

Problem 16.1

Monobromination of toluene gives a mixture of three bromotoluene products. Draw and name them.

Problem 16.3

How many products might be formed on chlorination of *o*-xylene (*o*-dimethylbenzene), *m*-xylene, and *p*-xylene?

Problem 16.5

Which of the following alkyl halides would you expect to undergo Friedel-Crafts reaction with rearrangement and which without? Explain.

- (a) $\text{CH}_3\text{CH}_2\text{Cl}$ (b) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
 (d) $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$ (e) Chlorocyclohexane

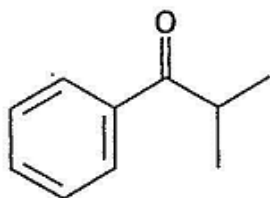
Problem 16.6

What is the major monosubstitution product from the Friedel-Crafts reaction of benzene with 1-chloro-2-methylpropane in the presence of AlCl_3 ?

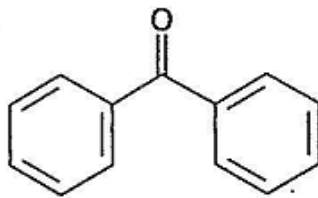
Problem 16.7

Identify the carboxylic acid chloride that might be used in a Friedel-Crafts acylation reaction to prepare each of the following acylbenzenes:

(a)



(b)

**Problem 16.8**

Rank the compounds in each of the following groups in order of their reactivity to electrophilic substitution:

- (a) Nitrobenzene, phenol, toluene, benzene
 (b) Phenol, benzene, chlorobenzene, benzoic acid
 (c) Benzene, bromobenzene, benzaldehyde, aniline

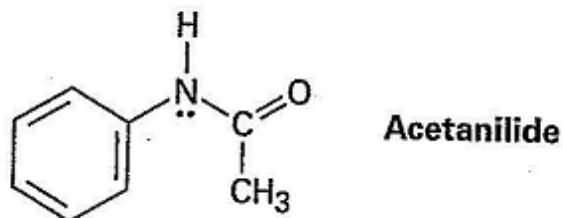
Problem 16.9

Predict the major products of the following reactions:

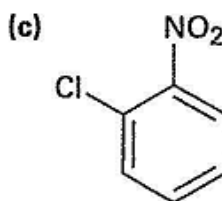
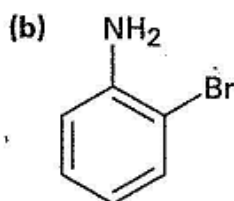
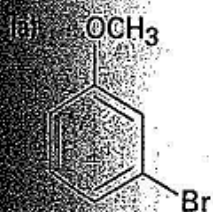
- (a) Nitration of bromobenzene (b) Bromination of nitrobenzene
 (c) Chlorination of phenol (d) Bromination of aniline

Problem 16.12

Acetanilide is less reactive than aniline toward electrophilic substitution. Explain.

**Problem 16.14**

At what position would you expect electrophilic substitution to occur in each of the following substances?

**Problem 16.39**

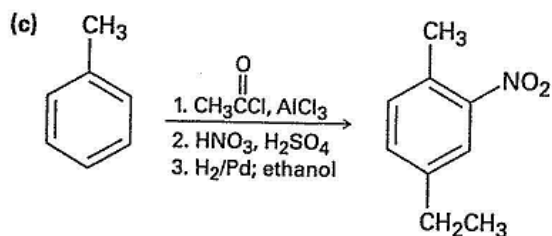
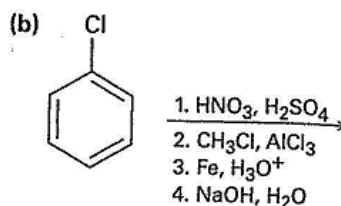
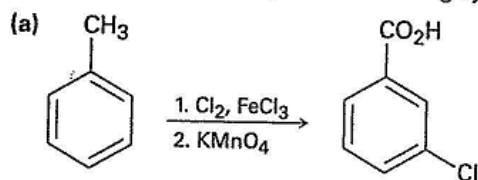
The carbocation electrophile in a Friedel-Crafts reaction can be generated in ways other than by reaction of an alkyl chloride with AlCl_3 . For example, reaction of benzene with 2-methylpropene in the presence of H_3PO_4 yields *tert*-butylbenzene. Propose a mechanism for this reaction.

Problem 16.43

Using resonance structures of the intermediates, explain why bromination of biphenyl occurs at ortho and para positions rather than at meta.

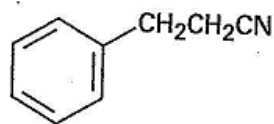
**Problem 16.48**

As written, the following syntheses have flaws. What is wrong with each?

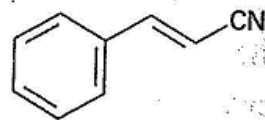


Problem 16.50

▲ Electrophilic substitution on 3-phenylpropanenitrile occurs at the ortho and para positions, but reaction with 3-phenylpropenenitrile occurs at the meta position. Explain, using resonance structures of the intermediates.



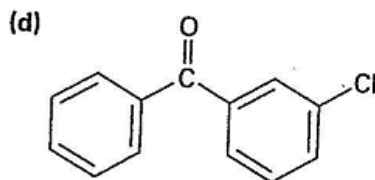
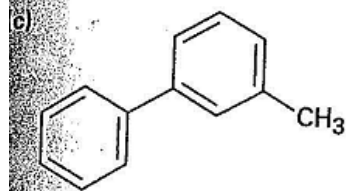
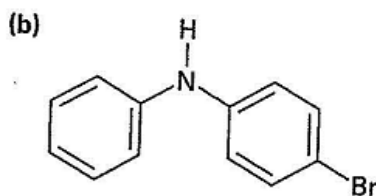
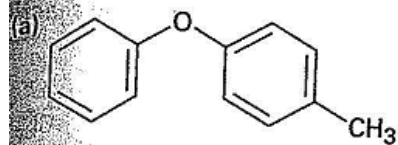
3-Phenylpropanenitrile



3-Phenylpropenenitrile

Problem 16.52

At what position, and on what ring, would you expect the following substances to undergo electrophilic substitution?



Problem 16.65

Propose a mechanism to account for the following reaction:

