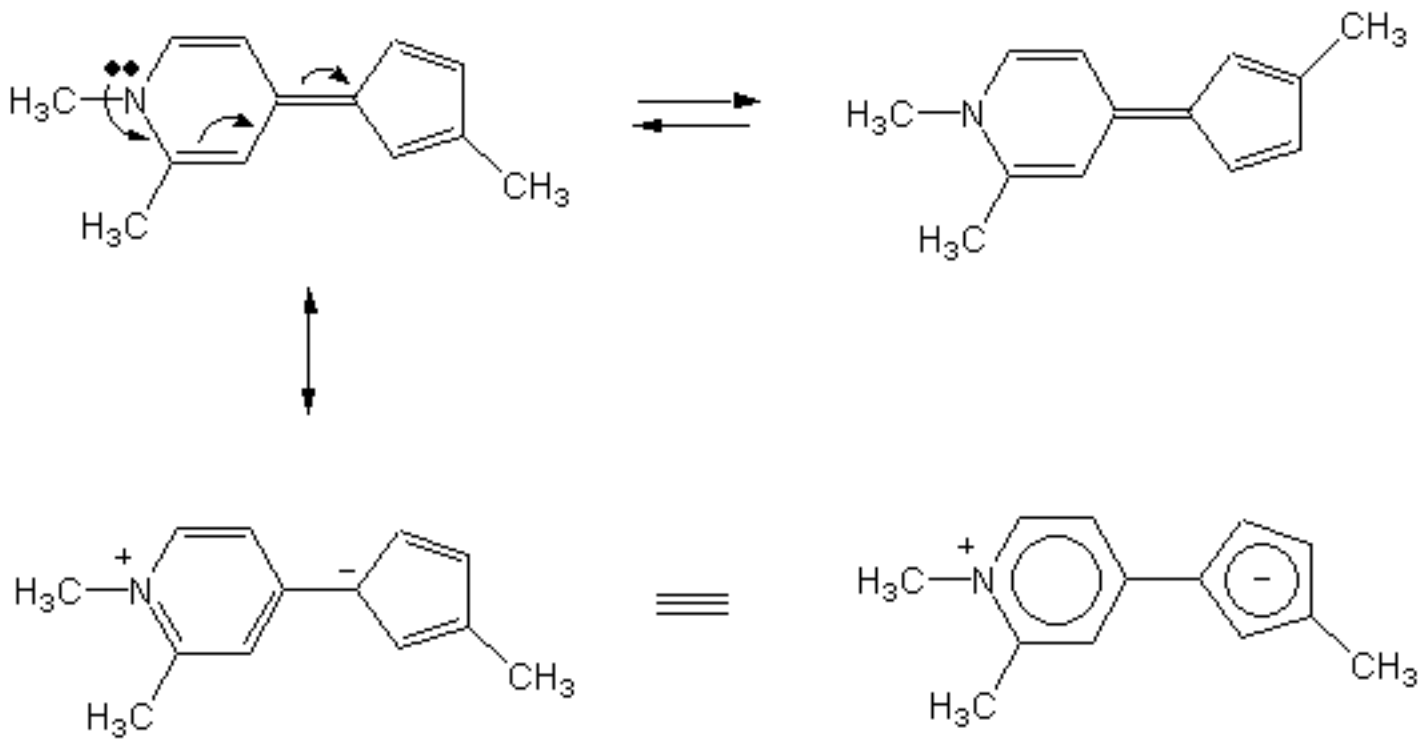
Organic Chemistry c3444y

1st Hour Exam

Answer Key

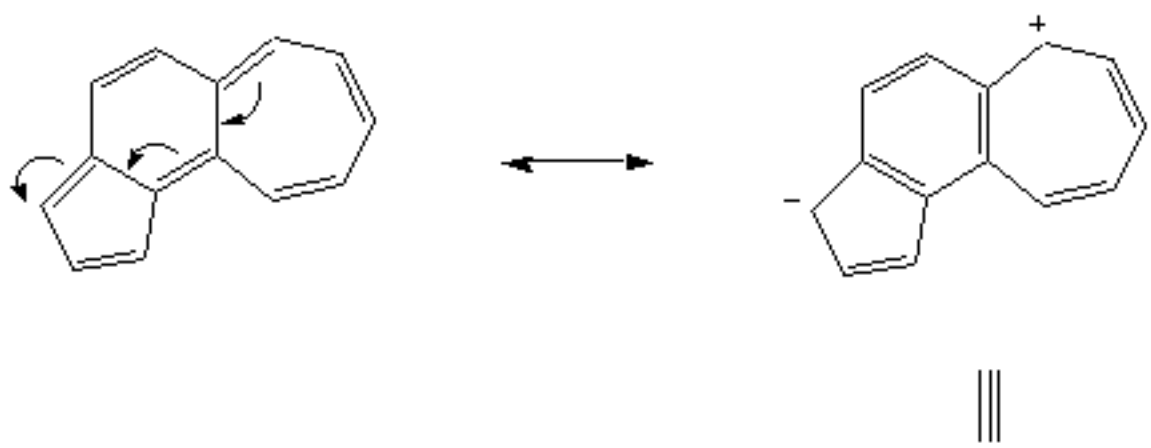
Name: _____

1. a. (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.

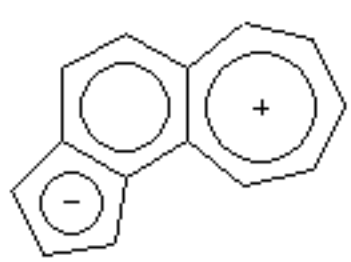


This resonance structure, with both rings aromatic, is a strong contributor. Therefore, there is a substantial amount of single bond character to the central bond. Thus rotation is possible.

b. (10 pts) Make a prediction as to the relative stability of the illustrated compound. Would you expect it to be unusually stable, unusually unstable, or about the same as a regular polyene? Use resonance structures to provide a simple explanation for your answer.

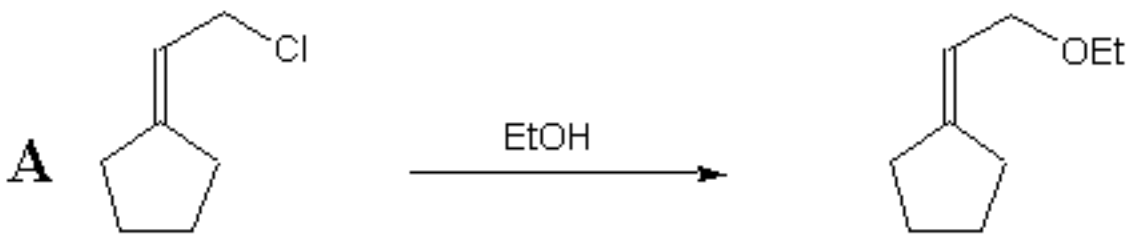


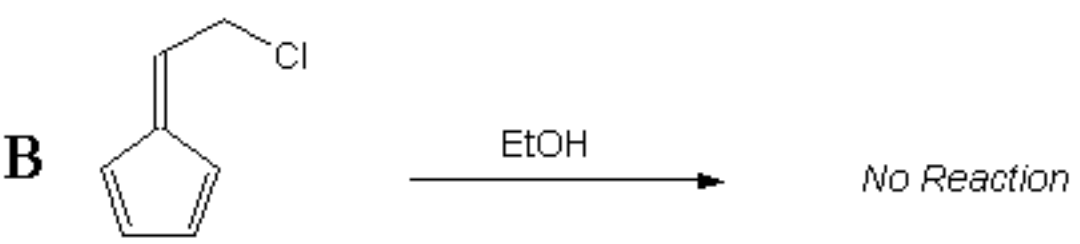
This molecule would be expected to be unusually stable, since we can draw a resonance structure with all three rings aromatic.

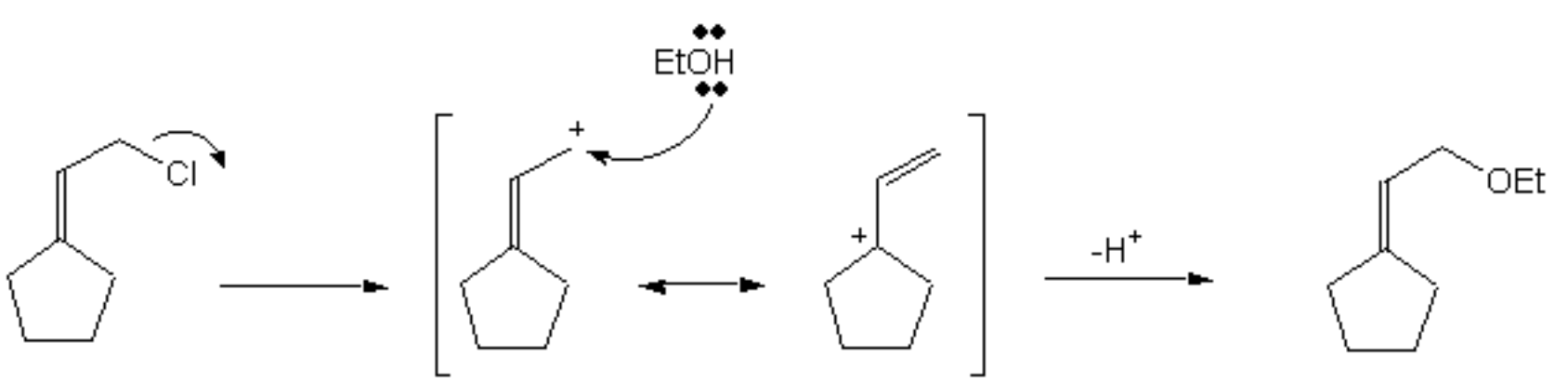


Name: _____

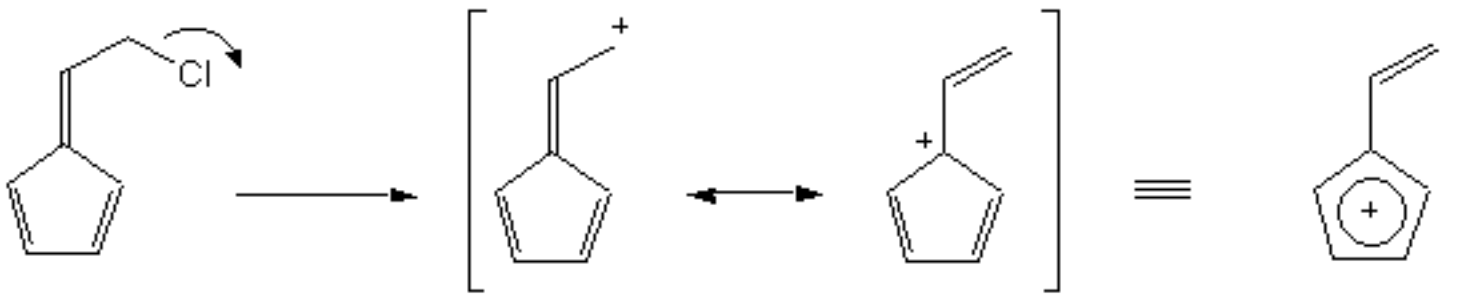
2. (10 pts) Consider the S_N1 reactions of the illustrated allylic chlorides. As expected, compound **A** reacts quite readily. However, under the same conditions compound **B** is quite inert. Recalling that the rate-determining step in the S_N1 reaction is the loss of chloride to form a cation, explain why compound **B** does not readily undergo S_N1 reaction.







Normal allylic cation

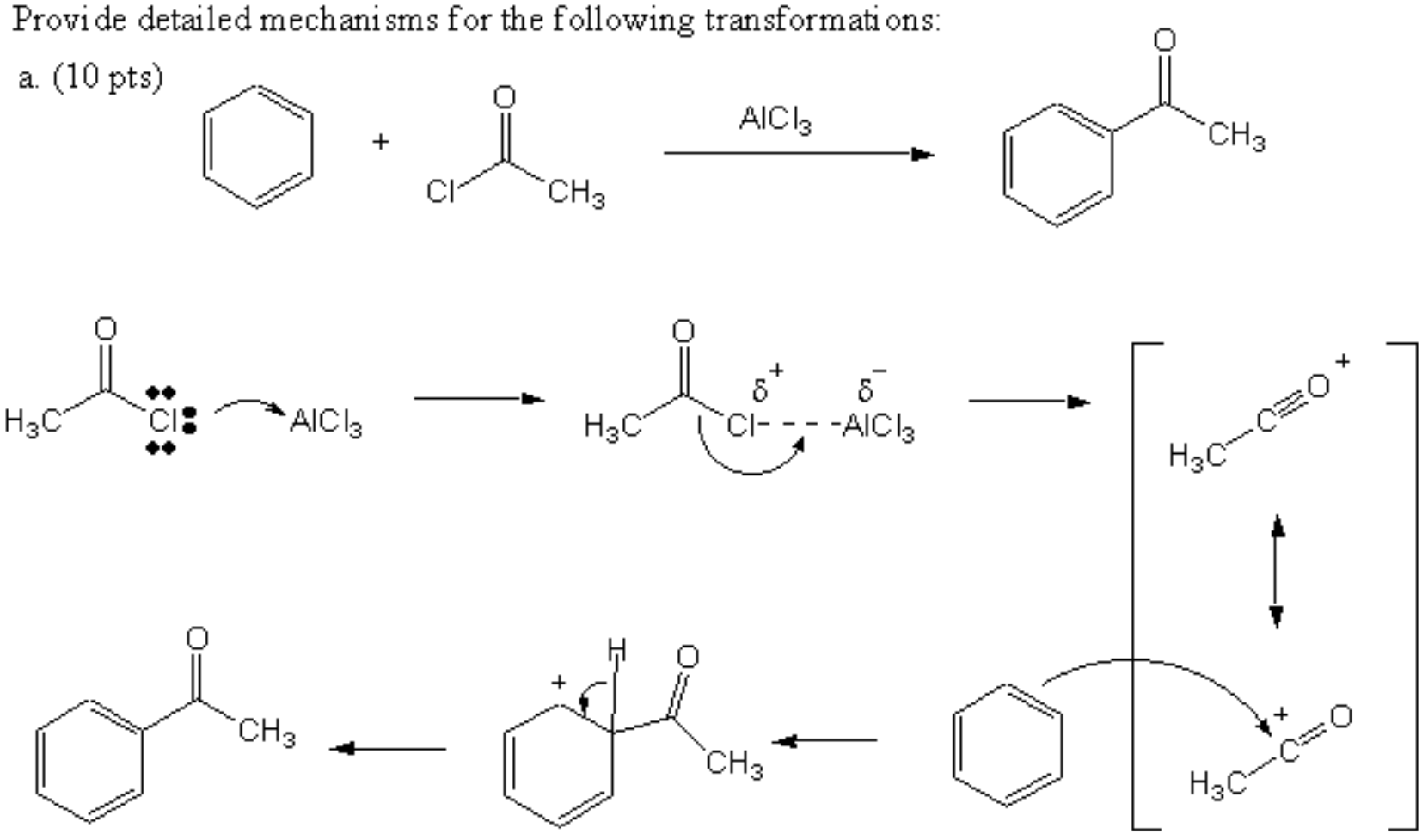


Highly unstable antiaromatic cation. Will not form.

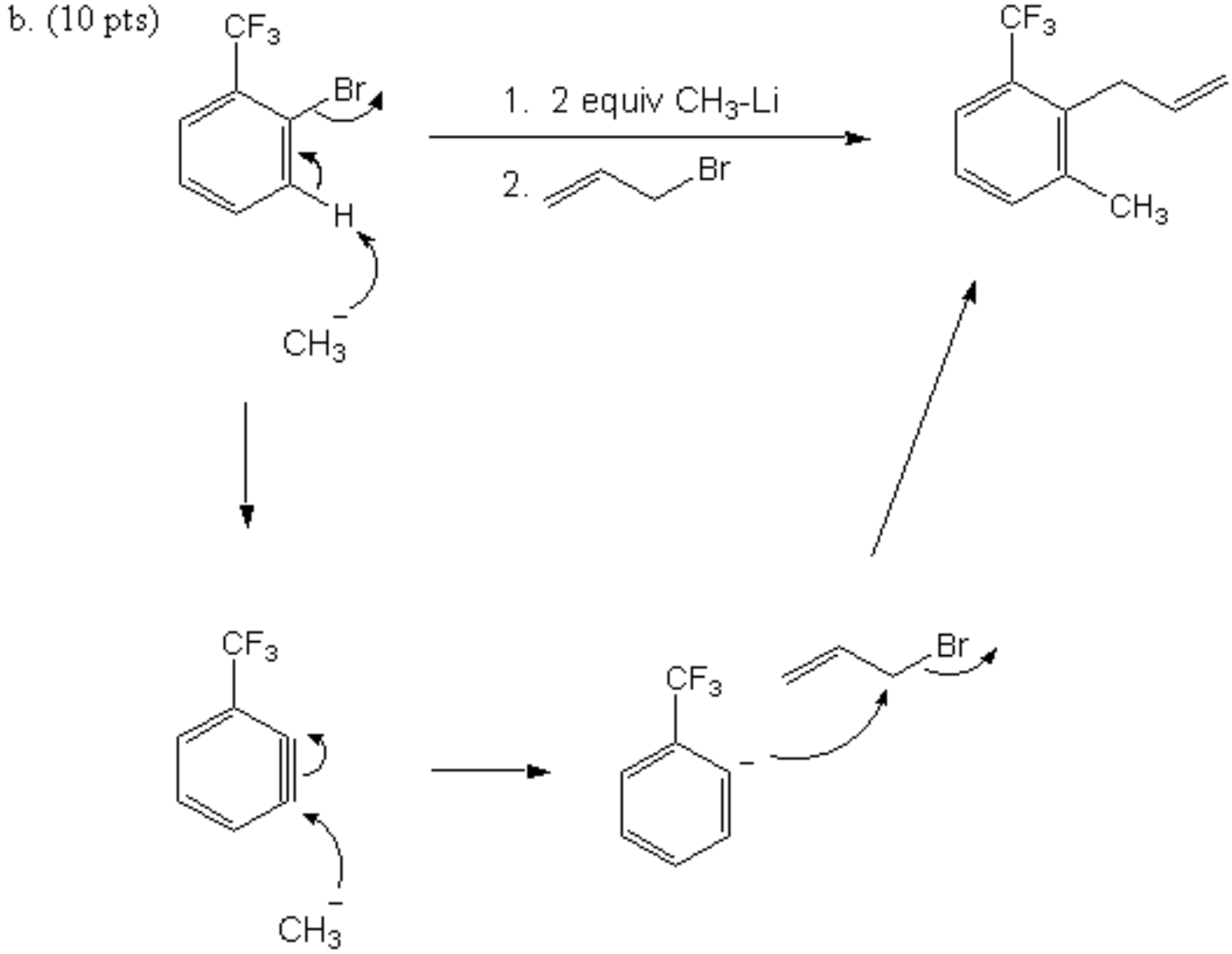
Name: _____

3. Provide detailed mechanisms for the following transformations:

a. (10 pts)

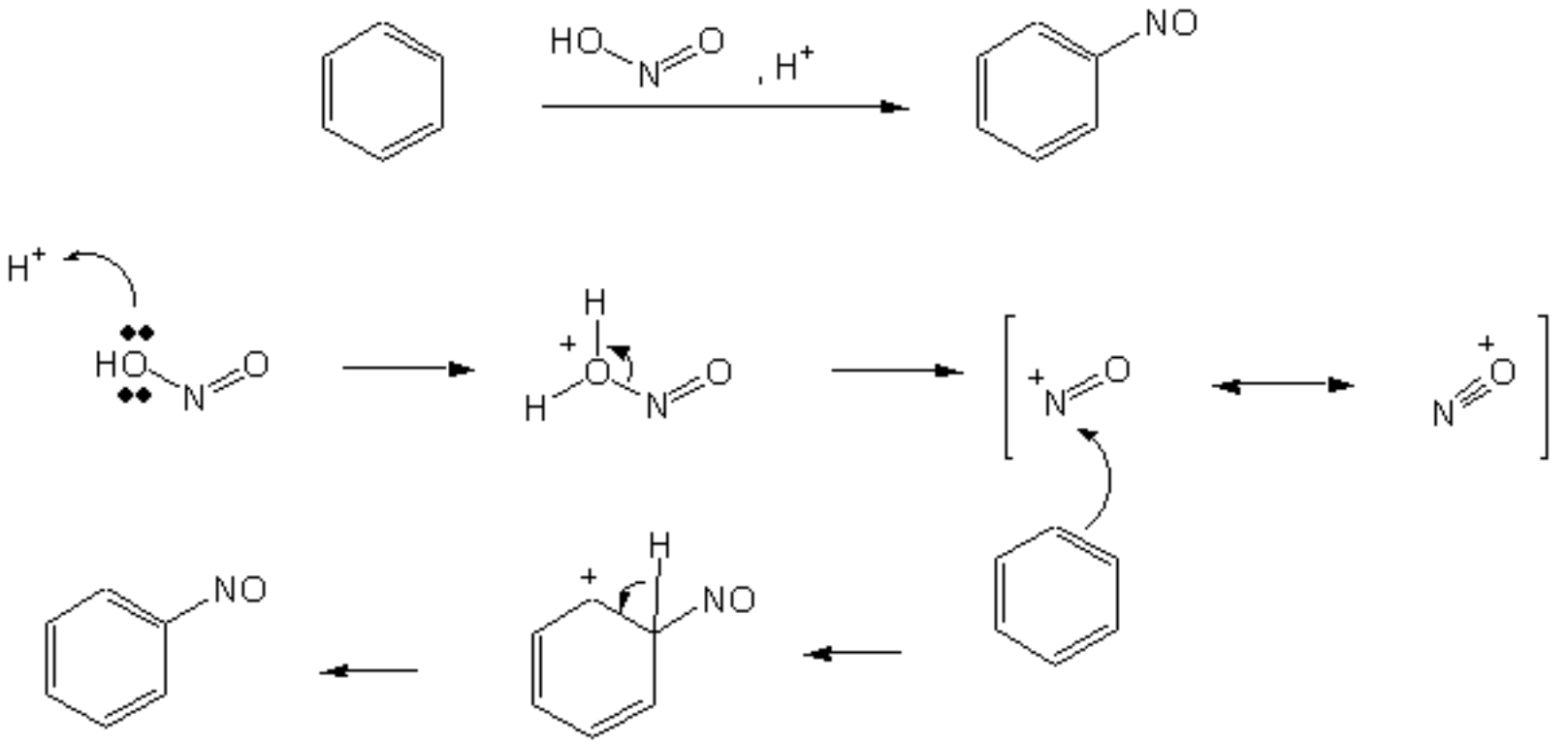


b. (10 pts)



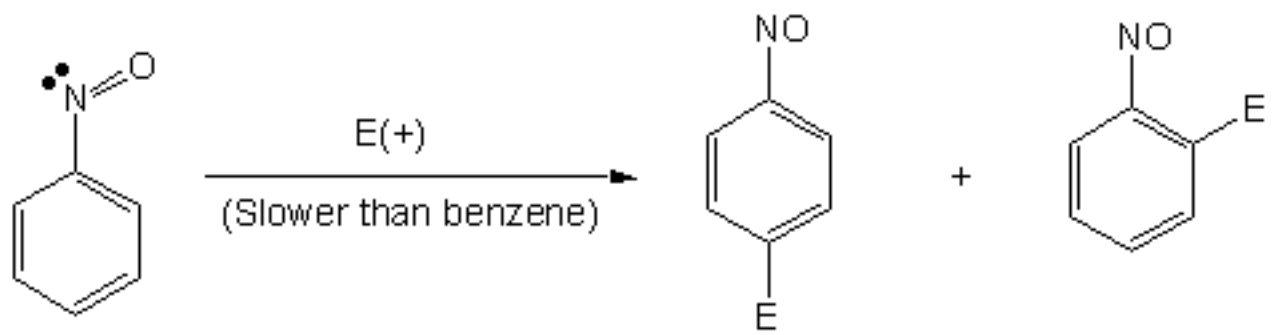
Name: _____

4. a. (10 pts) There is another type of electrophilic aromatic substitution called *nitrosation*. Provide a mechanism for this reaction. First, you must decide what is the actual electrophile here, and how it is formed.

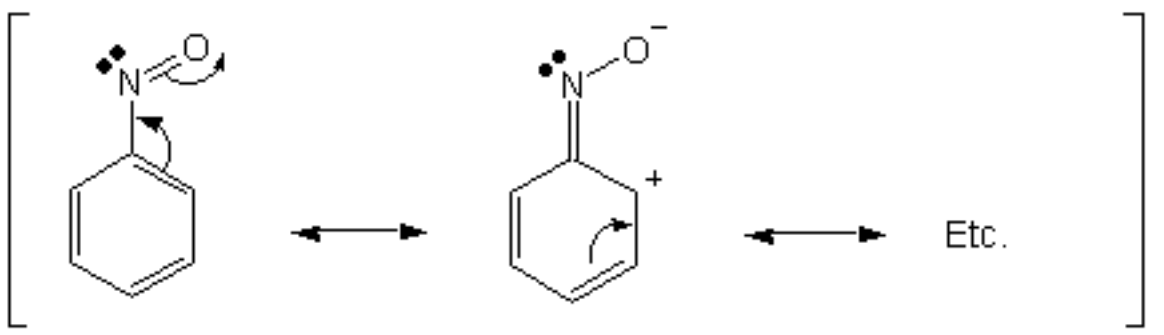


b. (10 pts) Provide an explanation for the fact that the nitroso group (NO) is a deactivator, but an *ortho/para* director.

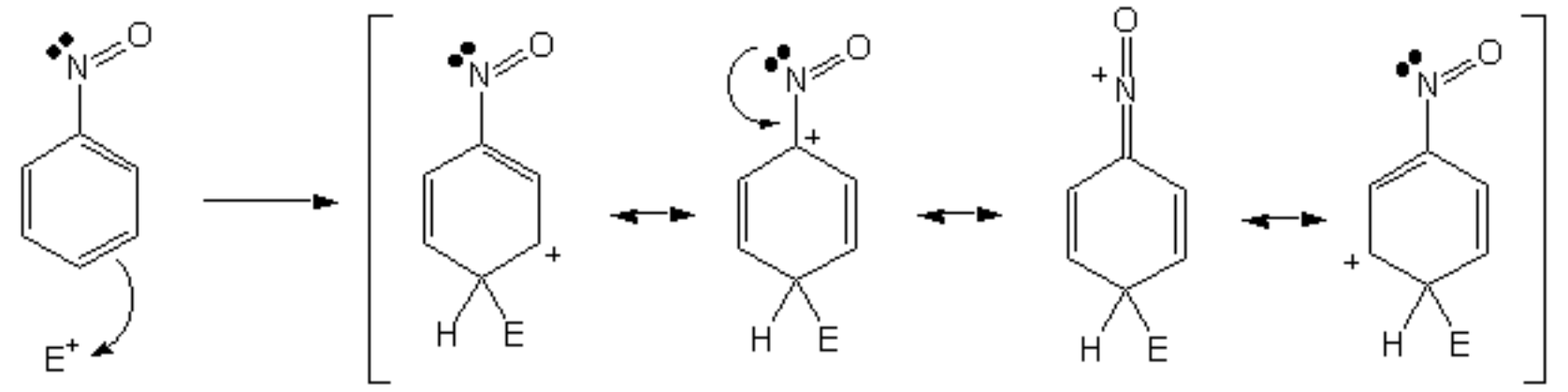
We must begin by drawing a proper Lewis dot structure:



The NO group is a deactivator because it is an electron withdrawing group, just like a caboryl or a nitro:



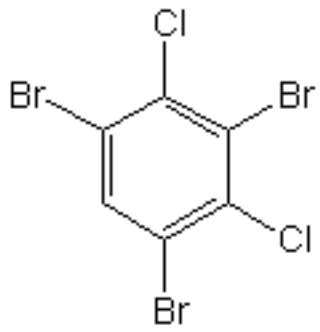
Like the halogens, however, if it is forced to react it will choose ortho/para to take advantage of the extra resonance structure that we can draw using the lone pair on the N:



Name: _____

5. Propose syntheses of the following compounds from the given starting materials.

a. (15 pts)



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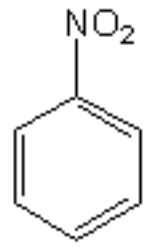
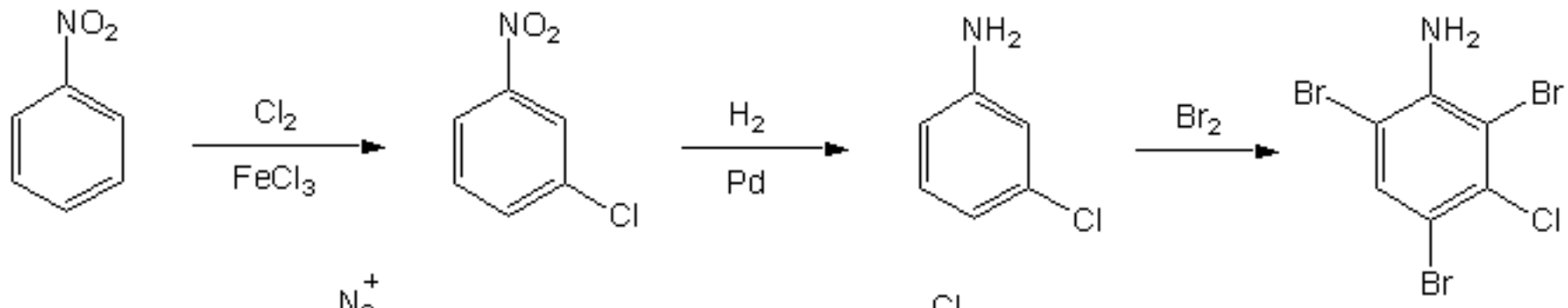
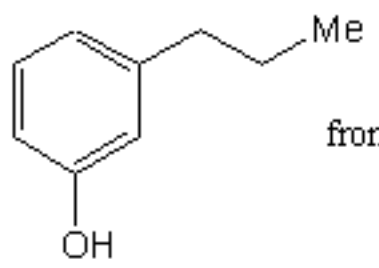




b. (15 pts)



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