16.0 Introduction

16.1 Electrophilic Aromatic Substitution Reactions: Bromination

16.2 Other Aromatic Substitutions

16.2 Exercises

Questions

Q16.2.1
In each case, how many products would be expected for the bromination of p-xylene, o-xylene, and m-xylene?

Q16.2.2
If toluene is treated with D₂SO₄ all the hydrogen’s are replaced with deuterium. Explain. (might need to draw mechanism)

Solutions

S16.2.1

S16.2.2
The deuterium is added to the ring. When the ring “re-aromatizes” the base scavenges the hydrogen before the deuterium and therefore is left on the ring. Continues for the rest of the hydrogen on the ring.

16.3 Alkylation and Acylation of Aromatic Rings: The Friedel-Crafts Reaction

16.3 Exercises

Questions

Q16.3.1
Which of the following will NOT undergo a rearrangement in a Friedel-Crafts reaction?

A) CH₂Cl

B) CH₂Cl

C) CH₂Cl

D) CH₂Cl

E) CH₂Cl

Q16.3.2
Suggest an acyl chloride that was used to make the following compounds:
A, B, and E will not undergo a rearrangement.

16.4 Substituent Effects in Substituted Aromatic Rings

16.4 Exercises

Questions

Q16.4.1

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

Q16.4.2

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

Solutions

S16.4.1
16.5 An Explanation of Substituent Effects

16.5 Exercises

Questions

Q16.5.1

(Trichloromethyl)benzene has a strong concentration of electrons at the methyl substituent. Comparing this toluene, which is more reactive toward electrophilic substitution?

Q16.5.2

The following compound is less reactive towards electrophilic substitution than aniline? Explain.

Q16.5.3

Consider the intermediates of the following molecule during an electrophilic substitution. Draw resonance structures for ortho, meta, and para attacks.

Solutions

S16.5.1

The trichloromethyl group is an electron donor into the benzene ring, therefore making it more stable and therefore more reactive compared to electrophilic substitution.
As seen in resonance the electron density is also localized off of the ring, thereby deactivating it compared to aniline.

**16.6 Trisubstituted Benzenes: Additivity of Effects**

**16.6 Exercises**

**Questions**

Q16.6.1
Predict the products of the following reactions:

Solutions
S16.6.1
16.7 Nucleophilic Aromatic Substitution

16.7 Exercises

Questions

Q16.7.1

Propose a mechanism for the following reaction:

Solutions

S16.7.1
When \( p \)-chlorotoluene is reacted with NaOH, two products are seen. While when \( m \)-chlorotoluene is reacted with NaOH, three products are seen. Explain this.

You need to look at the benzyne intermediates. The para substituted only allows for two products, while the para produces two different alkynes which give three different products.
16.9 Oxidation of Aromatic Compounds

16.9 Exercises

Questions

Q16.9.1

Predict the products.

Q16.9.2

Consider a benzyl radical. Would it be more stable than an alkyl radical? Explain.
Q16.9.3

How would you make the following molecule?

Solutions

S16.9.1

The second one leads to no reaction because it requires a hydrogen just off the phenyl ring.

S16.9.2

Yes it would be more stable than an alkyl radical, consider the pi system able to stabilize through resonance.

S16.9.3

The following is just one possibility.

16.10 Reduction of Aromatic Compounds
16.10 Exercises

Questions

Q16.10.1

How would you make the following from benzene and an acid chloride?

![Chemical structure]

Solutions

S16.10.1

16.11 Synthesis of Polysubstituted Benzenes

16.11 Exercises

Questions

Q16.11.1

How would you make the following compounds from benzene?

A) $m$-bromonitrobenzene

B) $m$-bromoethylbenzene

Q16.11.2
There is something wrong with the following reaction, what is it?

\[
\text{O} \quad 1) \text{HNO}_3, \text{H}_2\text{SO}_4 \\
\text{\textbf{A}16.11.1}} \\
\text{2) Br}_2, \text{FeBr}_3 \\
\text{3) H}_2 / \text{Pd} \\
\text{Br} - \text{NO}_2
\]

**Solutions**

**S16.11.1**

This is just one possible way to synthesize it.

(A) \[
\begin{align*}
\text{HNO}_3, \text{H}_2\text{SO}_4 & \quad \rightarrow \quad \text{NO}_2 \\
\text{Br}_2, \text{FeBr}_3 & \quad \rightarrow \quad \text{Br}
\end{align*}
\]

**S16.11.2**

The bromine should be in the meta position. Right now it is in the ortho position, from perhaps having the ethyl group present first and then the having it substituted there. BUT the ethyl group is last to form, and the aldehyde and nitro groups would both encourage a meta substitution.