A substituent on a benzene ring can effect the placement of additional substituents on that ring during \textbf{Electrophilic Aromatic Substitution}. How do we know where an additional substituent will most likely be placed? The answer to this is through inductive and resonance effects. Inductive effects are directly correlated with electronegativity. Substituents can either be meta directing or ortho-para directing.

\textbf{Introduction}

The three general positions of a disubstituted benzene ring are \textbf{ortho}, \textbf{meta} and \textbf{para}.

\textbf{Figure 1: The Effect of an Electron Donating Groups on a Benzene Ring}

The first scenario for adding an electrophile to a monosubstituted benzene ring is when the substituent is an \textbf{electron donating group}. Electron donating groups are alkyl groups, phenyl groups or substituents that have a lone pair of electrons on the atom directly bonded to the ring. Electron donating groups are donating by induction (Activating and Deactivating Benzene Rings) and resonance. Examples of electron donating groups: -CH$_3$, -OCH$_3$, -OH, -NH$_2$

Electron donating groups cause the second substituent to add on to the \textbf{para} or \textbf{ortho} position on the benzene ring. The reason for this can be explained by the different carbocation resonance structures of the ortho, meta and para positions.

Some electron donating groups have an extra resonance form in which there is a double bond between the atom and the carbon on the benzene. This is a very stable resonance form. This is due to directing effects of substituents in conjugation
with the benzene ring.

When the electrophile is added to the ortho position, three different resonance forms are possible. Carbocation forms 1 and 2 are secondary carbocations, but position 3 forms a tertiary carbocation and the positive charge is on the carbon directly attached to the electron donating group, which is the most stable. This carbocation is also stabilized by the electrons from the electron donating group. *More stable intermediates (the carbocation) have lower transition state energies and therefore a faster reaction rate, forming more of this product.* This is the reason that the ortho position is one of the major products.

If the electrophile is added to the monosubstituted benzene ring in the para position one of the three resonance forms of the carbocations will be a tertiary carbocation which is highly stable because of the +I effect if the three -CH₃. This carbocation intermediate is the same as the one formed from ortho substitution.

For the meta substituted carbocation resonance structures, there are three possible resonance forms that are secondary carbocations. These forms are not as stable as the tertiary carbocation form in the ortho and para substituted carbocations.

Therefore, the two major products of the reaction of a monosubstituted benzene ring with an electron donating group and additional electrophile are the **ortho** and **para** positions. *It's important to note that the para product is slightly more common than the ortho product due to steric hindrance.*

H-NMR spectroscopy can be used to determine whether or not a compound has a second substituent at the ortho or para position. At the ortho position there are four distinct signals, but for the para position there are only two signals because the molecule is symmetrical. Electron donating groups on a benzene ring are said to be **activating**, because they increase the rate of the second substitution so that it is *higher* than that of standard benzene.
The Effect of an Electron Withdrawing Group on a Benzene Ring

The other circumstance is when you have add an additional electrophile to a monosubstituted benzene ring with an electron withdrawing group on it. Electron withdrawing groups have an atom with a slight positive or full positive charge directly attached to a benzene ring. Examples of electron withdrawing groups: -CF_3, -COOH, -CN. Electron withdrawing groups only have one major product, the second substituent adds in the meta position. Again, this can be explained by the resonance forms of the carbocation intermediates.

When the second electrophile is added on to the benzene ring in the ortho position, the same three resonance forms of the carbocation are produced. Again, one form is a tertiary carbocation with the positive charge on the carbon directly attached to the electron withdrawing group. Unlike in the case with an electron donating group, this resonance form is much less stable. This is due to the electron withdrawing group pulling away electrons from the carbon, creating an even stronger positive charge. This situation holds true for the para substituted tertiary carbocation resonance form as well.

For the meta position, all the carbocations formed are secondary. Although these are not entirely stable, they are more favored than the resonance forms of the ortho and para positions.

The major product of a monosubstituted benzene ring with an electron withdrawing group and an additional electrophile is a product with meta substitution. In contrast to electron donating groups, electron withdrawing groups are deactivating. This means that the rate of the second substitution is lower than that of standard benzene.
Table 1: Common Substituents

<table>
<thead>
<tr>
<th>Strong Activating</th>
<th>Moderately Activating</th>
<th>Weakly Activating</th>
<th>Weakly Deactivating</th>
<th>Moderately Deactivating</th>
<th>Strongly Deactivating</th>
</tr>
</thead>
<tbody>
<tr>
<td>-NH₂, -NHR, -OH</td>
<td>-NHCOR</td>
<td>-CH₃, -phenyl</td>
<td>-Cl, -Br, -I</td>
<td>-COH, -COCH₃</td>
<td>-NO₂, -CF₃, -CCl₃</td>
</tr>
<tr>
<td>-OCH₃</td>
<td>-OCOR</td>
<td></td>
<td></td>
<td></td>
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</tbody>
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Halogen: A Special Case

Halogen are very electronegative. This means that inductively they are electron withdrawing. However, because of their ability to donate a lone pair of electrons in resonance forms, they are activators and ortho/para directing. Resonance forms win out in directing. Because they are electron withdrawing, halogens are very weak activators.

Electron withdrawing groups are meta directors and they are deactivators.

References


Problems

1. 

2. 

3. 

a) 

b) Is the rate of secondary substitution going to be higher or lower than that of standard benzene? (Explain)

4. 

5. 


SO₃, H₂SO₄
Contributors

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