Benzene was first suspected to exist way back in 1825 when British scientist Michael Faraday first isolated it from an oily mixture used in gaslights. This, and other compounds similar to it, formed a group called aromatic compounds. They were named aromatic due to their pleasing aroma, although not all smelled as such. The unusual stability of benzene makes it ideal for many reactions. Among these reactions is one known as the Friedel-Crafts Alkylation. However, the reaction suffers from a group of limitations making it a poor candidate to achieve desired results. Friedel-Crafts Alkylation was first discovered by French scientist Charles Friedel and his partner, American scientist James Crafts, in 1877. This reaction allowed for the formation of alkyl benzenes from alkyl halides, but was plagued with unwanted supplemental activity that reduced its effectively.

Limitations of Friedel-Crafts Alkylation

- **Carbocation Rearrangement** - Only certain alkylbenzenes can be made due to the tendency of cations to rearrange.
- **Compound Limitations** - Friedel-Crafts fails when used with compounds such as nitrobenzene and other strong deactivating systems.
- **Polyalkylation** - Products of Friedel-Crafts are even more reactive than starting material. Alkyl groups produced in Friedel-Crafts Alkylation are electron-donating substituents meaning that the products are more susceptible to electrophilic attack than what we began with. For synthetic purposes, this is a big disappointment.

To remedy these limitations, a new and improved reaction was devised: The Friedel-Crafts Acylation, also known as Friedel-Crafts Alkanoylation.

The goal of the reaction is the following:

\[
\text{Acyl chloride} + \text{benzene} \rightarrow \text{acyl benzoate} + \text{HCl}
\]

The very first step involves the formation of the acylium ion which will later react with benzene:

The second step involves the attack of the acylium ion on benzene as a new electrophile to form one complex:

The third step involves the departure of the proton in order for aromaticity to return to benzene:
During the third step, AlCl₄ returns to remove a proton from the benzene ring, which enables the ring to return to aromaticity. In doing so, the original AlCl₃ is regenerated for use again, along with HCl. Most importantly, we have the first part of the final product of the reaction, which is a ketone. The first part of the product is the complex with aluminum chloride as shown:

The final step involves the addition of water to liberate the final product as the acylbenzene:

Because the acylium ion (as was shown in step one) is stabilized by resonance, no rearrangement occurs (Limitation 1). Also, because of the deactivation of the product, it is no longer susceptible to electrophilic attack and hence, no longer goes into further reactions (Limitation 3). However, as not all is perfect, Limitation 2 still prevails where Friedel-Crafts Acylation fails with strong deactivating rings.

References


Problems

Problem 1:
Problem 2:

Problem 3:

Problem 4:

Problem 5:
Solutions

Solution to Problem 2:

Solution to Problem 3:

Solution to Problem 4:

Solution to Problem 5:
Contributors

- Mario Morataya (UCD)