Organic Chemistry c3444y

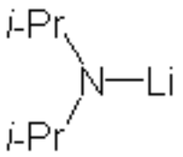
1st Hour Exam

Answer Key

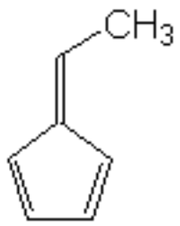
Name: _____

1. 6-methylfulvene is unusually acidic, and can be cleanly deprotonated with lithium diisopropylamide (LDA). (By contrast, propene cannot be deprotonated with LDA.)

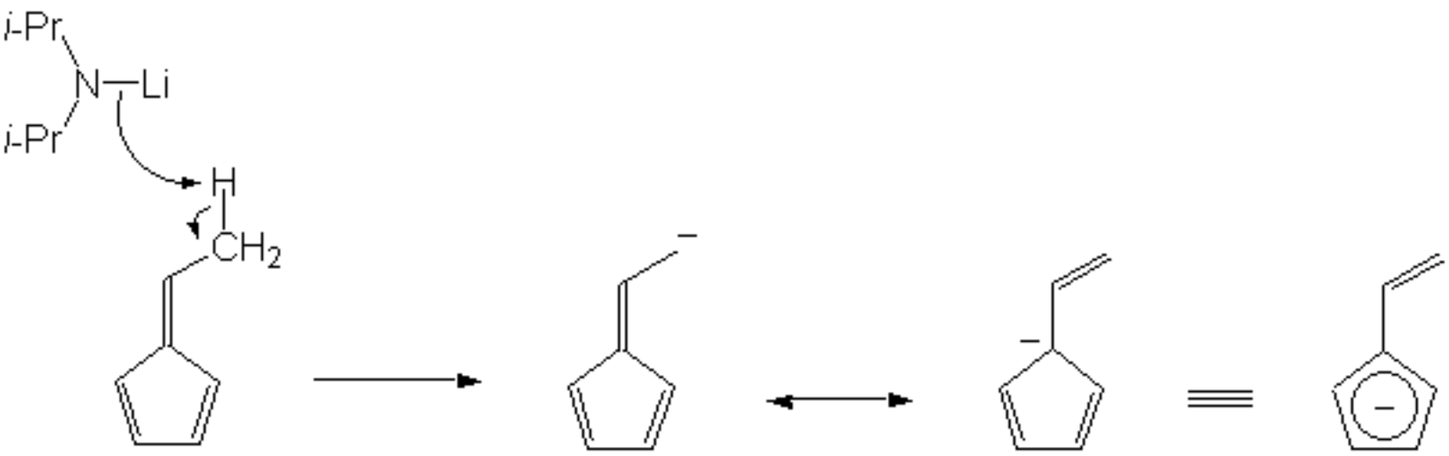
a. (10 pts) Indicate at which site you would expect 6-methylfulvene to be deprotonated. Is there any special stability associated with the anion that is generated upon deprotonation of 6-methylfulvene? Explain concisely with clear drawings.



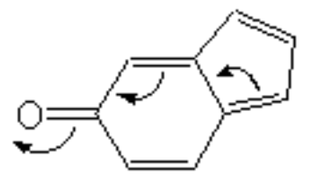
LDA, a strong base



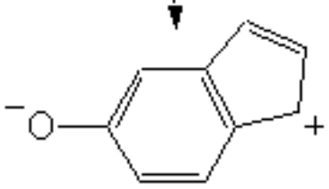
6-Methylfulvene



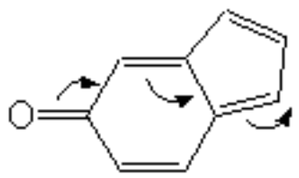
b. (10 pts) Make a prediction as to the relative stability of the illustrated compounds. Would you expect either of them to have any significant aromatic character? Use resonance structures to clarify your *briefly* worded answer.

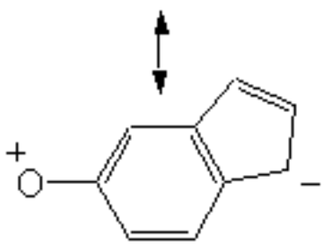


Relatively unstable.

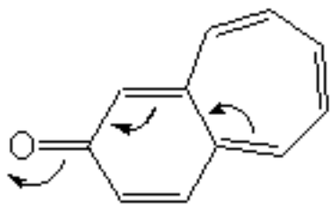


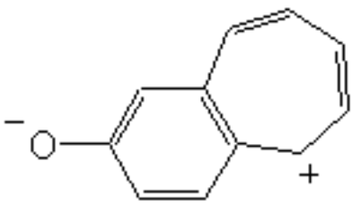
Antiaromatic!

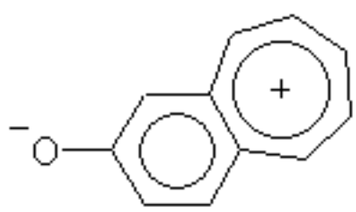




Tempting, but not a strong contributor. Oxygen has been deprived of its octet and bears a + charge.





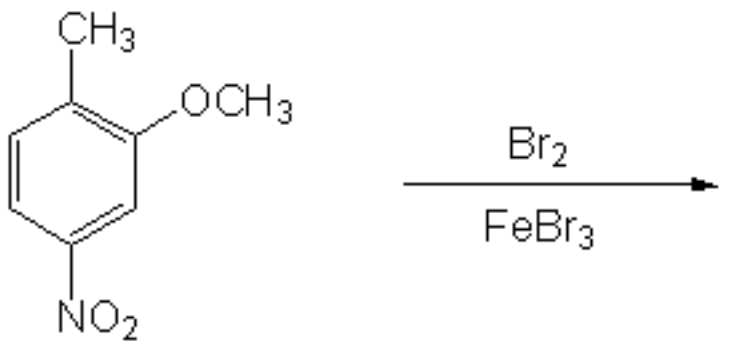


Relatively stable, significant aromatic character.

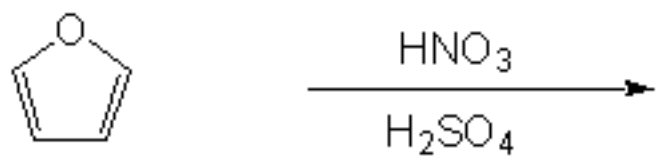
Name: _____

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

a. (7 pts)



b. (7 pts)



c. (6 pts)

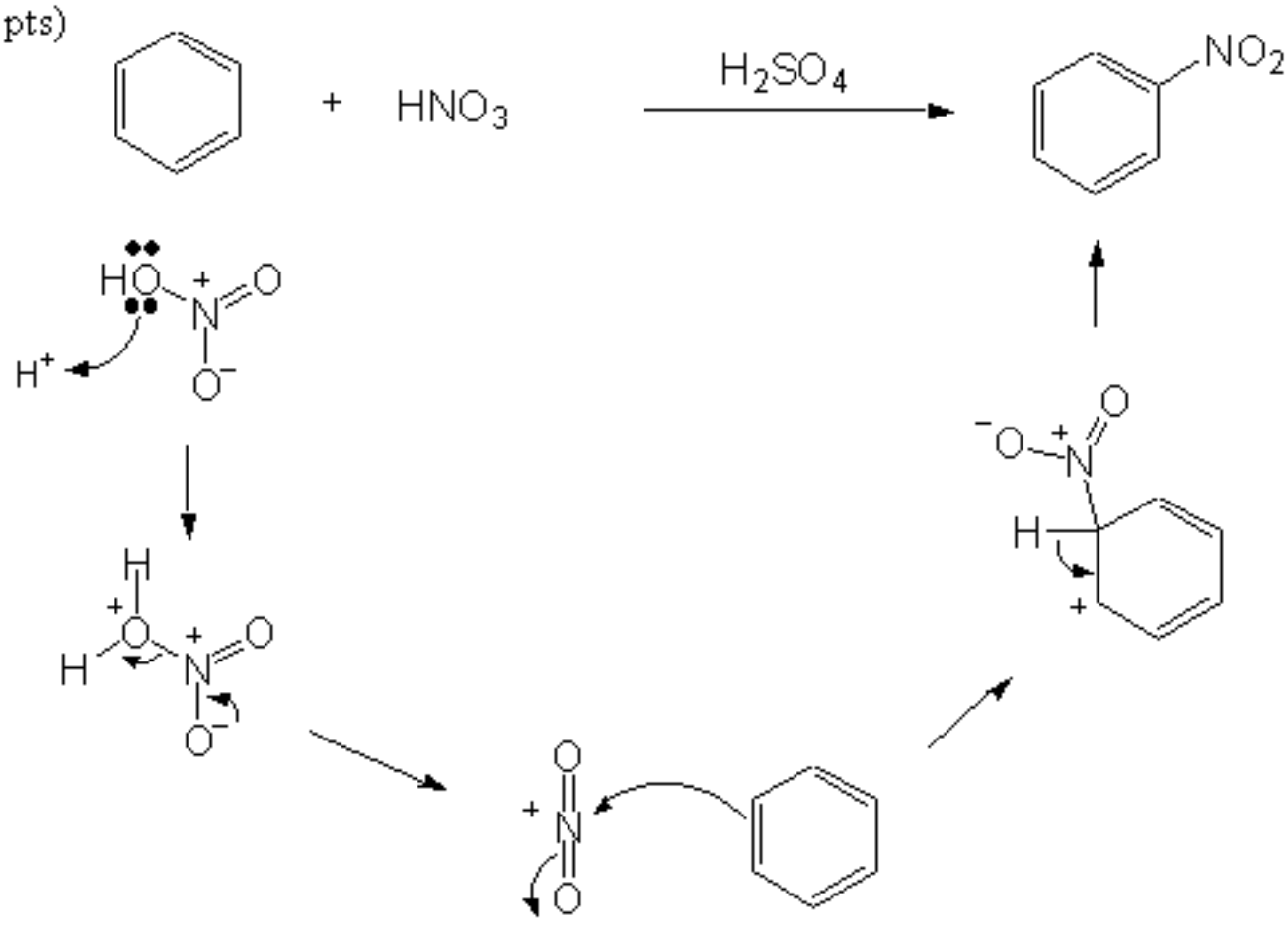
No Reaction.

These are the conditions for an S_N1 reaction, but in this case the intermediate carbocation would be antiaromatic.

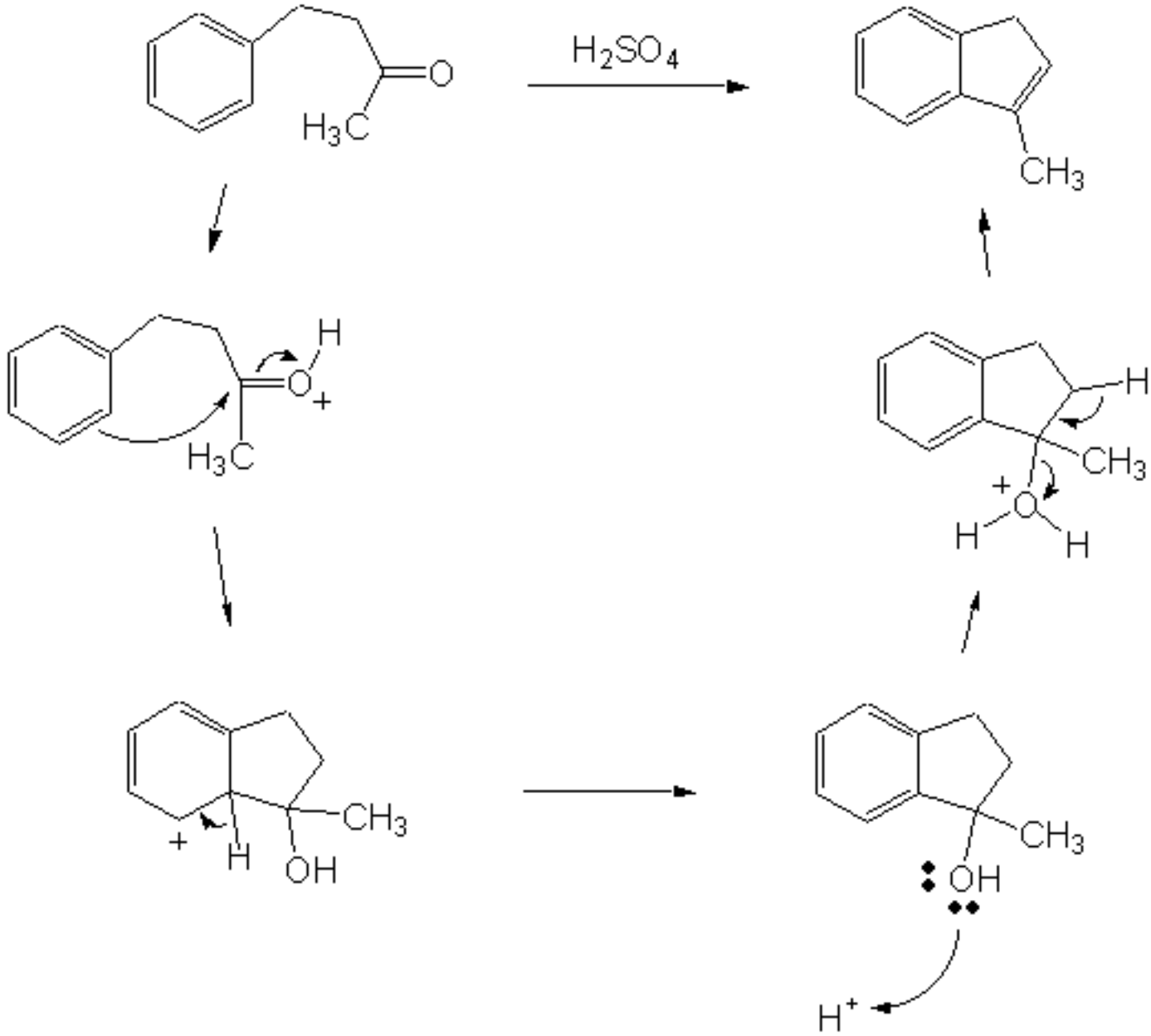
Name: _____

3. Provide detailed mechanisms for the following transformations:

a. (10 pts)

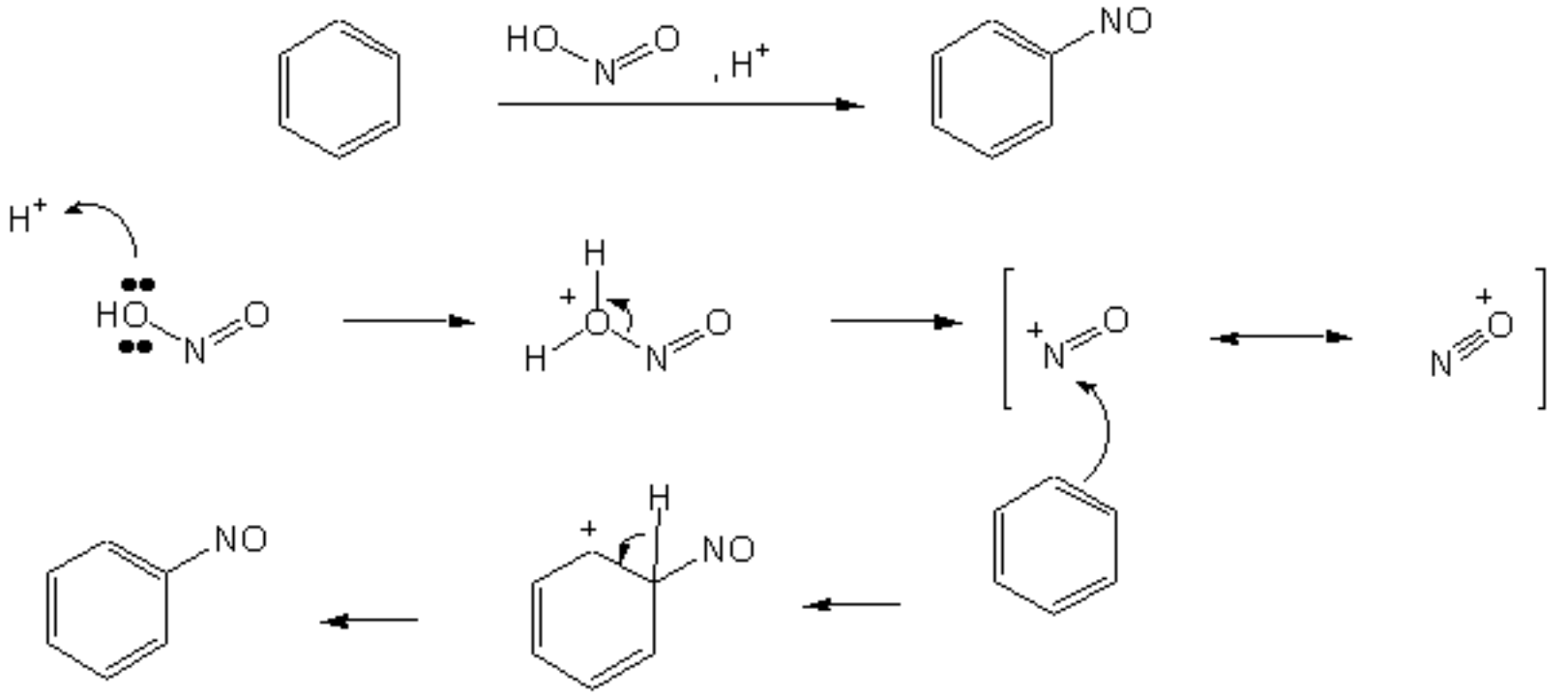


b. (10 pts) (You haven't seen this before, but you know enough to do it.)



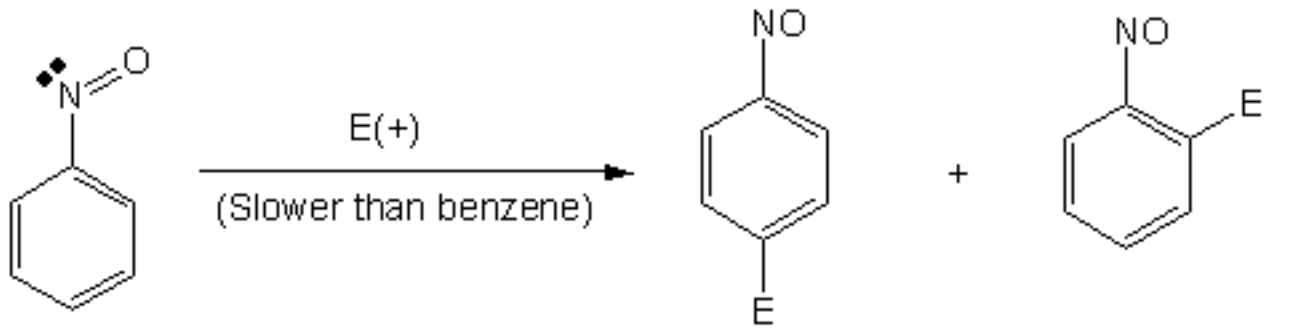
Name: _____

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.

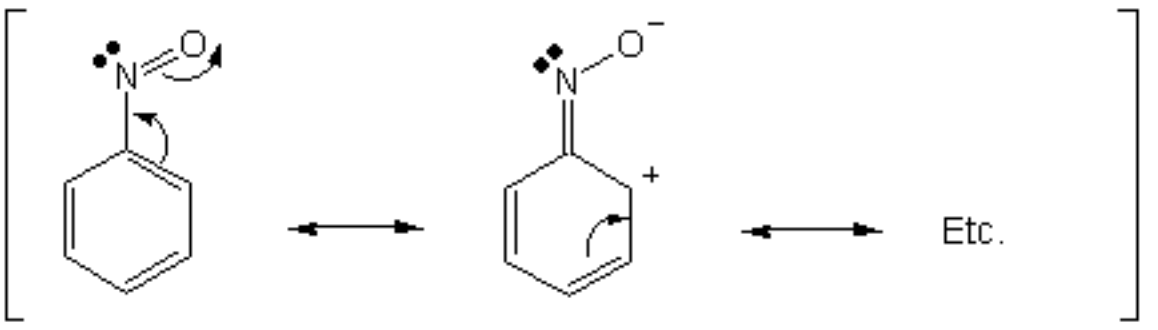


b. (10 pts) Provide an explanation for the fact that the nitroso group (NO) is a deactivator, but an *ortho/para* director.

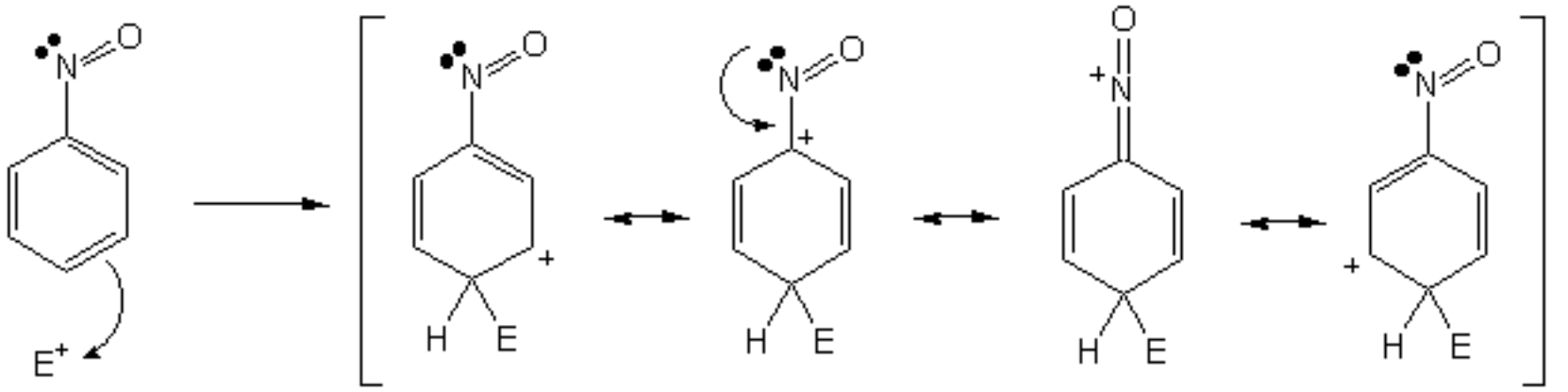
We must begin by drawing a proper Lewis dot structure:



The NO group is a deactivator because it is an electron withdrawing group, just like a cabonyl 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:



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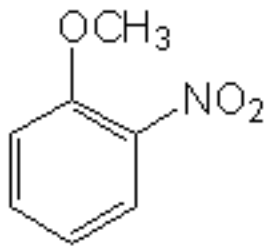
5. Propose syntheses of the following compounds from the given starting materials.

a. (10 pts)



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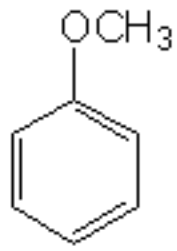
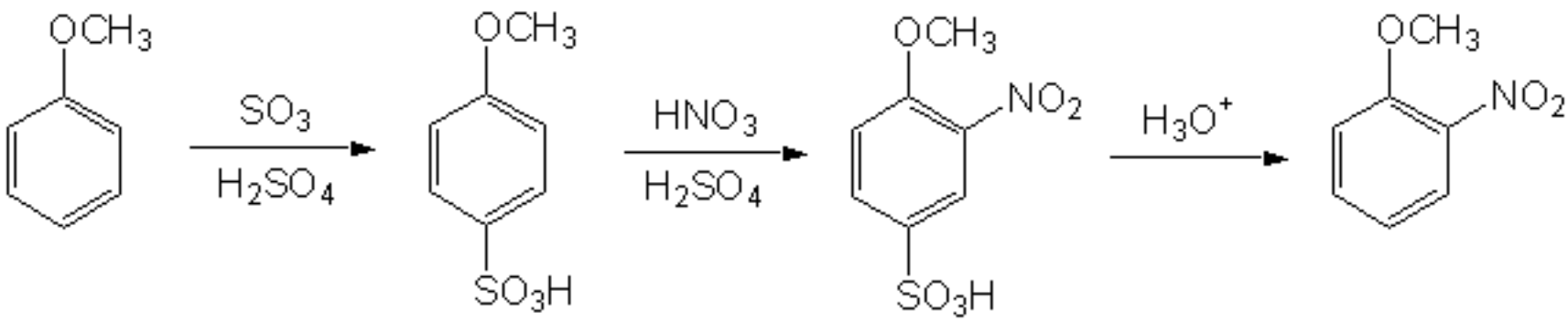
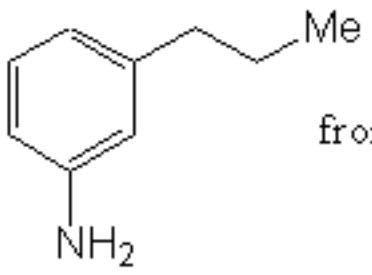




b. (10 pts)



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