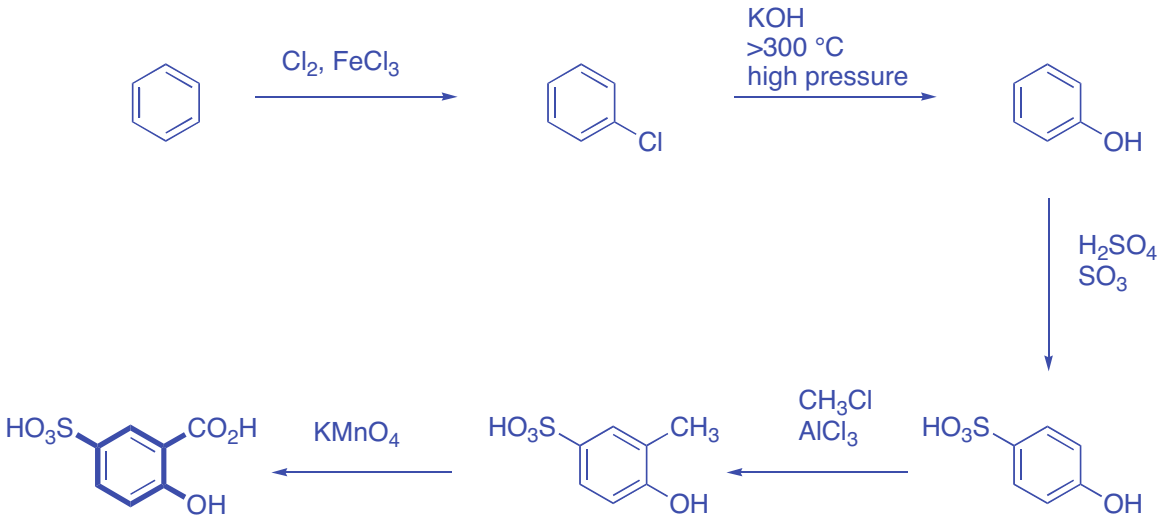

viagra




synthesize this from benzene

**There are a number of different ways you can do this synthesis that would be correct. Here is one way to make the target compound.**

**First we need to make phenol. To do this, start by making a halide and then doing a nucleophilic substitution (benzyne reaction).**




**Both groups direct to the same place**