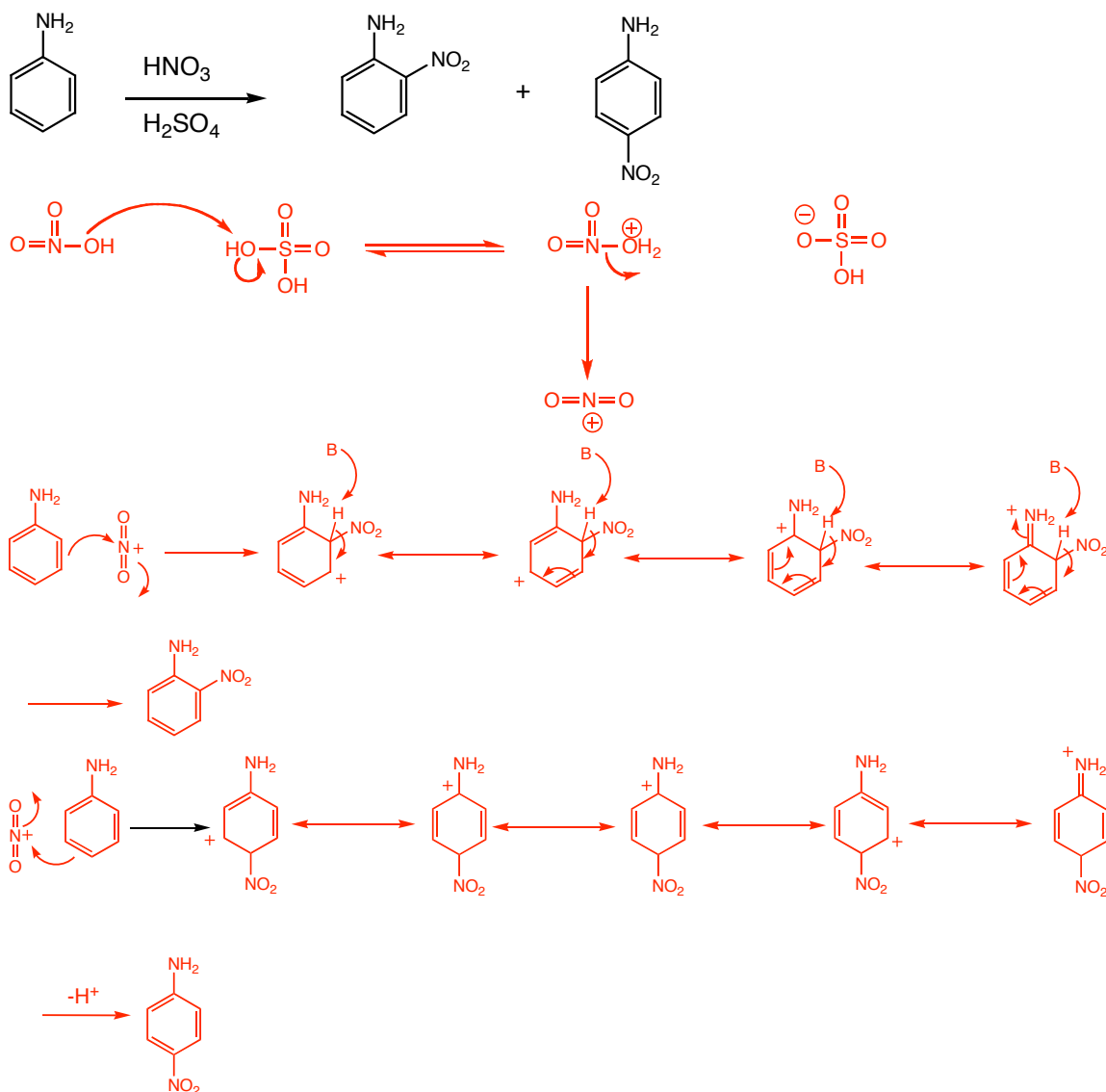


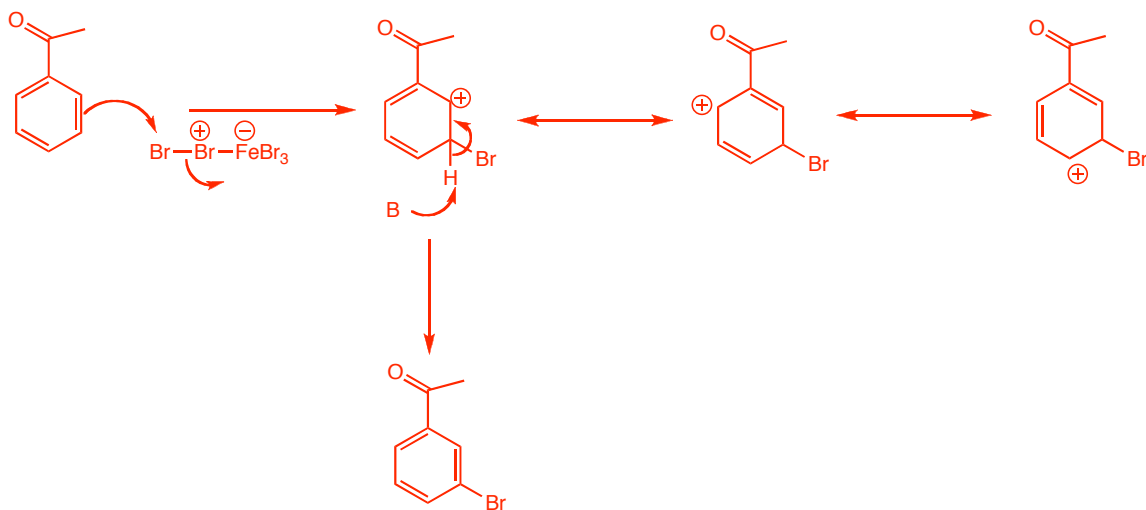
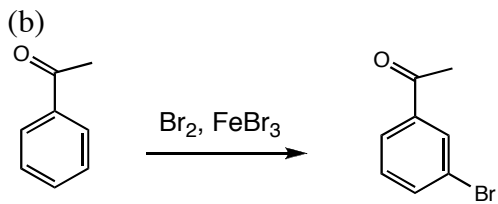
## Chemistry 218, Problem Set 6

Recommended problems from the text: 17.3-17.4, 17.10, 17.12-17.16, 17.18-17.22, 17.25-17.31, 17.33-17.42, 17.44-17.45, 17.53, 18.1-18.24, 18.32 (a-g), 18.33-18.37, 18.40-18.48, 18.51, 18.54 (a-e), 18.64-18.65

(Recommended problems from the text, 1<sup>st</sup> ed.: 17.3-17.4, 17.9, 17.11-17.15, 17.17-17.21, 17.24-17.31, 17.33-17.44, 17.50, 18.1-18.25, 18.34 (a-g), 18.35-18.39, 18.42-18.51, 18.54, 18.57 (a-e), 18.66-18.67)

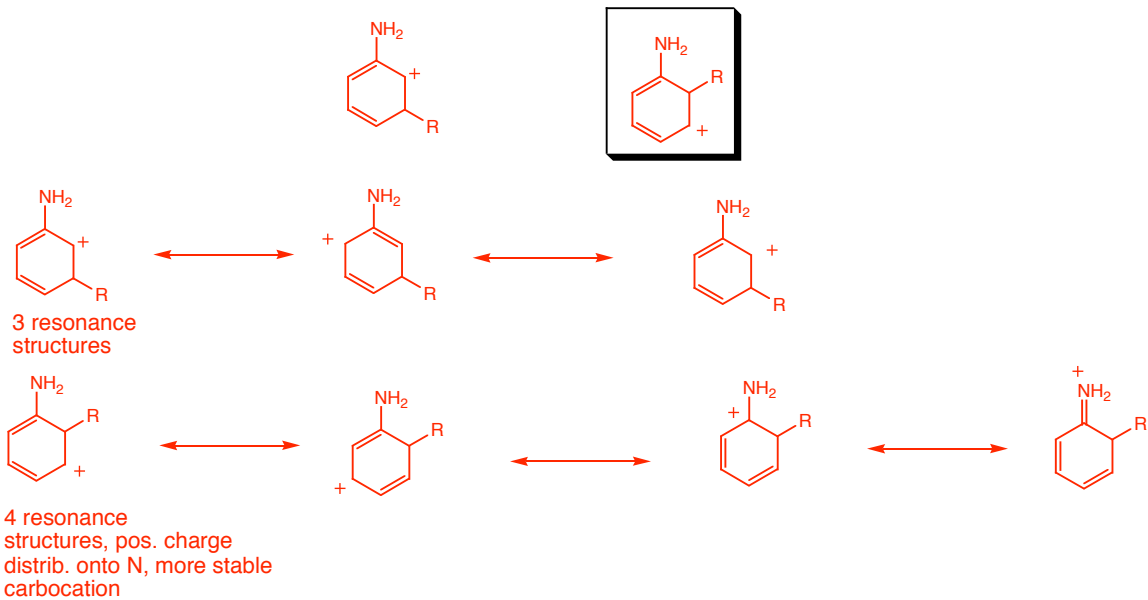
1. Draw mechanisms for each product formed in the following transformations. Include ALL resonance structures of carbocation intermediates.



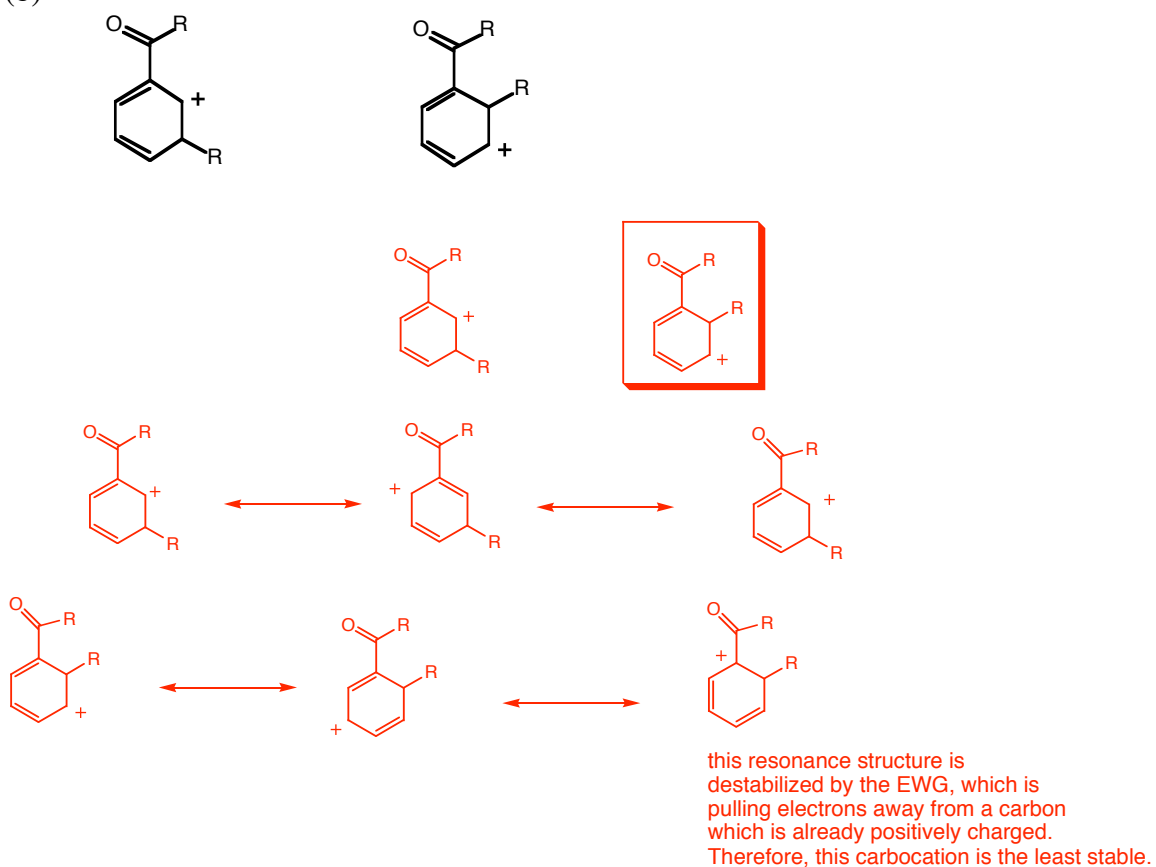


2. Choose the most stable carbocation from each of the following pairs.

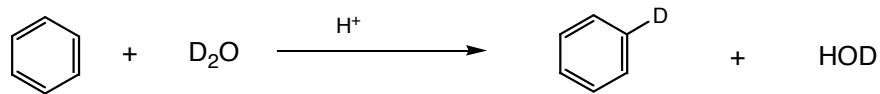
(a)



(b)



3. (a) If benzene is treated with sulfuric acid for several days at room temperature in the presence of  $D_2O$ , the following reaction occurs:

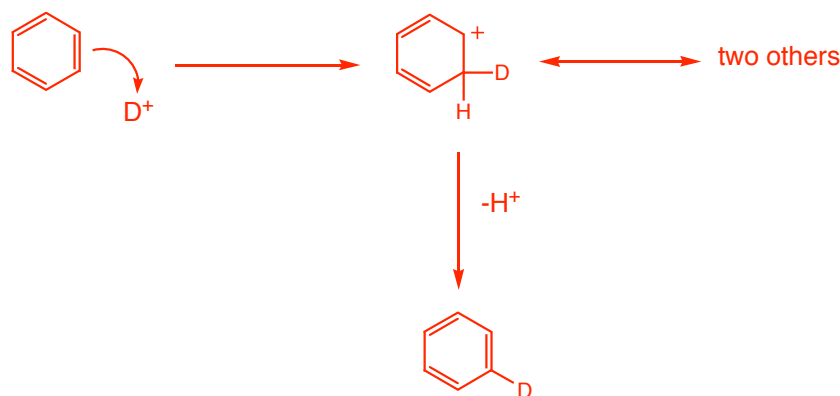


Draw a mechanism to explain the reaction. (Hint: what happens first when you put acid into water?)

First, an acid/base reaction occurs:



Benzene is then protonated by sulfuric acid. It is likely that some if not all will be protonated with deuterium.

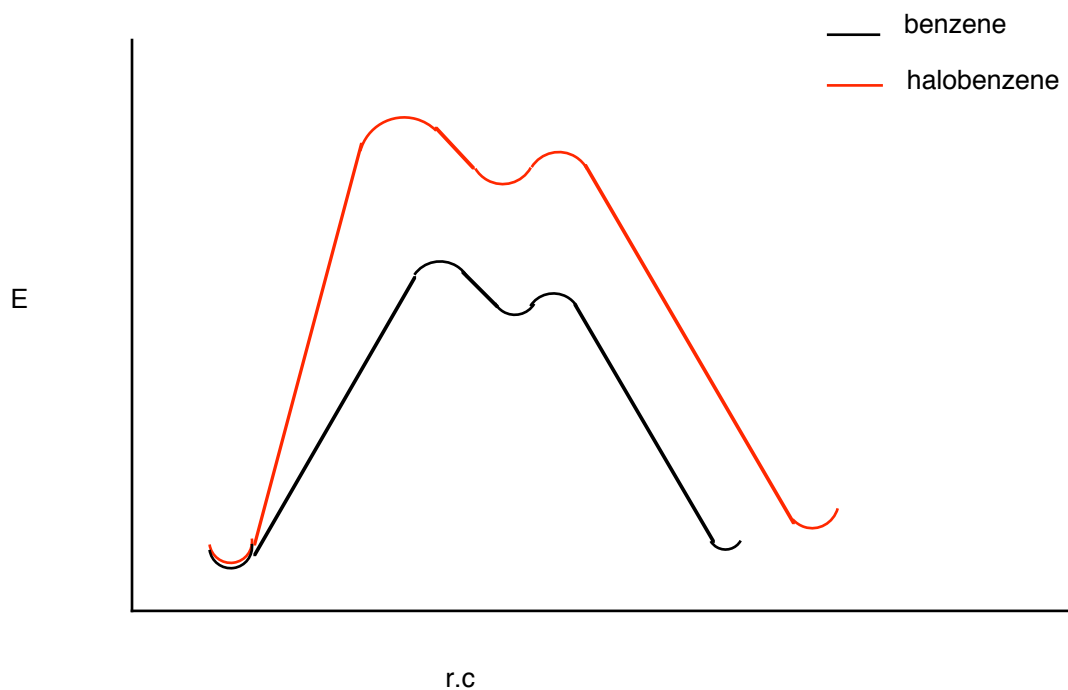


4. Predict whether single or multiple substitution is expected for the following reactions with benzene, if the reagents are used in a large excess, Explain WHY.

- (a) Nitration Only mono substitutions will occur because nitro groups are strongly deactivating groups. After one nitro group is introduced, the ring is deactivated toward further substitution.
- (b) Sulfonation  $SO_3H$  groups are moderately deactivating, so it is unlikely that a second substitution would occur.
- (c) Friedel-Crafts alkylation Alkyl groups are activating groups, so further alkylations will occur. The more alkyl groups that are installed, the more activated the ring will be.
- (d) Friedel-Crafts acylation Acyl groups are moderately deactivating groups, so it is unlikely that further acylations will occur.

(e) bromination Bromines are weakly deactivating, so a second bromination is possible, though it will be much more difficult than the first.

5. Draw a reaction coordinate for an EAS reaction with a halobenzene compared to benzene.



6. Each intersection of the following table represents a reaction. What products (if any) are formed in each reaction? Which reactions occur more rapidly than the analogous reaction on benzene itself? Assume only mono substitutions occur.

