Organic Chemistry c3444y

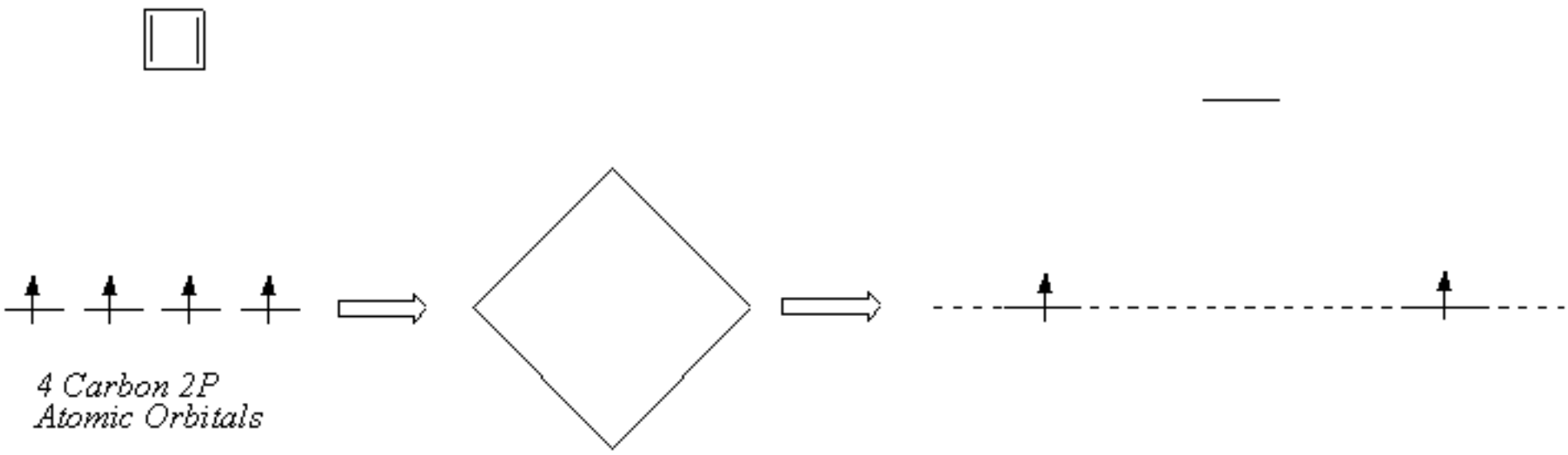
1st Hour Exam

Wednesday, Feb. 13, 2002
Prof. Leighton

Answer Key

Name: _____

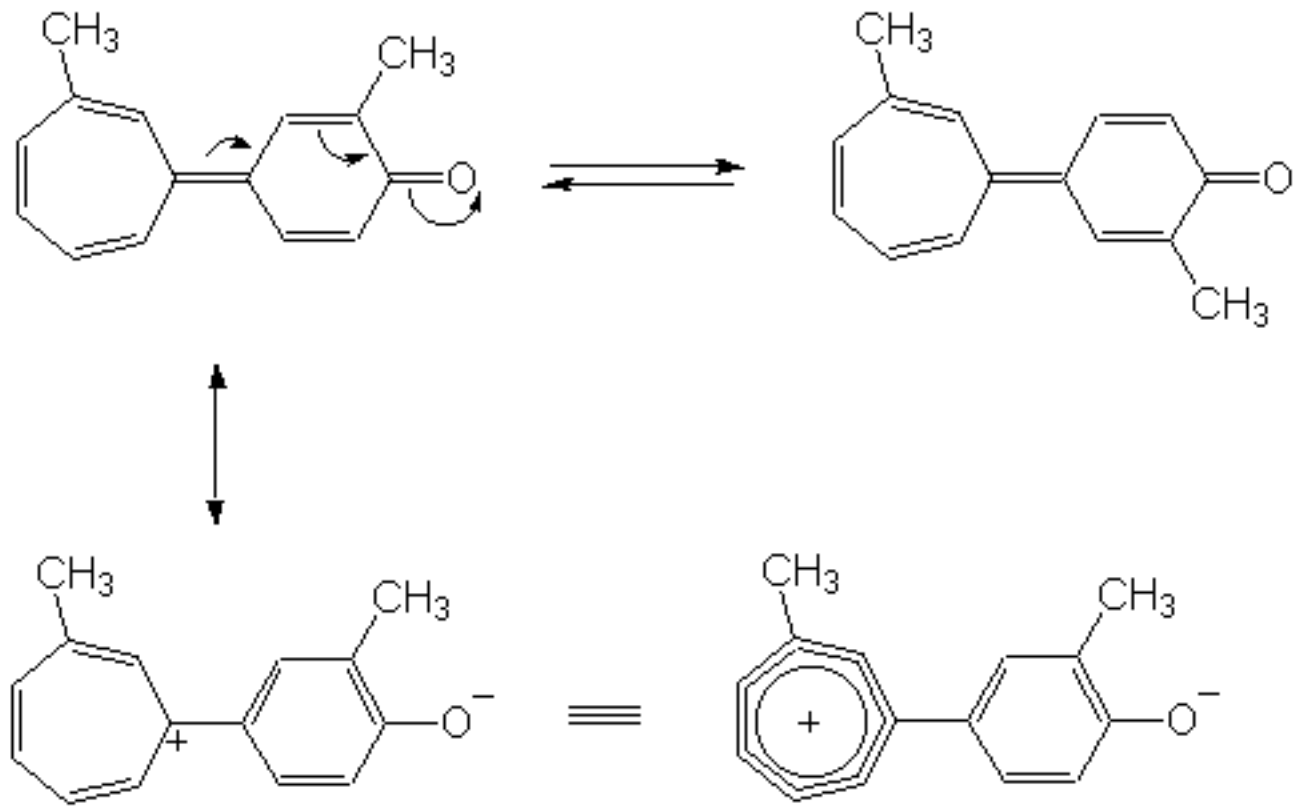
1. a. (10 pts) Demonstrate the use of the Frost circle method to determine whether or not the illustrated compound is aromatic or antiaromatic.



4 Carbon 2P Atomic Orbitals

Unpaired electrons, and electrons in non-bonding orbitals: ANTIAROMATIC

b. (10 pts) 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.

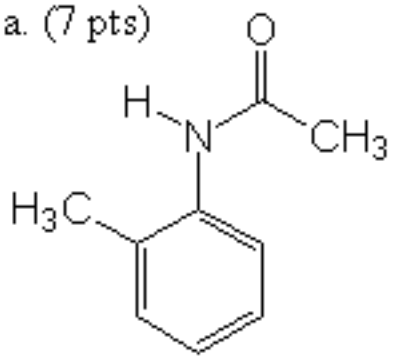


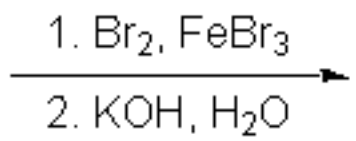
This resonance structure, in which both rings are aromatic, would be expected to make a significant contribution to the structure of this molecule. Thus, we would expect that the central double bond in question should have significant single bond character, and therefore should undergo unusually facile rotation.

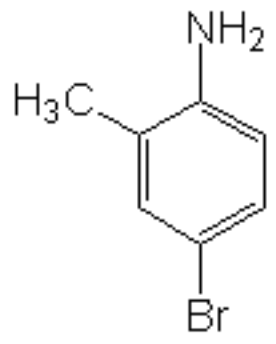
Name: _____

2. Predict the major product, if any, of the following reactions:

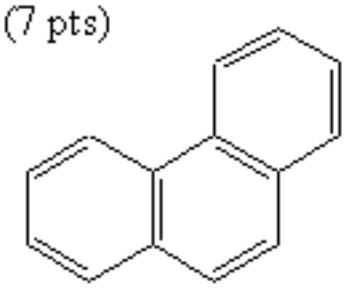
a. (7 pts)

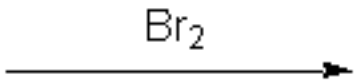


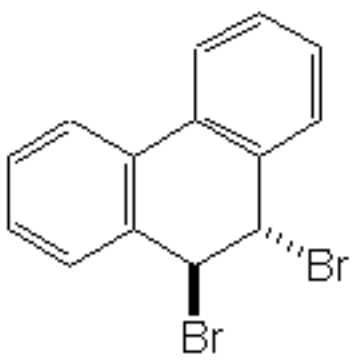




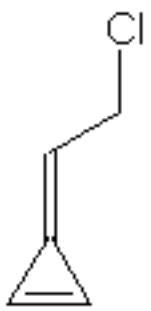
b. (7 pts)

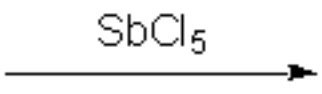


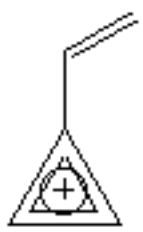




c. (6 pts)



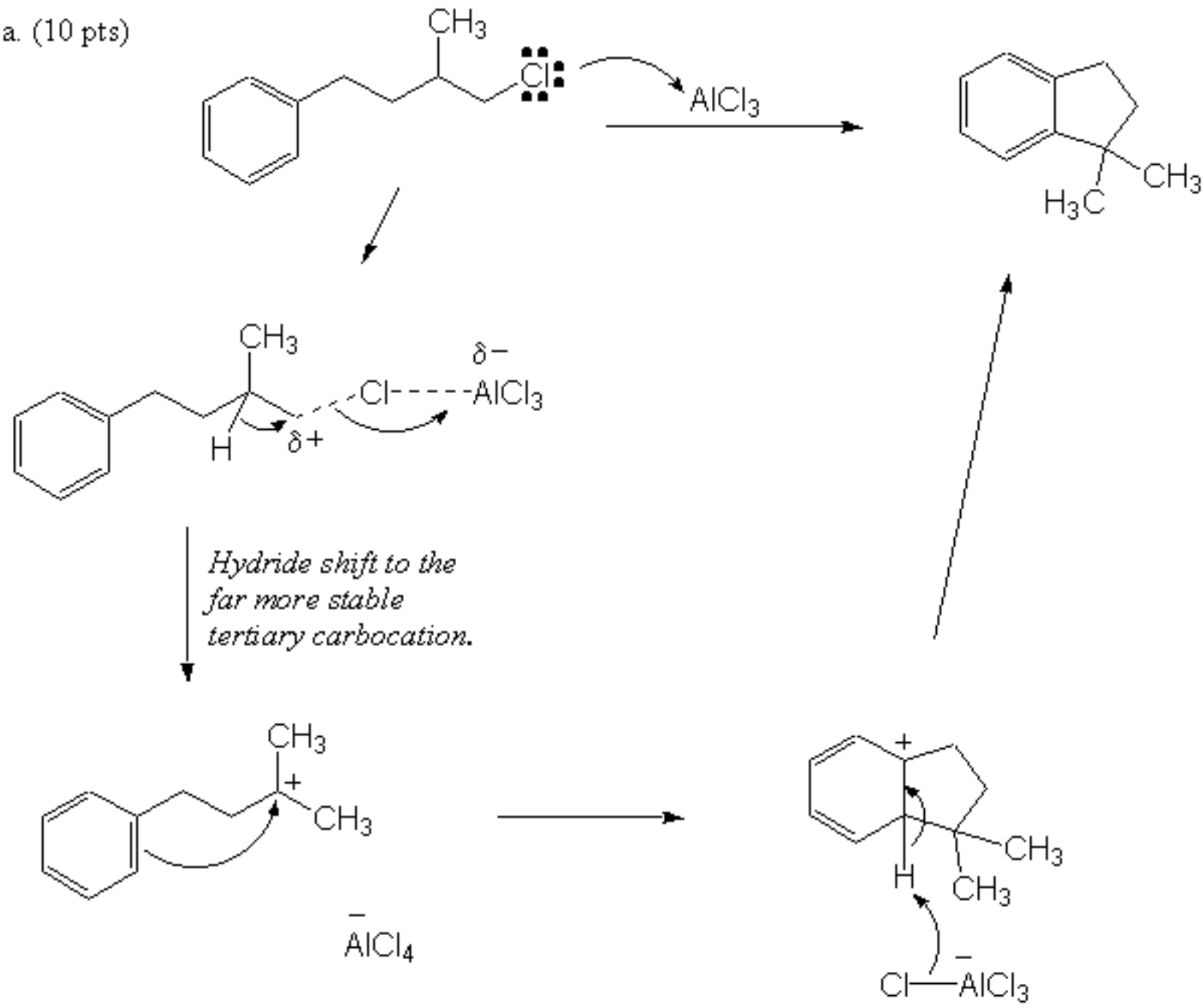




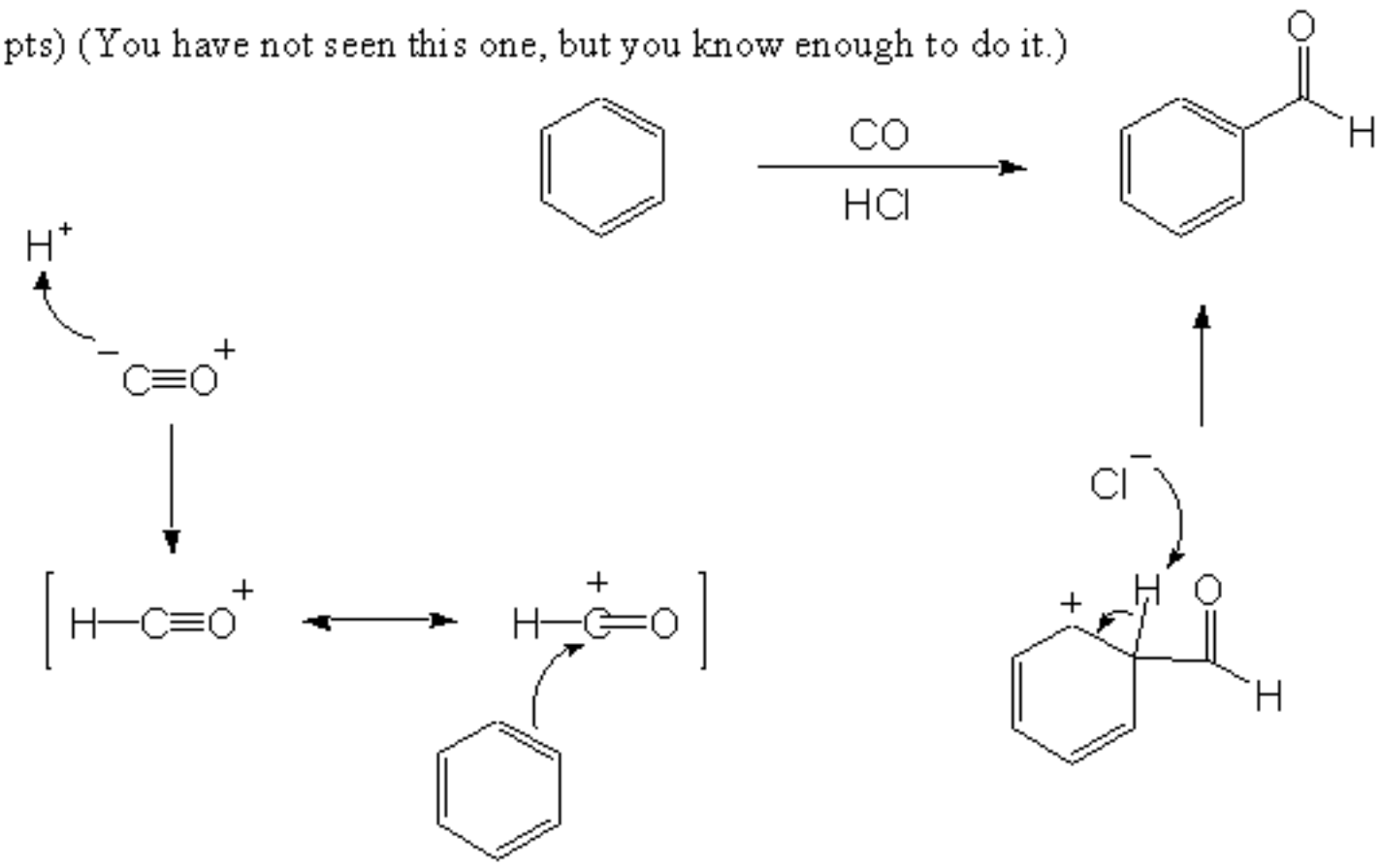
Name: _____

3. Provide detailed mechanisms for the following transformations:

a. (10 pts)

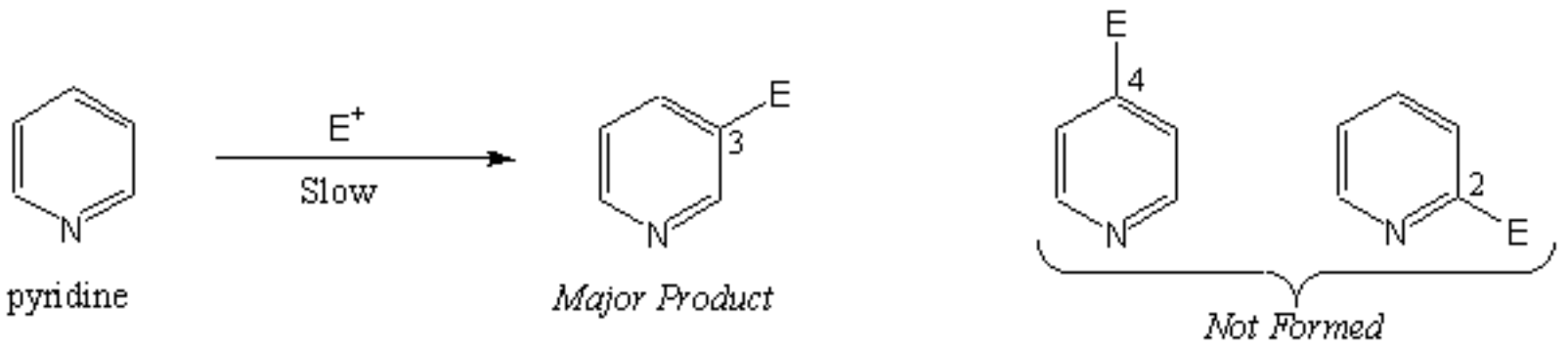


b. (10 pts) (You have not seen this one, but you know enough to do it.)

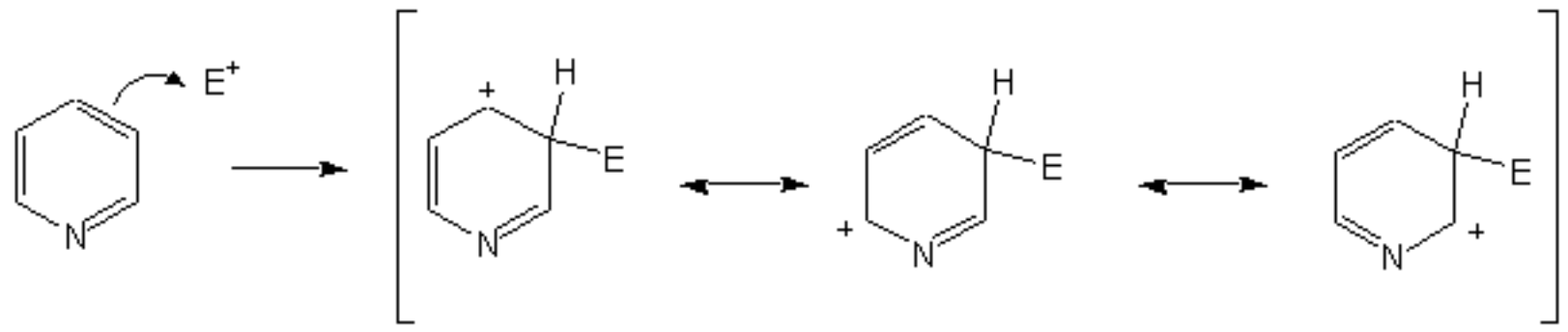


Name: _____

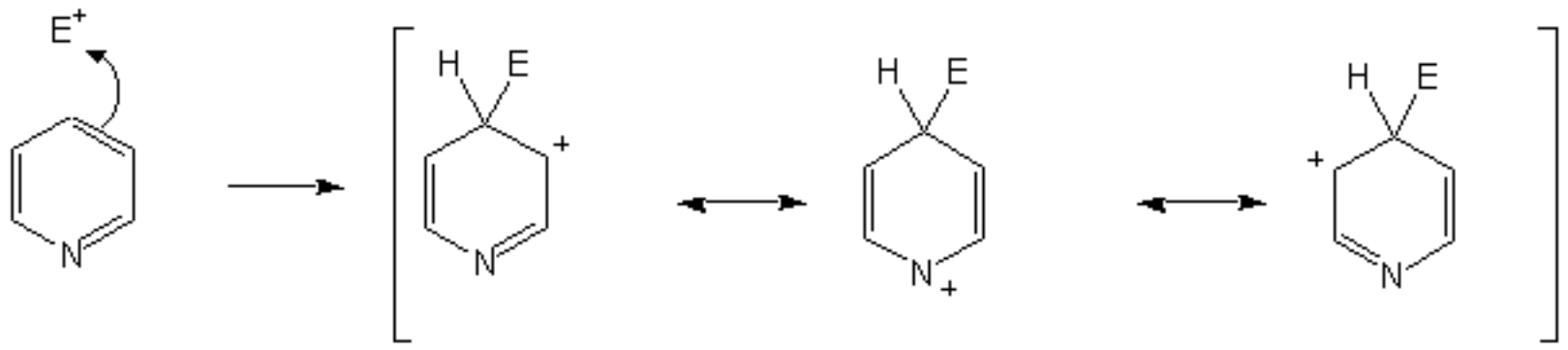
4. Pyridine can undergo electrophilic aromatic substitution. When it does, the reaction is slower than the corresponding reaction with benzene itself, and is quite selective for the 3 position rather than the 2 or 4 positions.



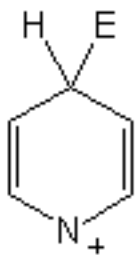
a. (7 pts) Draw the resonance structures for the intermediate arenium ion formed from attack at the 3 position:



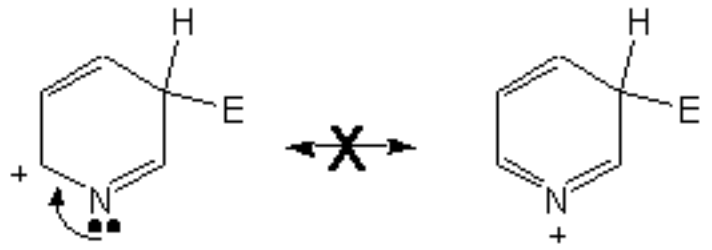
b. (7 pts) Draw the resonance structures for the intermediate arenium ion formed from attack at the 2 (or 4) position:



c. (6 pts) What is it that makes attack at the 2 (or 4) position especially slow relative to attack at the 3 position?

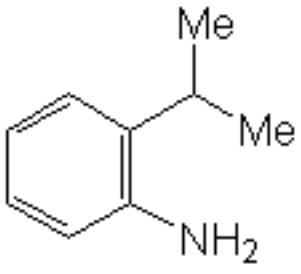


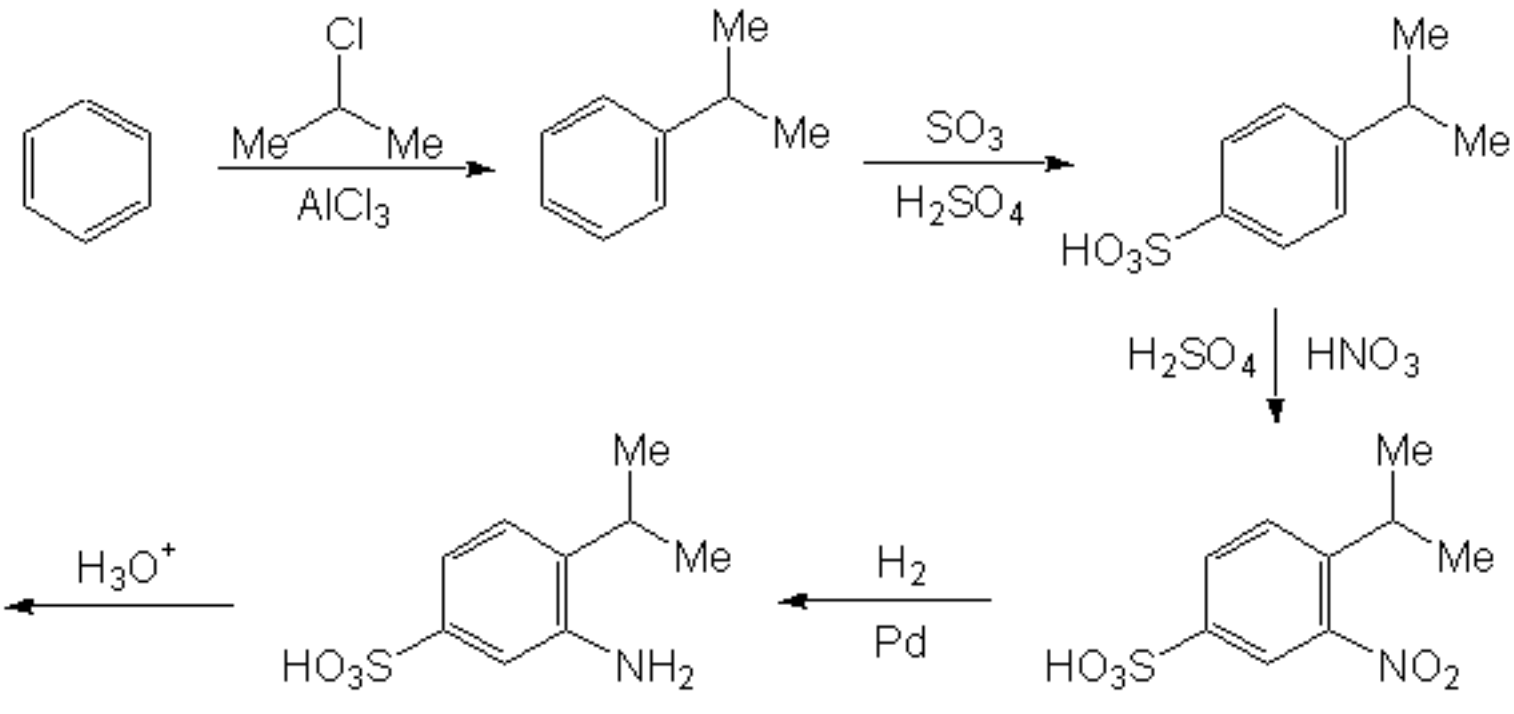
Especially poor contributor. Positive charge (does not have full octet) on relatively electronegative nitrogen.



Note: For anyone that drew the resonance structure on the right, make sure you understand why that is wrong: The lone pair on the Nitrogen is not properly aligned to engage in resonance. Another way to look at it is that two double bonds in a row in a six membered ring is not a reasonable structure.

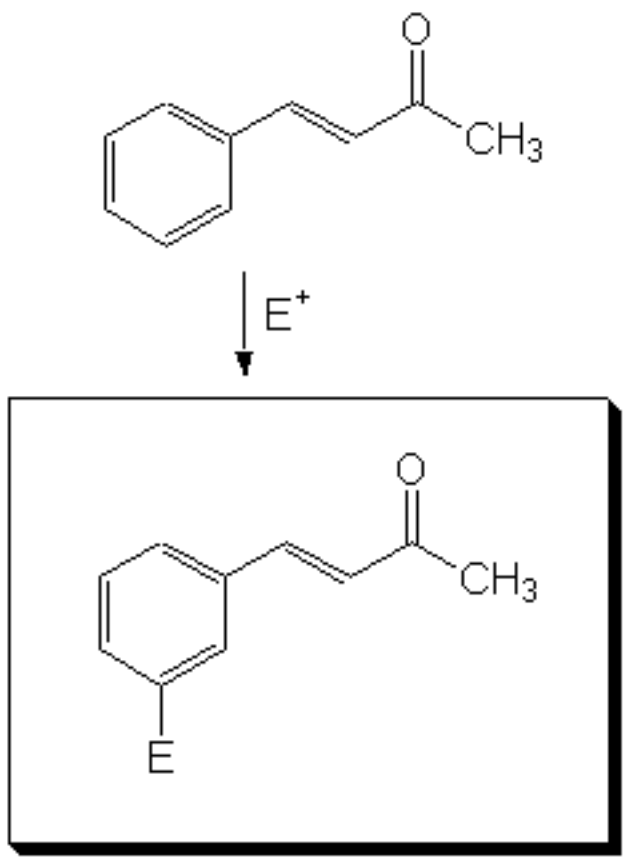
5. a. (10 pts) Propose a synthesis of the following compound from benzene and any other reagents that you need.



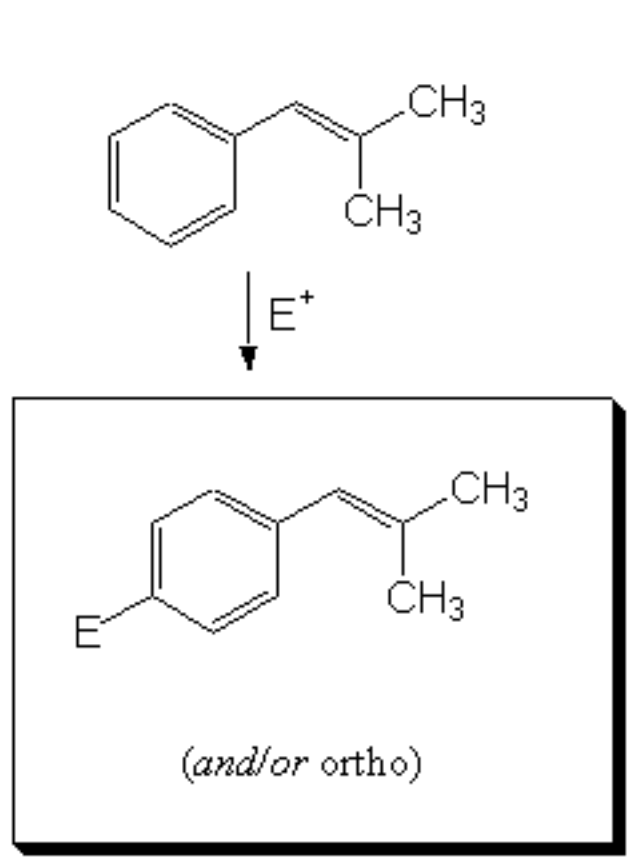


Note: In principle the amino group could be put on first, followed by the same blocking group strategy and then the Friedel-Crafts alkylation. But the latter does not work in the presence of an amino group, and/or in the presence of an electron withdrawing group (e.g. SO_3H).

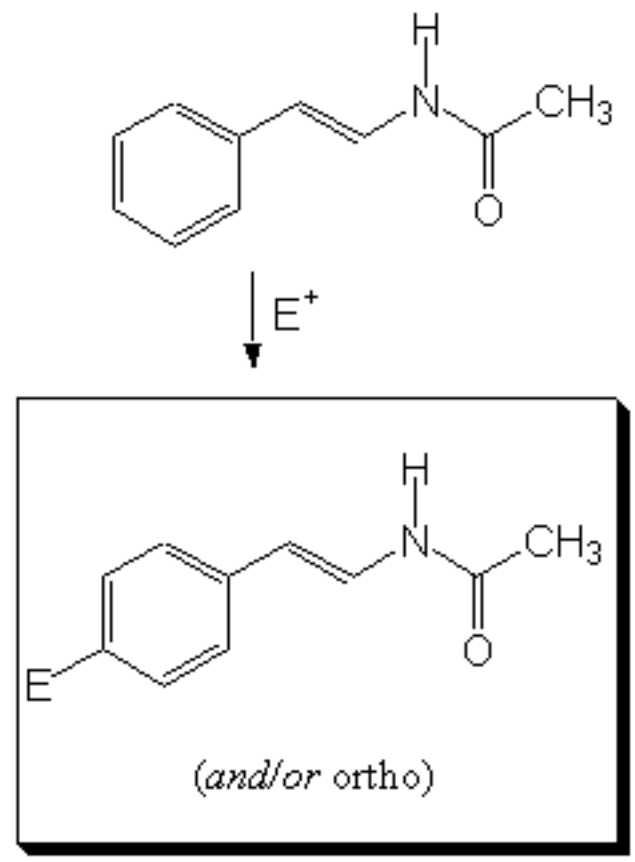
b. (10 pts) For each of the following electrophilic aromatic substitution reactions draw the expected product in the big box, and indicate in the smaller box whether you would expect the reaction to be faster or slower than the corresponding reaction with benzene.



Slower



Faster



Faster