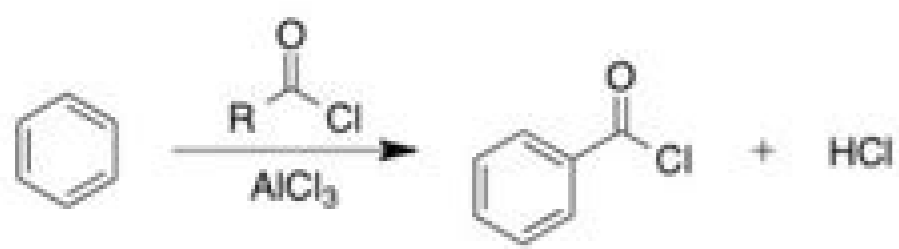


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## The Friedel-Crafts Alkylation Reaction



## The Friedel-Crafts Acylation Reaction

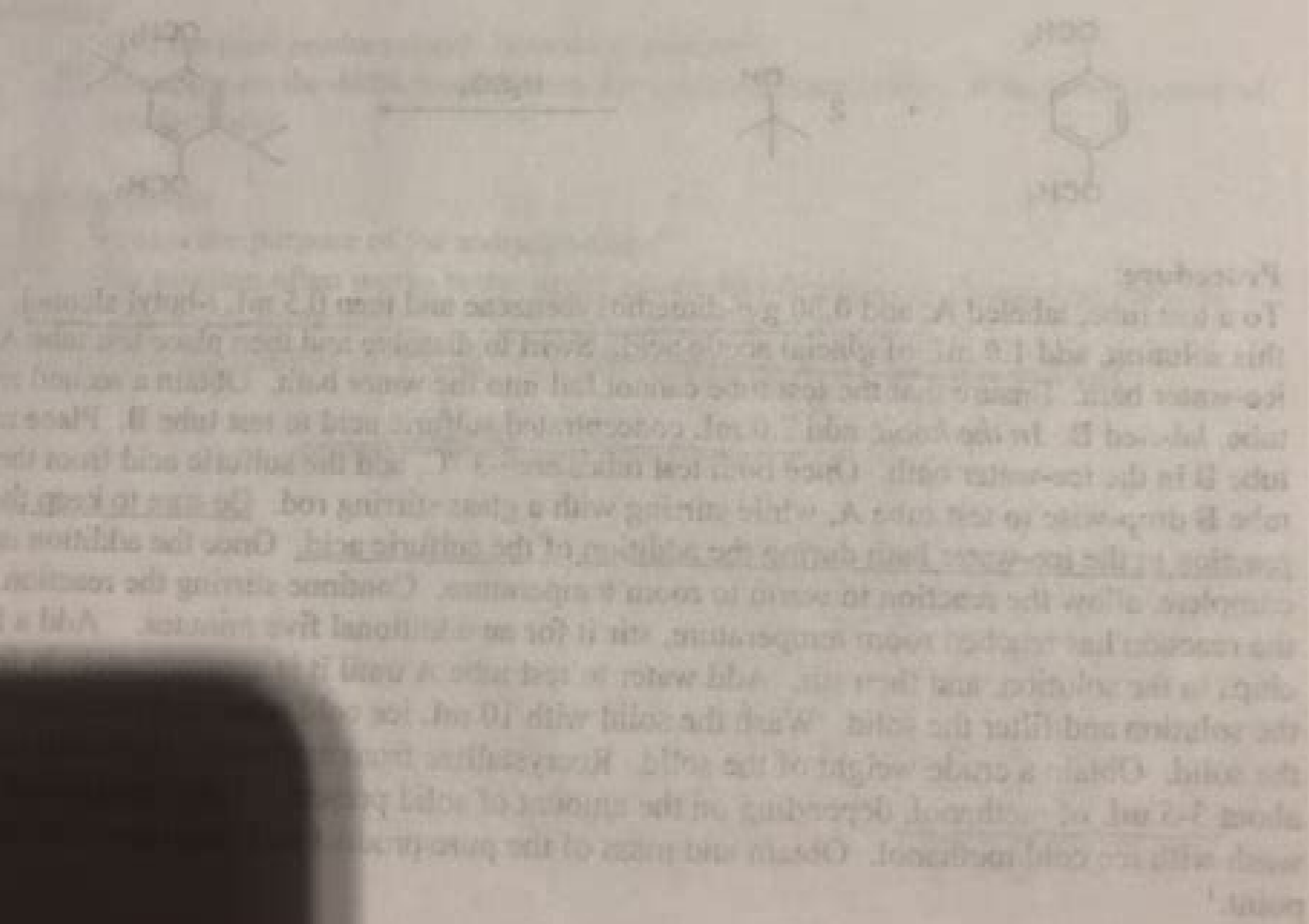
Throughout the process of the Friedel-Crafts reaction, a carbocation is also generated on the aromatic ring. The rate determining step is the first step in the reaction to break the aromatic pi bonds. In an effort to regain aromaticity, the final step of the reaction is a rapid elimination.

In Friedel-Crafts reactions, substituents on an aromatic ring play an important part of determining where new substituents will add, just as in other electrophilic aromatic substitution reactions. In general, those substituents that can donate electrons into an aromatic ring (either via the inductive effect or through the donation of lone pairs) activate an aromatic ring towards substitution and have an overall directing effect towards the *ortho* and *para* positions. Conversely, those that withdraw electrons (again, either inductively or through resonance) deactivate the ring towards substitution and generally direct towards the *meta* position.

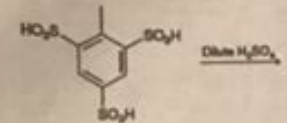
In this experiment, you will use two aromatic substrates and need to determine the separate products obtained. You will determine the product structures using proton

**Discussion:**  
1) Was the final product pure? How do you know?  
2) Comment on the difference between the crude and pure yields. What is the source of loss for both?

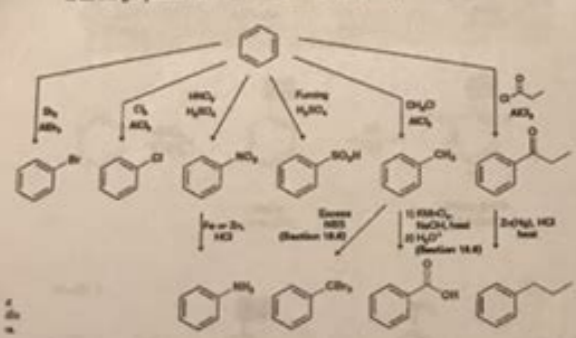
**Post-lab Questions:**  
1) Two equivalents of *t*-butanol are used in this reaction. What is the problem if only one equivalent is used?  
2) Draw a mechanism to show how *t*-butanol is activated to make the electrophile.  
3) Would IR be a useful tool in identifying the product? Why or why not?  
4) What is the reason for adding cold methanol to wash the crystals?  
5) What are the factors influencing selectivity in this reaction?



12. Predict the major product of the following reaction:



Monosubstituted Benzene Rings  
The simplest kind of synthesis problem is one that requires formation of a monosubstituted benzene ring. Drawing what you know about the reactivity of the benzene ring is the first step. The next step is to identify the reagents that will give you the desired product. In this case, we have seen 10 different groups that can be installed on an aromatic ring. Take special notice of the four groups shown in blue. Installation of these groups requires care.



13. Identify the reagents necessary to convert benzene into each of the following compounds

- Chlorobenzene
- Bromobenzene
- Propylbenzene
- Aniline (aminobenzene)
- Toluene

14. Identify the product obtained when benzene is treated with each of the following reagents

- Fuming sulfuric acid
- $Cl_2, AlCl_3$
- $Br_2, Fe$

### Lab #6: Friedel-Crafts Acylation of Ferrocene

Preparation: Wade chapter 17 (reactions of aromatic compounds); Zubrick chapter (column chromatography)

- Objectives:**
- To execute a Friedel-Crafts acylation on an aromatic ring
  - To become proficient using the technique of column chromatography

**Background:**

Friedel-Crafts alkylation and acylation reactions are powerful tools for substituting aromatic reactions. In the absence of strong activating groups, powerful Lewis acid catalysts such as  $AlCl_3$  must be used. However, activated aromatic compounds will undergo substitution under much milder conditions. Ferrocene, a common organometallic compound, is highly activated and undergoes acylation readily using a milder Brønsted-Lowry acid catalyst. In fact, ferrocene is so reactive that a diacyl derivative usually forms as a minor product (Figure 1).

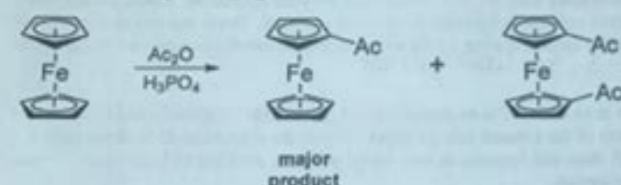


Figure 1. Acylation of ferrocene.

After the acylation reaction is complete, unreacted ferrocene starting material and diacylferrocene will be removed using column chromatography. Column chromatography allows for the separation of materials based on their relative solubility (mobile phase) and attractions to a packed solid column (stationary phase).

Table 1. Physical properties.

compound	molar mass	mp
ferrocene	186.04	173°C
acetic anhydride	102.09	
monoacetylferrocene	228.08	82°C
diacetylferrocene	247.09	126°C

**Experimental Procedure:**

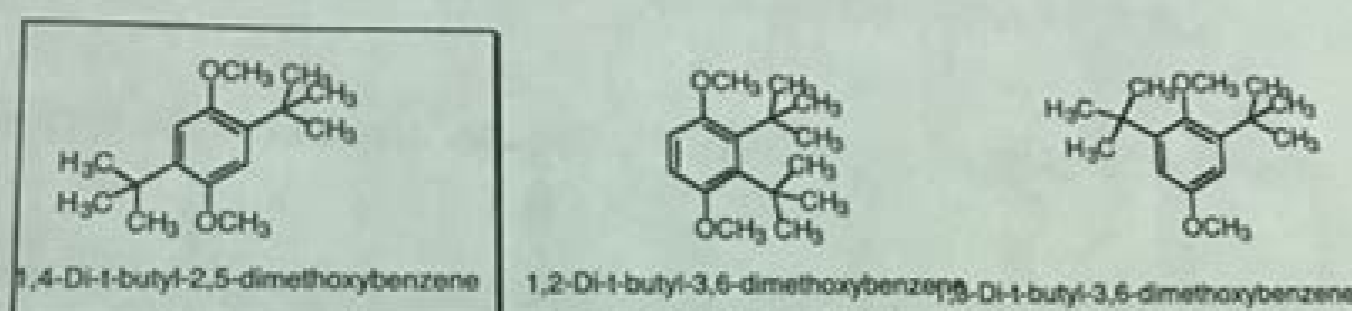
1. Chemical reaction

Weigh 200 mg of ferrocene into a conical vial and add in 2 mL of acetic anhydride. Attach an air condenser and heat gently in a warm water bath while stirring until the ferrocene is dissolved. Once dissolved, allow the solution to cool and disconnect the condenser so that you may carefully add 10 drops of phosphoric acid. Reattach the condenser and stir the reaction while heating in a hot water bath at approximately 100°C for 10 minutes.

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Friedel-Crafts Alkylation Lab

**Questions:**

1. Draw a detailed mechanism for the formation of *t*-butyl-2,5-dimethoxybenzene. (In other words, for the first alkylation, but not the second...)



2. The actual dialkylation product is 1,4-di-*t*-butyl-2,5-dimethoxybenzene. Why is this isomer preferred rather than the alternative isomer 1,2-di-*t*-butyl-3,6-dimethoxybenzene (see above)?
3. The actual dialkylation product is 1,4-di-*t*-butyl-2,5-dimethoxybenzene. Why is this isomer preferred rather than the alternative isomer 1,3-di-*t*-butyl-2,5-dimethoxybenzene (see above)?
4. What was your molar ratio of *t*-butanol to dimethoxybenzene?
5. Why do you think you did not stop after just a single alkylation? In other words, why were you able to add two *t*-butyls, not just one?
6. Why do you think you did stop after two alkylations? In other words, why were you able to add two *t*-butyls, but did not continue on to add a third *t*-butyl group at least to some of your molecules?
7. You used *t*-butanol and acid to generate the *t*-butyl cation used to form 1,4-di-*t*-butyl-2,5-dimethoxybenzene. Suggest two organic precursors other than *t*-butanol that could be used as precursors for *t*-butyl cation?

The Friedel-Crafts Alkylation reaction from 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 and picks up the hydrogen from the alkylbenzenium ion to reform the aromatic ring. The final 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 RCl then RBr and finally RI. This means that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend have similar halogen combinations such as  $BF_3$ ,  $SbCl_5$ ,  $AlCl_3$ ,  $SbCl_5$ , and  $AlBr_3$ , all of which are commonly used in these reactions. 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  $NH_2$ ,  $NHR$ , or  $NR_2$  substituent. The lone pair electrons on the amines react with the Lewis acid  $AlCl_3$ . 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. The prevents further acylations. 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. 1st 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,  $AlCl_4$  returns to remove a proton from the benzene ring, which enables the ring to return to aromaticity. In doing so, the original  $AlCl_3$  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 product forms a complex with aluminum chloride as shown below. 2nd 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

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