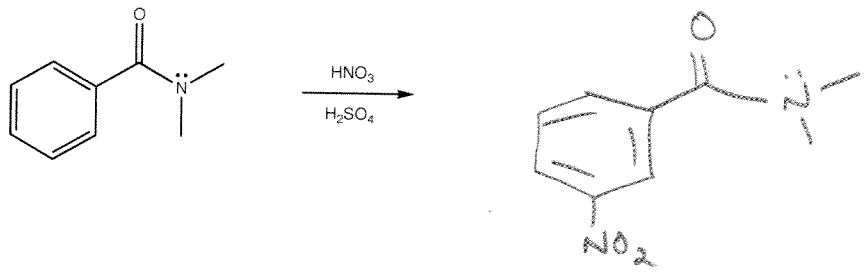
Exam #2 – CHEM 235 – Spring 2007

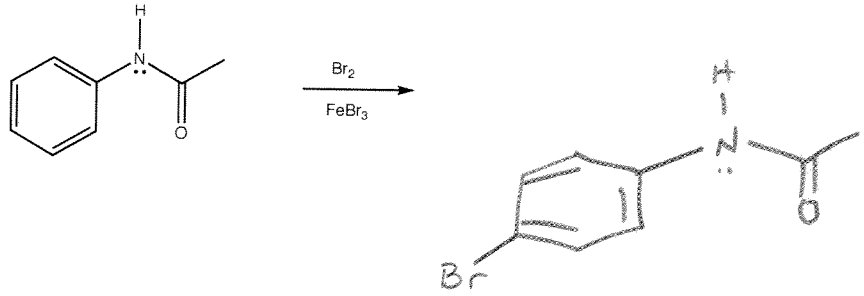
Name: Key

1. (35 points) Predict the major product for each of the following reactions. If no reaction is expected, briefly explain why. You may neglect stereochemistry. Where an EAS reaction takes place, you may assume that only one substitution takes place.

A)

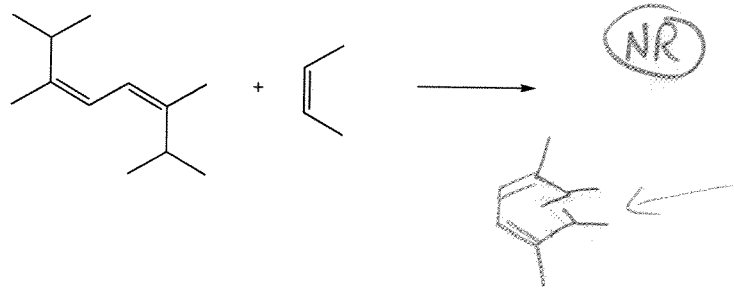


B)



(ortho subst. also pass)

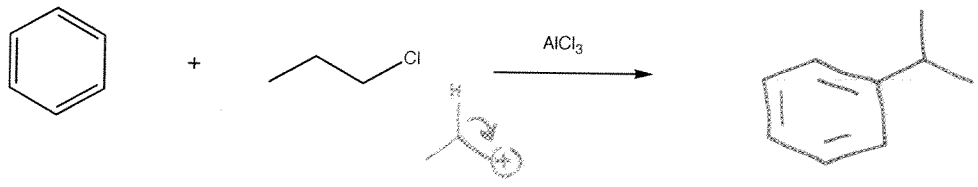
C)



NR

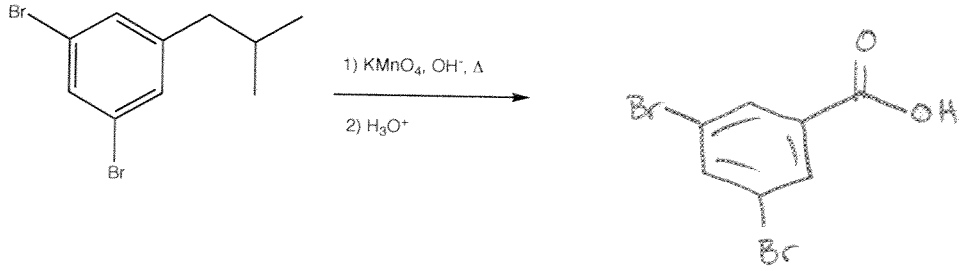
diene is too sterically hindered to assume s-cis conformer.

D)

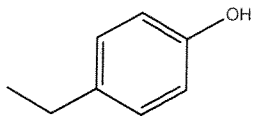


(for monoalkylated product (dialkylation likely))

E)

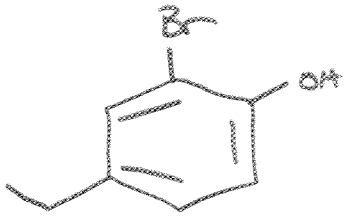


F)

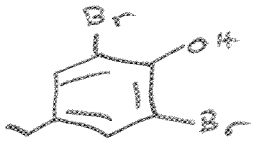


Br_2

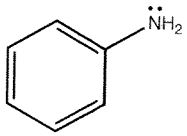
$FeBr_3$



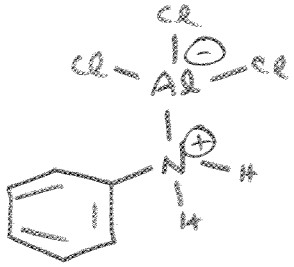
dibrominated likely:



G)



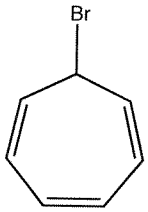
$AlCl_3$

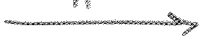


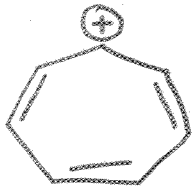
(lewis acid-base reaction)

2. (8 points) In the presence of a strong acid in ethanol, the compound shown below, (1*Z*,3*Z*,5*Z*)-7-bromocyclohepta-1,3,5-triene, will dissociate to form a cation and bromide.

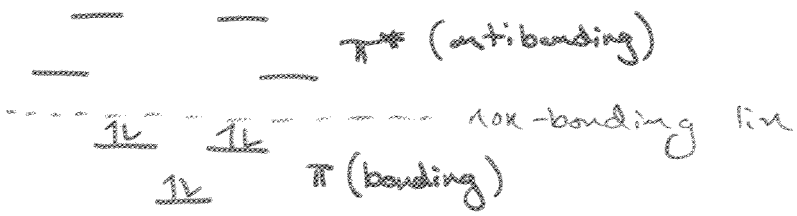
- Give the structure of the cation.
- Draw an orbital energy level diagram showing the relative energies of all of any π, π(non-bonding) and π* orbitals, and fill with electrons. (for the CATION)
- Do you predict this cation will be aromatic? Explain.







+ 6 resonance structures

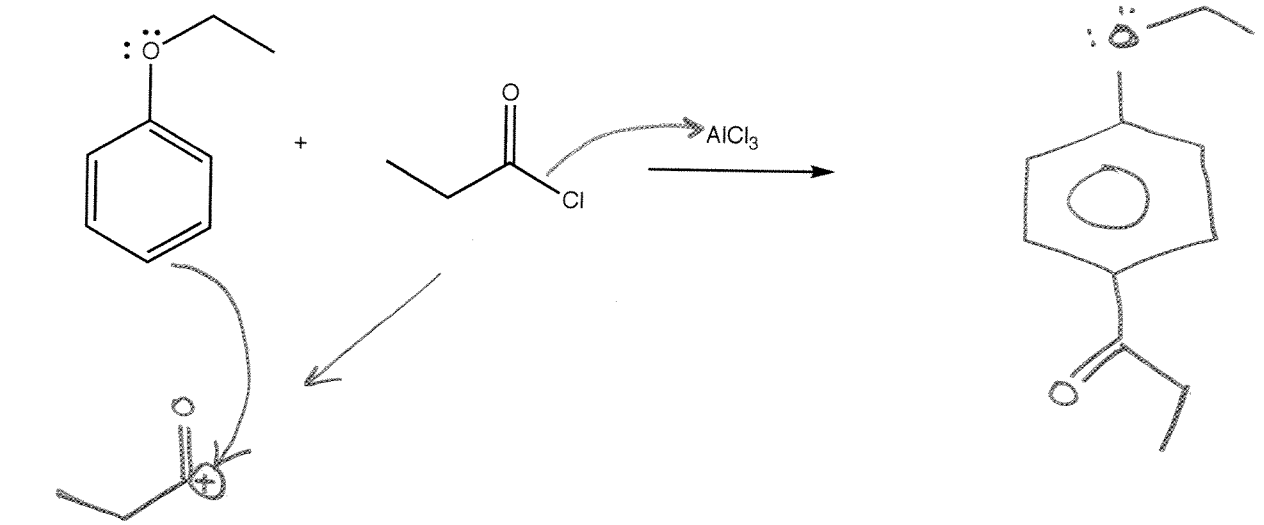


Aromatic

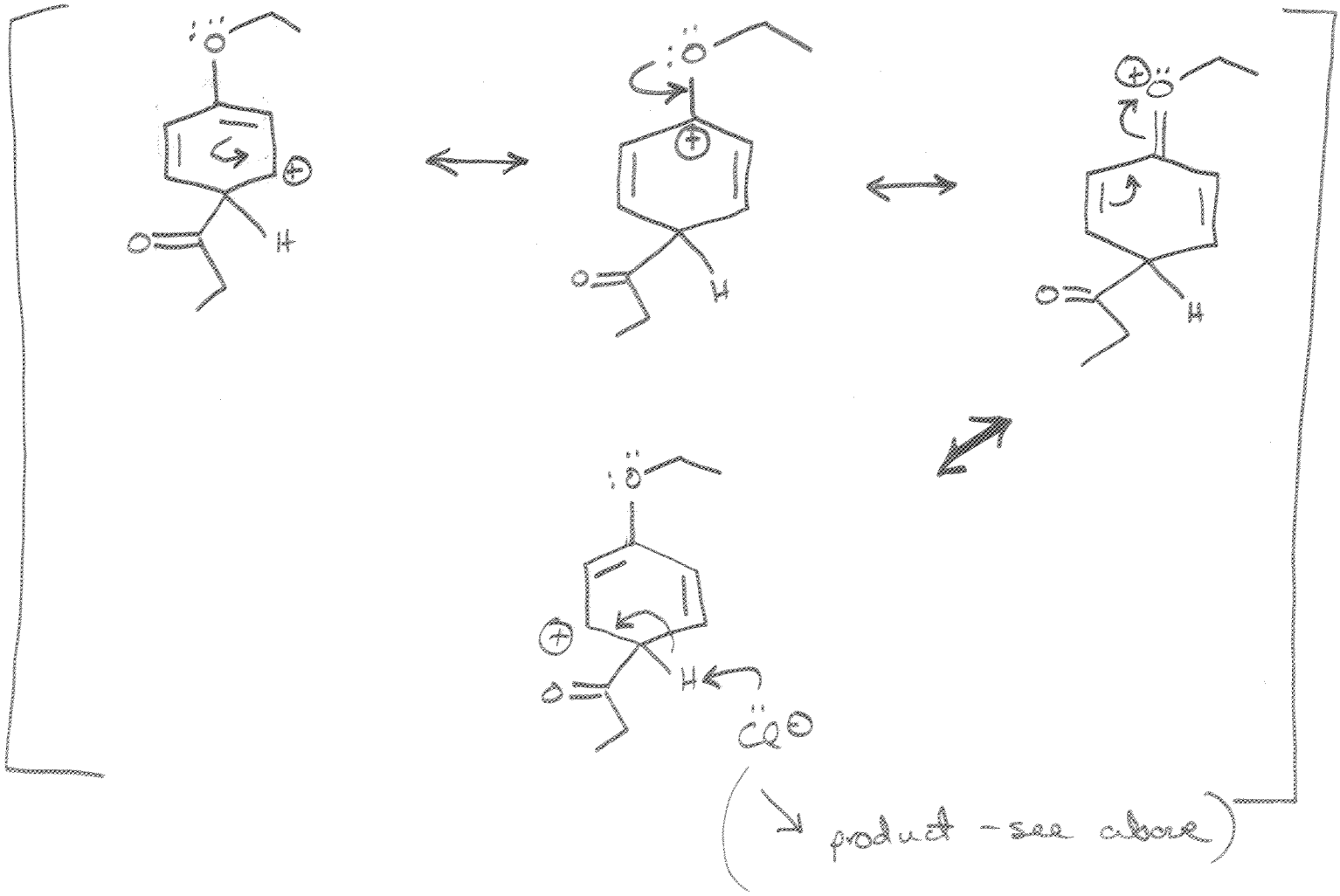
- Cyclic
- planar p-orbital (π) system
- Hucked # of e's (6)
- Electrons completely fill π orbitals & no electrons are in π^{*} orbitals

3. (12 points) Predict the major product for the following reaction.

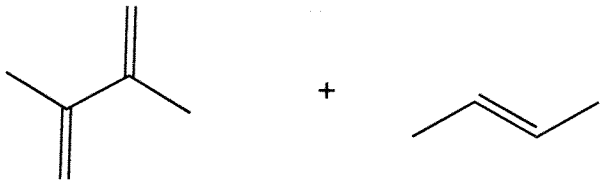
Write a complete arrow-pushing mechanism for the formation of that compound, including all important resonance structures for any intermediates.

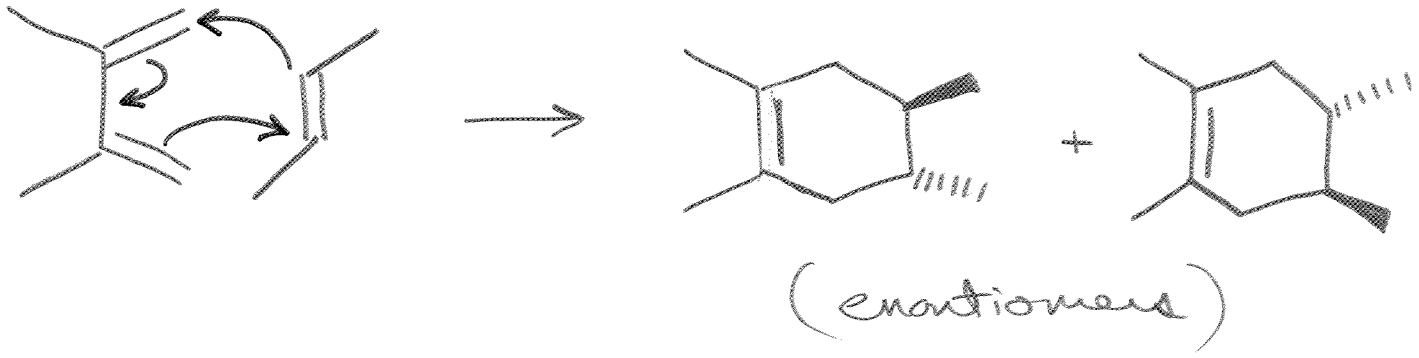


Intermediate:



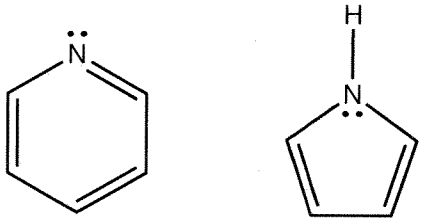
4. (8 points) Predict the structures of the two stereoisomers formed in the following reaction. Show the mechanism by which one of the stereoisomers is formed.





(enantiomers)

5. (8 points) Pyridine (on the left) has a basicity similar to ammonia and most alkyl amines (like methylamine). Pyrrole (on the right) is much less basic. Explain both of these observations.

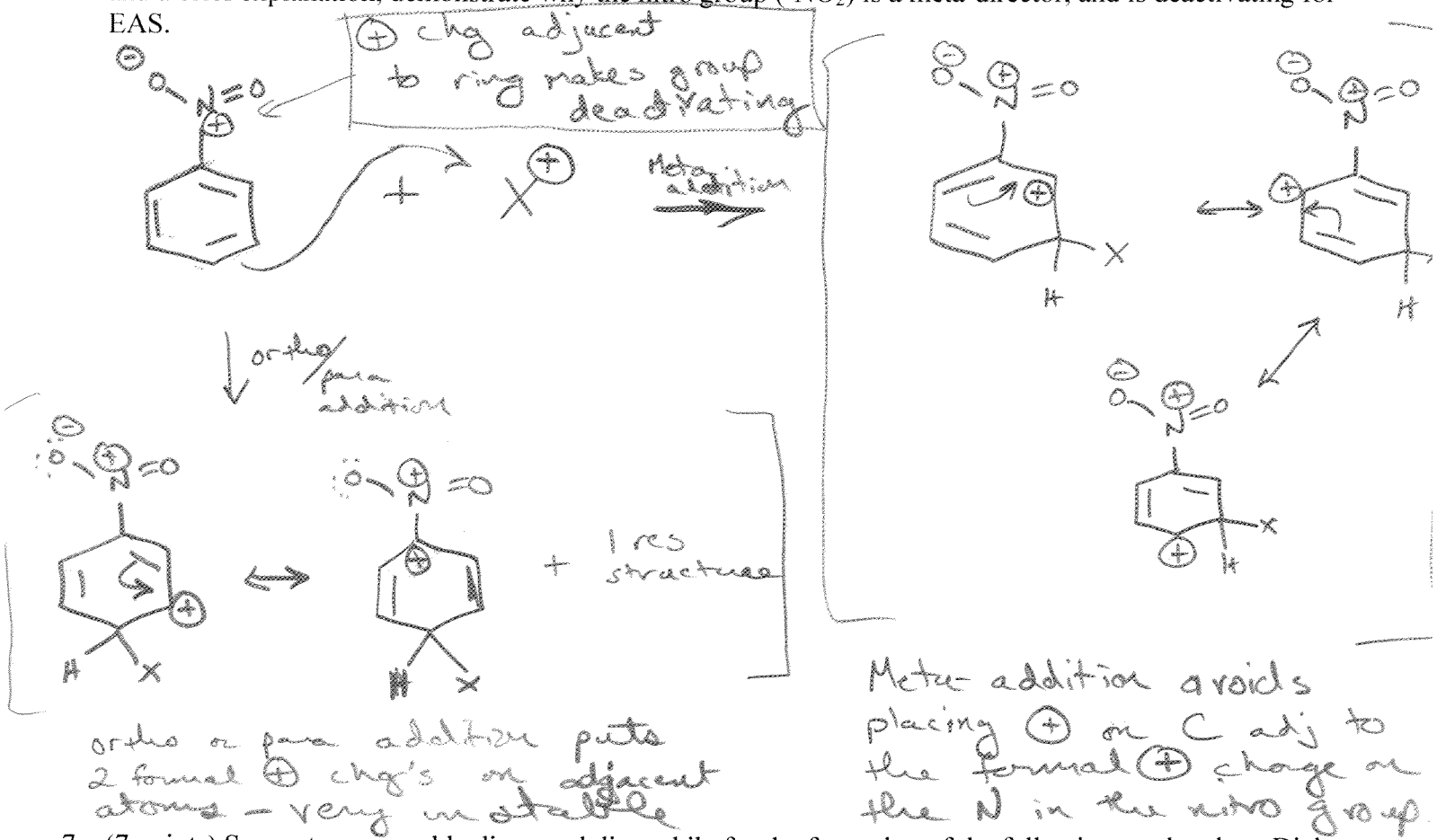


pyridine pyrrole

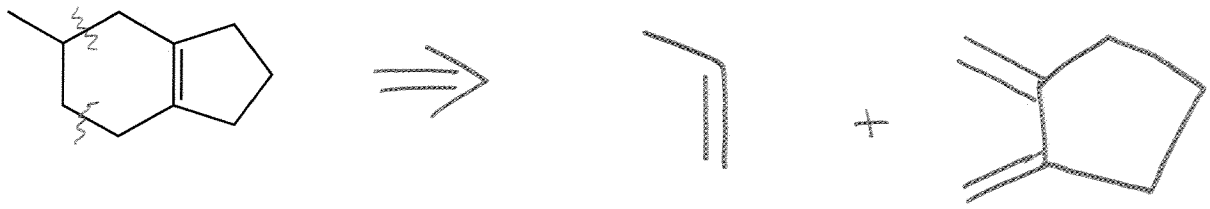
The lone pair on the pyridine are not tied up in the ring aromaticity. They are in an sp^2 orbital and are available to accept a H^+.

The lone pair on the pyrrole is participating in π conjugation in the aromatic ring. They are in p orbital (maj. into π system) and unavailable to accept a H^+.

6. (10 points) Using resonance structures for the intermediate in an electrophilic aromatic substitution (EAS) and a brief explanation, demonstrate why the nitro group ($-NO_2$) is a meta-director, and is deactivating for EAS.



7. (7 points) Suggest a reasonable diene and dienophile for the formation of the following product by a Diels-Alder reaction.



8. (12 points) Suggest a reasonable scheme for the preparation of the following compound using toluene, carboxylic acids, or alkyl chlorides as your only sources of carbon. You may use any other reagents or solvents you require.