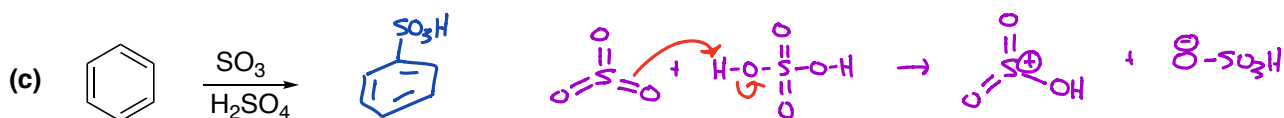
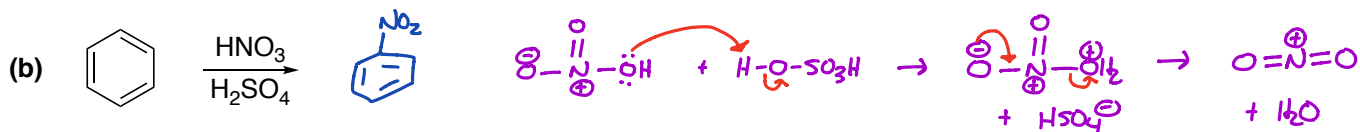
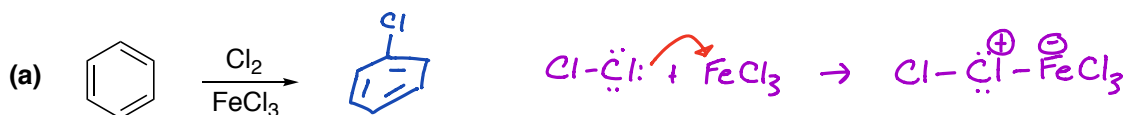


Answer Key  
Chemistry 234  
Chapter 16 Problem Set

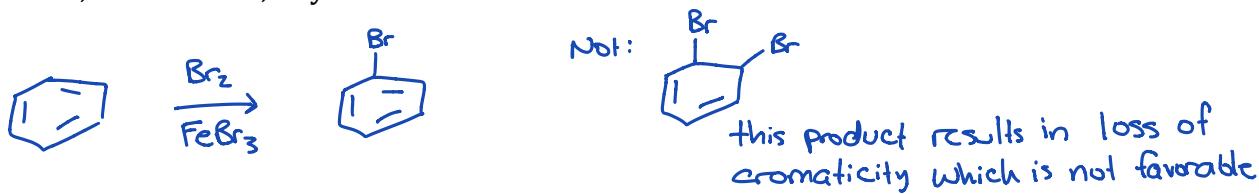
---

**Electrophilic Aromatic Substitution**

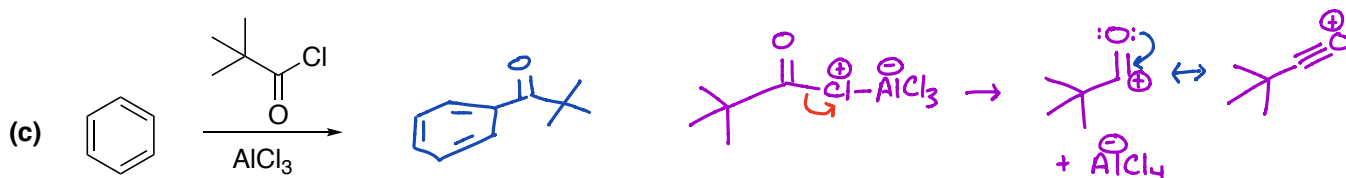
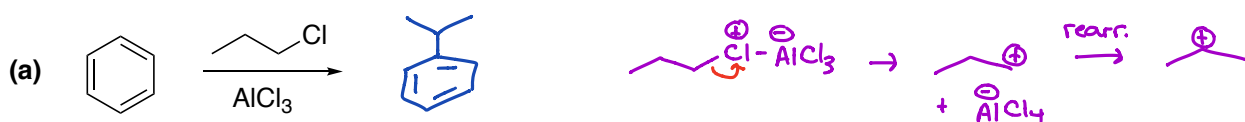
1) Predict the product and draw the mechanism for electrophile generation for each of the following reactions.



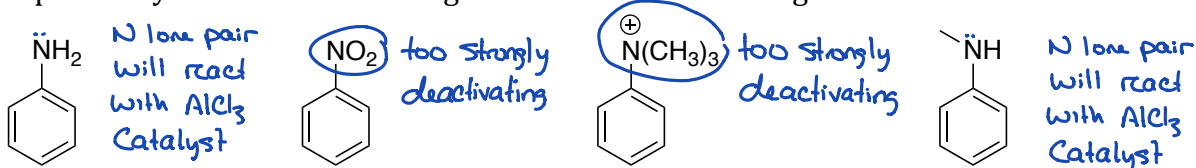
2) Explain why reaction of benzene with  $\text{Br}_2/\text{FeBr}_3$  results in the product bromobenzene instead of 5,6-dibromo-1,3-cyclohexadiene.



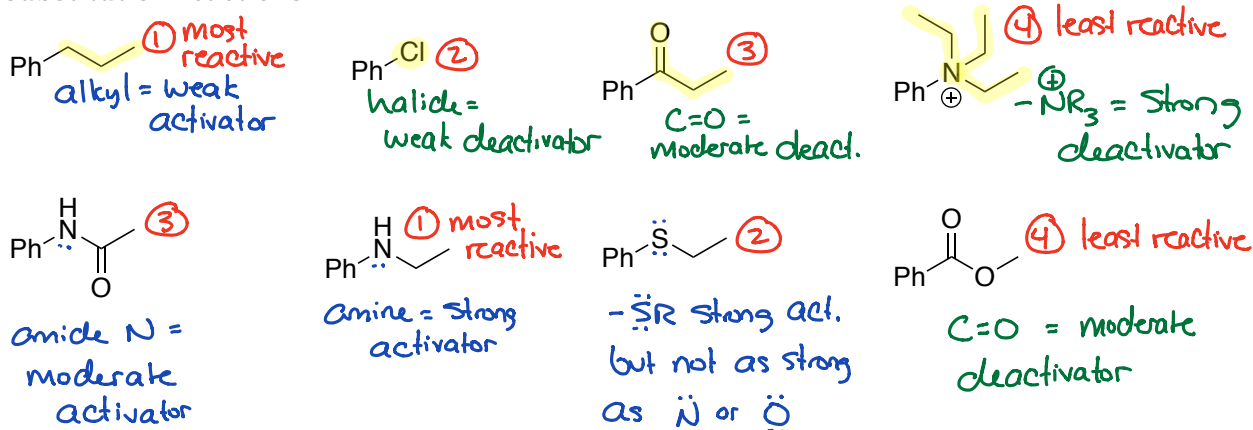
3) Predict the product and draw the active electrophile for each reaction shown below.



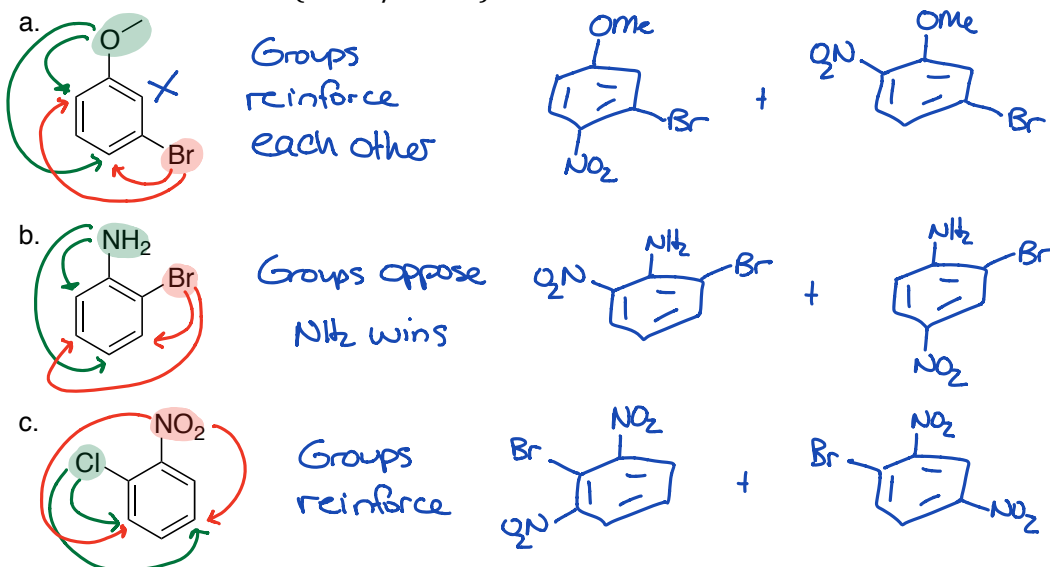
- 4) Explain why each of the following substrates do not undergo Friedel-Crafts reactions.



- 5) Arrange the following benzene substituents in order of reactivity in electrophilic aromatic substitution reactions.

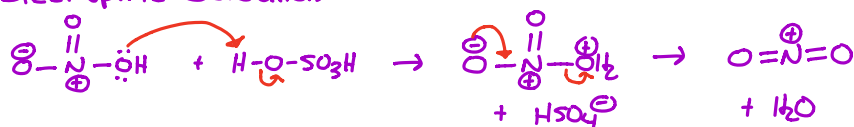


- 6) Predict the major products when the following benzene derivatives are treated to nitration conditions ( $\text{HNO}_3/\text{H}_2\text{SO}_4$ ).

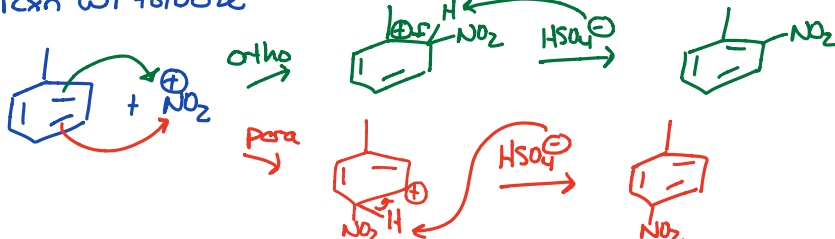


- 7) Write the full electron pushing mechanism for the nitration of toluene.

Electrophile Generation



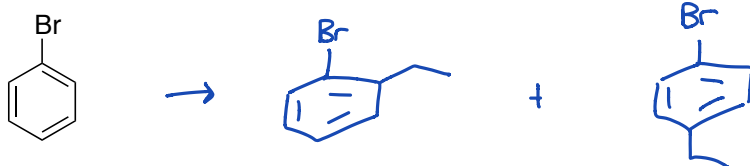
Rxn w/ toluene



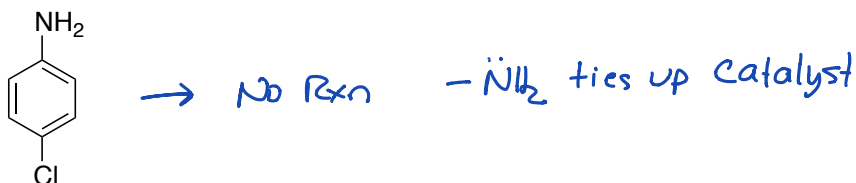
8) Predict the product(s) when each of the following benzene derivatives is treated to chloroethane and  $\text{AlCl}_3$ .



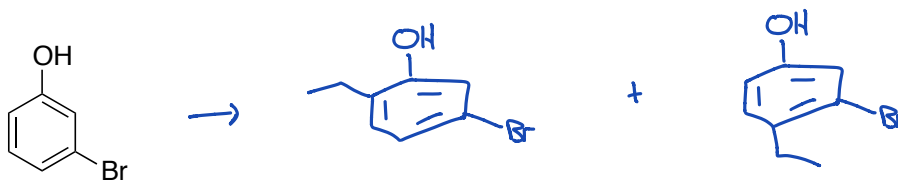
a.



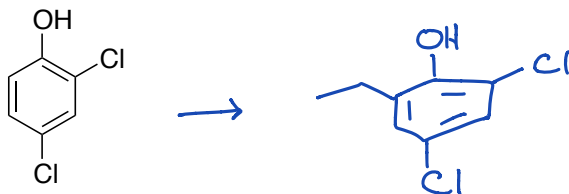
b.



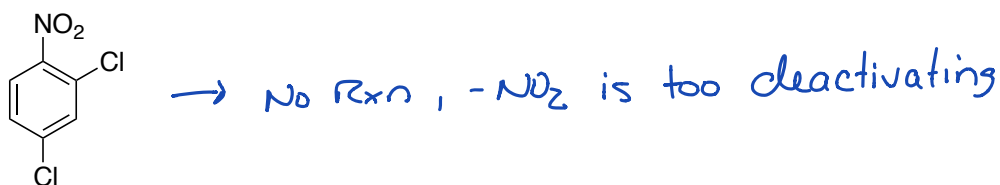
c.



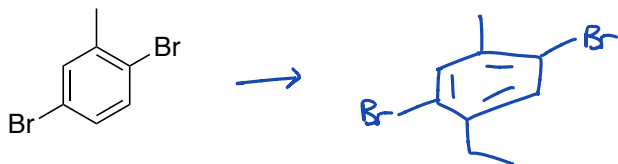
d.



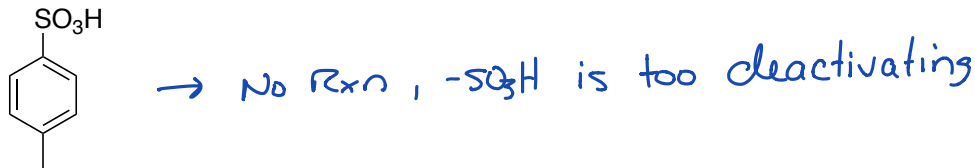
e.



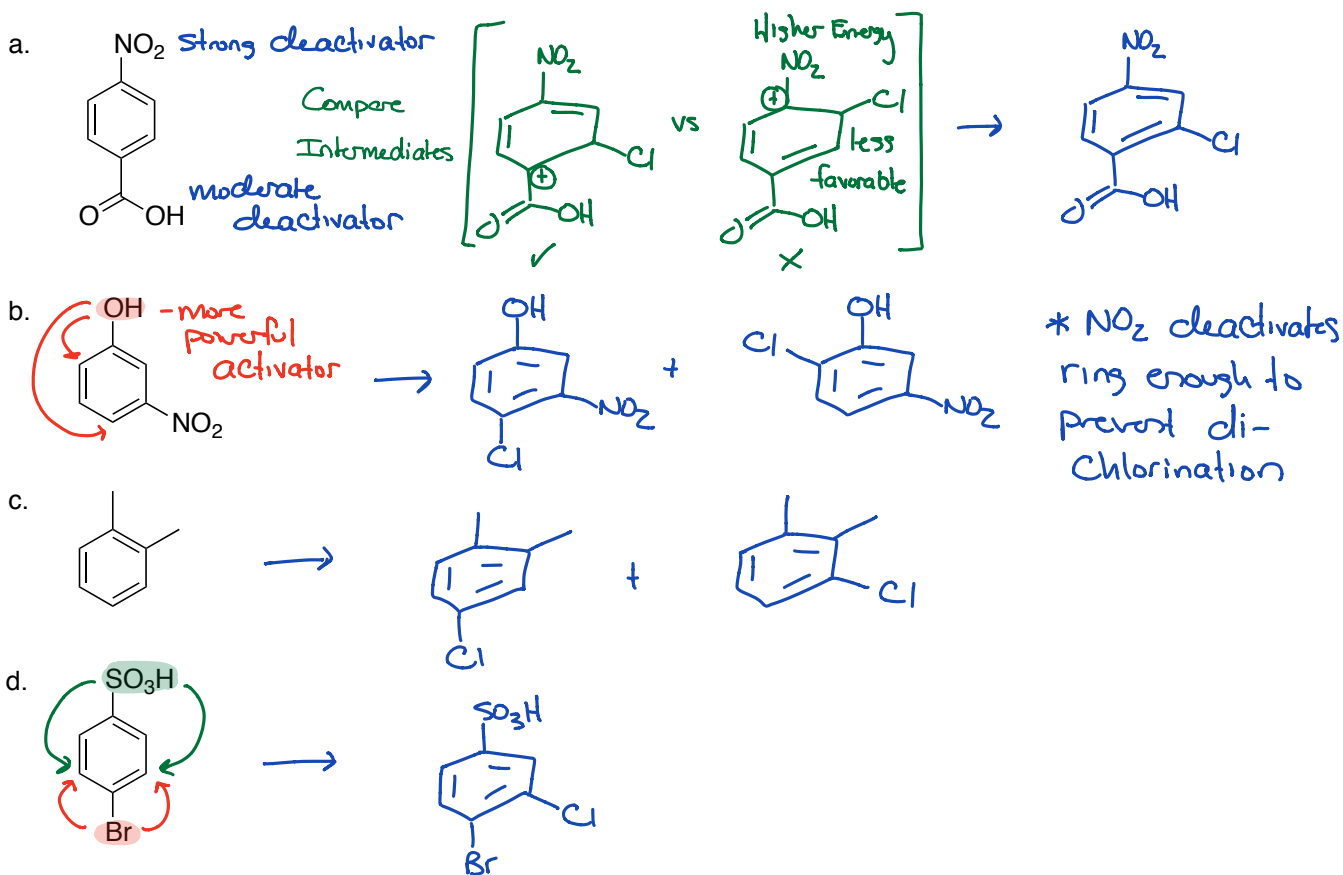
f.



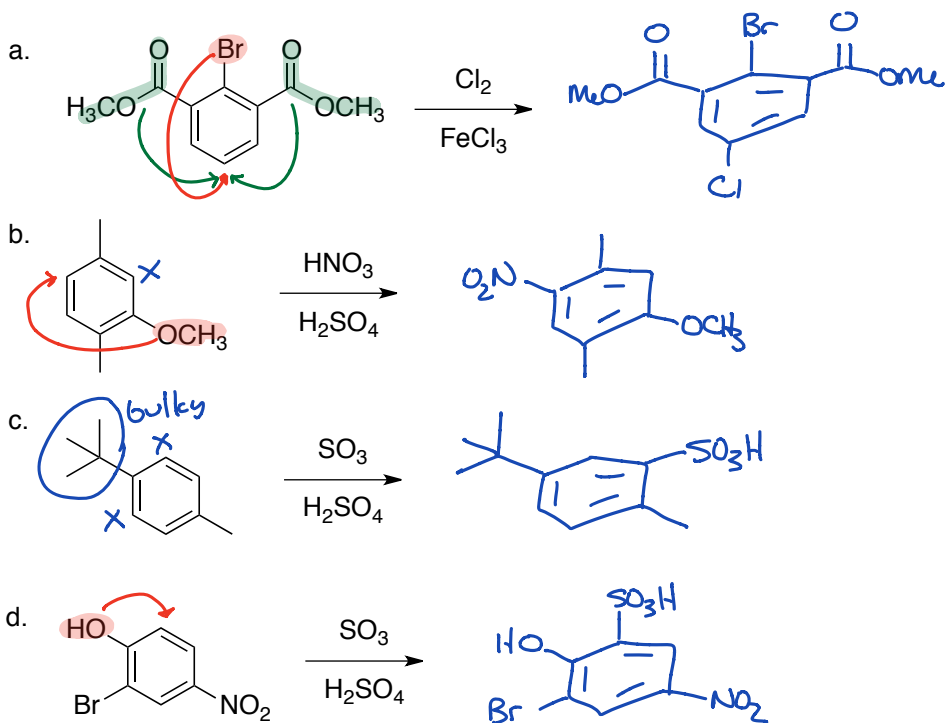
g.



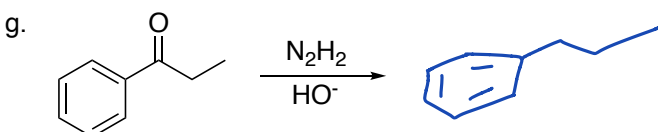
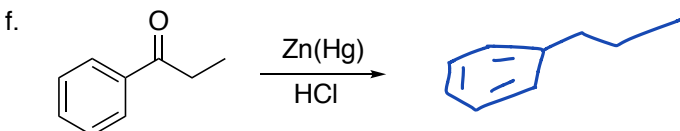
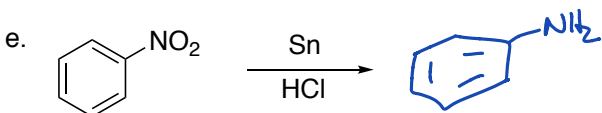
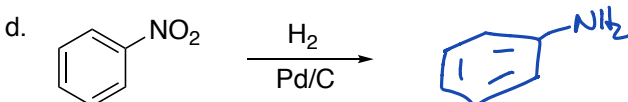
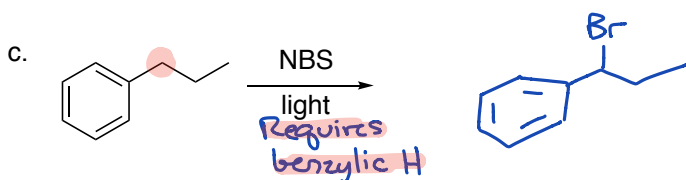
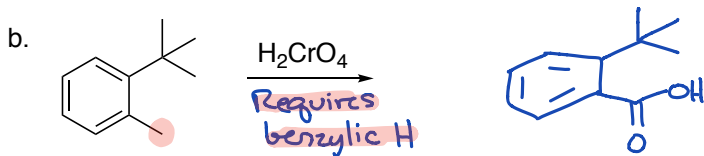
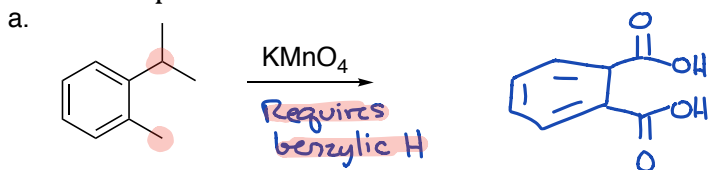
9) Predict the product(s) when the following benzene derivatives are subjected to electrophilic chlorination conditions ( $\text{Cl}_2$ ,  $\text{FeCl}_3$ ).



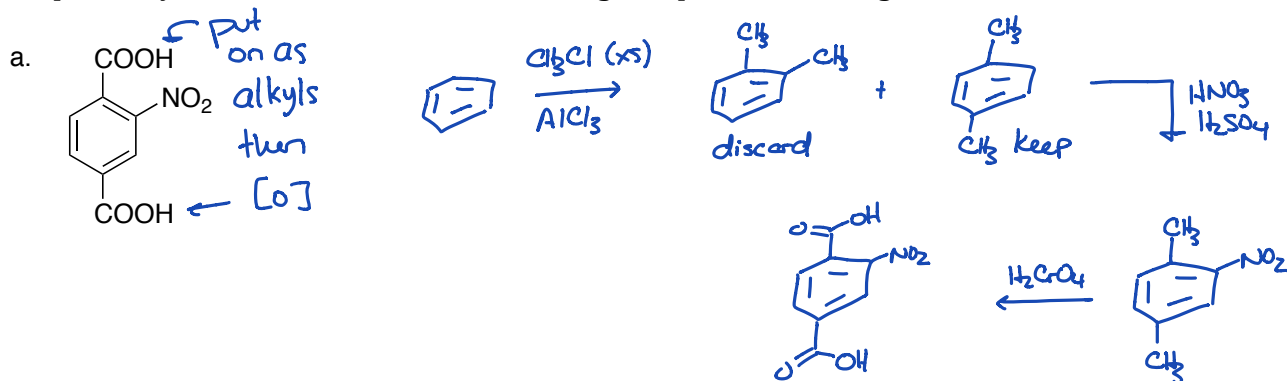
10) Predict the product(s) for each of the following reactions.

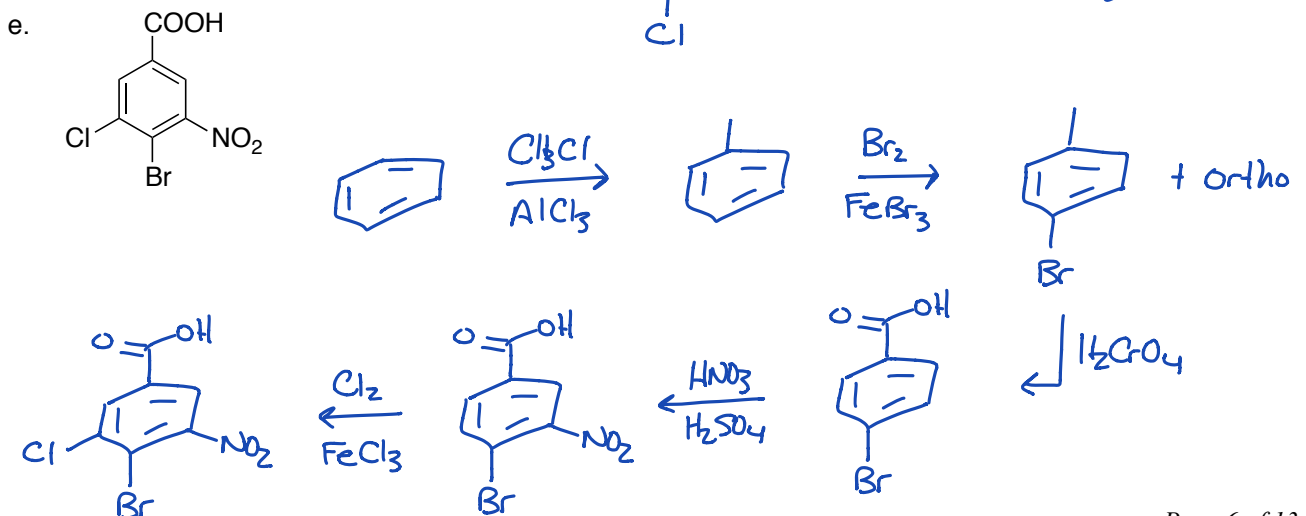
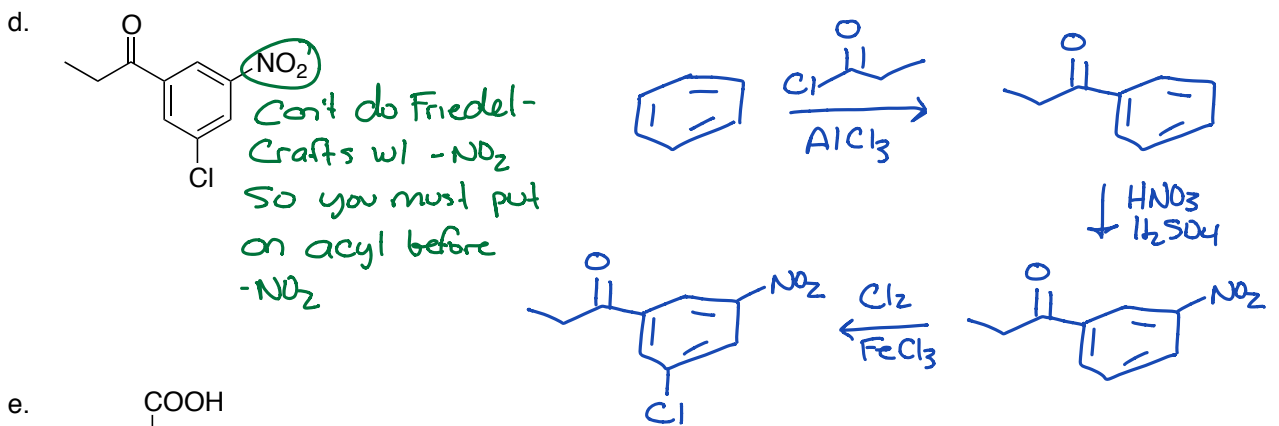
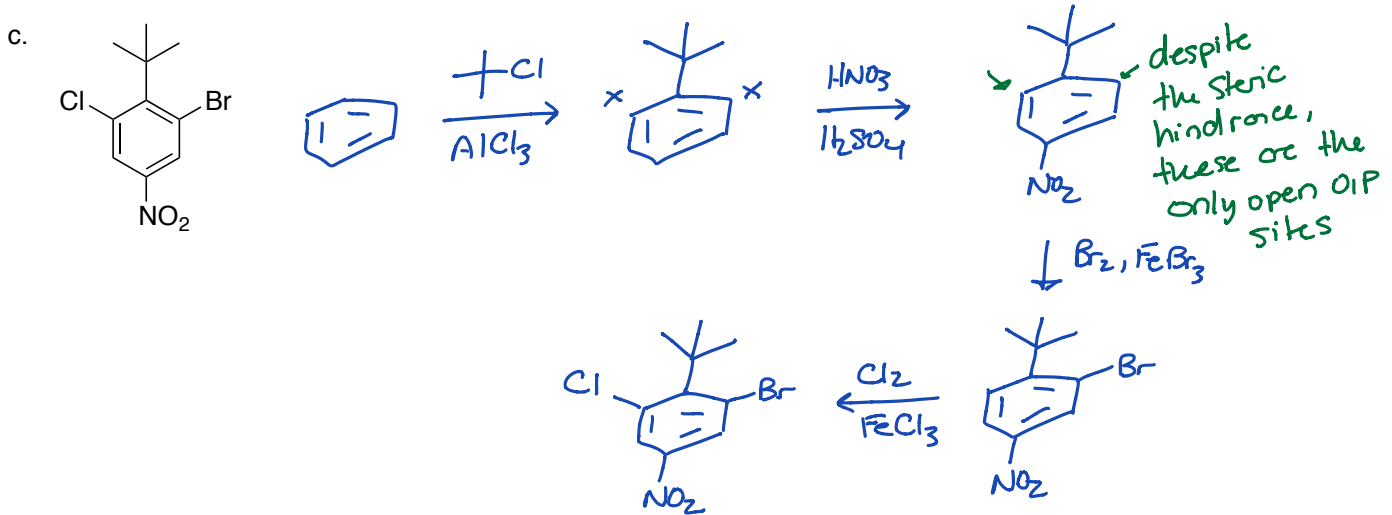
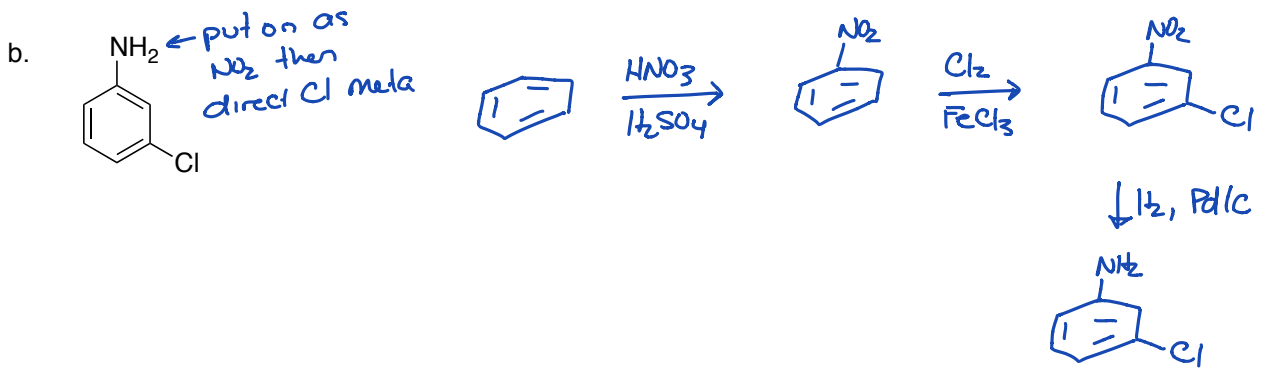


11) Predict the product for each benzene side-chain modification reaction shown below.

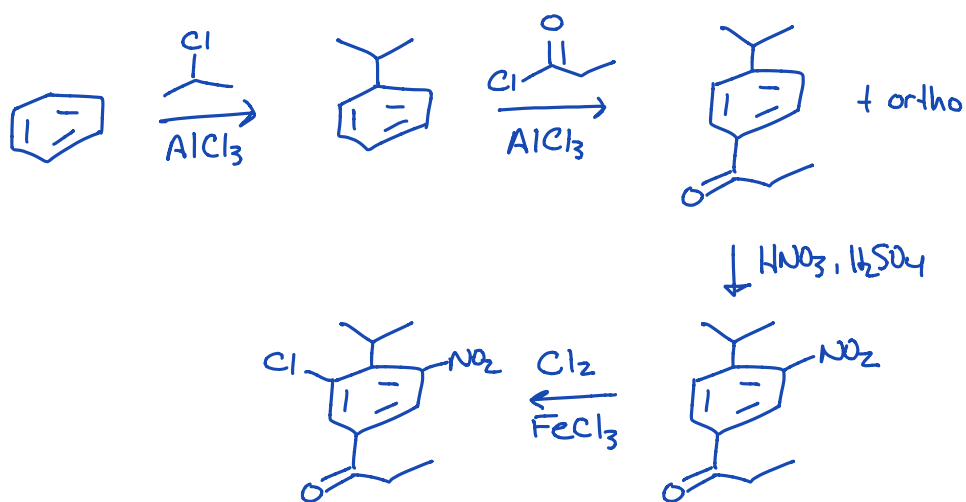
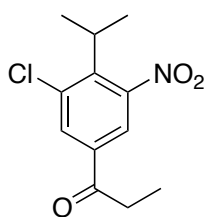


12) Propose a synthesis for each of the following compounds starting with benzene.

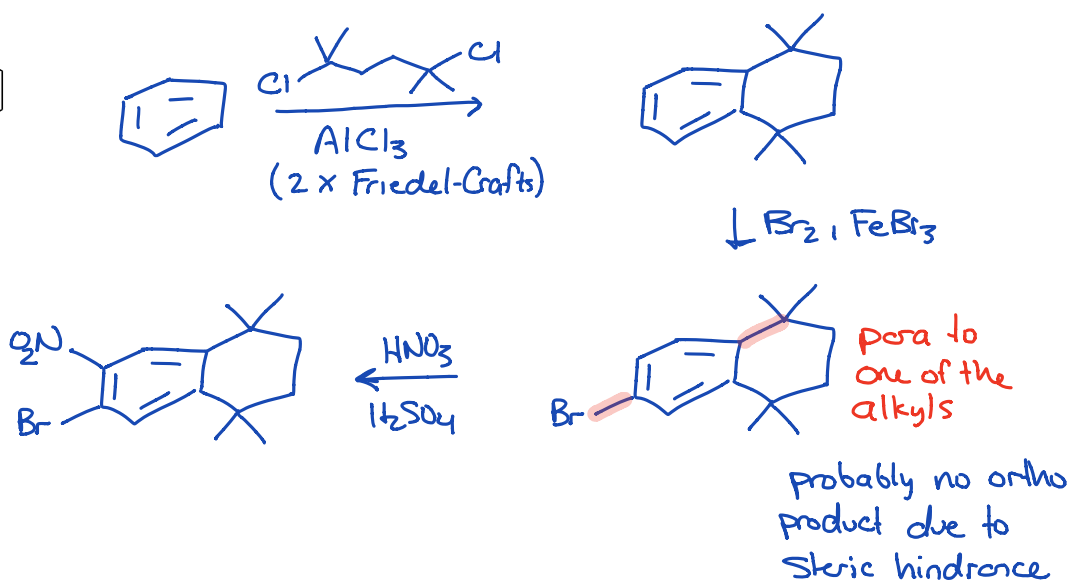
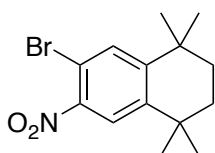




f.

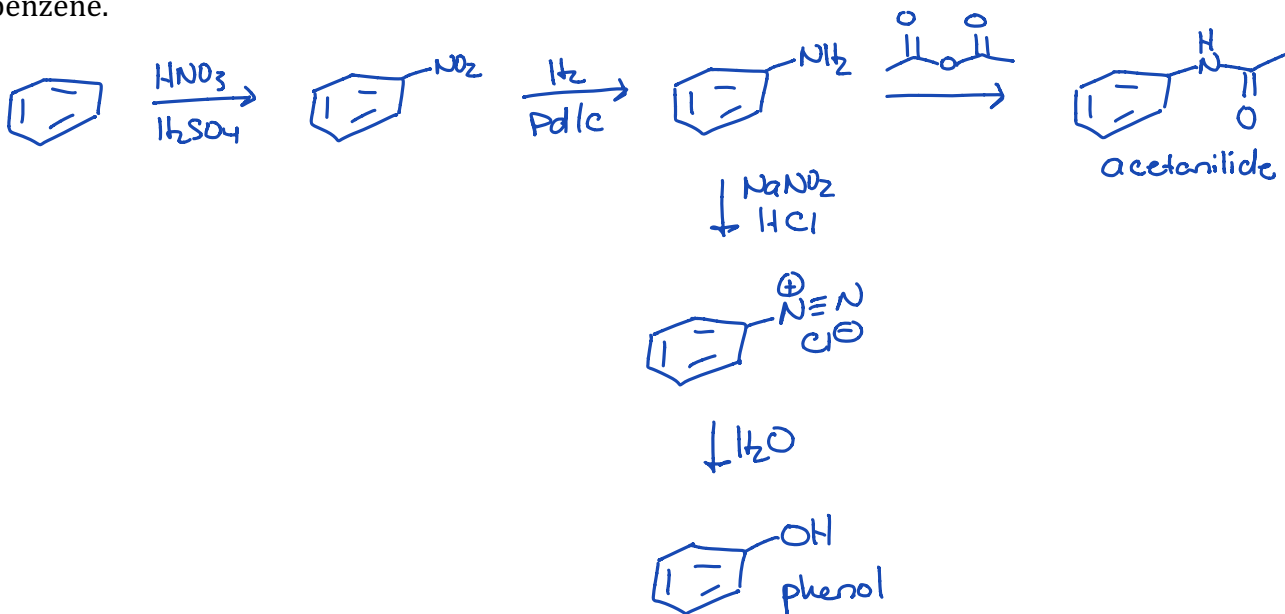


g.

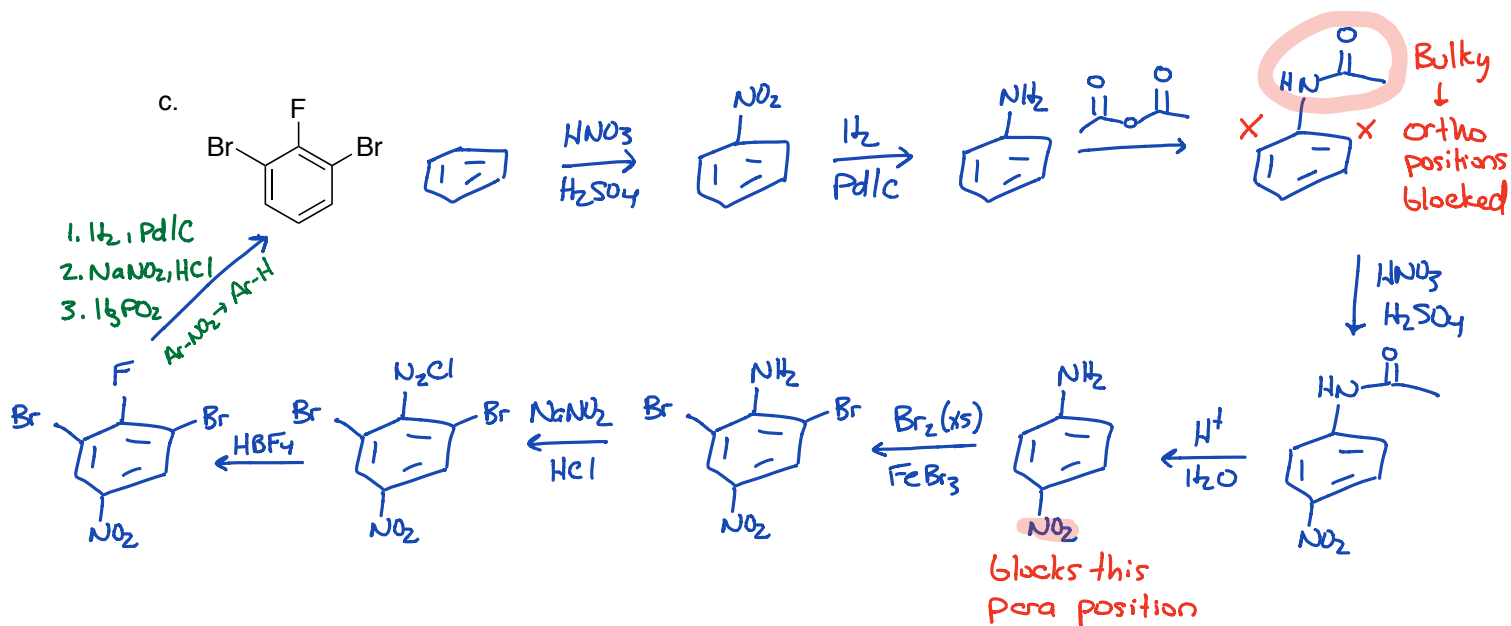
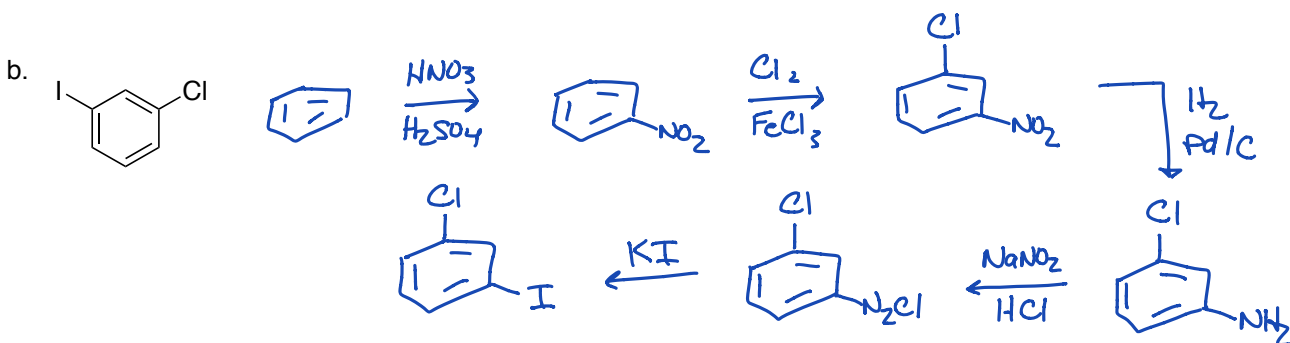
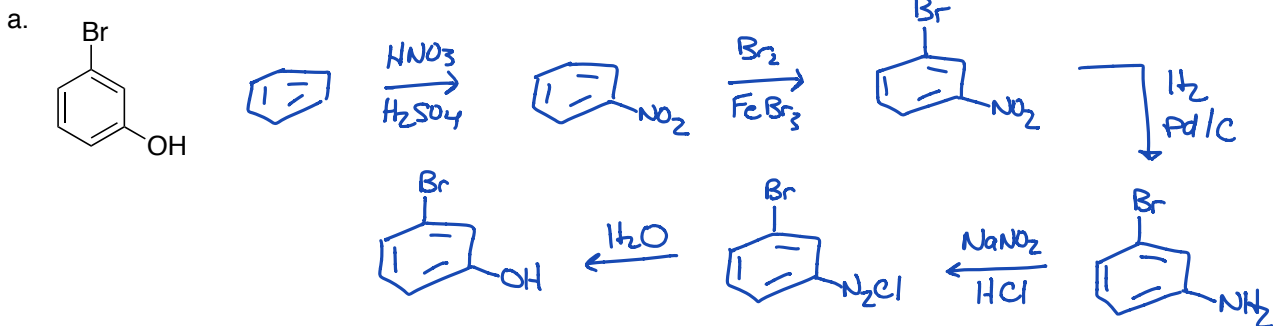


### Diazonium Ion Reactions

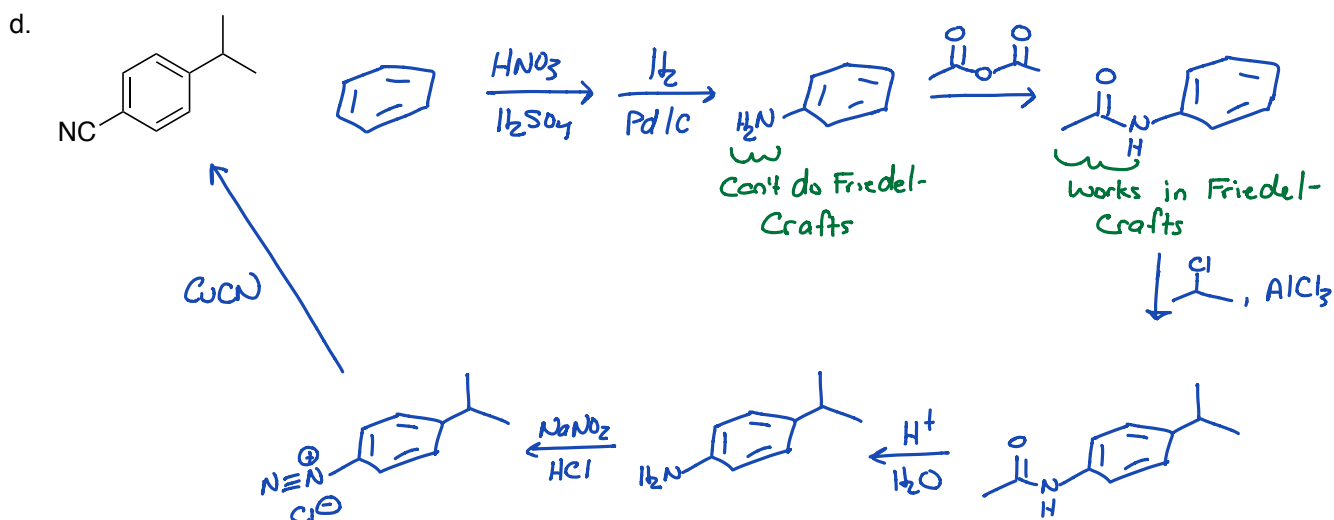
13) Write out the synthetic sequence to prepare phenol and acetanilide (Ph-NHCOCH<sub>3</sub>) from benzene.



14) Provide syntheses for each of the following compounds, free of other isomers. Your starting material should be benzene in each case.

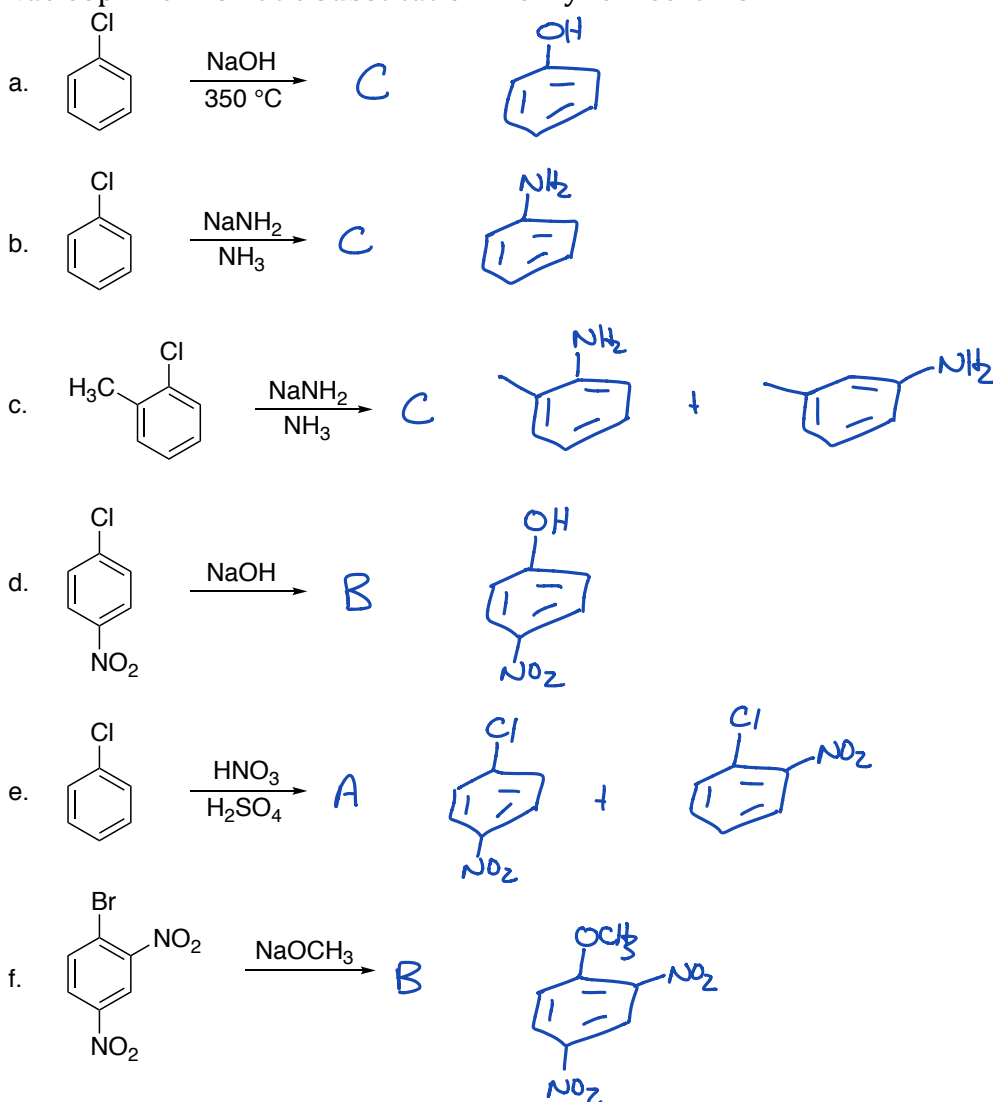




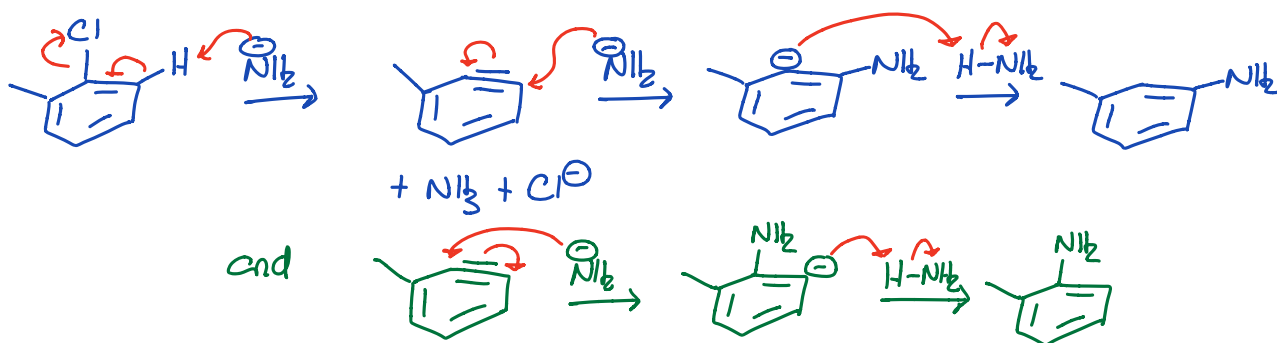


### Nucleophilic Aromatic Substitution

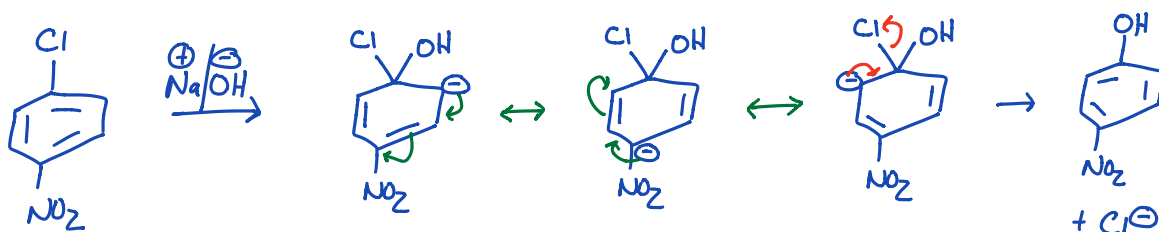
15) For each reaction shown below, determine if the reaction is (a) electrophilic aromatic substitution, (b) Nucleophilic Aromatic Substitution: Addition-Elimination, or (c) Nucleophilic Aromatic Substitution: Benzyne Mechanism.



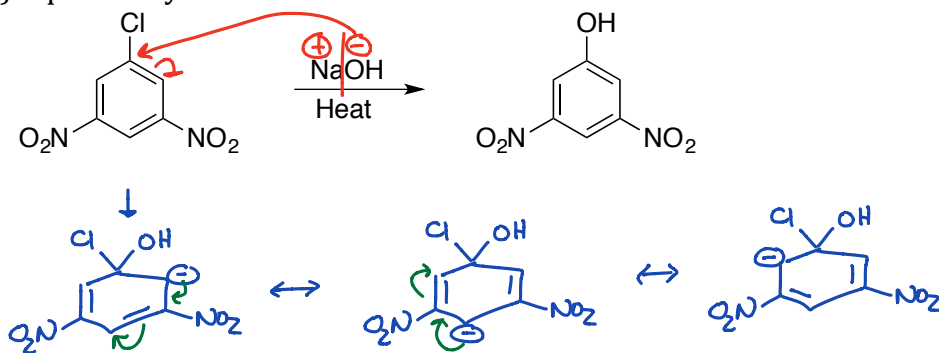
16) Show the full electron pushing mechanism for reaction 15c.



17) Show the full electron pushing mechanism for reaction 15d.

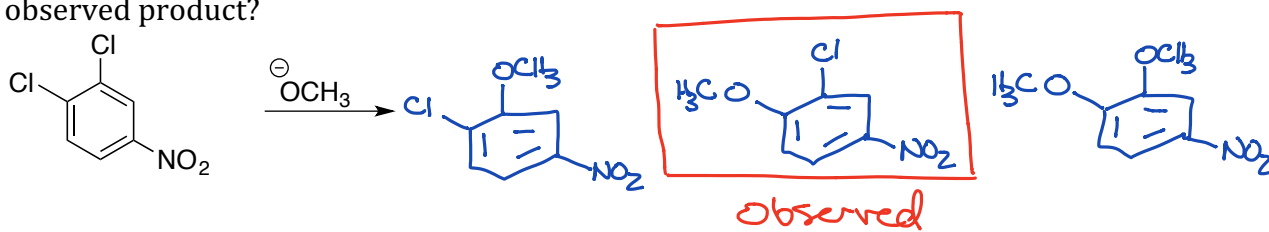


18) Explain why the reaction shown below does not occur.



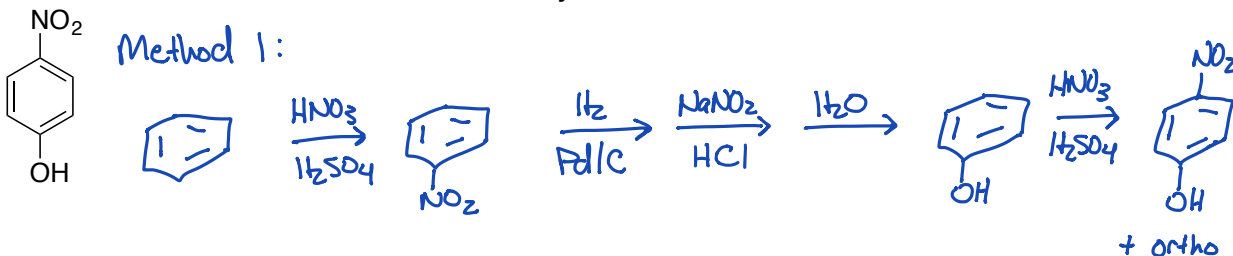
When  $-\text{NO}_2$  groups are meta to Cl, you don't get a stabilizing resonance structure that puts the  $\ominus$  on a carbon with a  $-\text{NO}_2$ .

19) Consider the reaction shown below. Theoretically, there are three possible products. Draw each of these products. In reality only one of these products is formed. Which one is the observed product?

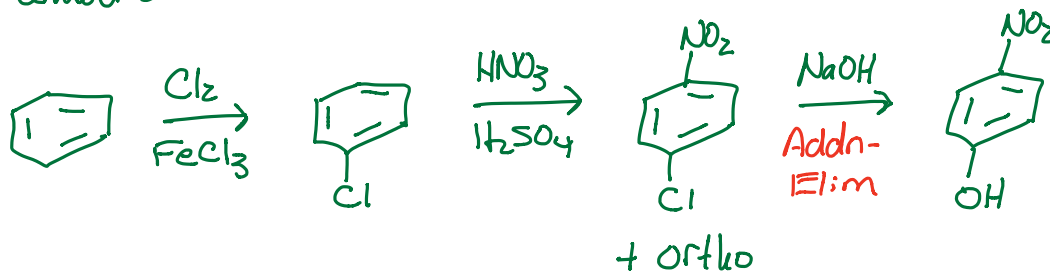


Only get addn-elim at the Cl that is para to  $\text{NO}_2$ .  
(or ortho)

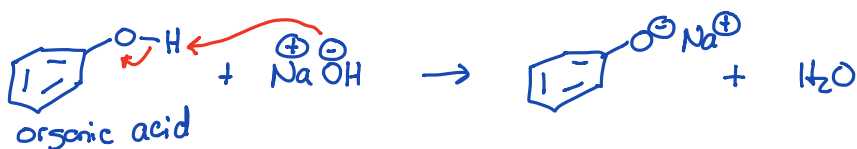
20) Show two methods to synthesize the molecule shown below starting with benzene. One route should use diazonium ion chemistry while the other route should not.



Method 2:



21) Show the reaction of phenol with NaOH.

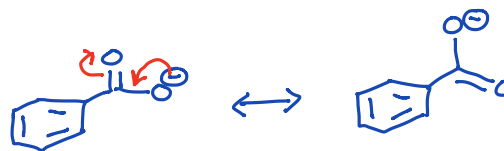


22) Show the reaction of benzoic acid with NaOH.

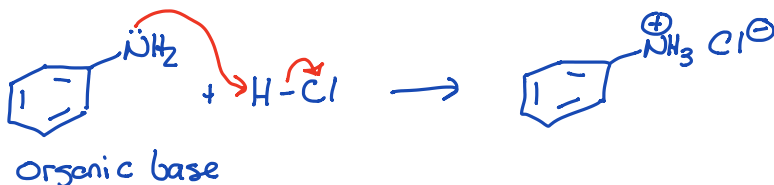


23) Is phenol or benzoic acid a stronger acid? Explain.

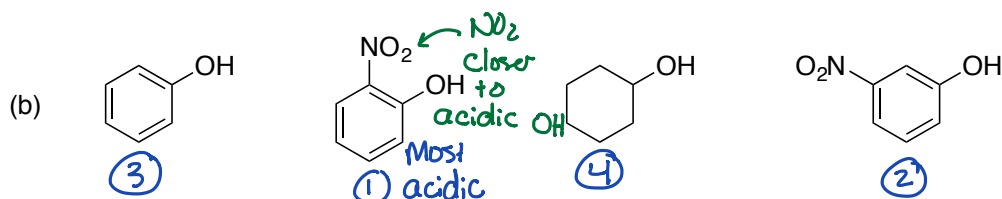
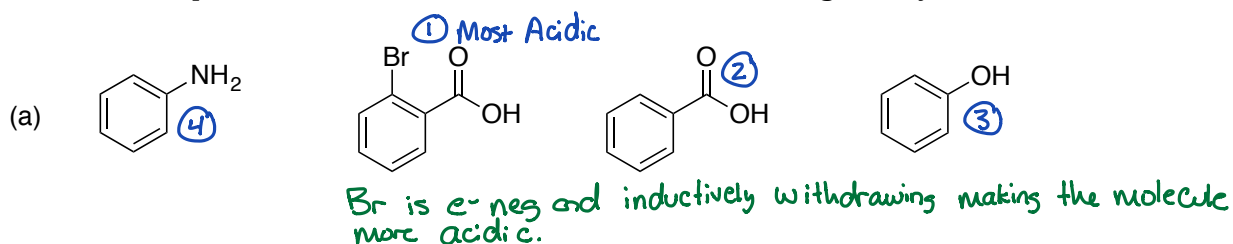
Benzoic acid. The  $\ominus$  of the conjugate base is delocalized over three atoms including two e-neg oxygen atoms.



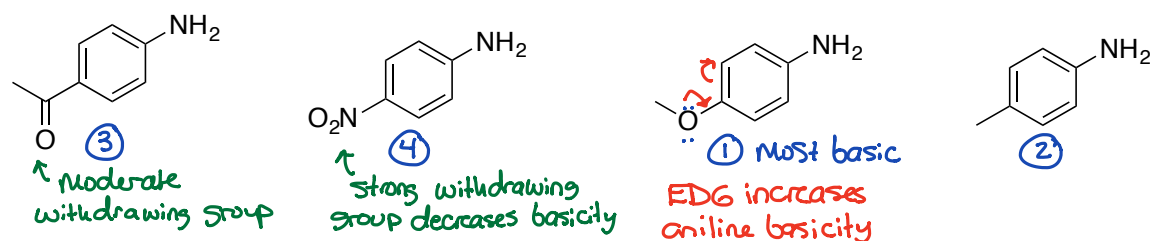
24) Show the reaction of aniline with HCl.



25) Rank the compounds in each set below in order of increasing acidity.

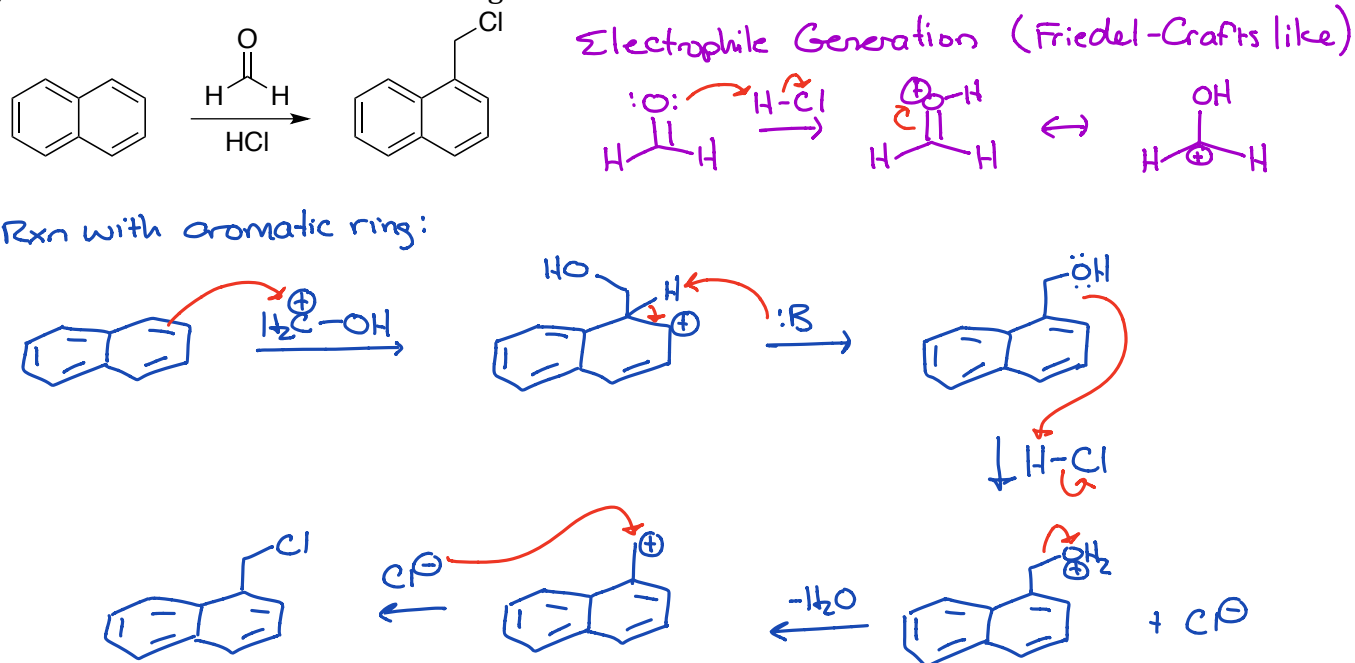


26) Rank the aniline derivatives below in order of increasing basicity.

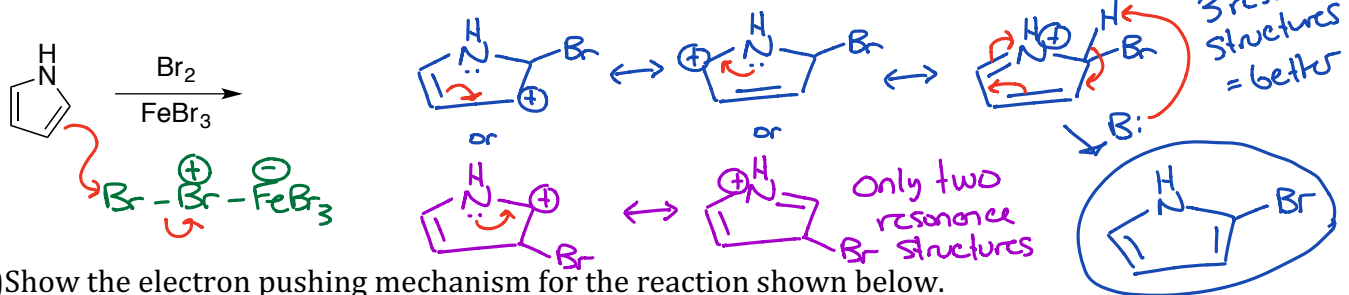


### Challenge Problems

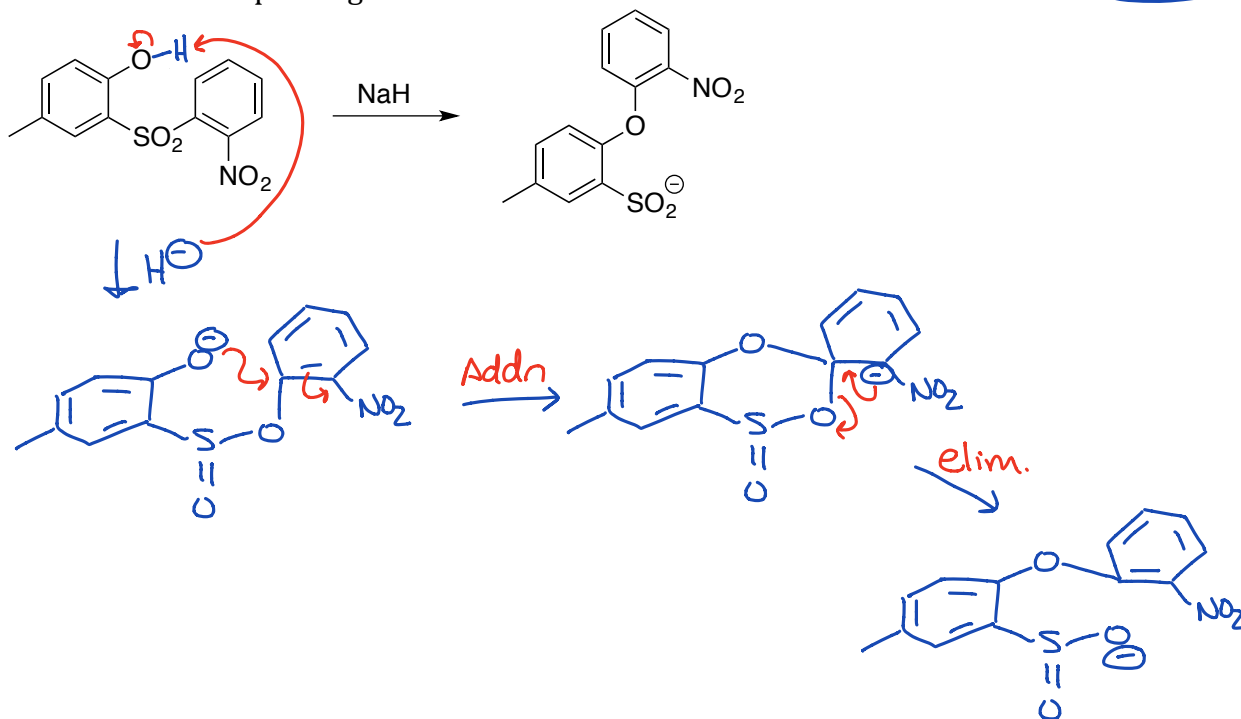
27) Write a mechanism for the following reaction.



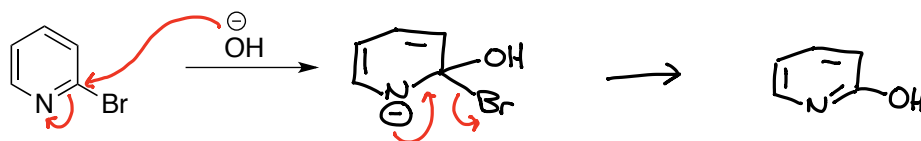
28) Predict the major product for the reaction of pyrrole with  $\text{Br}_2$ ,  $\text{FeBr}_3$ . *Hint: use resonance analysis of the intermediate to determine the preferred regioselectivity of the reaction.*



29) Show the electron pushing mechanism for the reaction shown below.



30) Substituted pyridines are known to undergo nucleophilic aromatic substitution via an addition-elimination mechanism. Predict the product and show the mechanism for the reaction shown below.



The pyridine nitrogen stabilizes the  $\ominus$  intermediate.