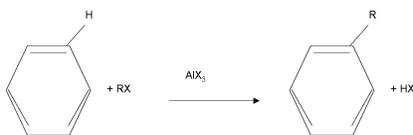


## 16.11: Friedel–Crafts Alkylation and Friedel–Crafts Acylation

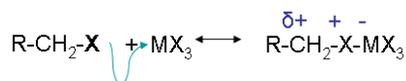
### Friedel-Crafts Alkylation

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 efficiency.



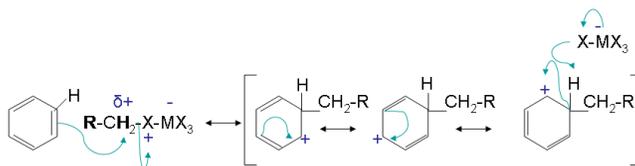
The mechanism takes place as follows:

*Step one:*



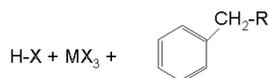
The first step creates a carbocation that acts as the electrophile in the reaction. This step activates the haloalkane. Secondary and tertiary halides only form the free carbocation in the step.

*Step two*



The second step has an electrophilic attack on the benzene that results in multiple resonance forms. The halogen reactions with the intermediate and picks up the hydrogen to eliminate the positive charge.

*Finish*



The final step shown above is the results of the end of step and shows the final products.

The reactivity of haloalkanes increases as you move up the periodic table and increase polarity. This means that an RF haloalkane is most reactive followed by RCl then RBr and finally RI. This means that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend to have similar halogen combinations such as BF<sub>3</sub>, SbCl<sub>5</sub>, AlCl<sub>3</sub>, SbCl<sub>5</sub>, and AlBr<sub>3</sub>, all of which are commonly used in these reactions.

### Some limitations of Friedel-Crafts Alkylation

There are possibilities of carbocation rearrangements when you are trying to add a carbon chain greater than two carbons. The rearrangements occur due to hydride shifts and methyl shifts. For example, the product of a Friedel-Crafts Alkylation will show an iso rearrangement when adding a three carbon chain as a substituent. Also, the reaction will only work if the ring you are adding a substituent to is not deactivated. For a look at substituents that activating or deactivating Benzene Rings.

The three key limitations of Friedel-Crafts alkylation are:

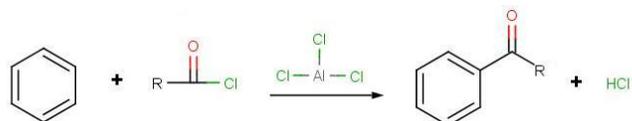
1. Carbocation Rearrangement - Only certain alkylbenzenes can be made due to the tendency of cations to rearrange.

- 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.

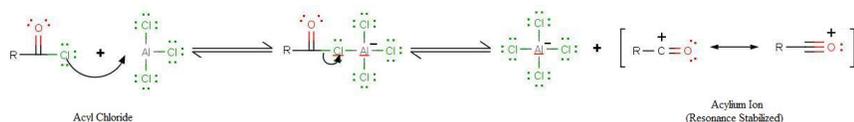
To remedy these limitations, a new and improved reaction was devised: The Friedel-Crafts Acylation. (also known as Friedel-Crafts Alkanoylation).

## Friedel-Crafts Acylation

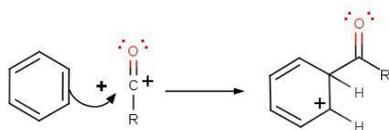
The goal of the reaction is the following:



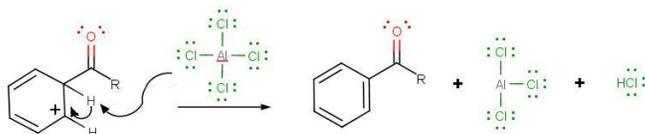
The very first step involves the formation of the acylium ion which will later react with benzene:



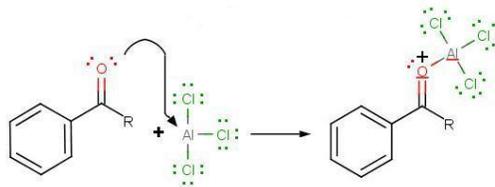
The second step involves the attack of the acylium ion on benzene as a new electrophile to form one complex:



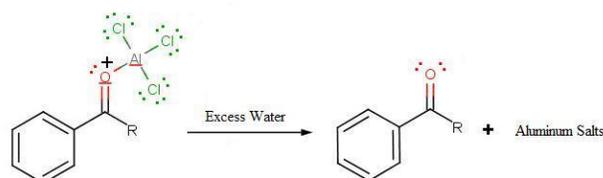
The third step involves the departure of the proton in order for aromaticity to return to benzene:



During the third step,  $\text{AlCl}_4$  returns to remove a proton from the benzene ring, which enables the ring to return to aromaticity. In doing so, the original  $\text{AlCl}_3$  is regenerated for use again, along with  $\text{HCl}$ . Most importantly, we have the first part of the final product of the reaction, which is a ketone. This 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, 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.

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