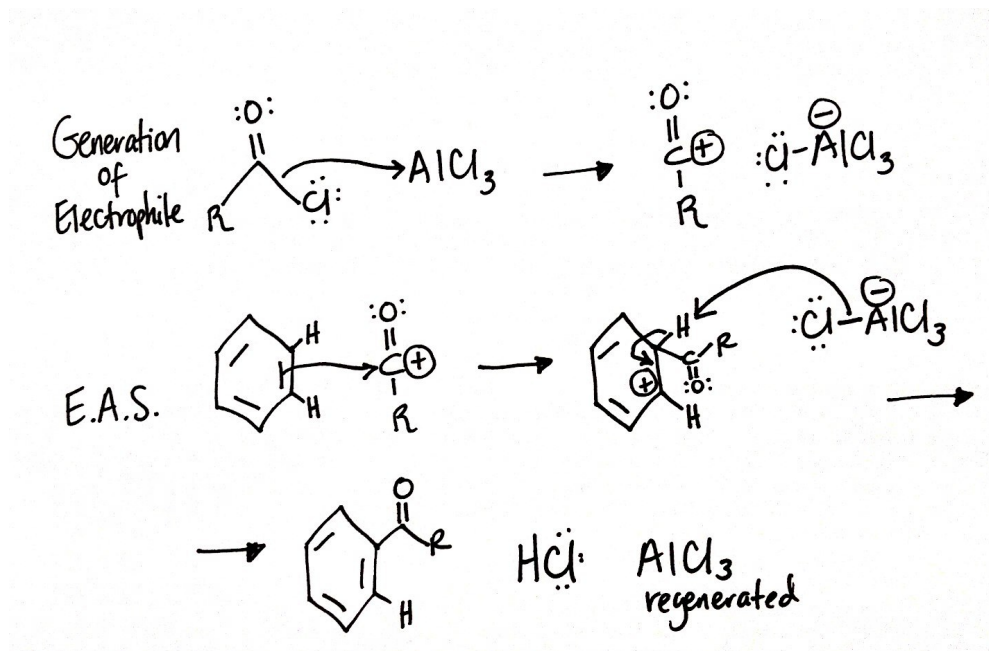
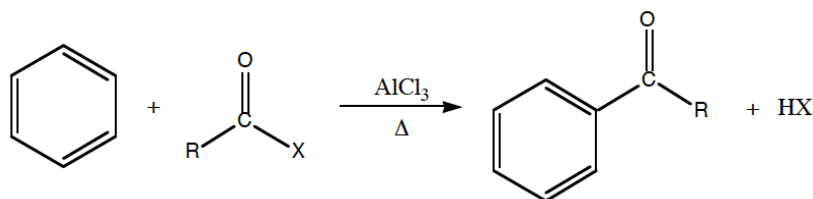


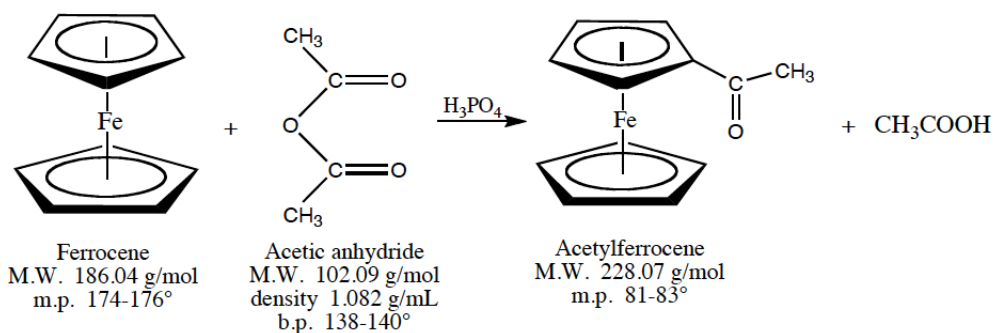
## 12BL Experiment 10: Friedel Crafts Acylation – An EAS Reaction

**Safety:** Proper lab goggles/glasses must be worn (even over prescription glasses). WEAR GLOVES! Acetic anhydride is corrosive and a lachrymator (tear gas). Its fumes are highly irritating, and it can react violently with water. Dispense the liquid under a hood; avoid contact, do not breathe its vapors and keep it away from water. Phosphoric acid can cause serious burns, particularly to the eyes; do not allow it to contact your eyes, skin or clothing. As always, ask where organic waste containers are located in the lab.

**Background:** A Friedel-Crafts Acylation is an electrophilic aromatic substitution reaction which introduces an acyl group onto an aromatic ring, whereas a Friedel-Crafts alkylation introduces an alkyl group onto the aromatic ring. In Acylation, the electrophile is an acyl carbocation that formed by reaction with a Lewis acid catalyst, such as aluminum chloride or many other metal halides. In alkylation, the electrophile is an alkyl carbocation that formed by reaction with a Lewis acid catalyst, also commonly aluminum chloride. However, keep in mind that you have learned a variety of methods to form carbocations that can be used in alkylation like alkenes/acid or alcohols/acid. In order for the reaction to take place, the aromatic ring system must be very electron rich and thus cannot contain any electron withdrawing groups.



Ferrocene was discovered by accident in 1951 and is an example of the now well-known metallocene or "sandwich" compounds. The highly electron rich cyclopentadienyl rings in ferrocene are aromatic and undergo many of the same reactions as benzene. In fact, most metallocenes are more reactive toward electrophilic reagents than is benzene, which indicates that the electrons are more readily available. Thus, while the Friedel-Crafts acylation of benzene requires aluminum chloride as a catalyst, ferrocene can be acylated by acetic anhydride under milder conditions using phosphoric acid as the catalyst. In addition, the second ring may also be acetylated to give 1,1'-diacetylferrocene,  $\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)_2$ .



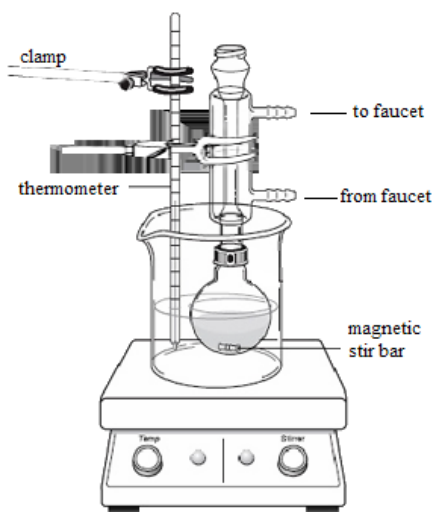
<http://www.bc.edu/schools/cas/chemistry/undergrad/org/spring/FriedelCrafts.pdf>

**Objective:** 1. To successfully synthesize an acylated aromatic ring. 2. To understand mechanisms of Friedel Crafts acylation and alkylation.

### Procedure:

#### Reaction:

- 1) Place 0.28 g of ferrocene in a 20ml round-bottom flask containing a magnetic stir bar. Prepare a hot water bath, heating the water to nearly the boiling point while preparing the following reaction mixture.
- 2) In a fume hood, add 1.0 mL of acetic anhydride.
- 3) Add 0.3 mL (approx. 15 drops) of 85% phosphoric acid, your catalyst, to the flask (Is this reaction endothermic or exothermic?).  
Note: The reaction mixture should heat up and darken in color.



- 4) Swirl the flask, heating occasionally in a hot water bath, if necessary, until all the ferrocene dissolves (use a small glass rod to break up any remaining clumps).
- 5) Attach a reflux condenser (as shown above), then heat the reaction mixture, with stirring, in the hot water bath prepared in step 1. Heat for *ONLY* 10 minutes (any longer could lead to decomposition of products and reactants). Note: during this time a purple color may develop (don't worry if it doesn't).
- 6) Place flask in ice and cool to room temperature.

**Workup:**

- 7) Pour the reaction mixture onto 1.5ml of ice water in a 25ml Erlenmeyer flask. Rinse the reaction flask with two 5 mL portions of ice water and add to 25ml flask.
- 8) Add 1.5 ml of 3 M NaOH to any remaining residue in reaction flask (20ml), stir vigorously with stirring rod to dislodge anything remaining. Then add this to the contents of the 25 ml Erlenmeyer flask and stir for a few minutes.
- 9) Check the pH. *Slowly* add solid sodium bicarbonate in drop wise until the remaining acid has been neutralized. This step can be done with magnetic stirring, but make sure to use a stirring plate that is *not hot*. Note: the reaction mixture should be a dark brown suspension at this time.
- 10) Allow reaction mixture to cool to room temperature then collect the crude product by vacuum filtration and continue to pull air through the product for a few minutes to dry it.
- 11) Clean both empty flasks with acetone and pour remains into specified waste jar for this lab.

**Purification:**

- 12) You will purify your product by recrystallizing it from hexane. Transfer the solid and a stir bar to a clean 25 mL beaker and add 5 mL of hexane. Boil for roughly 5 minutes with stirring until dissolved. You may add more hexane if needed.
- 13) Your solution may be a dark orange color that may have a black gummy substance (insoluble). You may decant the hot dark orange solution into another beaker. The insoluble black substance can be discarded in waste beaker.

- 14) Add a small amount of decolorizing charcoal to the decanted solution and swirl (roughly a small spatula full—too much of this will reduce your yield). Decant again to remove the decolorizing carbon.
- 15) Set the flask aside to cool slowly. Red-brown crystals of acetylferrocene should begin to form. Once the flask has reached room temperature, cool it in ice.
- 16) Collect the crystalline product by vacuum filtration, washing with a small quantity of cold hexane, and dry it by continuing to pull air through it for a few minutes.
- 17) Obtain its melting point & IR.

Procedure adapted by Shasta Ott

<http://oclab.wikispaces.com/Acetylation+of+Ferrocene>

<http://www.chm.uri.edu/bdeboef/chm292/Acetylferrocene.pdf>

<http://chemlab.truman.edu/OrganicLabs/acetylation-ferrocene-2012.pdf>

<http://greenchem.uoregon.edu/PDFs/GEMsID72.pdf>

[https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0CDUQFjAB&url=https%3A%2F%2Fmcla.instructure.com%2Fcourses%2F955075%2Ffiles%2F29675160%2Fdownload%3Fwrap%3D1&ei=a6s4UrSfD8\\_siQK9zYGABg&usq=AFQjCNF0TuL4NfWxqoyFDDHTyLgarp-7g&sig2=E5SKvG3dXybmOFeN2t26IA](https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0CDUQFjAB&url=https%3A%2F%2Fmcla.instructure.com%2Fcourses%2F955075%2Ffiles%2F29675160%2Fdownload%3Fwrap%3D1&ei=a6s4UrSfD8_siQK9zYGABg&usq=AFQjCNF0TuL4NfWxqoyFDDHTyLgarp-7g&sig2=E5SKvG3dXybmOFeN2t26IA)

## 12BL Prelab Experiment 10: Friedel Crafts Acylation – An EAS Reaction

1. Why are metal halides, such as aluminum chloride, considered Lewis Acids?

2. Give an example *mechanism* of a carbocation electrophile formed from..

a. an alkene and acid (with no rearrangement of carbocation possible)

b. an alcohol and acid

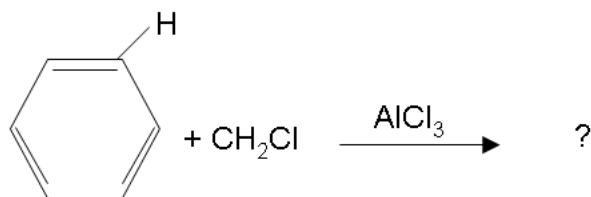
c. an alkene and acid & the resulting carbocation undergoes rearrangement to a more stable carbocation

d. an acyl carbonyl compound and a metal halide acid catalyst

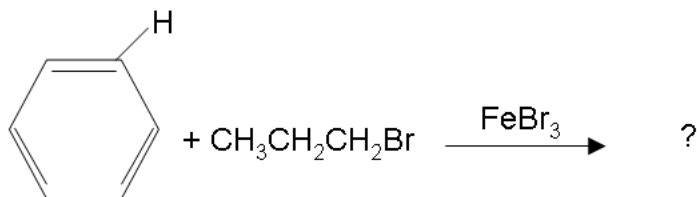
## 12BL Postlab Experiment 10: Friedel Crafts Acylation – An EAS Reaction

1. Melting Point Range of Pure Product \_\_\_\_\_ °C
2. Is your product Acetylferrocene or 1,1'-diacetylferrocene?
3. Attach your completely analyzed IR with all bonds and wavenumbers shown in their appropriate positions on the IR; include structure of product on IR.
4. For the following problems, give the major Friedel Crafts Alkylation product.

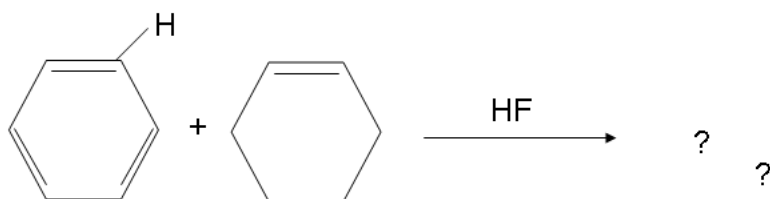
Problem 1:



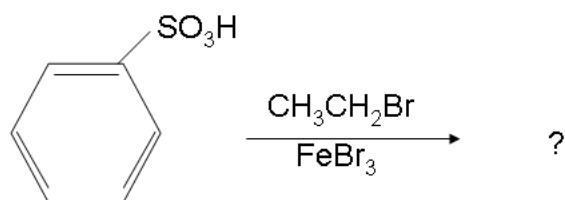
Problem 2:



Problem 3:



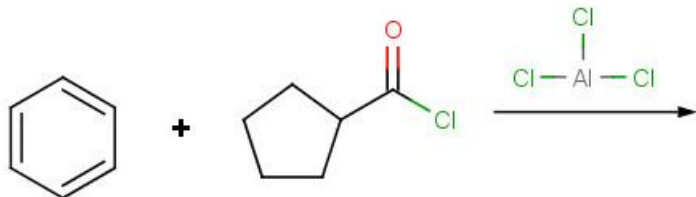
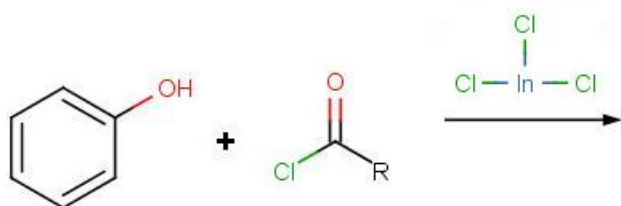
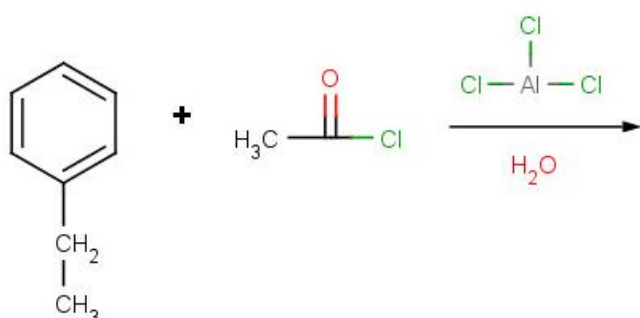
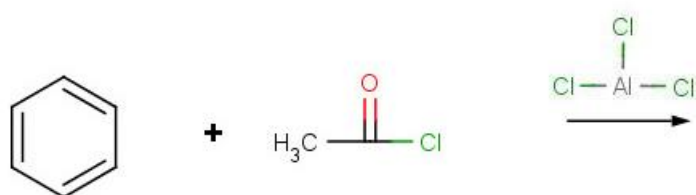
Problem 4:



Problem 5:

Show the mechanism for the Friedel-Crafts Alkylation of benzene and  $\text{CH}_2\text{Cl}_2$  with  $\text{SbCl}_5$  catalyst.

5. For the following, give the major Friedel Crafts Acylation product.



6. Show the mechanism for the following Friedel Crafts Acylation reaction.

