

## REACTIONS OF AROMATIC COMPOUNDS

A STUDENT WHO HAS MASTERED THE MATERIAL IN THIS SECTION SHOULD BE ABLE TO:

1. Predict the product or products of electrophilic aromatic substitution reactions and reactions involving side chains.

Important reactions include:

Electrophilic aromatic substitution: halogenation, nitration, sulfonation, Friedel-Crafts alkylation and acylation.

Side chain reactions: permanganate oxidation, Clemmensen reduction, free radical halogenation, and the addition and elimination reactions you're familiar with from previous sections.

Important effects include:

The directive effects of the substituent already on the ring controls the location of incoming groups.

When two or more groups are present, the strongest activating group on the ring controls the location of the incoming group. If the only groups present are deactivating, the weakest deactivating group controls the location of the incoming group. You will need to memorize the table of substituent activating-deactivating and ortho/para and meta-directing properties.

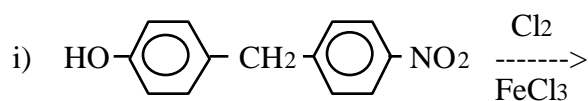
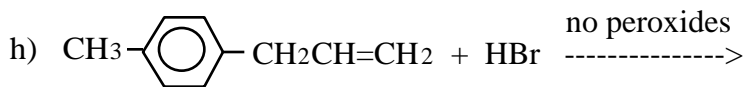
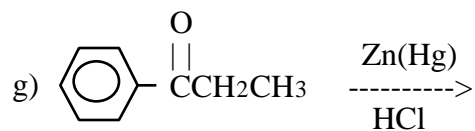
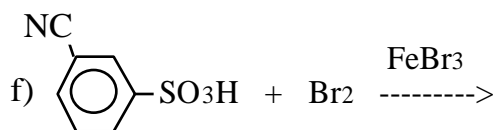
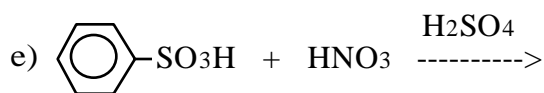
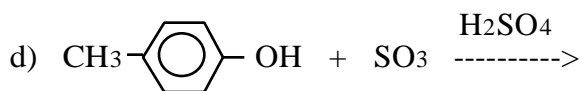
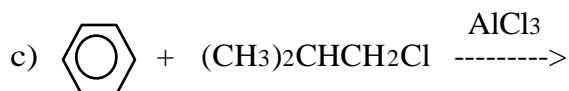
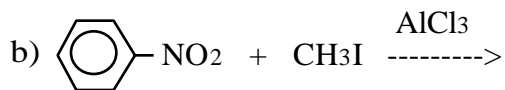
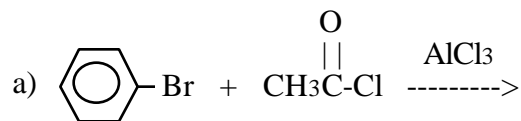
Substitution does not occur between groups meta to one another if there are any other possibilities.

Keep in mind the limitations of the Friedel-Crafts reactions: No reaction occurs with benzene rings containing meta directing groups or amino groups ( $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ ), and rearrangement of side chains may occur.

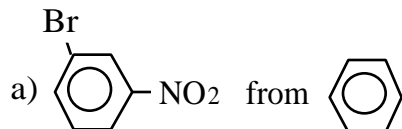
2. Using the reactions of Objective 1 above, propose syntheses of substituted benzene derivatives. (The order in which reactions are performed is often important).
3. Propose mechanisms for the reactions of objective 1 above (except permanganate oxidation and Clemmensen reduction) and of other electrophilic aromatic substitution reactions. Also, predict the relative reactivity of compounds toward electrophilic aromatic substitution.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

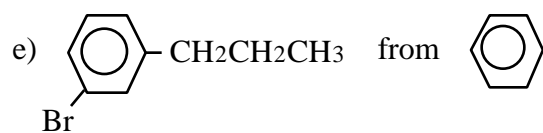
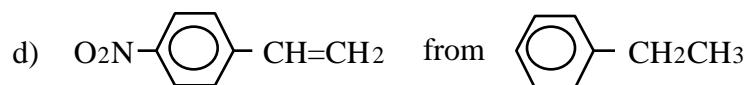
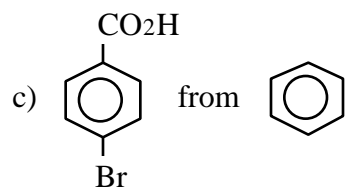
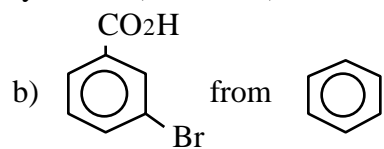
1. Predict the product or products of the reactions shown (if any):



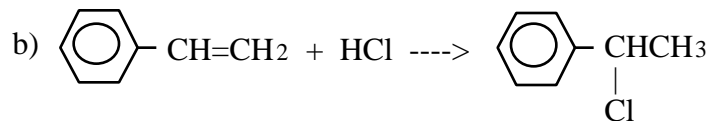
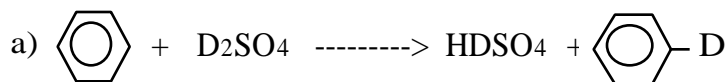
2. Propose a synthesis of each of the following compounds, from the given starting material(s) and any other needed reagents.



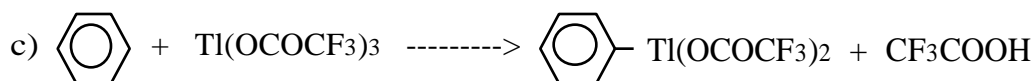
2. Synthesis (continued)



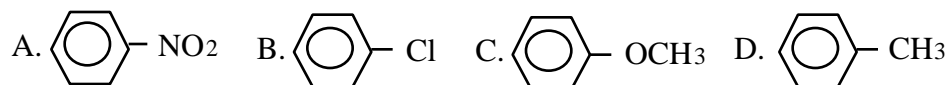
3.1 Propose a mechanism of each of the following reactions.



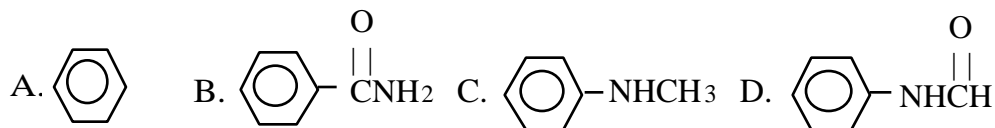
3.1 Propose a mechanism, continued.



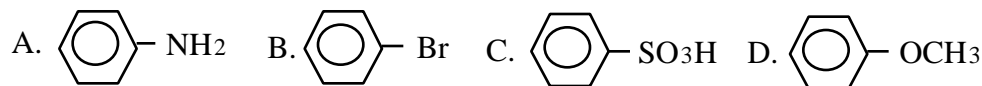
3.2 Which of the following compounds reacts MOST RAPIDLY with  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ?



3.3 Which of the following compounds reacts MOST RAPIDLY with  $\text{CH}_3\text{I}/\text{AlCl}_3$ ?

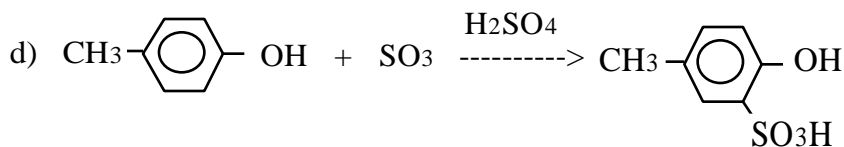
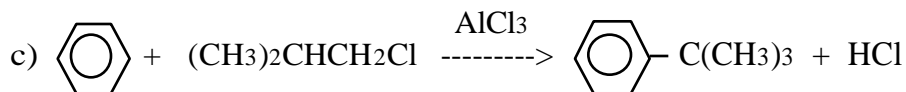
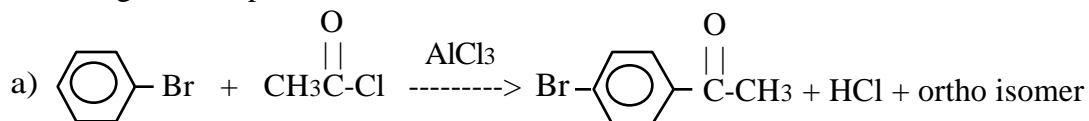


3.4 Which of the following compounds reacts MOST SLOWLY with  $\text{Br}_2/\text{FeBr}_3$ ?

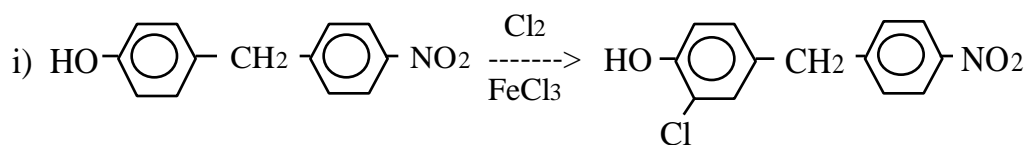
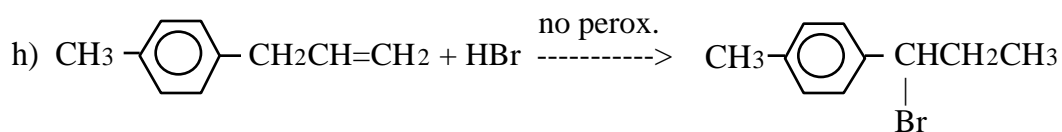
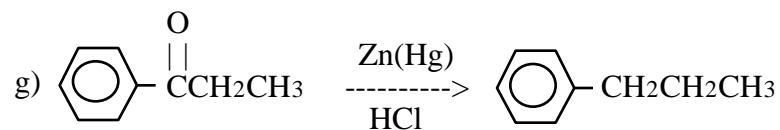
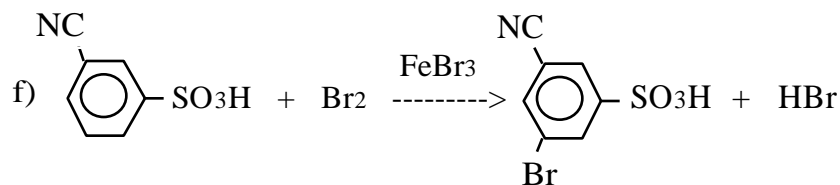
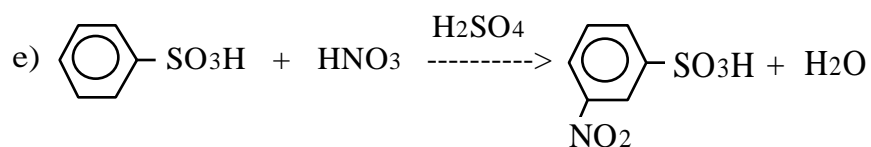


#### ANSWERS TO THE PROBLEMS:

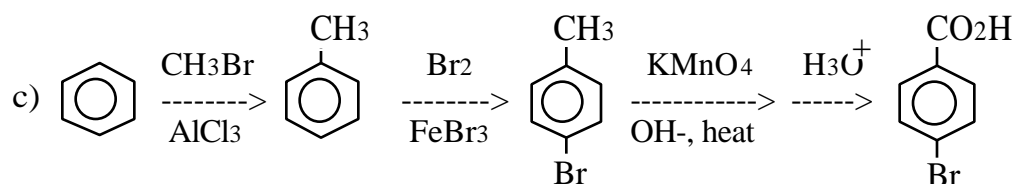
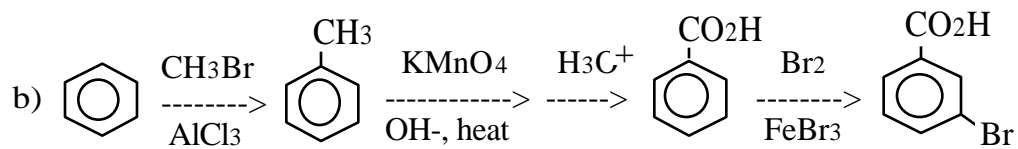
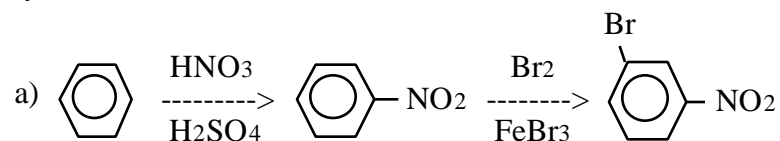
1. Predicting reaction products:



1. Predicting reaction products, continued.

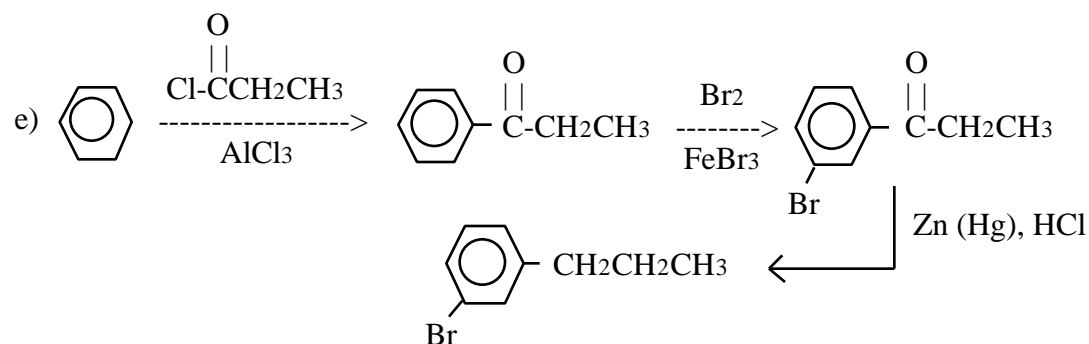
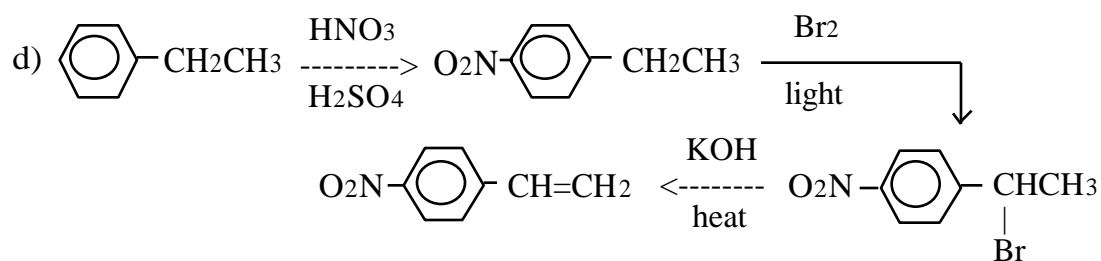


2. Synthesis:

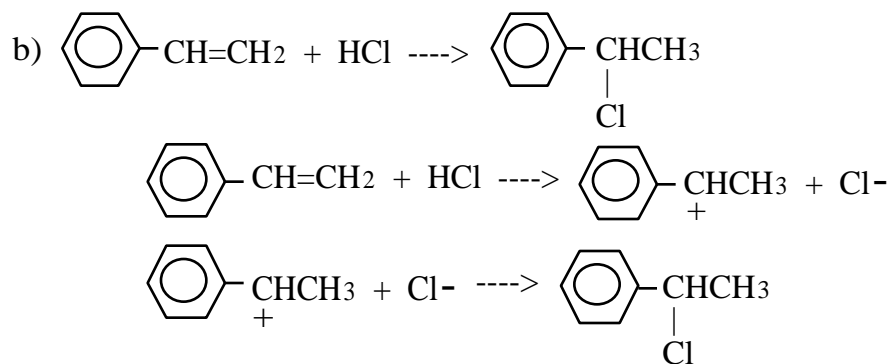
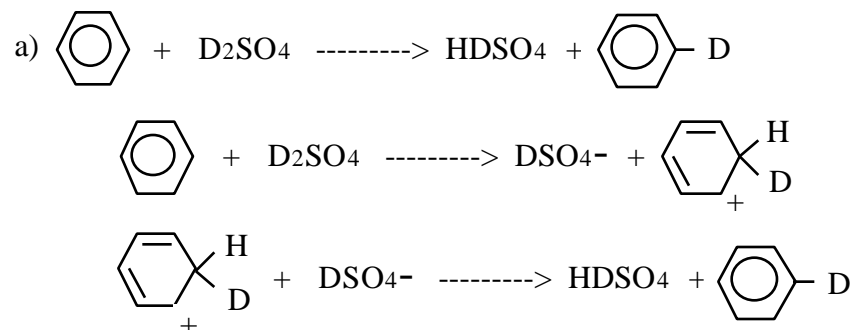


You can also brominate first and do the Friedel-Crafts reaction second.

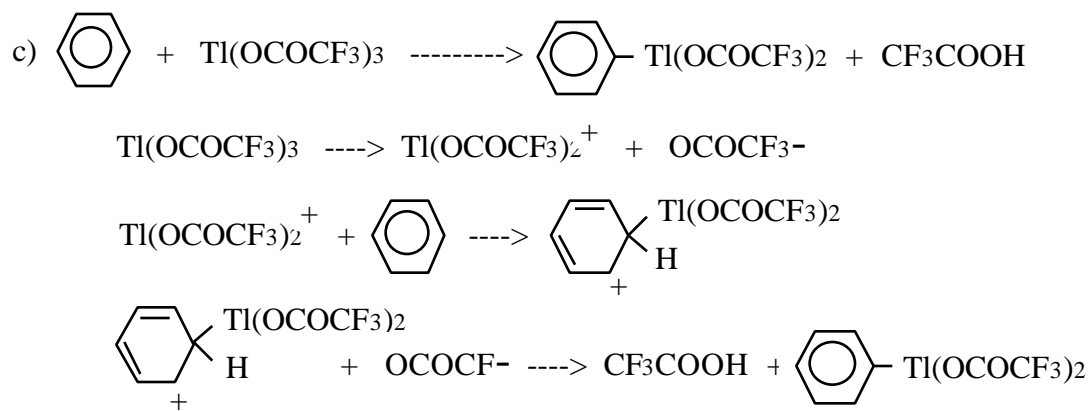
2. Synthesis, continued.



3.1 Mechanisms:

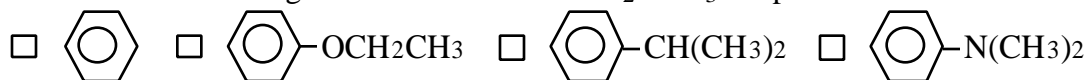


3.1 Mechanisms, continued.

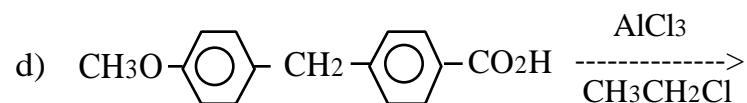
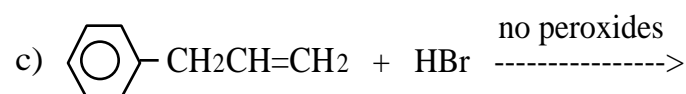
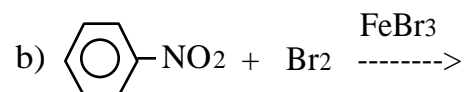
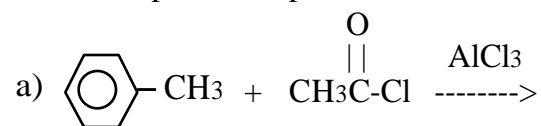


- 3.2 C  
 3.3 D  
 3.4 C

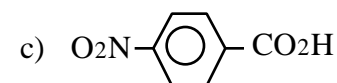
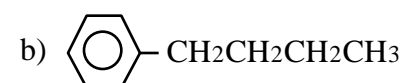
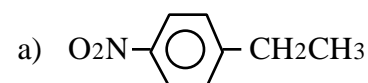
1) Which of the following reacts FASTEST with  $\text{Cl}_2/\text{FeCl}_3$ ? 5 pts



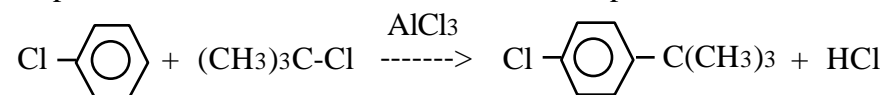
2) Predict the product or products of each of the following reactions. 5 pts each.



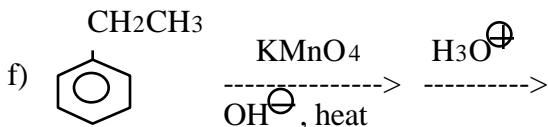
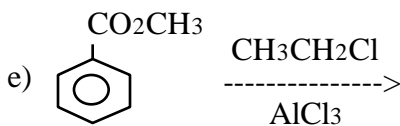
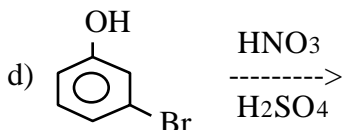
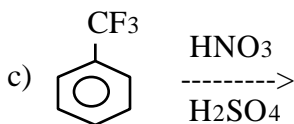
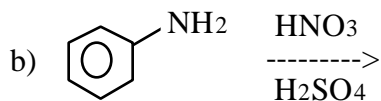
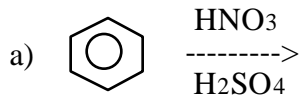
3) Propose a synthesis of each of the following compounds from benzene and any other needed reagents. 5 pts each.



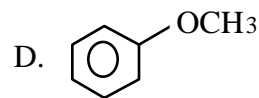
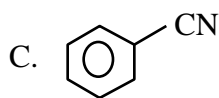
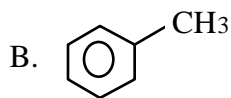
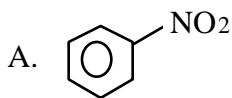
4) Propose a mechanism of the reaction shown. 5 pts.



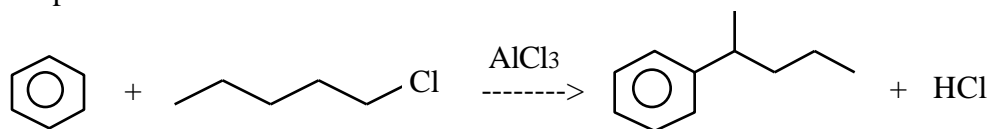
1. Draw the structures of all of the major organic products of each of the following reactions. If no reaction occurs, write "NR".



2. Which of the following compounds reacts most rapidly with  $\text{I}_2/\text{HNO}_3$ ?



3. Propose a mechanism for the reaction shown.



4. Propose syntheses of each of the following compounds from the indicated starting materials and any other needed reagents.

