This is your report cover. Please fill this form out and attach it to your form.
Experiment 11a and b

General Safety Considerations

1. AlCl₃ reacts violently with H₂O liberating HCl gas. Be careful when you open AlCl₃ bottle (keep your nose out of it). Make sure you tightly cap the bottle when you are finished. Do not allow your AlCl₃ to sit around exposed to the atmosphere. It will react with the atmospheric H₂O and deactivate. When you measure out the AlCl₃ you should immediately transfer it into a very dry round-bottom (the reaction flask) already containing the xylene. The xylene will create a barrier to the atmospheric H₂O. Generally, wear gloves and goggles. In the event of a spill, consult your instructor immediately.

2. p-Xylene, 1-bromobutane and 1-bromopropane are irritants and toxic. Take all the normal precautions to avoid exposure. Keep the chemicals in the hood as much as possible. Wear gloves and goggles. In the event of a major spill, consult your instructor. If you come in contact with these substances, flush the exposed area for fifteen minutes with cold water.
Experiment 11
Flow Chart

Apparatus

1. add 1.0 g aluminum chloride
2. add 12.5 mL p-xylene
3. add 1-bromopropane dropwise over 15 minutes
4. stir for 30 minutes
5. pour on ~10g ice
6. separate layers

organic

aqueous

1. add calcium chloride
2. wait 5 minutes
3. decant org. into 100 mL r.b.
4. GC analysis
discard hood sink

11-3
Experiment 11

Aromatic Substitution: Friedel-Crafts Alkylation Science repulses the indefinite.

Claude Bernard (1813-78), Introduction à l'Etude de la Medecine Experimentale (1865)

In preparation for this investigation, carefully study pages 710-731 of Loudon and answer the pre-lab questions on the form that follows the procedures in this lab.

This exercise is an excellent example of the kind of experiments that are done in order to investigate the mechanism of a reaction. Your objectives are to carry out the Friedel-Crafts alkylation of p-xylene with 1-bromopropane and analyze the products by GC. The expected products are n-propyl-p-xylene and iso-propyl-p-xylene. You will determine the ratio of these products by GC. The extent of isomerization of the alkyl group from n-propyl to iso-propyl gives information on the rate of rearrangement versus the rate of alkylation. You will compare that information with the ratio of products found in the alkylation of benzene.

A. Procedure:

1. Set up the apparatus shown on the top of the next page in the hood using drierite in the adapter. Set a magnetic stirrer under the round bottomed flask. Take the addition funnel to the hood and add to it 0.025 mole of 1-bromopropane. Cork or stopper the funnel and reconnect it to the apparatus. Place a magnetic stirring bar in the 25 mL roundbottom flask and bring it and a cork to the hood. Place 0.5 g of aluminum chloride in the flask and immediately cover it with 6.3 mL of dry p-xylene (the point is to minimize exposure of AlCl₃ to moisture in the air). Quickly reconnect the flask to the apparatus.

2. With the stirrer and vacuum line on, add the 1-bromopropane dropwise (1-2 drops per second). After addition is complete (about 15 minutes), allow the mixture to react an additional 30 minutes.
3. Pour the mixture into a 50 mL beaker containing about 5 g of ice. Stir until the ice has melted, then transfer to a 25 or 30-mL separatory funnel, separate the layers, and discard the aqueous layer. Dry the organic layer over anhydrous CaCl₂ for about 5 minutes.

4. Filter or decant the solution into a small flask and carry out a preliminary GC analysis of the solution. If you have sensitivity problems with the GC, adjustment of the concentration of the sample may be necessary. Please see your instructor if you are having trouble with the GC.

B. Lab Report

A standard lab report will not be required for this lab. If you complete the attached form, you have finished the lab write-up.

-- Formyl benzene
by Liza Donlon & Heather Campbell
Experiment 11
Form Write-up

Name: ___________________________  Exp. name: ___________________________

T.A. Name: ________________________  Date: ___________________________

I. Pre-lab Exercises

A. Why is it essential to use a gas trap and to work in the hood while carrying out this experiment? (5 points)

B. Why is a drying tube used in this experiment? (5 points)

C. What side reaction will occur if the glassware used is not dry? (5 points)

D. Why is an excess of p-xylene used in this experiment? (5 points)
II. Experiment and Results

A. Attach the required GC to the back of the report. Assign a structure to each peak on the GC. (10 points)

B. Calculate the ratio of products in percent form for the reaction excluding unreacted p-xylene. (8 points)
III. Discussion/Conclusions

A. Discussion of Rate of Rearrangement vs. Rate of Substitution. (20 points)

B. Error Analysis. Focus on errors that might alter the ratio of products. (10 points)
IV. Post-lab Questions

A. Analyze the $^1$H NMR spectrum of n-propyl p-xylene and isopropyl p-xylene. Copies of the spectra will be available in the lab and on reserve in the Collier Science Library. (10 points)

B. Write a complete mechanism (arrow formalism, resonance structures) explaining the formation of the two products. (8 points)

C. Why was the reaction mixture poured on ice at the end of the reaction. Write equations to describe any chemistry occurring in this step. (4 points)
D. Approximately what ratio of rearranged to unarranged products do you expect if toluene (methyl benzene) is subjected to the reaction carried out in this lab? (8 points)

E. Given the fact that the reaction you just did is kinetically controlled, what do you suppose might happen if the temperature of the reaction was raised enough to cause equilibration. (8 points)

V. Quality of Results (20 points)
Experiment 11b: The Friedel-Crafts Reaction (Thermodynamic Control) – A Discovery Based Lab

This project will involve doing a Friedel-Crafts alkylation of xylene similar to that done earlier in the semester, but at elevated temperature and extended time so that the reaction will be under thermodynamic control. The product mixture will be analyzed using GC/Mass Spectrometry (GCMS). Dr. Nierz will assist you in operating the GC/Mass Spec instrument. You should work in pairs or at most in groups of three on this project. It is acceptable to work alone if you wish, but consider this option seriously before committing to it.

Please do the following to prepare for your project:

1. Go over the Friedel-Crafts procedure in your lab book and adapt it so that the reaction will be done at 50°C for two hours rather than the given time at room temperature. You should also consider using 1-bromobutane in lieu of 1-bromopropane in the reaction because it gives better resolved products on the GCMS. What control reaction should you run?

2. Read up on the mass spectra of aromatic compounds in Loudon, Chapter 12. For more advanced reading see Parikh, V. M. Absorption Spectroscopy of Organic Molecules and Silverstein, Bassler and Morrill, Spectrometric Identification of Organic Compounds. Both of these books are on reserve in Collier and relevant selections will be available electronically with a pass word that will be supplied in class or via email.

3. Write down the monoalkylation products you would expect to obtain if the reaction were under thermodynamic control (there are at least six). Hint: Realize that thermodynamic control means that the reaction is in equilibrium. When the reaction goes backwards methyl groups can come off and reattach in new and exciting locations!!

4. When you have some proposed products, look up their boiling points. This will be helpful in assigning the GC/Mass Spec peaks. You can try the web or there is a very good book in the reference section of Collier: Rossini, Pitzer, Arnett, Braun, Pimentel, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds.

5. It will also be helpful to get some specific information about how the sorts of compounds you will be making fragment when under mass spectrometric conditions. A good book for this is Budzikiewicz, Djerassi, and Williams, Mass Spectrometry of Organic Compounds. This will be on reserve in Collier. You should focus on the sections devoted to aromatic compounds.

Alternatively, information about fragmentation patterns can be obtained from the web. We have links (see course website at www.brynmawr.edu/Acads/Chem/menzsfo/index.html) to several websites that have Mass spectral data. You should be most interested in the different fragmentation of propyl or butyl benzenes vs. isopropyl or sec-butylbenzenes. It is OK to work with model compounds rather than the specific compounds you are making.

Knowing how the compounds fragment will be very useful in identifying the GC peaks.

6. After you have carried out your experiment and have interpreted your data, you should propose a mechanism for the formation of the various products. You can also check your assignments by searching out a paper on this topic (GC/Mass Spectrometry study of the Friedel Crafts Alkylation of p-Xylene) that was published in the early 1990’s. To find this paper you will have to do a Chemical Abstracts search.
Upon completion of your project, your results will be presented orally to Dr. Nerz. Please make an appointment within two weeks of completing the work. Your presentation should include the following.

I. What you were trying to discover
II. An interpretation of your results
III. Mechanistic explanation for the formation of the products considering the thermodynamic nature of the reaction conditions.

It is expected that all members of the group will have a strong knowledge of all the above areas. The idea is to have the knowledge and understanding of the work, not to make a fancy presentation. The idea is also to cut some of the time you would need to do a write-up so don’t get carried away with this.