REACTIONS OF AROMATIC COMPOUNDS

A STUDENT SHOULD BE ABLE TO:

1. Predict the product(s) of Electrophilic Aromatic Substitution (EAS), Nucleophilic Aromatic Substitution (S_NAr) and Elimination-Addition reactions.

   Important reactions include:
   Electrophilic aromatic substitution: halogenation, sulfonation and desulfonation, nitration, Friedel-Crafts alkylation and acylation, and aryldiazonium salts
   Side-chain reactions: Clemmensen reduction and all reactions from previous sections including free radical halogenation, oxidations, addition and elimination reactions.

   Important effects include:
   The substituent already on the ring directs the location of the incoming group.
   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.
   Strong activators possess a lone pair of electrons adjacent to the aromatic ring (except halogens). Moderate activators possess a lone pair adjacent to the aromatic ring that is participating in resonance outside the ring. Weak activators are typically alkyl groups. Deactivators are electron-withdrawing groups.
   All activating groups are *ortho*, *para* directors. Most deactivating groups are *meta* directors. Halogens are weak deactivators and *ortho*, *para* directors.
   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 aromatic rings only containing deactivating groups or amino groups ($-NH_2$, $-NHR$, $-NR_2$), and rearrangement of side chains may occur with Friedel-Craft alkylations.

2. Predict the relative reactivity of compounds toward electrophilic aromatic substitution.

3. Determine whether a substitution will proceed by an electrophilic aromatic substitution (EAS), nucleophilic aromatic substitution (S_NAr), or an elimination-addition mechanism. If the reagent is an electrophile the reaction will be EAS. If the ring contains powerful electron withdrawing group(s) and a leaving group *ortho* or *para* to the withdrawing group, the reaction will be S_NAr.

4. Using the reactions of Objective 1, propose syntheses of substituted aromatic derivatives. The order in which reactions are performed is often important.

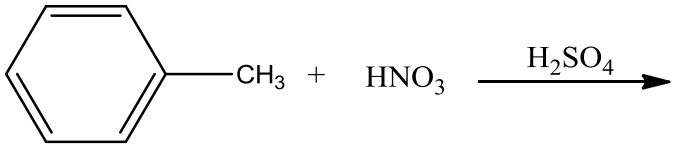
5. Understand and be able to draw the mechanism of an Electrophilic Aromatic Substitution (EAS) reaction, Nucleophilic Aromatic Substitution (S_NAr), and an Elimination-Addition mechanism. The mechanisms will include all intermediates and proper mechanistic arrows. Understand the chemistry dictating the observed regiochemistry.

To best prepare for this module, please work Chapter 19 and section 23.11 Skill Builder problems in the textbook.

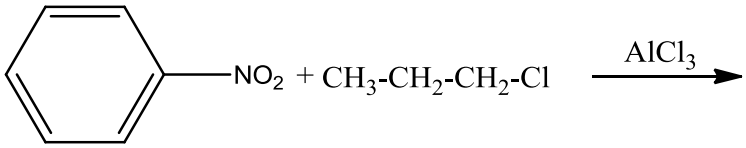
A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGES SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Predict the product or products of the reactions shown (if any)

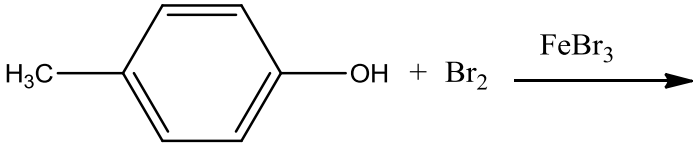
a)



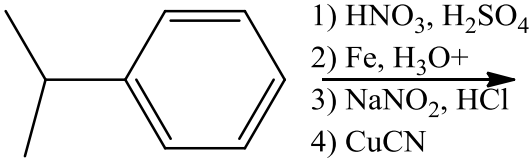
b)



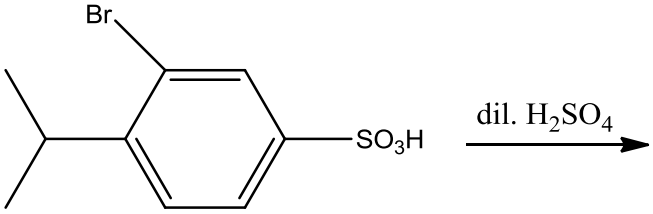
c)



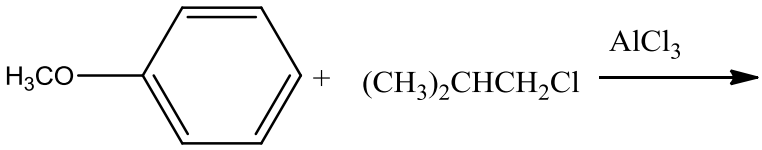
d)



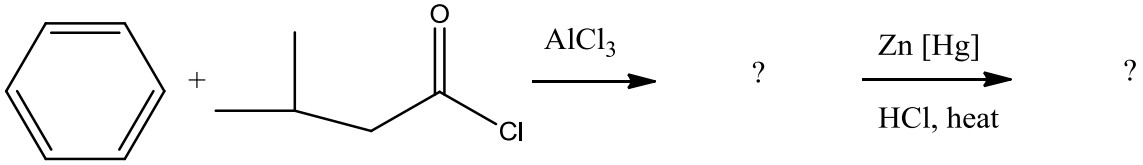
e)



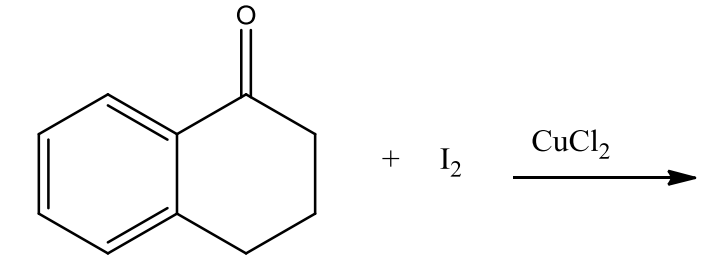
f)



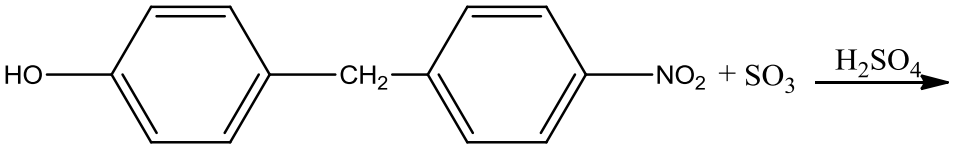
g)



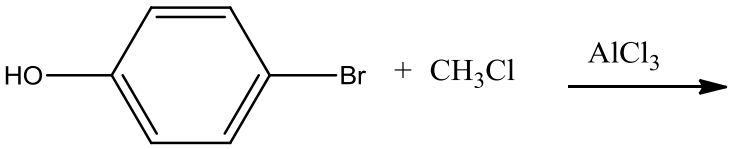
1.1 h)



i)



j)



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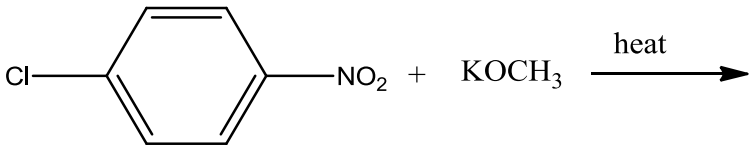
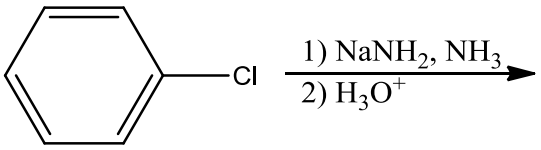
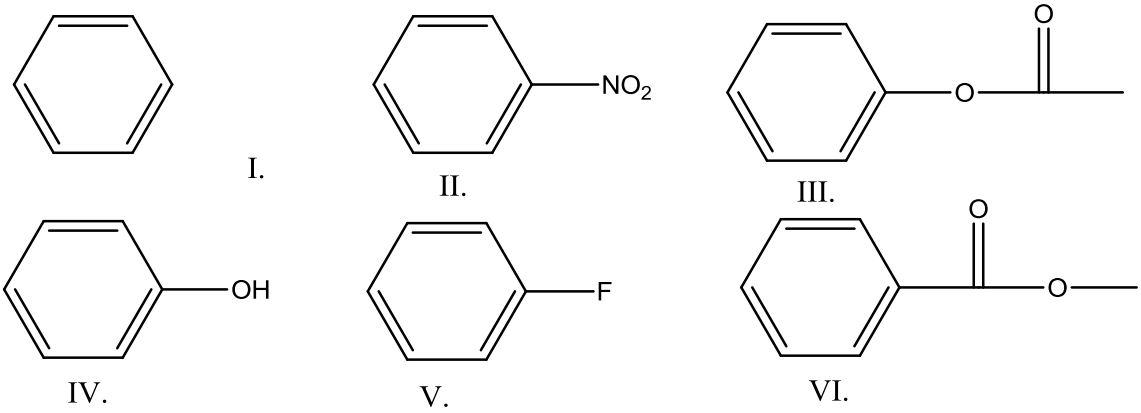


l)



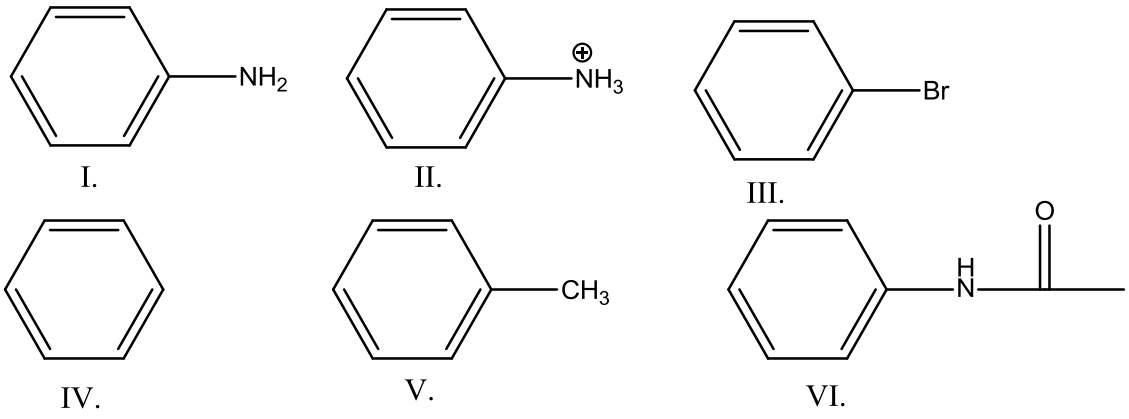
2. Rank the following compounds from fastest to slowest as they react in an EAS with $Br_2/FeBr_3$.

a)



fastest_____>____>___>___>____>____slowest

2. b)

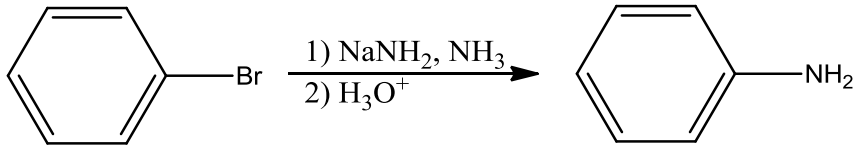


I. II. III. IV. V. VI.

fastest_____>____>___>___>____>____slowest

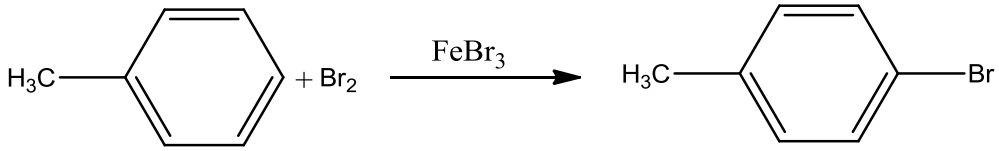
3. Under each reaction, circle the correct operating mechanism.

a)



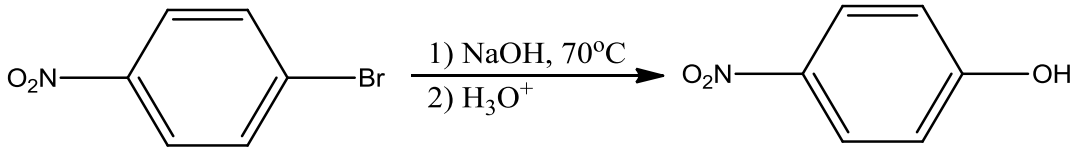
EAS, S_NAr, or Elimination-Addition

b)



EAS, S_NAr, or Elimination-Addition

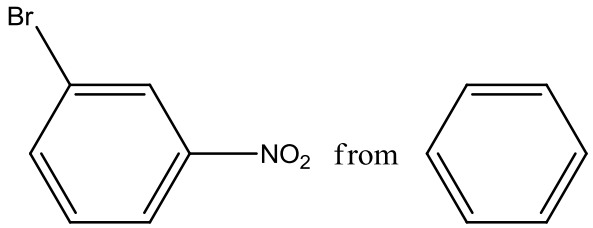
c)



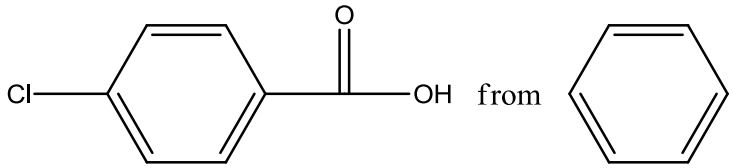
EAS, S_NAr, or Elimination-Addition

4. Propose a synthesis of each of the following compounds, from the given starting material and any other needed reagents.

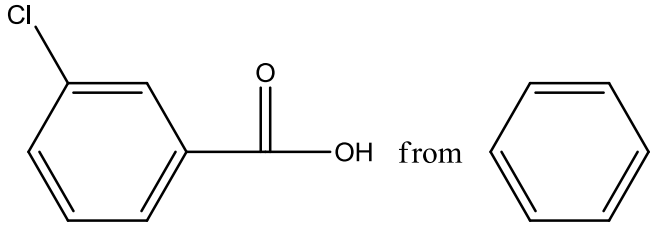
a)



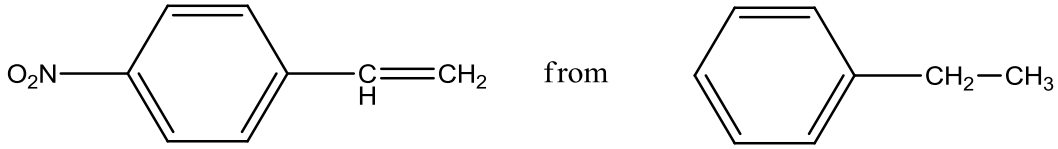
b)



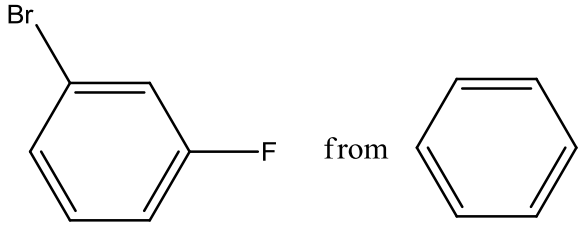
c)



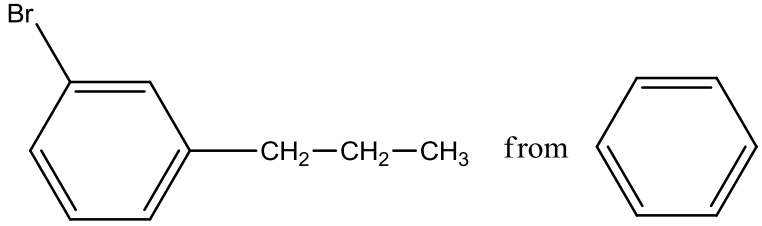
d)



e)

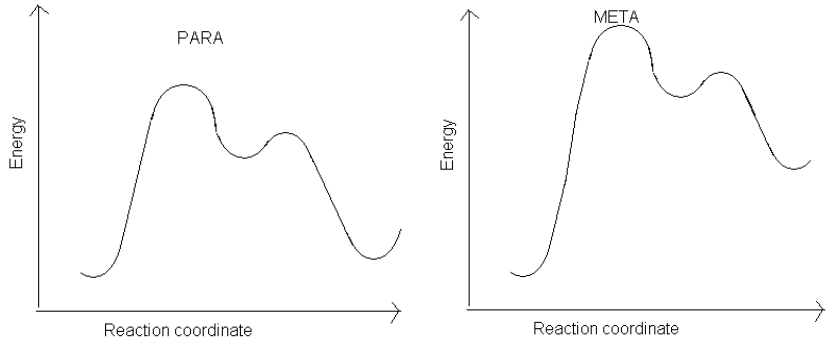


f)

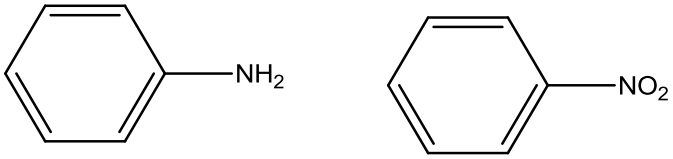


5.1 Draw the complete mechanism, using proper curved arrow notation, and all intermediates of both the *para* and *meta* bromination of nitrobenzene in the presence of ferric bromide. Two complete mechanisms will have to be drawn. Identify any particularly unstable intermediate with an asterisk (*). Based on this, which regiochemistry is preferred?

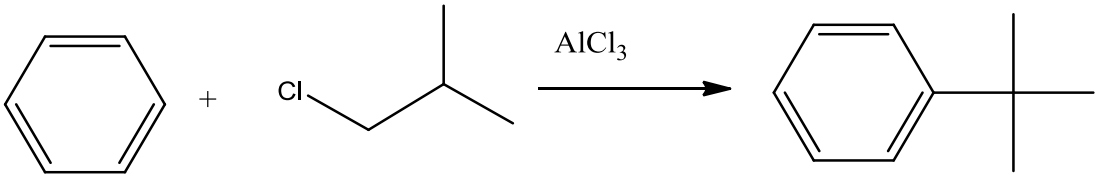
5.2 Below are two reaction energy coordinates for a *para* and *meta* chlorination of an aromatic substrate.



Which one of the two materials below could be responsible? Explain why.



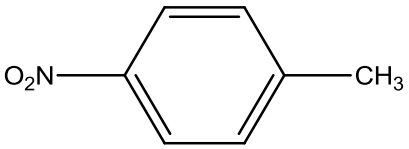
5.3 Propose a complete mechanism for the following reaction. Be sure to use correct curved arrow notation and show all intermediates.



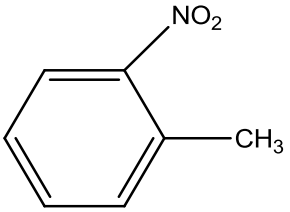
SOLUTIONS TO SAMPLE PROBLEMS:

1.1 Predict the product or products of the reactions shown (if any)

a)

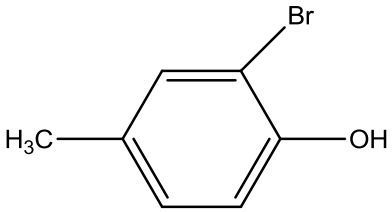


and

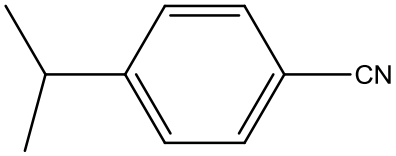


b) no reaction

c)

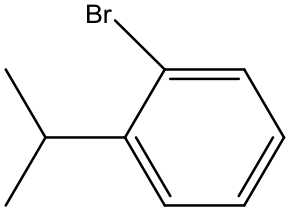


d)

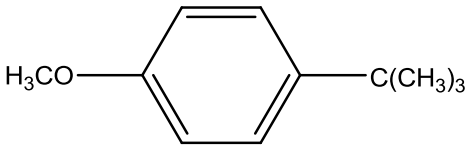


(+ *ortho* isomer as minor product, due to sterics)

e)

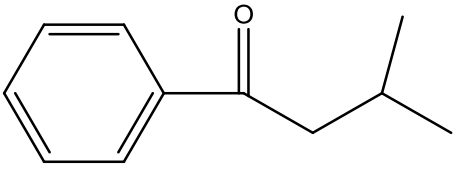


f)



+ *ortho* isomer

g)



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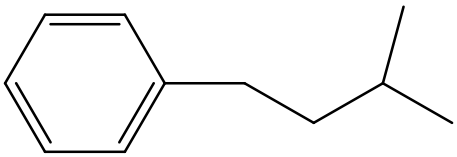
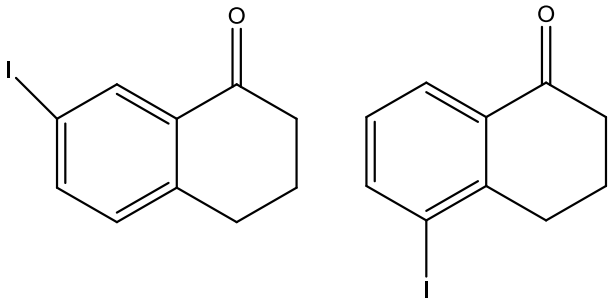
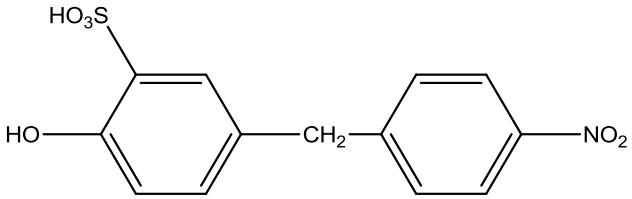


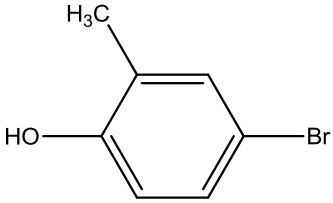
1.1 h)



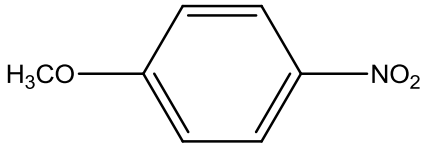
i)



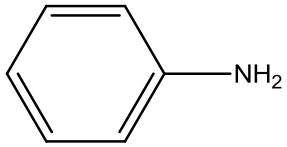
j)



k)



l)



2. a. fastest _IV_ > _III__ > _I__ > _V__ > _VI___ > _II_ slowest

b. fastest _I____ > _VI___ > _V__ > _IV__ > _III___ > _II__ slowest

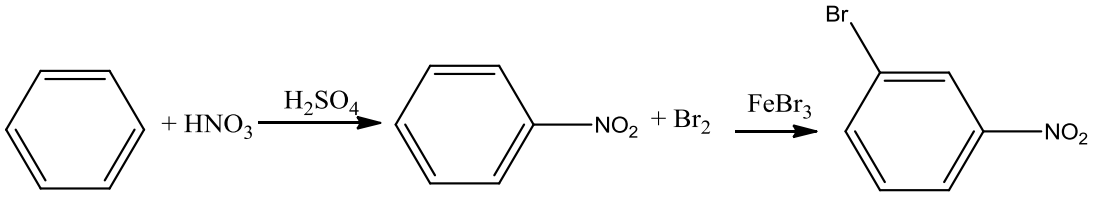
3. Next to each reaction circle the correct operating mechanism.

a) EAS, SNAr, or (Elimination-Addition)

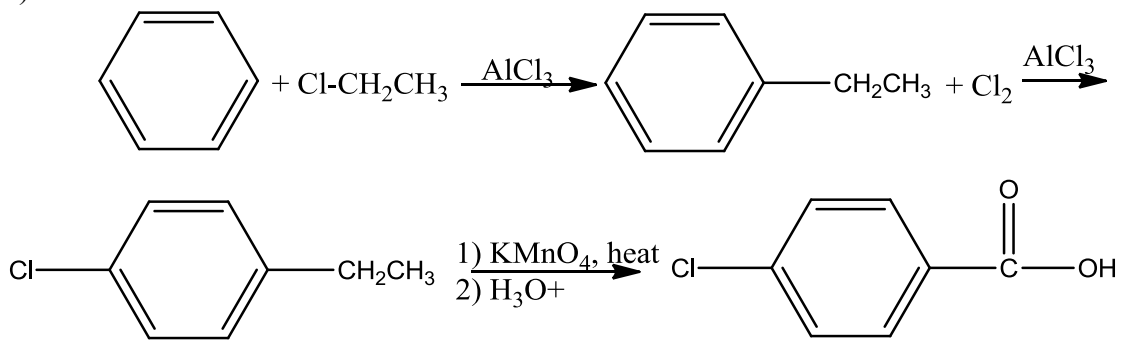
b) (EAS), SNAr, or Elimination-Addition

c) EAS, (SNAr), or Elimination-Addition

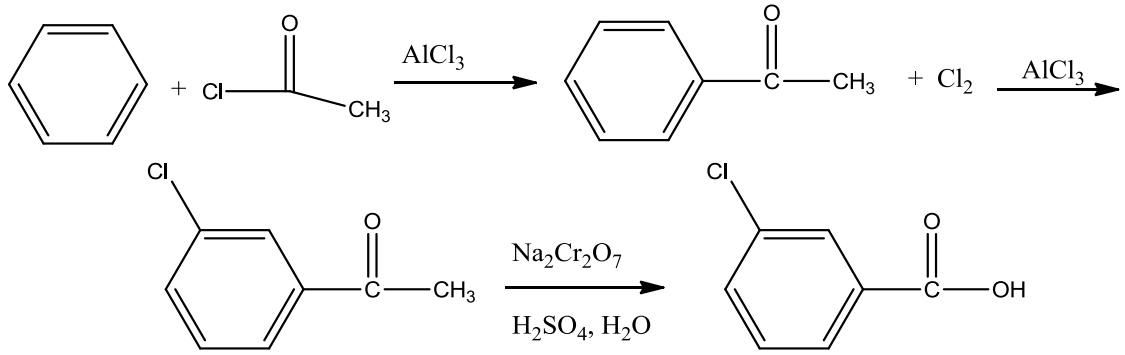
4. a)



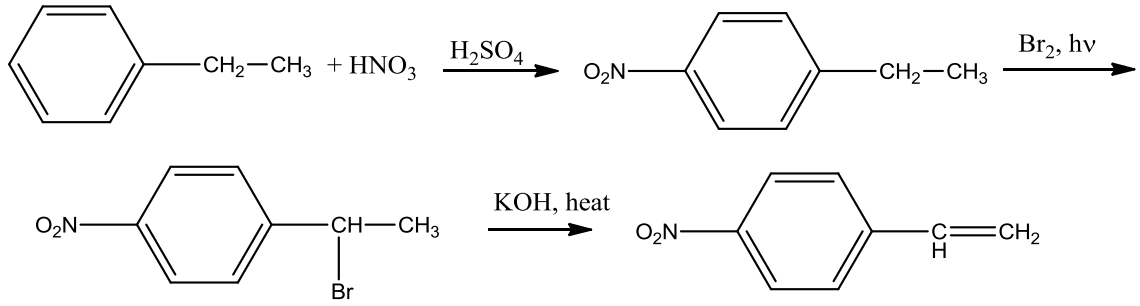
4. b)


+ Cl-CH2CH3
AlCl3
CH2CH3
+ Cl2
AlCl3
Cl
CH2CH3
1) KMnO4, heat
2) H3O+
Cl
O
C
OH

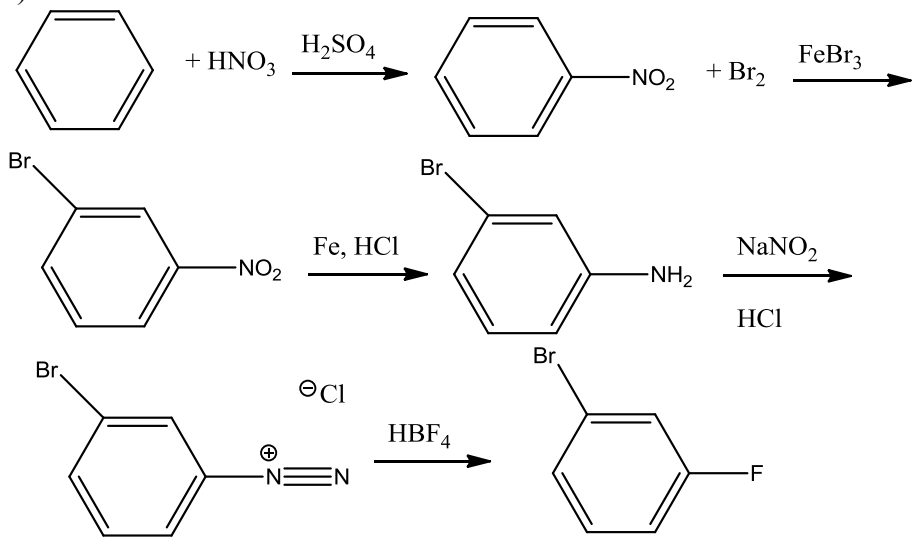
c)


+ Cl
O
CH3
AlCl3
O
C
CH3
+ Cl2
AlCl3
Cl
O
C
CH3
Na2Cr2O7
H2SO4, H2O
Cl
O
C
OH

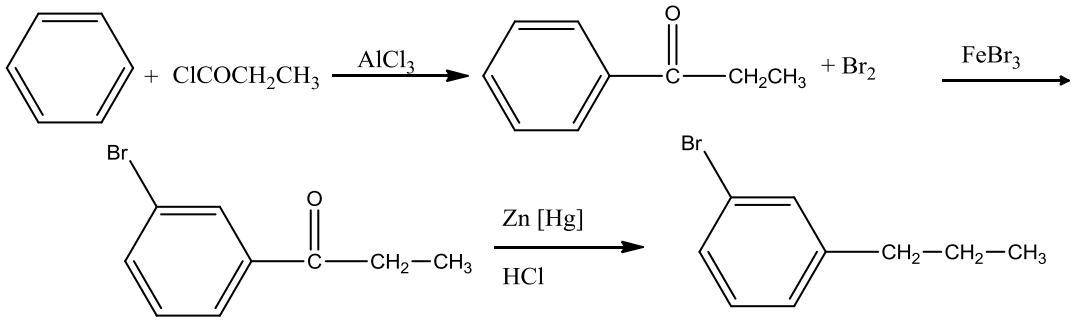
d)


CH2—CH3
+ HNO3
H2SO4
O2N
CH2—CH3
Br2, hν
O2N
CH—CH3
Br
KOH, heat
O2N
C
H
CH2

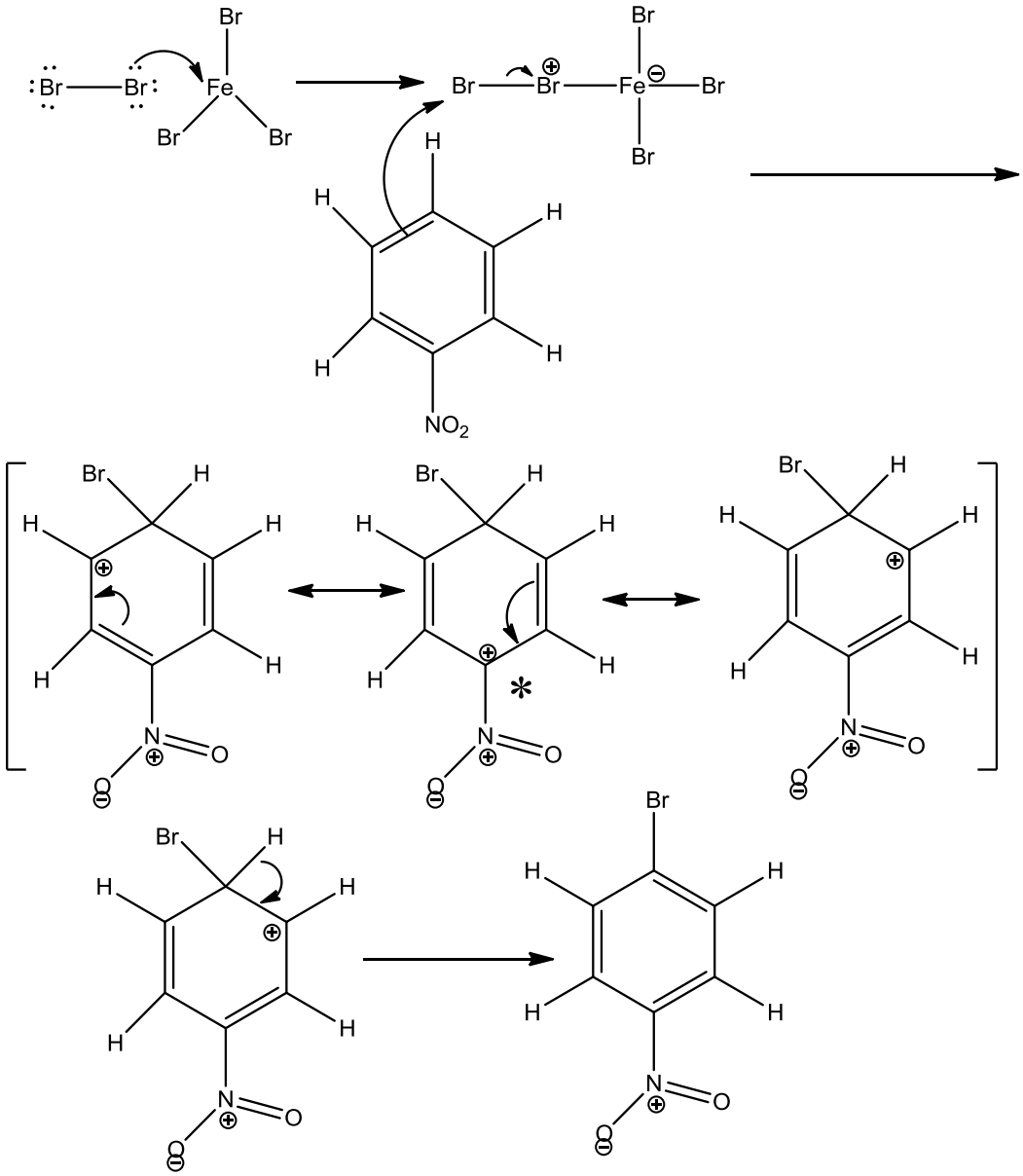
e)


+ HNO3
H2SO4
NO2
+ Br2
FeBr3
Br
NO2
Fe, HCl
Br
NH2
NaNO2
HCl
Br
⊖Cl
⊕
N≡N
HBF4
Br
F

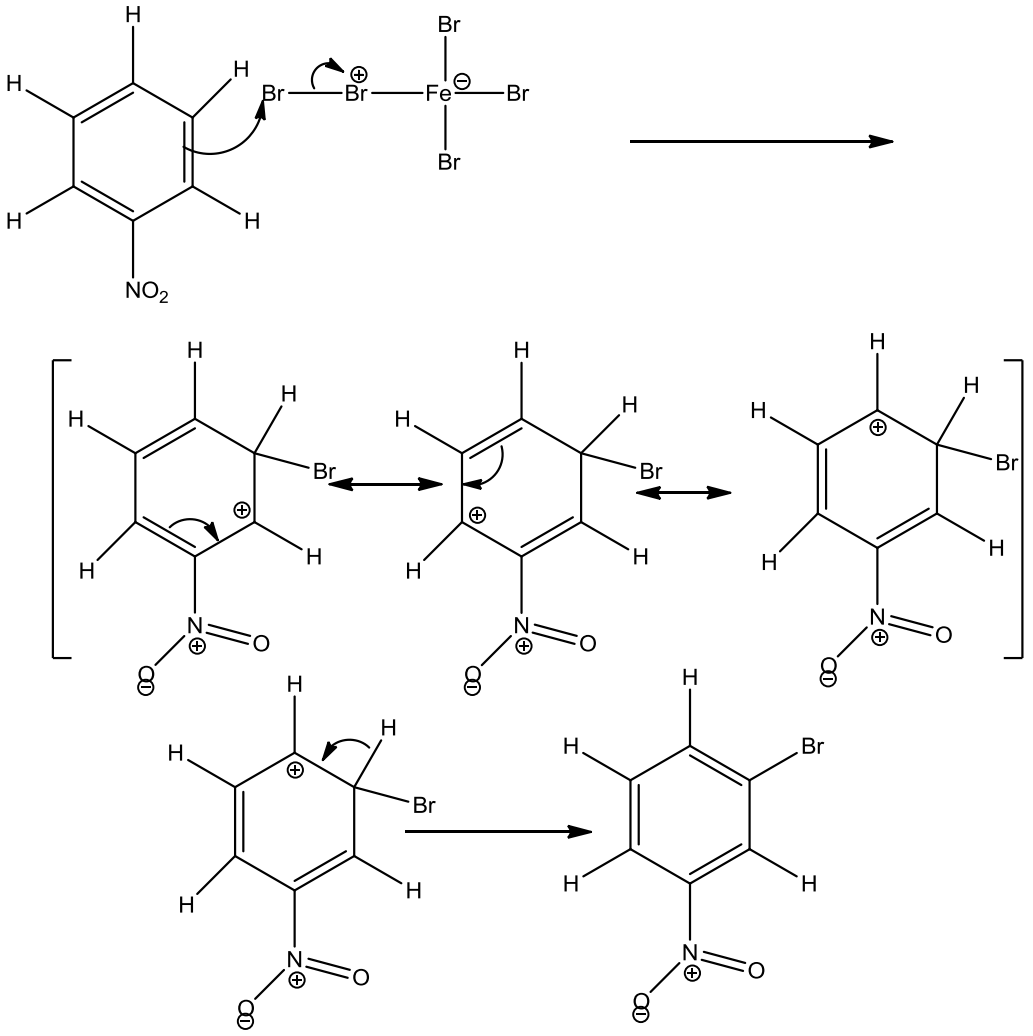
4. f)



5.1 *para*:



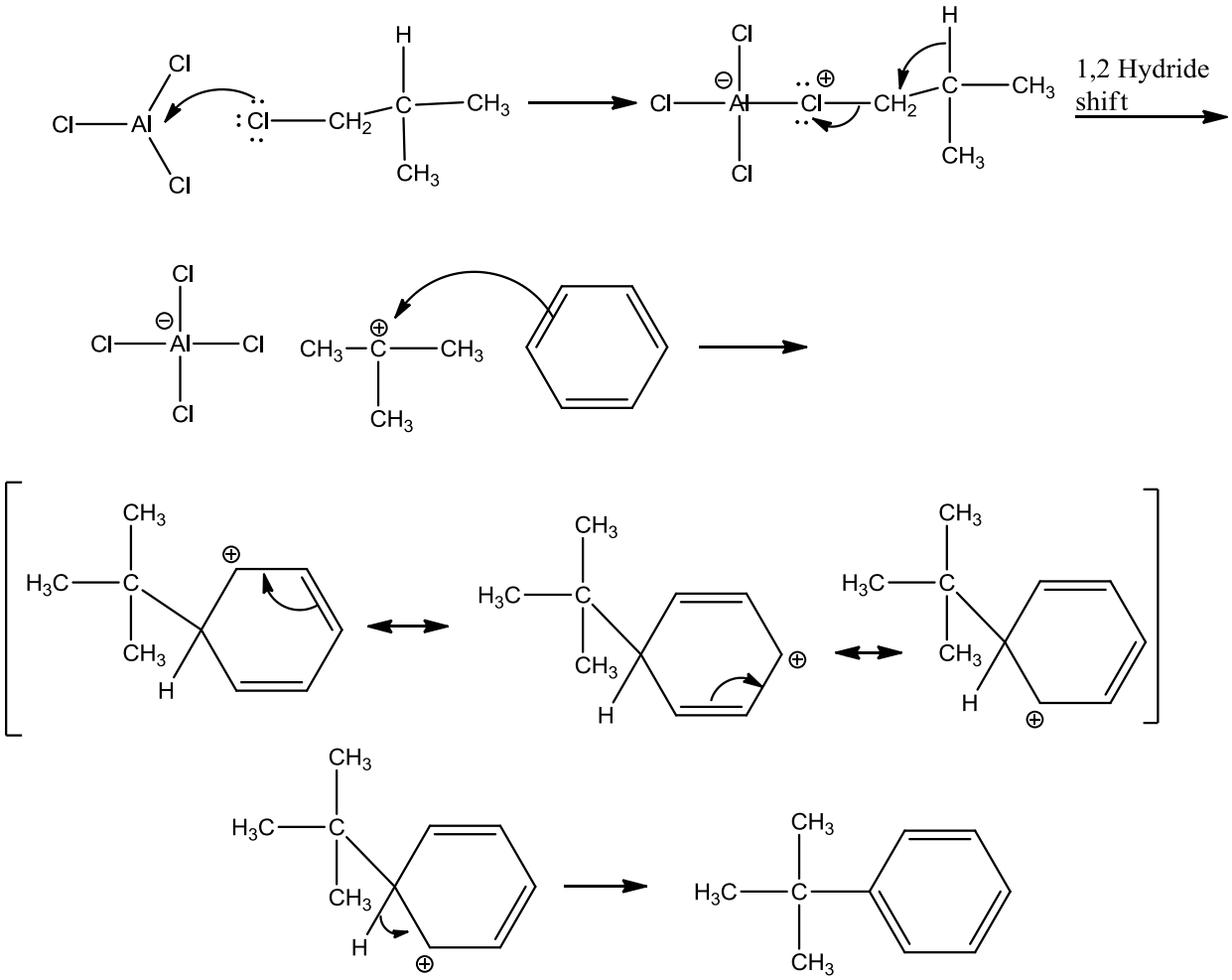
5.1 *meta*:



When a *para* substitution takes place on nitrobenzene, a very high energy intermediate results in which two formal positive charges are adjacent to each other (*) in one of the contributing resonance forms. The *meta* substitution has no particularly high energy intermediate. Based on these results, the *meta* substitution product would be predicted to form preferentially.

5.2 The examination of the two reaction coordinates shows that the activation energy for the *meta* substitution is greater than that for the *para* substitution. In addition, the energy of the intermediate of the *para* sigma complex is lower than that of the *meta* sigma complex. This shows that the substituent must be an activator, and *ortho*/*para* directing. Of the two choices the nitro is a very strong electron withdrawing group and a deactivator. The correct choice is aniline.

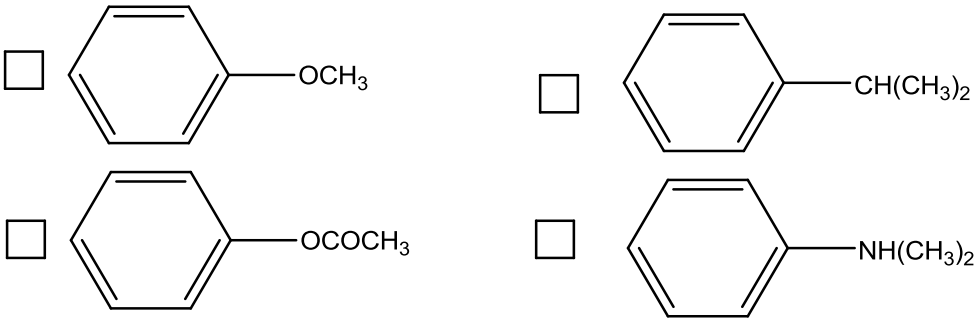
5.3 Propose a complete mechanism for the following.



The primary carbocation complex rearranges to a more stable tertiary carbocation.

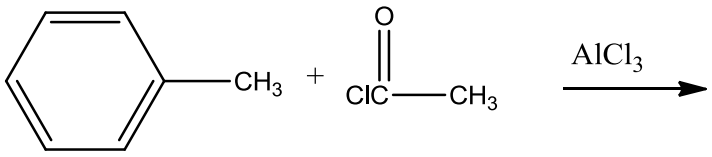
Name _____ Fifth Drill Test (Sample A)
Organic Chemistry 2220DR Answer All Questions

1. Which of the following reacts FASTEST with Cl_2/ $FeCl_3$?

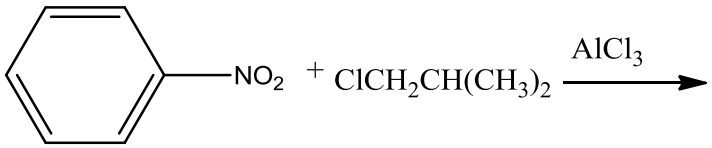


2. Predict the product of each of the following reactions.

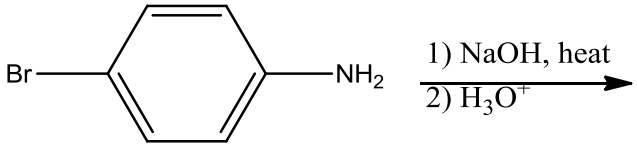
a)



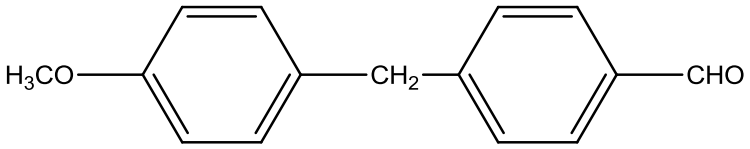
b)



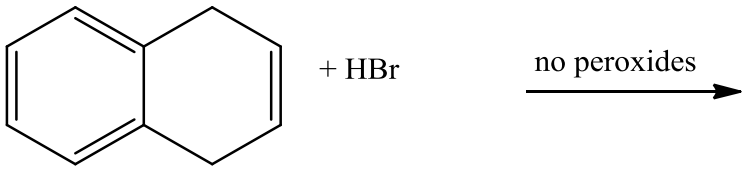
c)



d)

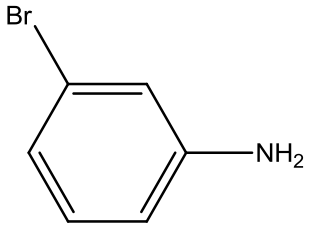


e)

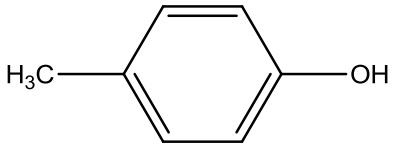


3. Propose a synthesis of each of the following compounds from benzene and any other needed reagents.

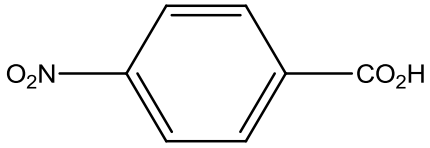
a)



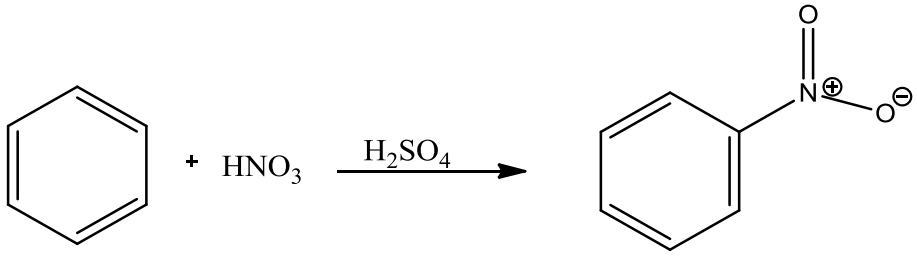
b)



c)

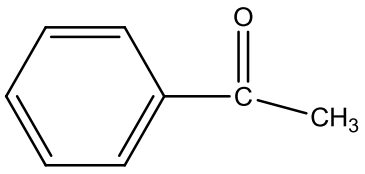


4. Provide a complete mechanism showing proper curved arrows and all intermediates for the reaction shown. Show the formation of the electrophile.

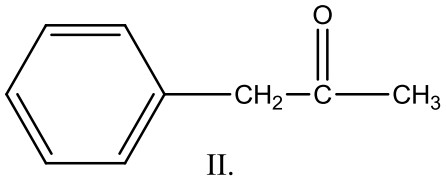


Name _____ Fifth Drill Test (Sample B)
Organic Chemistry 2220DR Answer All Questions

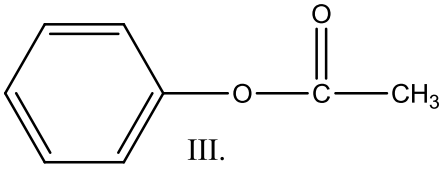
1. Circle the letter which correctly ranks the following compounds from fastest to slowest as they react in an EAS reaction with HNO_3 and H_2SO_4. (if a>b, a is faster than b)



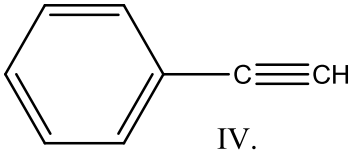
I.



II.



III.

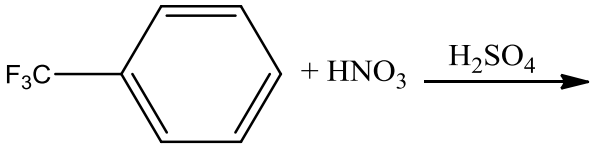


IV.

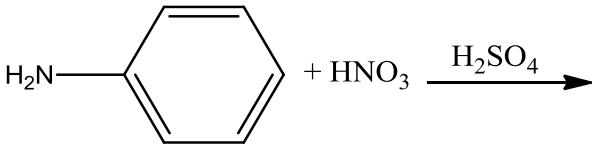
a) I > II >III > IV
b) IV > III > II > I
c) III > IV> II > I
d) III > II > I > IV

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

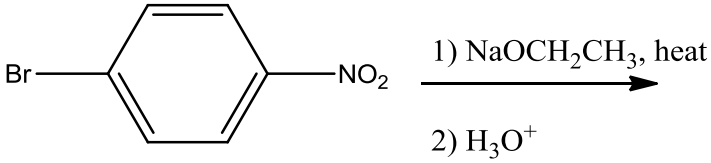
a)



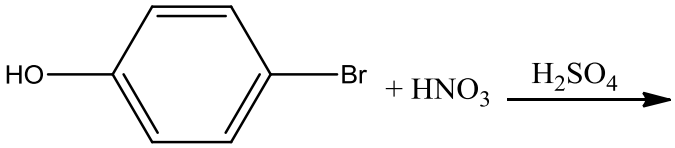
b)



c)

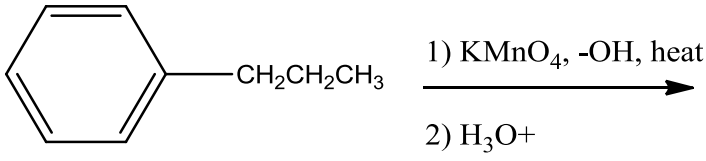


d)



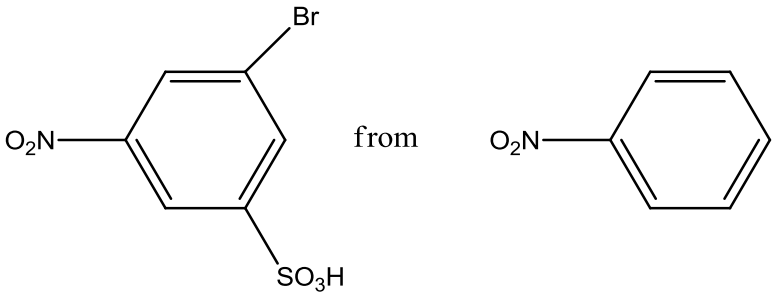
e)

f)

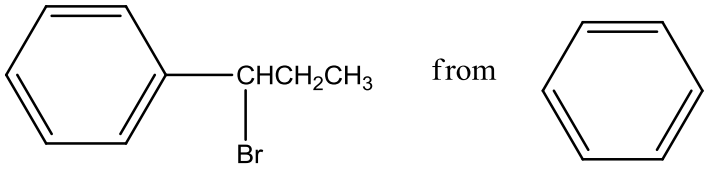


3. Propose a synthesis of each of the following compounds from the indicated starting materials and any other needed reagents.

a)



b)



4. Provide a complete mechanism showing proper curved arrows and all intermediates for the reaction shown.