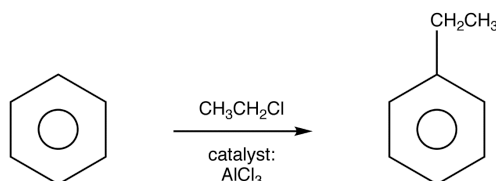


## 18.5: ALKYLATION AND ACYLATION OF BENZENE - THE FRIEDEL-CRAFTS EAS REACTIONS

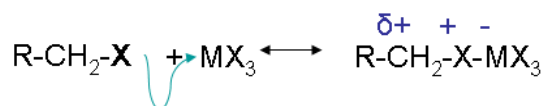
### FRIEDEL-CRAFTS ALKYLATION

The Friedel-Crafts Alkylation reaction forms alkyl benzenes from alkyl halides. The usefulness of this reaction is limited, because it can be difficult to stop the reaction at a single alkylation. Additionally, a carbocation intermediate is produced in Step 1 which brings the potential for carbocation rearrangements (ominous theme music).

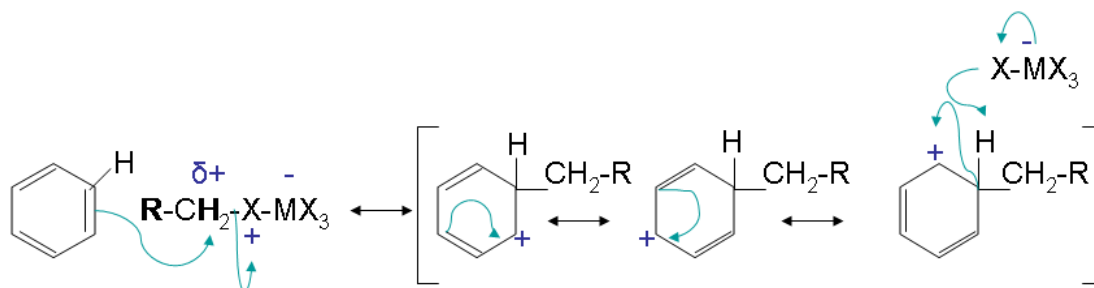


The mechanism takes place as follows:

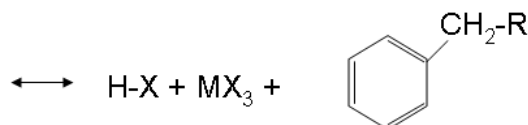
**Step 1:** A carbocation is created to form the electrophile. This step activates the haloalkane. Secondary and tertiary halides only form the free carbocation in this step.



**Step 2:** The pi electrons from benzene react with the electrophile to form the resonance stabilized alkylbenzenium ion.



**Step 3:** Any Lewis Base reacts picks up the hydrogen from the alkylbenzenium ion to reform the aromatic ring.

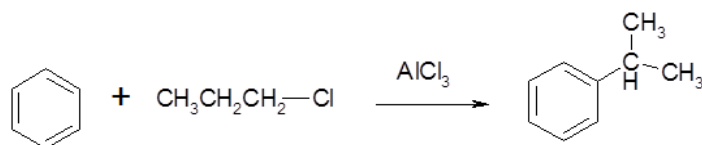


The finish step shown above is the two products.

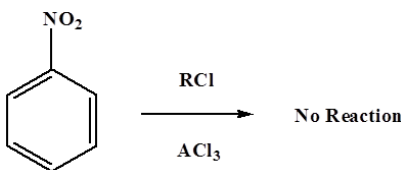
The reactivity of haloalkanes increases as you move up the periodic table and increase polarity. This means that an RF haloalkane is most reactive followed by  $\text{RCl}$  then  $\text{RBr}$  and finally  $\text{RI}$ . This means that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend have similar halogen combinations such as  $\text{BF}_3$ ,  $\text{SbCl}_5$ ,  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ , and  $\text{AlBr}_3$ , all of which are commonly used in these reactions.

### SOME LIMITATIONS OF FRIEDEL-CRAFTS ALKYLATION

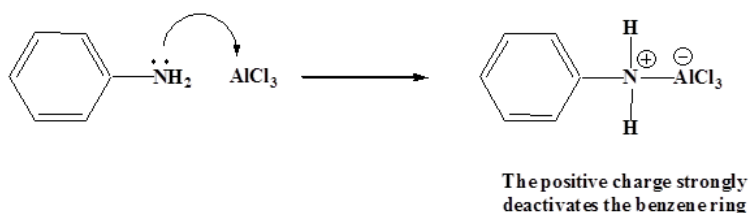
There are possibilities of carbocation rearrangements when you are trying to add a carbon chain greater than two carbons. The rearrangements occur due to hydride shifts and methyl shifts. For example, the product of a Friedel-Crafts Alkylation will show an iso rearrangement when adding a three carbon chain as a substituent. One way to resolve these problems is through Friedel-Crafts Acylation.



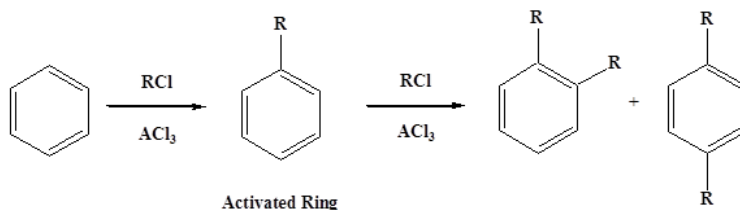
Also, the reaction will only work if the ring you are adding a substituent to is not deactivated. Friedel-Crafts fails when used with compounds such as nitrobenzene and other strong deactivating systems.



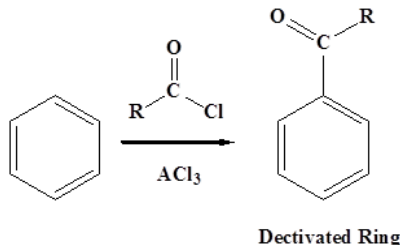
Friedel-Crafts reactions cannot be performed then the aromatic ring contains a  $\text{NH}_2$ ,  $\text{NHR}$ , or  $\text{NR}_2$  substituent. The lone pair electrons on the amines react with the Lewis acid  $\text{AlCl}_3$ . This places a positive charge next to the benzene ring, which is so strongly activating that the Friedel-Crafts reaction cannot occur.



Lastly, Friedel-Crafts alkylation can undergo polyalkylation. The reaction adds an electron donating alkyl group, which activates the benzene ring to further alkylation.

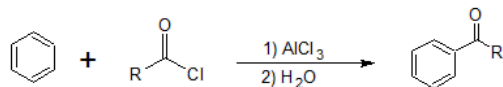


This problem does not occur during Friedel-Crafts Acylation because an acyl group is deactivating. This prevents further acylations.



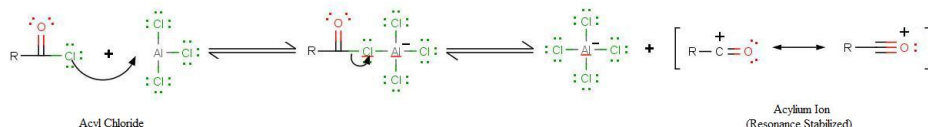
## FRIEDEL-CRAFTS ACYLATION

There is an additional reaction step for Friedel-Crafts Acylation. The acyl group of the product complexes with the aluminum chloride. Water is added to isolate the acyl benzene final product.

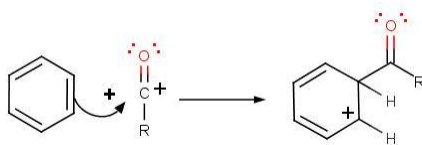


### 1<sup>st</sup> Reaction

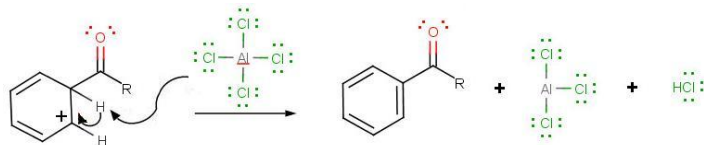
#### Mechanism Step 1: Acylium ion formation



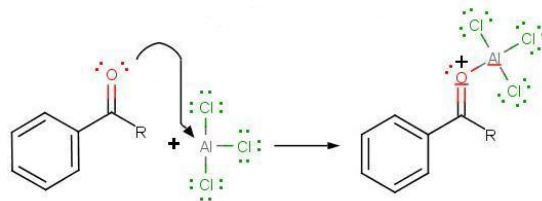
**Mechanism Step 2:**  $\pi$  electrons of benzene react with the acylium ion to form the sigma complex, resonance stabilized acylbenzenium intermediate:



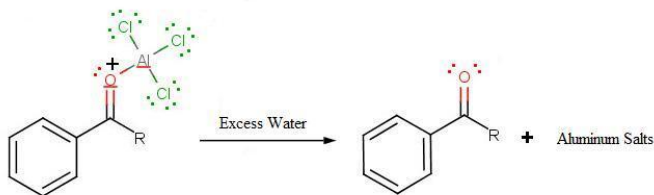
**Mechanism Step 3:** Deprotonation of the sigma complex to restore aromaticity.



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. The product forms a complex with aluminum chloride as shown below.



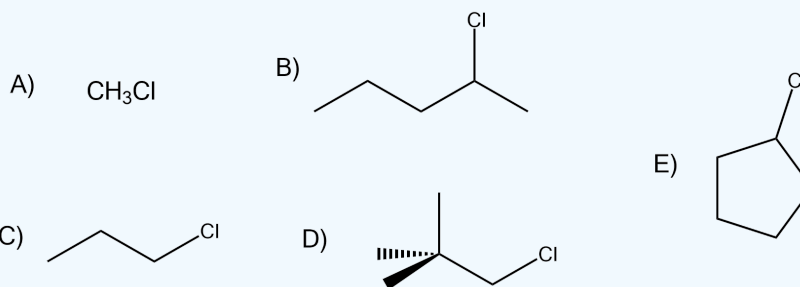
**2<sup>nd</sup> Reaction:** Water is added to liberate the final product as the acylbenzene:



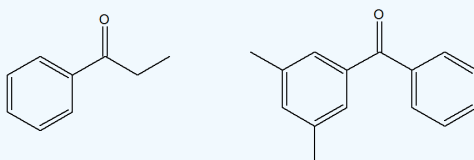
Friedel-Crafts Acylations offer several synthetic advantages over Friedel-Crafts Alkylation. These advantages provide greater control over the production of reaction products. The acylium ion is stabilized by resonance, so no carbocation rearrangement occurs. Additionally, acyl groups are deactivating with for EAS reactions, so the product does not undergo further reactions. However, Friedel-Crafts Acylations do not work with nitrobenzenes or other deactivated benzene rings. The concept of deactivated will be more fully explored in the next two sections of this chapter.

### Exercise

11. Which of the following will NOT undergo a rearrangement in a Friedel-Crafts reaction?



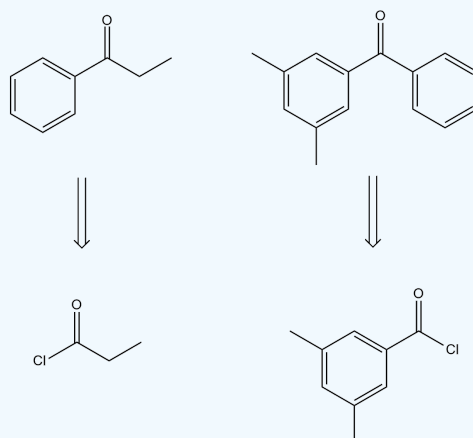
12. Suggest an acyl chloride that was used to make the following compounds:



**Answer**

11. A, B, and E will not undergo a rearrangement.

12.



## CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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