

## 18.13: ADDITIONAL EXERCISES

**18-1** Draw the resonance structures for benzaldehyde to show the electron-withdrawing group.

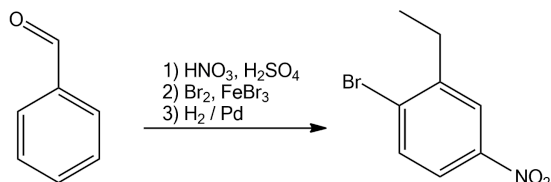
**18-2** Draw the resonance structures for methoxybenzene to show the electron-donating group.

**18-3** How would make the following compounds from benzene?

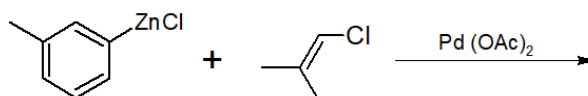
A) *m*-bromonitrobenzene

B) *m*-bromoethylbenzene

**18-4** There is something wrong with the following reaction, what is it?



**18-5** Choose the correct answer.



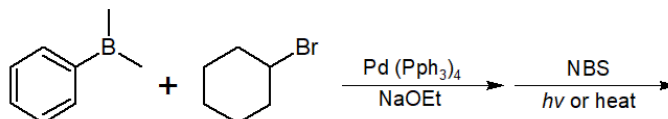
a) 1-methyl-3-(2-methylprop-1-en-1-yl)benzene

b) 2-chloro-4-methyl-1-(2-methylprop-1-en-1-yl)benzene

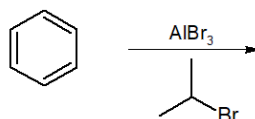
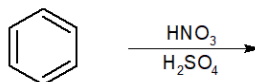
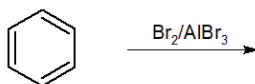
c) 1-chloro-3-(2-methylprop-1-en-1-yl)benzene

d) 1-(1-chloroethenyl)-3-methylbenzene

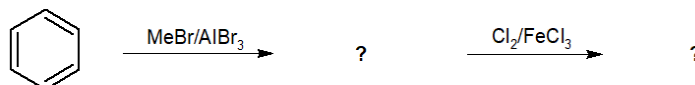
**18-6** Predict the final product of the following reaction chain.



**18-7** Provide the final product for the following reactions.

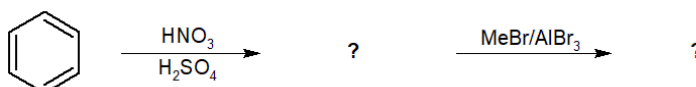


**18-8** For the following reaction chain, provide the intermediate and final product(s).



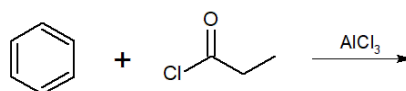
**18-9** Give the IUPAC name for the final product(s) of the previous problem, **18-8**.

**18-10** For the following reaction chain, provide the intermediate and final product(s).

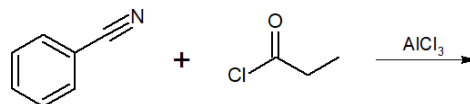


18-11 Give the final product of the following reactions.

a)

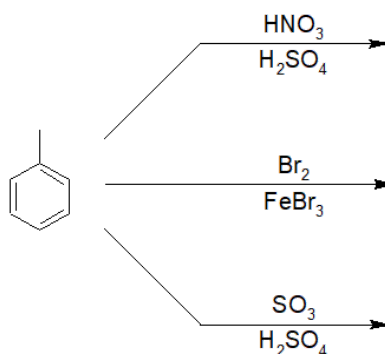


b)

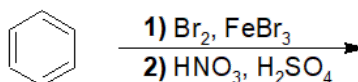


### Halogenation, Nitration, and Sulfonation of Benzene

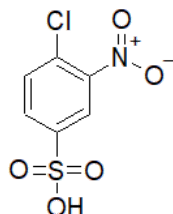
18-12 Predict the products of the following reactions.



18-13 Give the IUPAC nomenclature and structure of the product of the following reaction.



18-14 Choose the correct answer that describes the best route of synthesis of the following molecule.

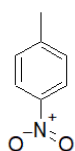


- a) Chlorination, sulfonation, nitration
- b) Sulfonation, nitration, chlorination
- c) Nitration, sulfonation, chlorination

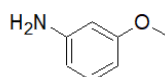
### Activating, Ortho-, Para-Directing Substituents

18-15 For the following compounds, point to the position(s) on the ring that are most likely to have a substituent added.

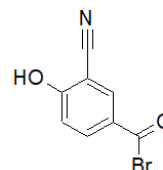
a)



b)

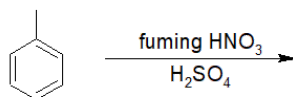


c)

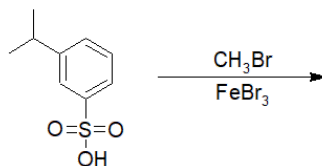


18-16 Predict the major product of the following reactions.

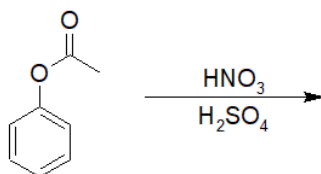
a)



b)



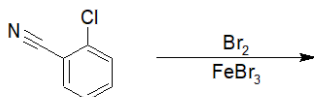
18-17 Provide the correct IUPAC nomenclature and structure of the product of the following reaction.



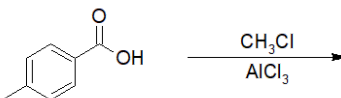
### Deactivating, Meta-Directing Substituents

18-18 Predict the products of the following reactions.

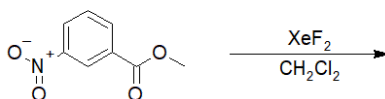
a)



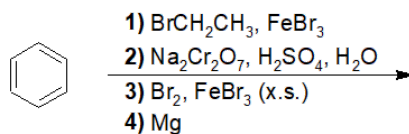
b)



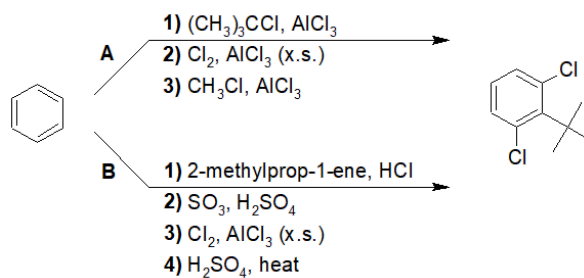
c)



18-19 Predict the product of the following reaction.



18-20 Choose the pathway that will lead to the product formed on the right.



### Halogen Substitutes: Deactivating, but Ortho, Para-Directing

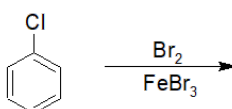
18-21 Choose the correct IUPAC nomenclature of one of the products of the following reaction.



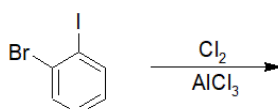
- a) 3-bromobenzene-1-sulfonic acid
- b) 4-bromobenzene-1-sulfonic acid
- c) 5-bromobenzene-1,3-disulfonic acid
- d) 4-bromophenyl hydrogen sulfate

**18-22** Predict the products of the following reactions.

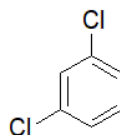
a)



b)



**18-23** Propose a route of synthesis for the following compound, starting with chlorobenzene (assume any desired intermediate compounds can be isolated for use in subsequent steps).

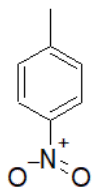


**1,3-dichlorobenzene**

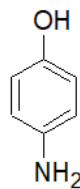
### Effects of Multiple Substituents on Electrophilic Aromatic Substitution

**18-24** For the following compounds, identify which substituent is the stronger activating group and predict the position(s) of a subsequent electrophilic aromatic substitution.

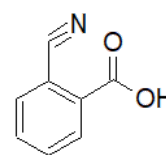
a)



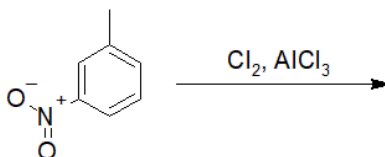
b)



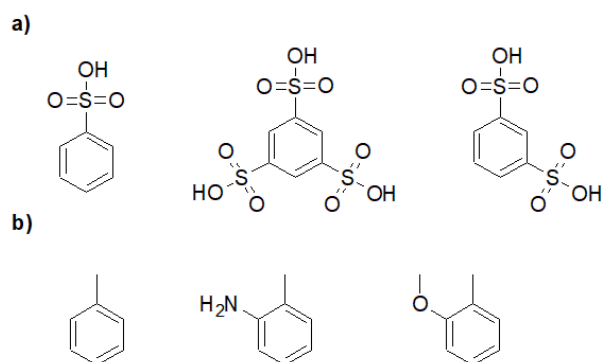
c)



**18-25** Predict all possible singly chlorinated products of the following reaction.

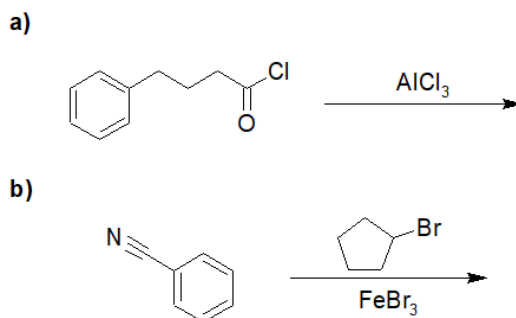


**18-26** Rank the following compounds in order from slowest to fastest to go through an electrophilic aromatic substitution reaction.

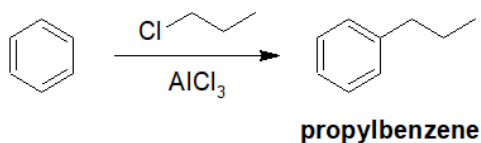


### Friedel-Crafts Alkylation/Acylation

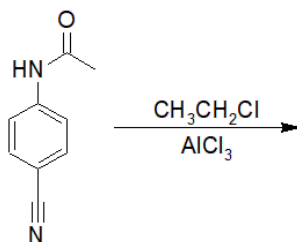
18-27 Predict the products of the following reactions.



18-28 Explain whether or not the following reaction is the best way to synthesize propylbenzene and if not, propose a better route of synthesis.



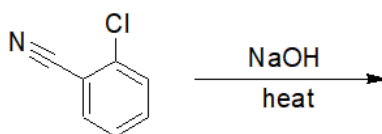
18-29 Choose the correct answer and if a product is formed, provide the structure of the product.



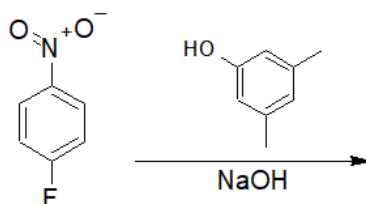
- a) No reaction
- b) 4-amino-2-methylbenzonitrile
- c) 4-amino-2-ethylbenzonitrile
- d) N-(4-cyano-2-ethylphenyl)acetamide

### Nucleophilic Aromatic Substitution

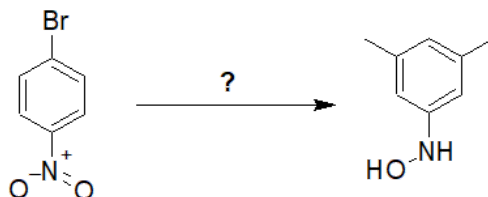
18-30 Predict the product of the following reaction and provide the correct IUPAC nomenclature.



18-31 Predict the product of the following reaction.

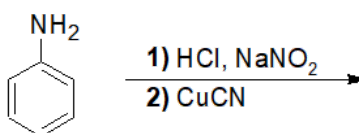


18-32 Suggest a route of synthesis to make *N*-hydroxy-3,5-dimethylaniline from 1-bromo-4-nitrobenzene.

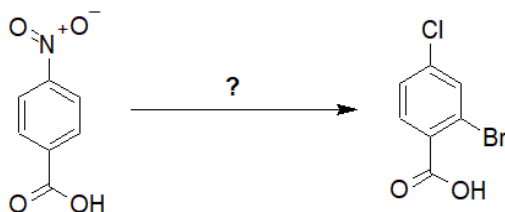


### Aromatic Substitutions Using Organometallic Reagents

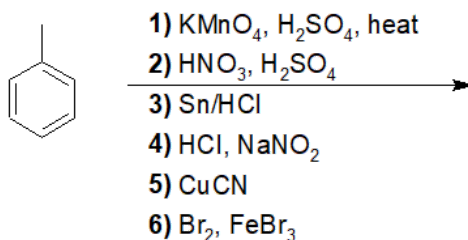
18-33 Provide the structure and IUPAC nomenclature of the product of the following reaction.



18-34 Suggest a route of synthesis to make 2-bromo-4-chlorobenzoic acid from 4-nitrobenzoic acid.



18-35 Choose the correct IUPAC nomenclature for the product of the following reaction.

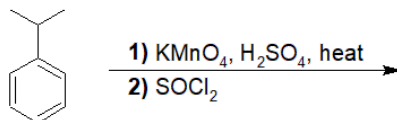


- a) 2-bromo-5-nitrobenzoic acid
- b) 2-bromo-5-cyanobenzoic acid
- c) 3-cyano-5-nitrobenzoyl bromide
- d) 3-bromo-5-cyanobenzoic acid

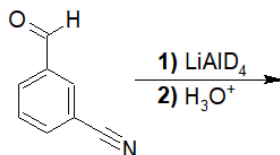
### Side-Chain Reactions of Benzene Derivatives

18-36 Predict the products of the following reactions.

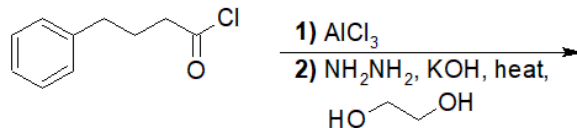
a)



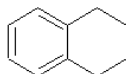
b)



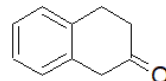
18-37 Choose the correct structure of the product of the following reaction.



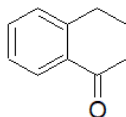
a)



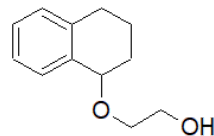
b)



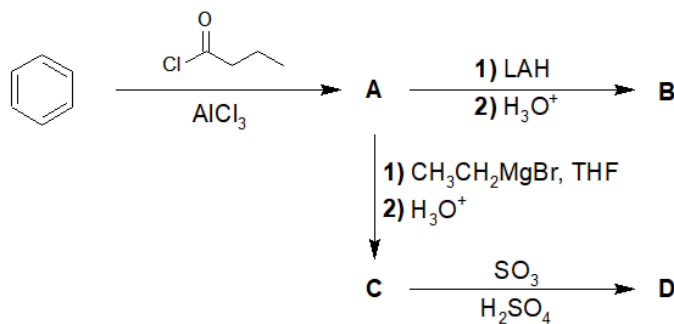
c)



d)



18-38 Provide the intermediate and final products of the following reactions.



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