This page looks at the facts about the nitration of benzene and methylbenzene. The mechanisms for these reactions are covered elsewhere on the site, and you will find links to these.

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The nitration of benzene

Nitration happens when one (or more) of the hydrogen atoms on the benzene ring is replaced by a nitro group, NO₂. Benzene is treated with a mixture of concentrated nitric acid and concentrated sulfuric acid at a temperature not exceeding 50°C. The mixture is held at this temperature for about half an hour. Yellow oily nitrobenzene is formed.

\[
\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}
\]

You could write this in a more condensed form as:

\[
\text{[C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}\]
\]

The concentrated sulfuric acid is acting as a catalyst and so is not written into the equations. At higher temperatures there is a greater chance of getting more than one nitro group substituted onto the ring. You will get a certain amount of 1,3-dinitrobenzene formed even at 50°C. Some of the nitrobenzene formed reacts with the nitrating mixture of concentrated acids.

Notice that the new nitro group goes into the 3 position on the ring. Nitro groups "direct" new groups into the 3 and 5 positions. It is also possible to get a third nitro group attached to the ring (in the 5 position). However, nitro groups make the ring much less reactive than the original benzene ring. Two nitro groups on the ring make its reactions so slow that virtually no trinitrobenzene is produced under these conditions.

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The nitration of methylbenzene (toluene)

Methylbenzene reacts rather faster than benzene - in nitration, the reaction is about 25 times faster. That means that you would use a lower temperature to prevent more than one nitro group being substituted - in this case, 30°C rather than 50°C. Apart from that, the reaction is just the same - using the same nitrating mixture of concentrated sulphuric and nitric acids.

You get a mixture of mainly two isomers formed: 2-nitromethylbenzene and 4-nitromethylbenzene. Only about 5% of the product is 3-nitromethylbenzene. Methyl groups are said to be 2,4-directing.

For 2-nitromethylbenzene:
and 4-nitromethylbenzene:

\[
\begin{align*}
\text{CH}_3 & \quad + \quad \text{HNO}_3 \quad \longrightarrow \quad \text{CH}_3
\text{NO}_2 & \quad + \quad \text{H}_2\text{O} \\
\text{CH}_3 & \quad + \quad \text{HNO}_3 \quad \longrightarrow \quad \text{CH}_3
\text{NO}_2 & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

Just as with benzene, you will get a certain amount of dinitro compound formed under the conditions of the reaction, but virtually no trinitro product because the reactivity of the ring decreases for every nitro group added (by the way, trinitromethylbenzene used to be called trinitrotoluene or TNT).

The reactivity of a benzene ring is governed by the electron density around the ring. Methyl groups tend to "push" electrons towards the ring - increasing the density, and so making the ring more attractive to attacking reagents. This is actually a simplification. In order to understand the rate effect properly you have to think about the stability of the intermediate ions formed during the reactions, because this affects the activation energy of the reactions.

Contributors

Jim Clark (Chemguide.co.uk)