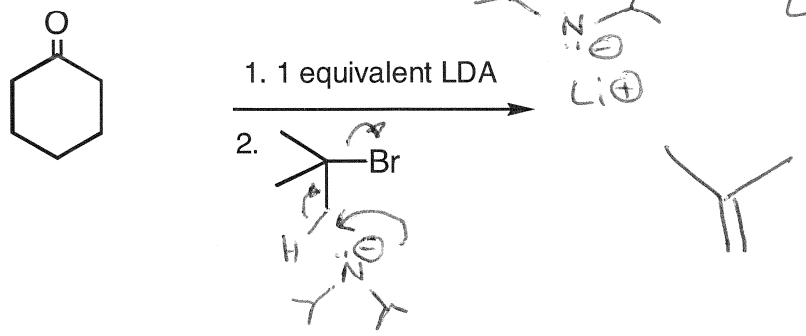
KEY practice problems May '03

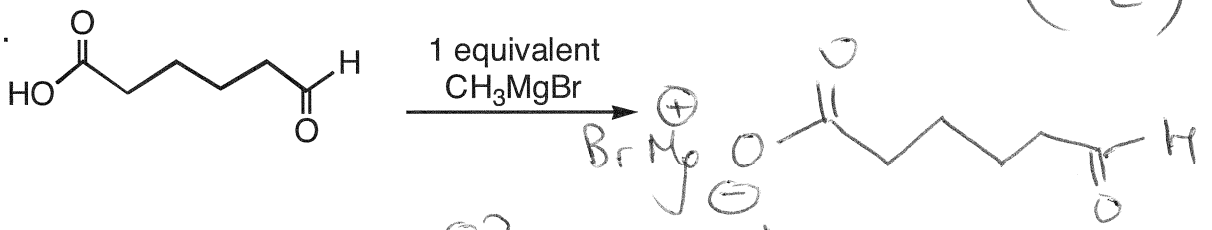
1. Give the principal organic products for the following reactions.

a.

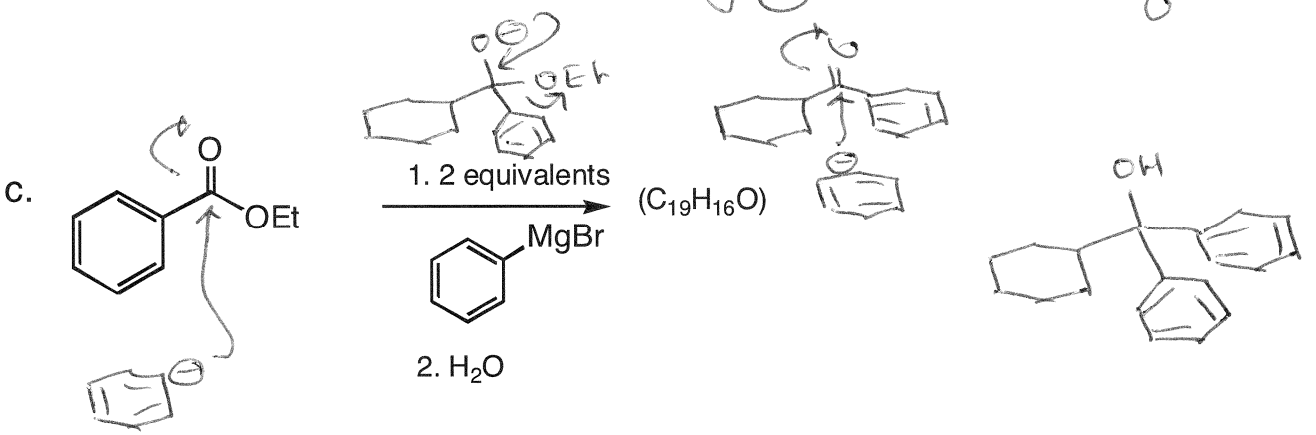


LDA is a strong base so it will just eliminate the bromide (E_2)

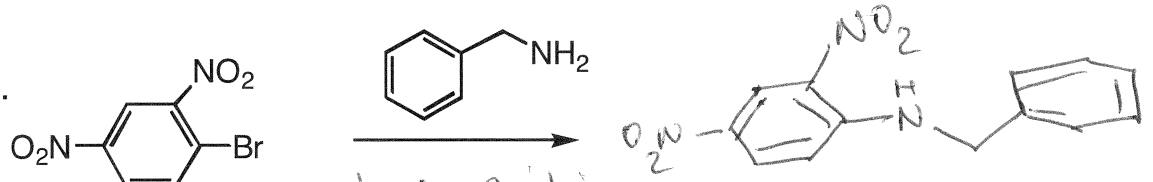
b.



c.

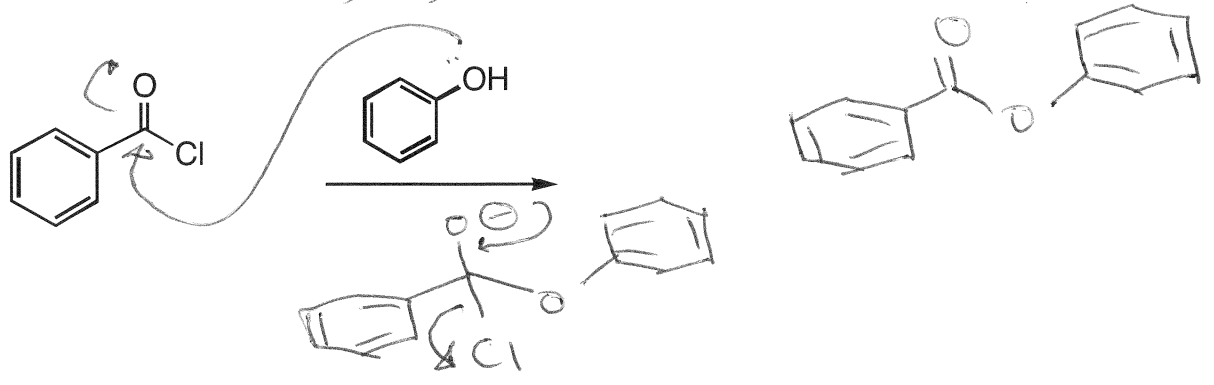


d.



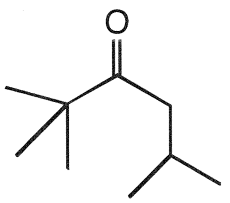
Nucleophilic aromatic substitution

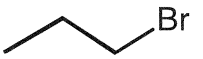
e.

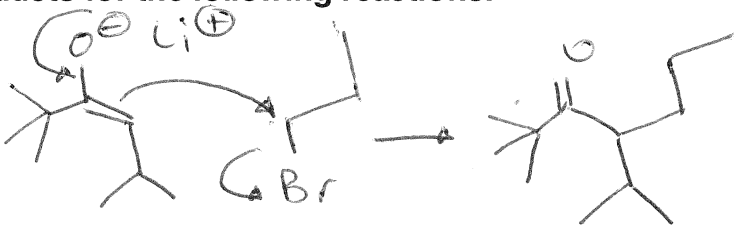


1. (continued) Give the principal organic products for the following reactions.

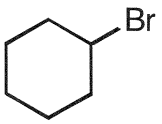
f.



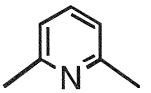
1. LDA
2. 
3. H_2O



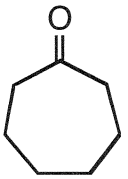
g.



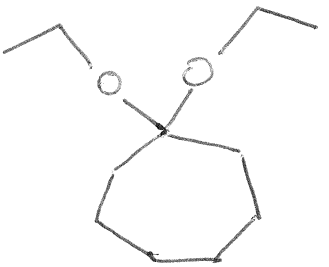
heat



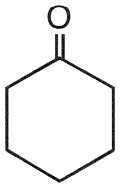
h.



excess EtOH/H^+

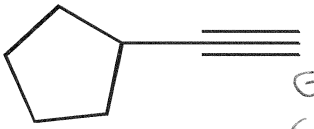


i.

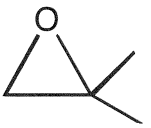


$tBuNH_2/H^+$

j.

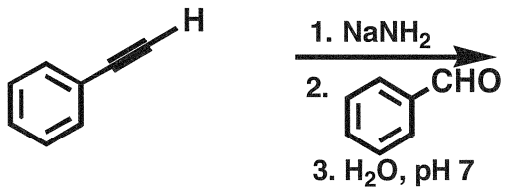


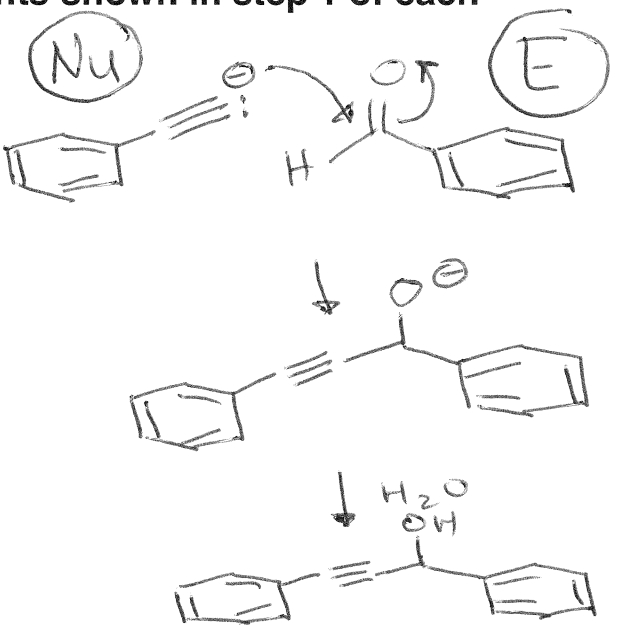
pK_a 25

1. $NaNH_2$
2. 
3. H_2O, pH7

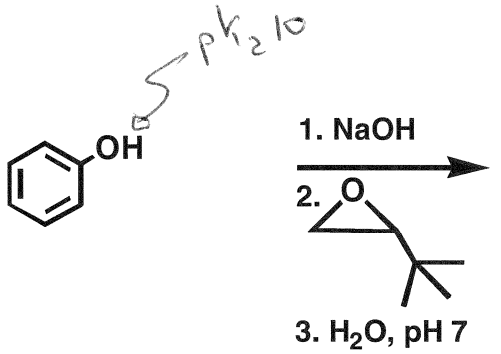
2. For the following pairs of reactants identify the ELECTROPHILIC and NUCLEOPHILIC components and the identity of the product. Note, the actual nucleophile and electrophile may be an intermediate that is formed after reaction with the reagents shown in step 1 of each transformation.

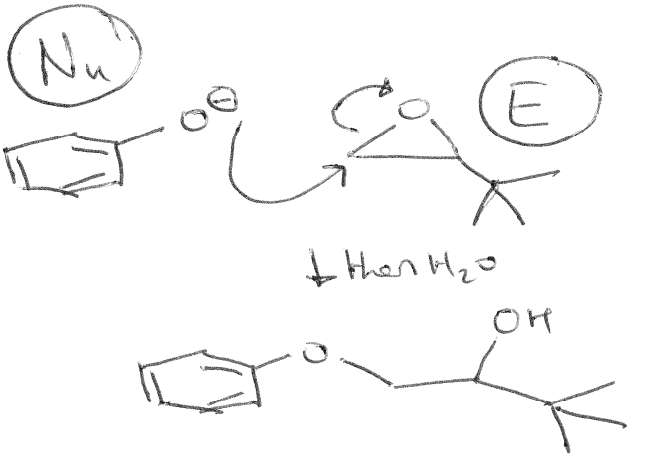
a.



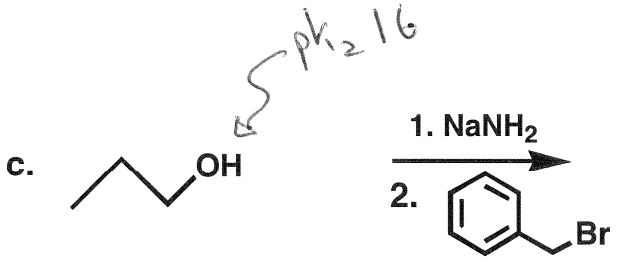


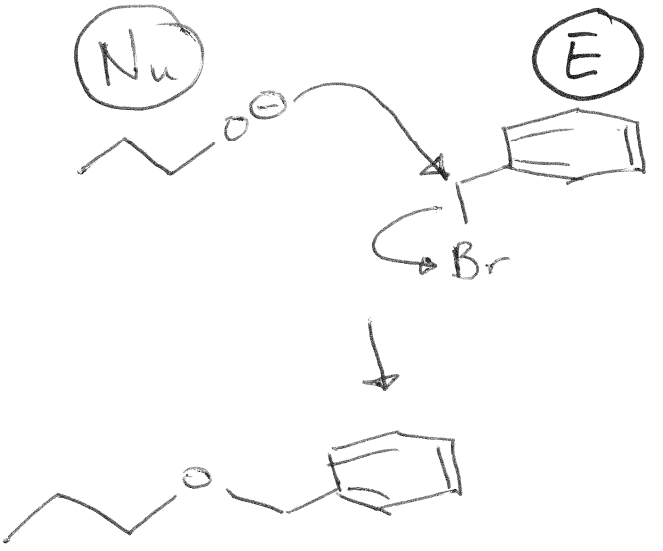
b.



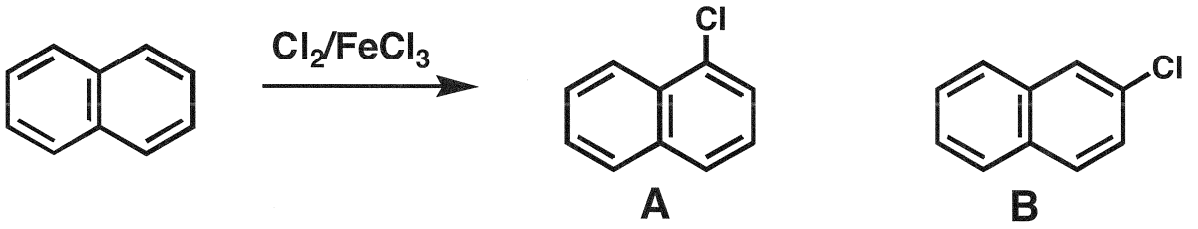


c.





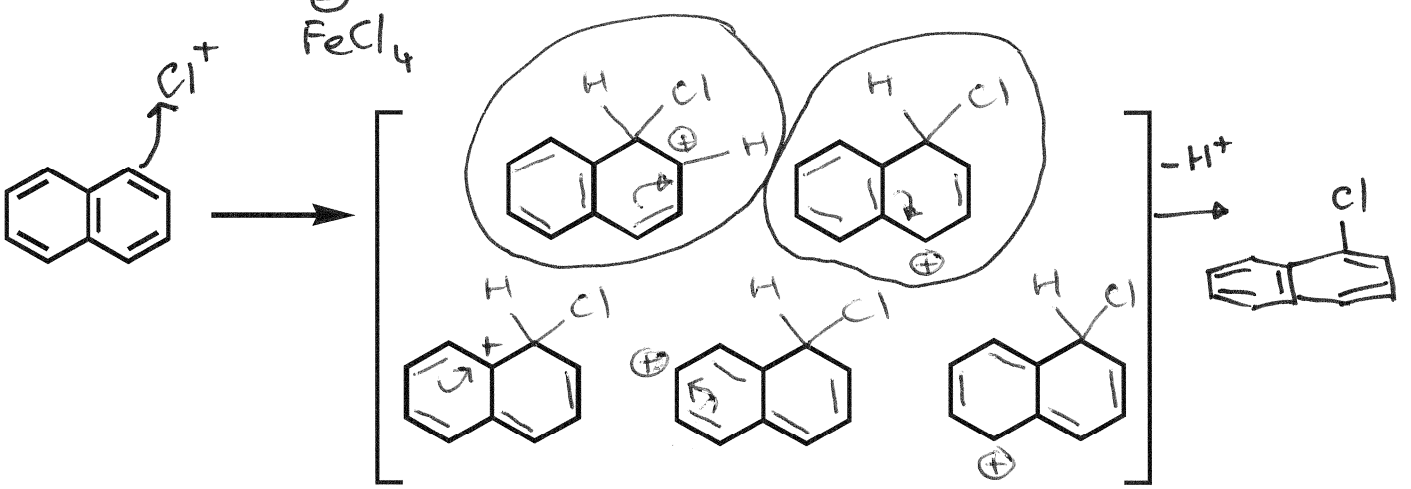
3. When naphthalene is treated with Cl_2 in the presence of $FeCl_3$ the major product from the reaction is product A and the minor product is B.



A **B**

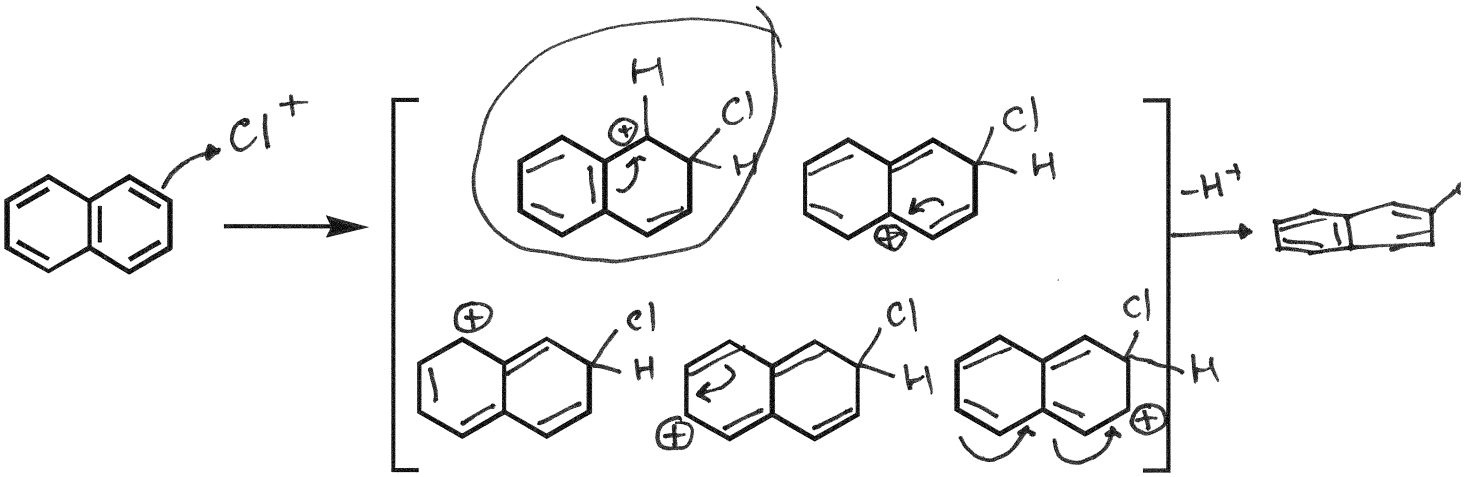
Using the mechanism of electrophilic aromatic substitution EXPLAIN the product outcome. Your answer must include a detailed stepwise mechanism and a discussion of the stability of the intermediates formed in the reaction.
The carbon framework of naphthalene is predrawn to save you time you just need to add the chlorine substituent, the double bonds and the charge.

A



σ complex

B

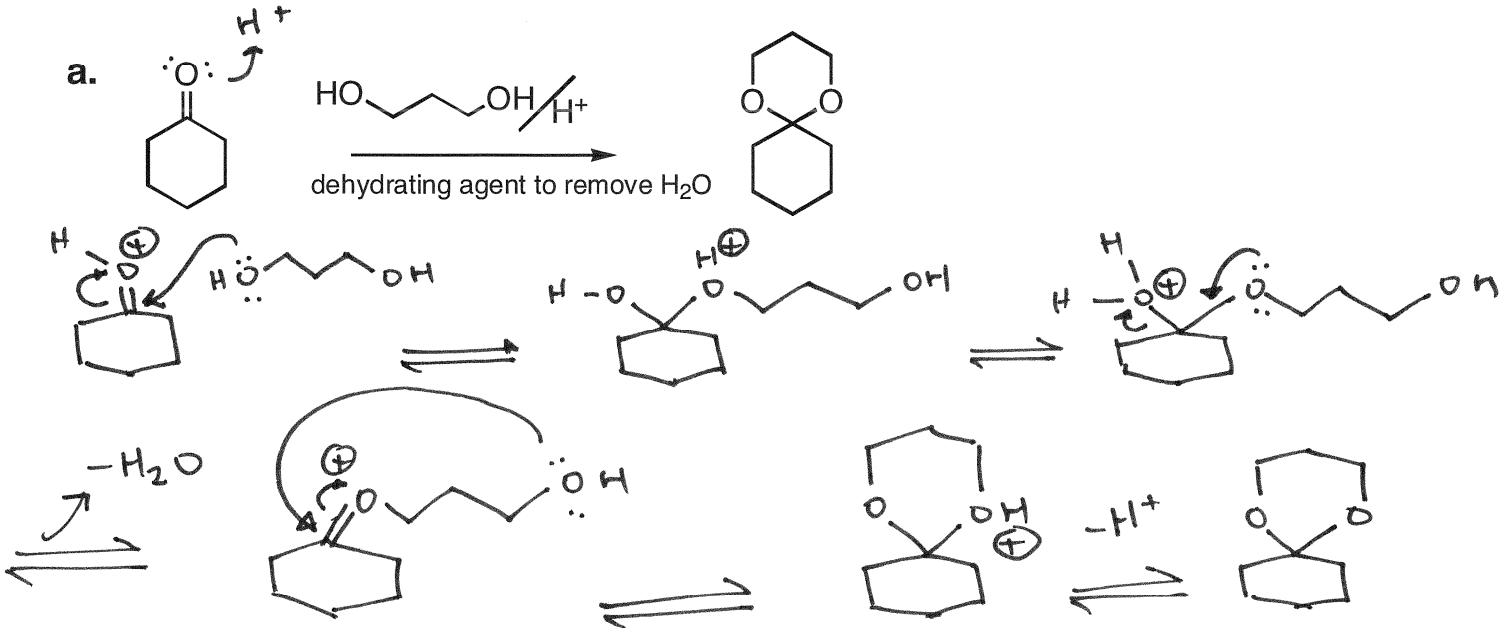


σ complex

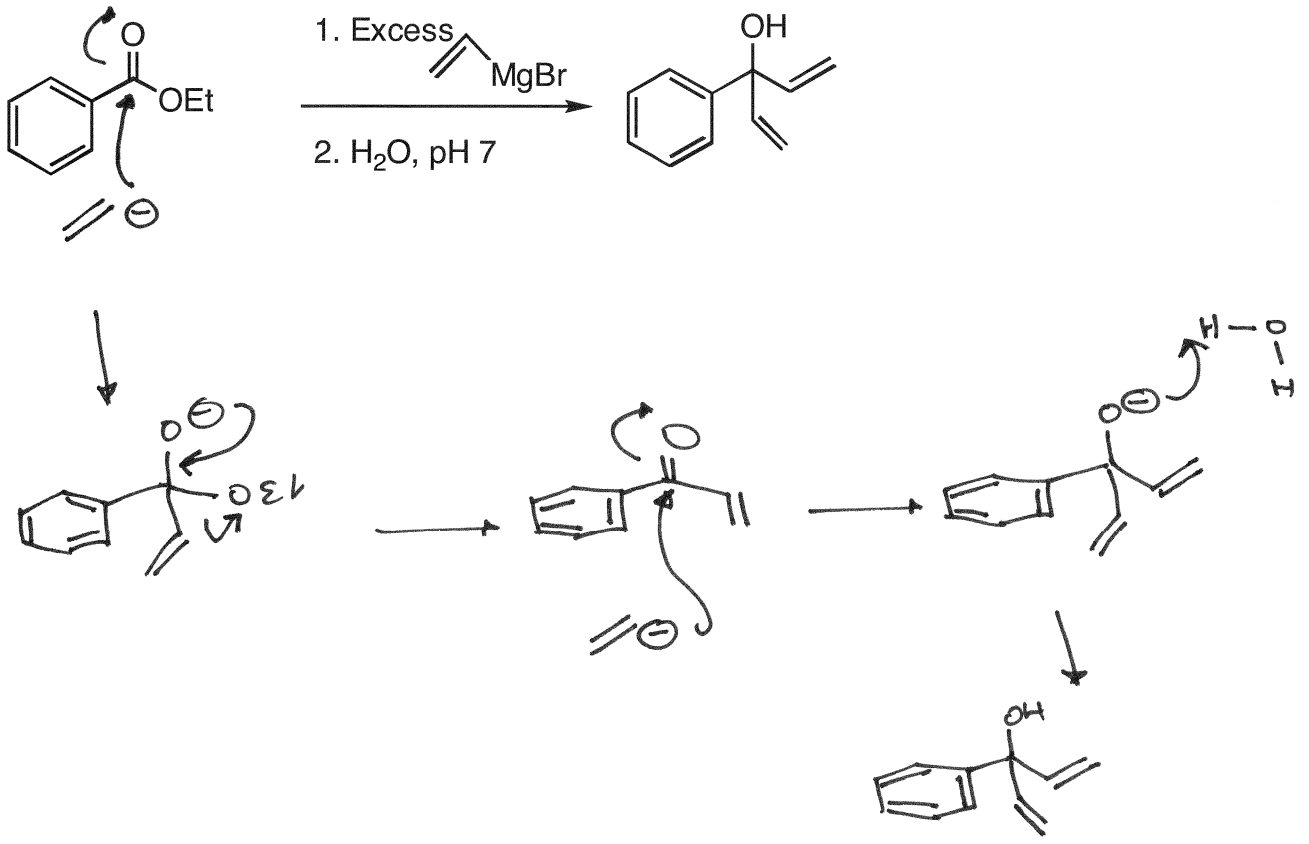
For A Two of the resonance structures contributing to the σ complex preserve aromatic stabilization in one of the two rings In contrast for B. aromaticity is only preserved in 1 of 5 resonance structures.
A has more stable σ complex so prod will be that from this high energy intermediate

4. Write the complete stepwise mechanism for the following reactions. Show all electron flow with arrows and include all intermediate stuctures.

a.



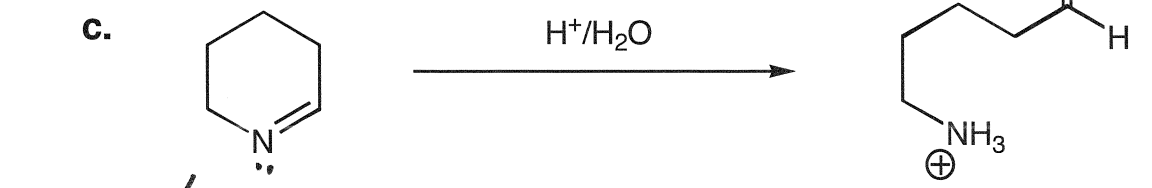
b.

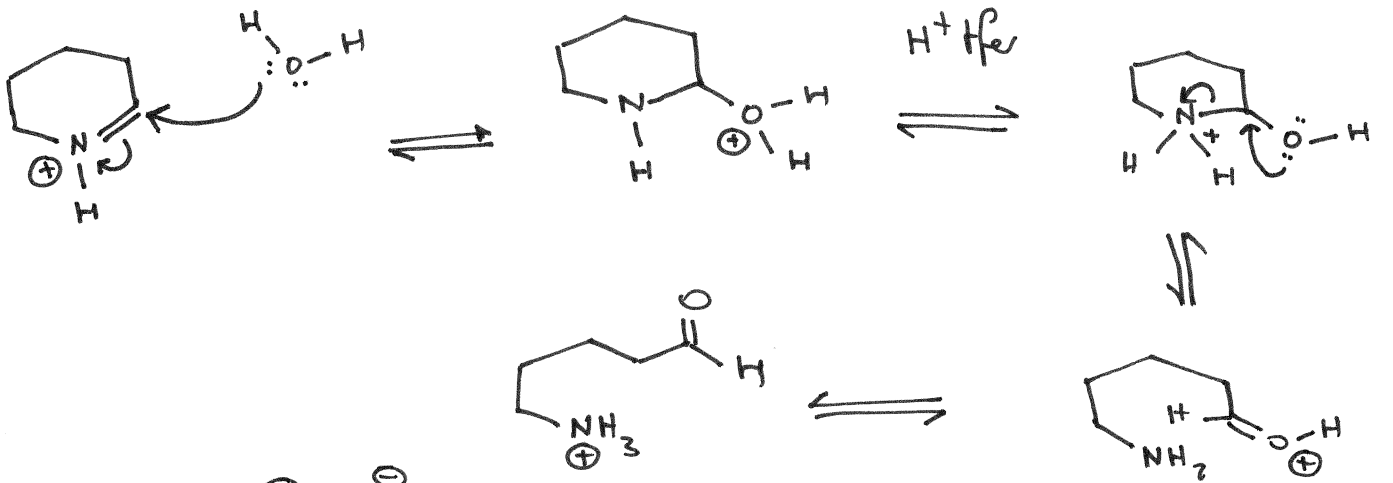


steps are just the reverse of imine formation

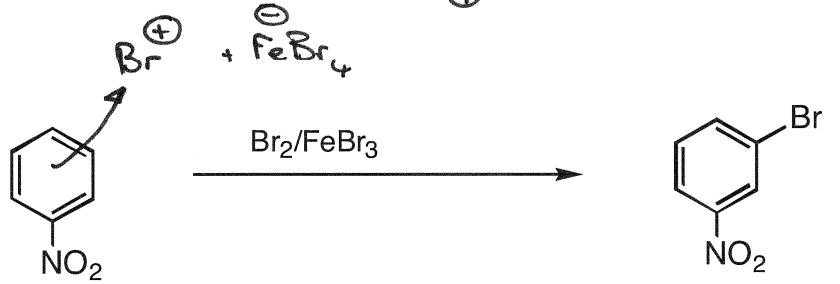
4. continued

c.



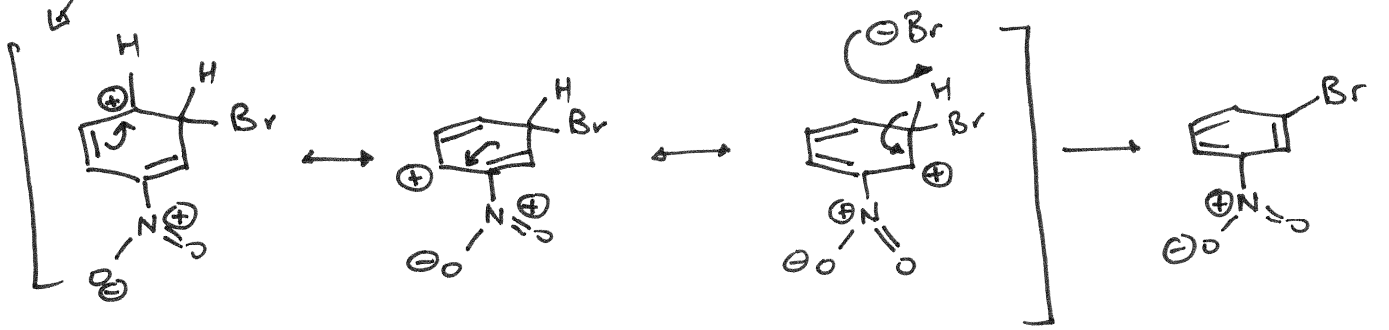


d.



Mechanism must account for formation of meta-substituted product.

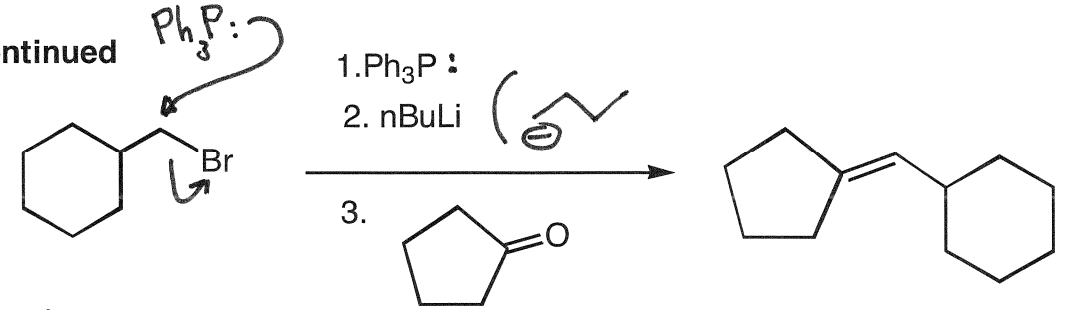
$FeBr_3 \; Br^{\ominus} \rightleftharpoons FeBr_4^{\ominus}$

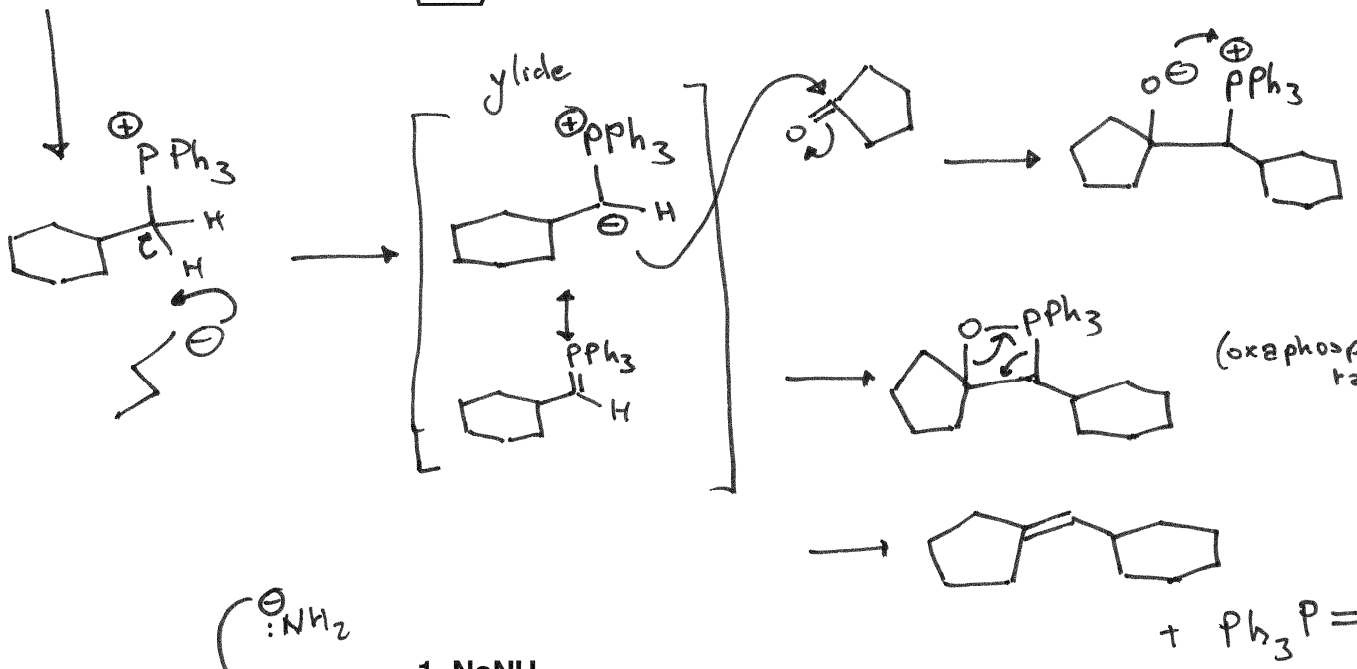


Substitution o or p to $-NO_2$ gives resonance structures in which +ve of σ complex is on adjacent atom to ⊕ of $-N^{\oplus}(=O)-O^{\ominus}$ which cannot contribute to the stability of the σ complex

4. continued

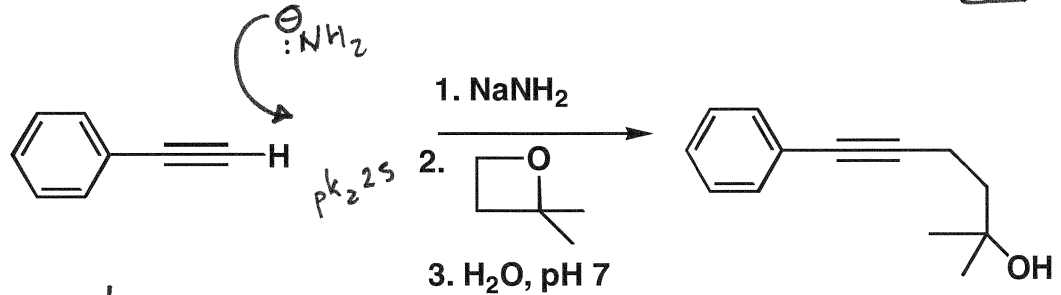
e.

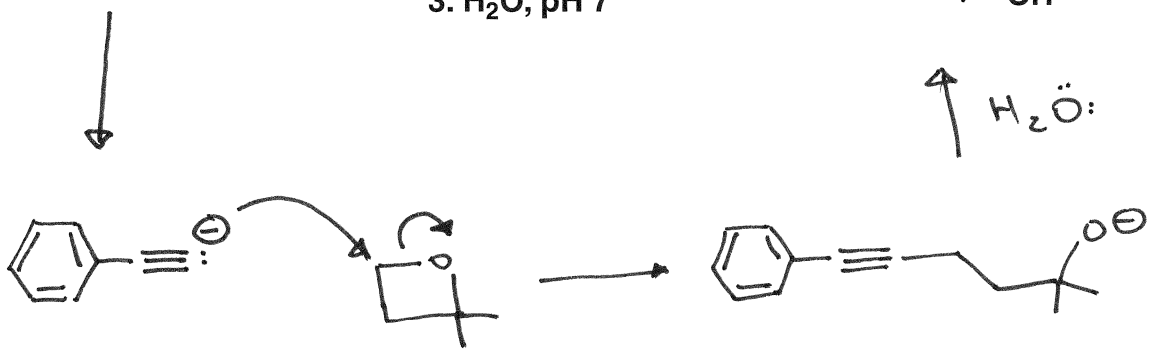




+ $Ph_3P=O$

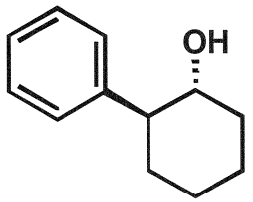
f.



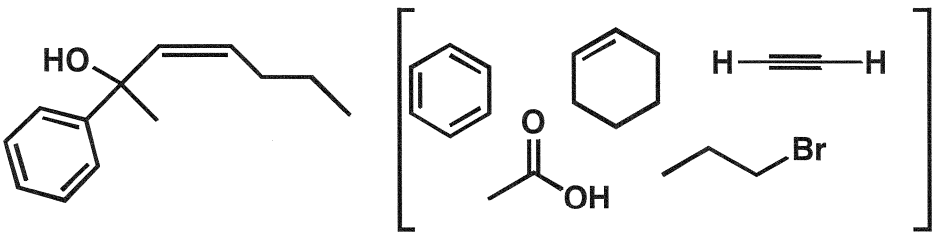


5.Design syntheses of compounds a, b and c.
The pool of carbon-containing starting materials that you can use are shown in the square brackets. You may use any other common reagents.

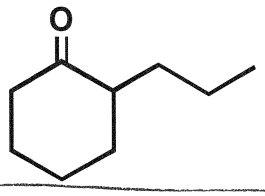
a.



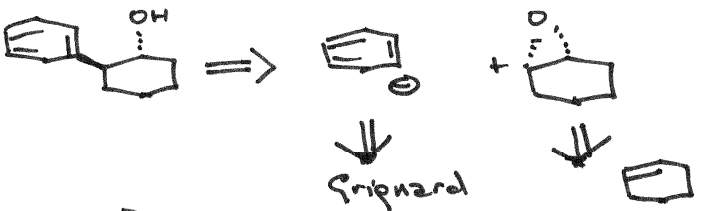
b.



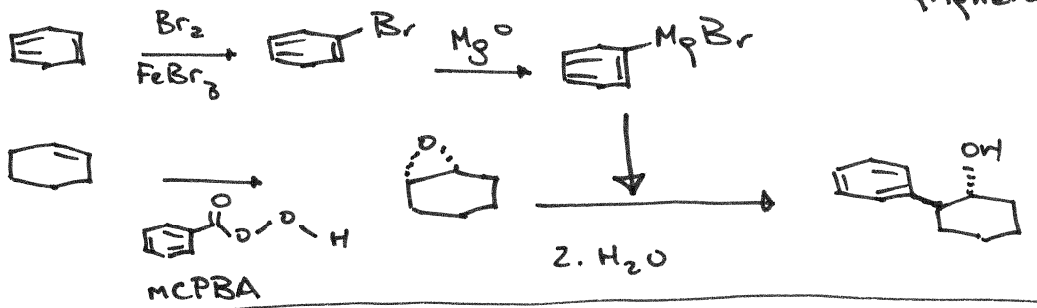
c.



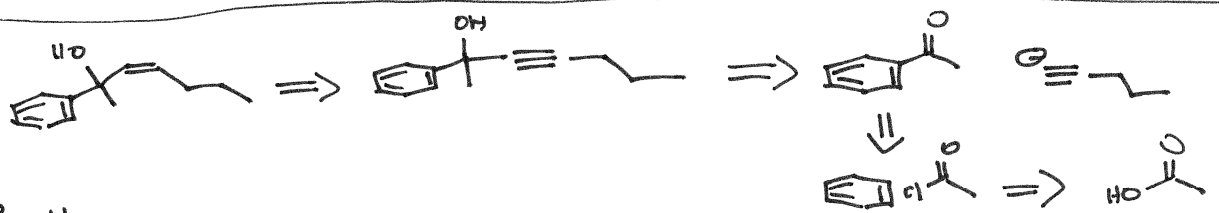
a.



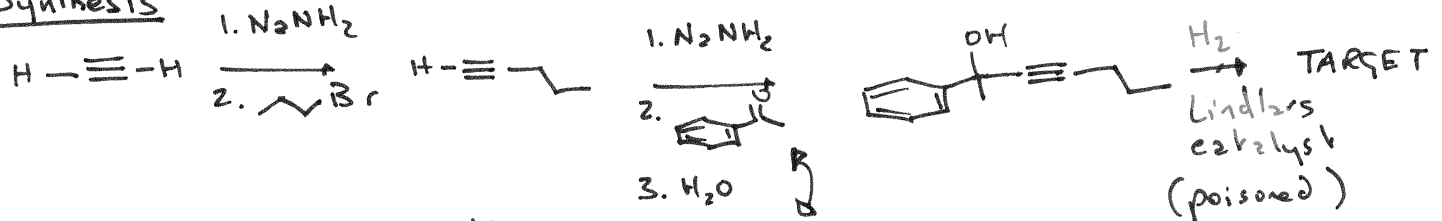
a. Synthesis

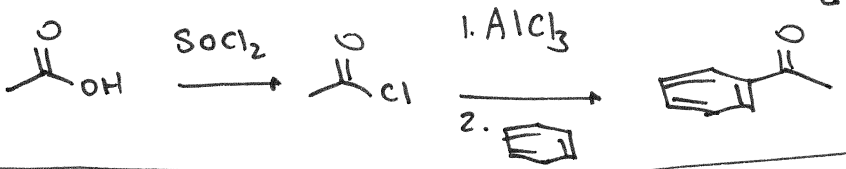


b.



Synthesis





c.