CHEMISTRY 344 - Organic Chemistry Laboratory II – Spring 2012
Lab #3: Friedel-Crafts Acylation (two weeks)

In this lab you will predict the directing effects of substituent groups in Electrophilic Aromatic Substitution. This is a 2-week lab, and the synthesis procedure is attached to this document. Your initial goal is to synthesize Compound A (an oil), formed by the Friedel-Crafts acylation reaction between 2-chlorotoluene and acetylchloride. You will then oxidize Compound A into compound B (a solid) that is easily identified by its melting point.

Pre-lab Reading: You are expected to read the following sections in Chapter 15 of your Solomons lecture text: Friedel-Crafts acylation (15.7); effect of substituents on reactivity and orientation (15.10, 15.10A, 15.10B, 15.10C, 15.10D). Also read about the haloform reaction, section 17.3C.

Pre-Lab Notebook Preparation: Complete the following information in your lab notebook before your pre-lab recitation. Use the numerals and headings as given.

Table of Contents: You will need to update the Table of Contents for each new lab with the date and brief title of each experiment, and the notebook page number on which the lab begins.

I. Title of the Experiment and Date.

II. Purpose of the experiment: One- or two-sentences describing what you are going to do and why. State your experimental goals.

III. Equations: Write the balanced equation for this reaction, ***including structures***.

IV. Table of Reagents: In your lab notebook create a table, like the one shown below, for the following reagents used in this lab: **2-chlorotoluene** and **acetyl chloride.** Your table must include the name, structure, and all physical data. You can find this information in the Aldrich Chemical Catalog, the Merck Index, or on-line from the **ChemIndex** web site. The link to ChemIndex and instructions can be found on Dr. Brush's Lab web site: **http://webhost.bridgew.edu/ebrush/CH343%20Lab.htm**.

Chemical name and formula	structure	molecular mass (g/mole)	melting point (solids) (^oC)	boiling point (liquids) (^oC)	density (liquids) (g/mL)

V. Procedure: Summarize the lab procedure in your notebook. Do not copy the procedure word-for-word.

VI. Health, Environmental, and Waste disposal: Look up and summarize some of the health and environmental hazards for **2-chlorotoluene** at the MSDS database: **http://hazard.com/msds/index.php**

***Laboratory Book*: The following should be completed before leaving lab, initialed and dated by you.**

VII. Data and Observations: Record a rough transcript of your experimental method in your lab notebook, indicating what you actually did and what you actually observed. Do not prepare this section in advance. This section should be written in a paragraph format and include: **experimental procedure, all reagent mass and volume measurements, observations, crude and pure product mass or volume, % yield calculations, and product analysis by melting point, chromatography analysis, or instrument analysis.** You will be judged on the depth of your observations and technical success (yields, purity, etc.).

VIII. Discussion and Conclusions: A brief, but critical evaluation of your results, and the success of your experiment. Address the experiments goals and purpose!

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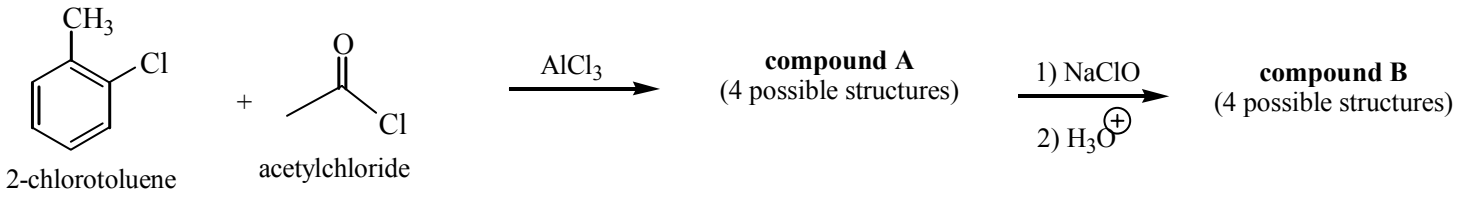
Experimental Procedure



NOTES: Compound A is formed by a **Friedel-Crafts Acylation**. The oxidation reaction that produces Compound B is an example of the **Haloform Reaction**, which converts methyl ketones into carboxylic acids.

Week 1. Add a circular stirring bar to a **DRY** 10 mL round bottom flask followed by 2 mL of CH_2Cl_2. While stirring, add 0.3g of **DRY** $AlCl_3$, 0.2 mL of 2-chlorotoluene, and 0.16 mL of acetyl chloride. Cap the reaction mixture and stir at room temperature for 90 minutes. If no red-orange color appears after 30 minutes, try adding an additional 0.2 g of $AlCl_3$. If this does not yield a red-ish color, start the reaction from the beginning again. Cool the reaction in an ice-water bath and slowly add 3 mL of **ice-cold water**. Stir this mixture with a glass rod, and add one mL of concentrated HCl (**CAUTION!**) to dissolve any Al salts which may have precipitated. Mix thoroughly, then remove the aqueous layer and wash the CH_2Cl_2 layer with 5 mL of water, followed by 5 mL of 5% Na_2CO_3 solution, and then twice more with water. Transfer the CH_2Cl_2 solution to a pre-weighted 25 mL Erlenmeyer flask, and evaporate the solvent with low heat in the sand bath with no gas for 15 min (drying with sodium sulfate is not necessary), leaving a yellow oil (compound A). Determine the mass of compound A. Cover your product and leave in your lab drawer for completion next week.

Week 2. Dissolve the yellow oil of Compound A in 5 mL of ethanol, add a stir bar, and slowly add 10 mL of Clorox bleach. The mixture is stirred and heated at 50°C for 2 minutes, then 1 mL of acetone is added to destroy excess ClO^-, and the mixture is reheated for 2-3 minutes. Compound B is precipitated when 3 mL of concentrated HCl (**CAUTION!**) is added. The solid product is isolated by vacuum filtration, and washed with 2 mL of ice-cold water. The wet solid is transferred to a 5 mL reaction vial and dissolved in 1-2 mL of 1 M NaOH. Pipet filter this solution into a clean 25 mL Erlenmeyer flask. Rinse the pipet filter with 1 mL of water, then acidify the filtrate with concentrated HCl, to obtain pure Compound B as a white precipitate. Cool in an ice-water bath for 10 minutes, and collect your product by filtration on a Hirsh funnel, and wash with 2 mL of ice-cold water. Scrape your damp product onto a watch glass and dry at 100°C for 15-20 minutes. Obtain an accurate melting point for Compound B, and be sure to heat the sample slowly!

Name:_____ **Lab Partner**_____

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Lab Report Grade _____(100 points)

The following questions are based on your pre-lab reading and the results of your experiment. You and your lab partner are encouraged to work together, but you must each turn in your own report! Answer each question in the space provided, and **show all calculation work below or on a separate sheet of paper**.

1. Experimental data for Compound A.

mass of 2-chlorotoluene used_____ grams _____ moles

Theoretical yield of product: _____grams _____moles

Experimental yield of your product: _____grams _____moles

% Yield_____

2. Experimental data for Compound B.

mass of 2-chlorotoluene used_____ grams _____ moles

Experimental melting point_____

Theoretical yield of product: _____grams _____moles

Experimental yield of your product: _____grams _____moles

% Yield_____

3. Draw the structures of all four possible products for **Compound A** formed by the Friedel-Crafts acylation of 2-chlorotoluene with acetylchloride.

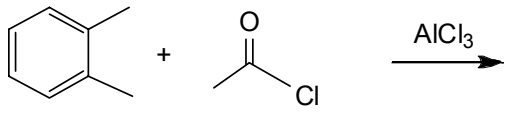
4. Draw the structures of all four possible products for **Compound B** formed by the subsequent oxidation of the acyl group of Compound A to a carboxylic acid by NaClO (haloform reaction).

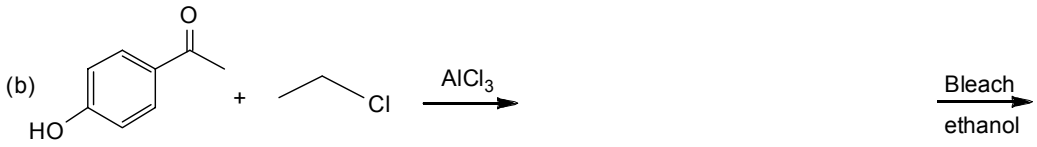
5. Identification of Compound B. To answer this question you must have an accurate melting point for pure Compound B. The melting points for the four possible Compound B products are: 2-chloro-3-methyl benzoic acid (141^{o}C), 3-chloro-4-methyl benzoic acid (209^{o}C), 4-chloro-5-methyl benzoic acid (201^{o}C), and 3-chloro-2-methyl benzoic acid (159^{o}C). Based on your experimental melting point, draw the actual structure for **Compound B** below.

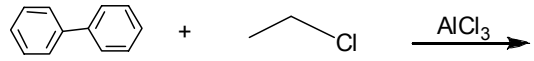
6. Compound A. Based on your answer above, draw the corresponding structure for **Compound A**, and the arenium (benzenonium) ion intermediate that results during the Friedel-Crafts acylation reaction with acetyl chloride and $AlCl_3$. Explain why this particular isomer was formed.

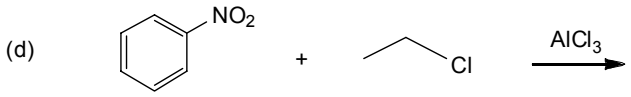
7. Evaluation. Was your experiment a success? Consider your goals, observations, mp, and yield data. A short paragraph is expected.

8. Reactions. Complete each reaction shown below with the structure of the major products. Points will be deducted for drawing duplicate structures. If you believe that no reaction occurs, write"NR".

(a) 

(b) 

(c) 

(d) 

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