Objectives

After completing this section, you should be able to

1. draw the resonance contributors for the carbocation intermediate formed during the reaction of a given monosubstituted benzene derivative with any of the electrophiles discussed in this chapter.
2. classify each of the substituents listed in Objective 2 of Section 16.4 as being either meta or ortho/para directing.
3. classify each of the substituents listed in Objective 2 of Section 16.4 as being ortho/para directing activators, ortho/para directing deactivators, or meta directing deactivators.
4. predict the product or products formed from the reaction of a given monosubstituted benzene derivative with each of the electrophiles discussed in this chapter.
5. explain, by drawing the resonance contributors for the intermediate carbocation, why the electrophilic substitution of an alkyl benzene results in a mixture of mainly ortho- and para-substituted products.
6. explain why the electrophilic substitution of phenols, amines and their derivatives proceeds more rapidly than the electrophilic substitution of benzene itself.
7. explain, by drawing the resonance contributors for the intermediate carbocation, why meta substitution predominates in electrophilic aromatic substitution reactions carried out on benzene derivatives containing one of the substituents R₃N⁺, NO₂, CO₂H, CN, CO₂R, COR or CHO.
8. explain why electrophilic aromatic substitution of benzene derivatives containing one of the substituents listed in Objective 7, above, proceeds more slowly than the electrophilic substitution of benzene itself.
9. explain, by drawing the resonance contributors for the intermediate carbocation, why the electrophilic aromatic substitution of halobenzenes produces a mixture of mainly ortho- and para-substituted products.
10. explain why the electrophilic aromatic substitution of halobenzenes proceeds more slowly than does the electrophilic substitution of benzene itself.
11. use the principles developed in this chapter to predict in which of the three categories listed in Objective 3, above, a previously unencountered substituent should be placed.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- steric effect
- steric hindrance

Study Notes

As you saw in Section 16.4, a substituent on a benzene ring can be an activator or a deactivator. At the same time, a substituent can also be a meta director or an ortho/para director. Of the four possible combinations, only three are known—there are no meta directing activators.

If you look at the data for the nitration of toluene, you will see that the yield of o-nitrotoluene is 63% and that of p-nitrotoluene is 34%. Statistically, we should expect to obtain twice as much ortho product as para product, because the former is produced by attack at either of two carbon atoms whereas the latter is produced by attack at only one carbon atom (see Figure 16.1, below).
ortho and para sites identified on a toluene ring

**Figure 16.1:** Proportions of o-nitrotoluene and p-nitrotoluene produced by the nitration of toluene

In this instance, the observed ortho/para ratio is almost 2:1, as we might expect. However, if we study the ortho/para ratio found in the nitration of a number of other arenes, we see that this is not always the case. Note that the data for the nitration of toluene given in the table below differ from those presented elsewhere. The variation may result from a difference in temperature, reaction conditions or reagent, and emphasizes the point that it is the trends which are important, not the numbers themselves.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>% ortho</th>
<th>% para</th>
<th>ortho/para ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>58</td>
<td>37</td>
<td>1.57:1</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>45</td>
<td>49</td>
<td>0.92:1</td>
</tr>
<tr>
<td>isopropylbenzene</td>
<td>30</td>
<td>62</td>
<td>0.48:1</td>
</tr>
<tr>
<td>tert-butylbenzene</td>
<td>16</td>
<td>73</td>
<td>0.22:1</td>
</tr>
</tbody>
</table>

*[Source: These data were taken from the audiocassette *Some Organic Reaction Pathways*, by Peter Sykes. London: Educational Techniques Subject Group, The Chemical Society, 1975.]*

**Table 16.1:** Nitration of arenes

The table above shows us that as the size of the alkyl substituent already present in the ring increases, attack at the ortho position becomes more difficult, and the percentage of ortho isomers in the mixture of products decreases. This is an example of a *steric effect*—an effect caused by the size of the substituent—and we would say that as the size of the alkyl group increases, attack at the ortho position becomes less favourable as a result of *steric hindrance*. Note that the size of the electrophile can also be a factor in determining the ortho/para ratio: the larger the electrophile, the less able it is to attack at the ortho position, particularly if the substituent already present in the ring is itself quite bulky.

When drawing the resonance contributors to the carbocation formed during an electrophilic aromatic substitution, bear in mind that those of the type

\[
\text{carbocation resonance form with positive charge on oxygen of ring hydroxide}
\]

are particularly important, because in such structures each atom possesses a complete octet of electrons.

Note that, as do the hydroxyl and amino groups, the halogens have an inductive electron-withdrawing effect and a resonance electron-releasing effect on a benzene ring. The difference in behaviour during electrophilic substitutions arises because, with the hydroxyl and amino groups, the resonance effect completely swamps the inductive effect, whereas with the halogens, there is a much finer balance. In the case of the latter, the inductive effect reduces the overall reactivity, but the resonance effect means that this reduction is felt less at the ortho and para positions than at the meta position.
Substituted rings are divided into two groups based on the type of the substituent that the ring carries:

- **Activated rings**: the substituents on the ring are groups that donate electrons.
- **Deactivated rings**: the substituents on the ring are groups that withdraw electrons.

### Introduction

Examples of activating groups in the relative order from the most activating group to the least activating:

-\( \text{-NH}_2\), \(\text{-NR}_2\) > \(\text{-OH, -OR> -NHCOR> -CH}_3\) and other alkyl groups

with \(R\) as alkyl groups (\(\text{C}_n\text{H}_{2n+1}\))

Examples of deactivating groups in the relative order from the most deactivating to the least deactivating:

-\(\text{-NO}_2\), \(\text{-CF}_3\) > \(\text{-COR, -CN, -CO}_2\text{R, -SO}_3\text{H > Halogens}\)

with \(R\) as alkyl groups (\(\text{C}_n\text{H}_{2n+1}\))

The order of reactivity among Halogens from the more reactive (least deactivating substituent) to the least reactive (most deactivating substituent) halogen is:

\[\text{F} > \text{Cl} > \text{Br} > \text{I}\]

The order of reactivity of the benzene rings toward the electrophilic substitution when it is substituted with a halogen groups, follows the order of electronegativity. The ring that is substituted with the most electronegative halogen is the most reactive ring (less deactivating substituent) and the ring that is substituted with the least electronegative halogen is the least reactive ring (more deactivating substituent), when we compare rings with halogen substituents. Also the size of the halogen effects the reactivity of the benzene ring that the halogen is attached to. As the size of the halogen increase, the reactivity of the ring decreases.

### The direction of the reaction

The activating group directs the reaction to the ortho or para position, which means the electrophile substitute the hydrogen that is on carbon 2 or carbon 4. The deactivating group directs the reaction to the meta position, which means the electrophile substitute the hydrogen that is on carbon 3 with the exception of the halogens that is a deactivating group but directs the ortho or para substitution.
Substituents determine the reaction direction by resonance or inductive effect

Resonance effect is the conjugation between the ring and the substituent, which means the delocalizing of the \(\pi\) electrons between the ring and the substituent. Inductive effect is the withdraw of the sigma (the single bond) electrons away from the ring toward the substituent, due to the higher electronegativity of the substituent compared to the carbon of the ring.

Activating groups (ortho or para directors)

When the substituents like -OH have an unshared pair of electrons, the resonance effect is stronger than the inductive effect which make these substituents stronger activators, since this resonance effect direct the electron toward the ring. In cases where the subtituents is esters or amides, they are less activating because they form resonance structure that pull the electron density away from the ring.

By looking at the mechanism above, we can see how groups donating electron direct the ortho, para electrophilic substitution. Since the electrons locatinn transfer between the ortho and para carbons, then the electrophile prefer attacking the carbon that has the free electron.

Inductive effect of alkyl groups activates the direction of the ortho or para substitution, which is when s electrons gets pushed toward the ring.
Deactivating group (meta directors)

The deactivating groups deactivate the ring by the inductive effect in the presence of an electronegative atom that withdraws the electrons away from the ring.

![Diagram of deactivating group mechanism]

we can see from the mechanism above that when there is an electron withdraw from the ring, that leaves the carbons at the ortho, para positions with a positive charge which is unfavorable for the electrophile, so the electrophile attacks the carbon at the meta positions.

Halogens are an exception of the deactivating group that directs the ortho or para substitution. The halogens deactivate the ring by inductive effect not by the resonance even though they have an unpaired pair of electrons. The unpaired pair of electrons gets donated to the ring, but the inductive effect pulls away the electrons from the ring by the electronegativity of the halogens.

Substituents determine the reactivity of rings

The reaction of a substituted ring with an activating group is faster than benzene. On the other hand, a substituted ring with a deactivated group is slower than benzene.

Activating groups speed up the reaction because of the resonance effect. The presence of the unpaired electrons that can be donated to the ring, stabilize the carbocation in the transition state. Thus; stabilizing the intermediate step, speeds up the reaction; and this is due to the decrease of the activating energy. On the other hand, the deactivating groups, withdraw the electrons away from the carbocation formed in the intermediate step, thus; the activation energy is increased which slows down the reaction.

The CH₃Group is and ortho, para Director

![Chemical reaction diagram]

Alkyl groups are Inductive activators
With o/p attack the form a tertiary arenium carbocation which speeds up the reaction

Ortho Attack

Meta Attack

Para Attack

The O-CH₃ Group is an ortho, para Director

Ortho and Para product produces a resonance structure which stabilizes the arenium ion. This causes the ortho and para products for form faster than meta. Generally, the para product is preferred because of steric effects.
Acyl groups are meta Directors

Acyl groups are resonance deactivators. Ortho and para attack produces a resonance structure which places the arenium cation next to and additional cation. This destabilizes the arenium cation and slows down ortho and para reaction. By default the meta product forms faster because it lacks this destabilizing resonance structure.
References


Outside Links

- [http://en.wikipedia.org/wiki/Activating_group](http://en.wikipedia.org/wiki/Activating_group)

Problems

1. Predict the direction of the electrophile substitution on these rings:

   ![Diagram of benzene ring with bromine substituent](image)
2. Which nitration product is going to form faster?

- nitration of aniline or nitration of nitrobenzene?

3. Predict the product of the following two sulfonation reactions:

A.

\[
\begin{array}{c}
\text{SO}_3 \\
\text{H}_2\text{SO}_4
\end{array}
\]

4. Classify these two groups as activating or deactivating groups:

A. alcohol

B. ester

5. By which effect does trichloride effect a monosubstituted ring?

**Answers**

1. The first substitution is going to be ortho and/or para substitution since we have a halogen substituent. The second substitution is going to be ortho and/or para substitution also since we have an alkyl substituent.

2. The nitration of aniline is going to be faster than the nitration of nitrobenzene, since the aniline is a ring with NH\textsubscript{2} substituent and nitrobenzene is a ring with NO\textsubscript{2} substituent. As described above NH\textsubscript{2} is an activating group which speeds up the reaction and NO\textsubscript{2} is deactivating group that slows down the reaction.

3. A. the product is

\[
\begin{array}{c}
\text{SO}_3\text{H} \\
\text{OH}
\end{array}
\]

B. the product is
4. A. alcohol is an activating group.
   B. ester is a deactivating group.

5. Trichloride deactivate a monosubstitued ring by inductive effect.

**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.

![Resonance structures](image)

**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.

**S16.5.2**
As seen in resonance the electron density is also localized off of the ring, thereby deactivating it compared to aniline.

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