

Lab Project: Electrophilic Aromatic Substitution Reactions/ Acylation
Chem 227 / Dr. Rusay / Spring '09

Because of the reputations of DVC and its skilled chemistry students, NSF has awarded your student research group a non-competitive π^2 starter grant, which covers the costs of demonstrating proficiency in all aspects of organic laboratory synthesis: *Preparation, Isolation, (π_1) Purification, and Identification (π_2)*. If the results of this initial investigative phase are acceptable, your group will be eligible for funding at a significantly higher level.

Your group is to prepare samples of 3 or 4 different acylated aromatic compounds, which will be assigned to the group. The group will be responsible to plan, prepare, purify, identify and turn-in samples of each of the synthetic products. How this is to be done is entirely the decision and responsibility of the group. General guidance, recommendations and final approval will be provided by Dr. R.

NSF has set a target quantity that is to be produced and delivered for each compound. It is 35 mmoles of each. The samples (amount, yield & purity) will constitute 25% of the contract. The remaining 75% will be based on intellectual performance/written communication: supporting physical/spectroscopic data & interpretation, calculations, answers to assigned questions and the quality of the group's final report, which is to be typed and be in journal format to include: **1)** reactions and structures, **2)** concise experimental procedures with % yield of each of the products, **3)** IR/NMR tables of spectroscopy data, **4)** answers to assigned questions, **5)** attached copies of each group member's raw lab research notebook pages, which should include their name, and be clearly and legibly written in the format described in the course syllabus, and **6)** a typed invoice for NSF that includes an itemized account of the man/woman hours for each group member devoted to the syntheses, the total hours for the group, the \$/hour charge that you think reasonable for re-imbursement. The **complete** package must be submitted by the deadline noted in the calendar. **LATE submissions will not be accepted.** All group members receive the same base grade for the project.

NSF's remittance will be translated into a grade for the group; all members receiving the same grade. (NOTE: *this grade will be subject to adjustment based on the results of a private, confidential survey within the group of each group member's performance and contribution.*)

Phase One (Worksheet, Background reading, Organization & Preparation)

1) Complete questions #1-4 **Electrophilic Aromatic Substitution** Worksheet. **2)** Refer to: in-class slides, and the Chem 227 *Web assignment page*. Decide who will be doing which synthesis. Select one member as team leader and spokesperson, who is to see Dr. R. with the worksheet and obtain a set of NMR handouts with questions for various electrophilic aromatic substitution reactions. These must be completed and turned-in with the final report. (*Four lab periods are allotted in total for the entire in-lab portion of the project including NMR/IR data acquisition.*)

Phase Two (Planning and Pre-Lab Proposal)

Consult the *Acylation* procedure. It is to be adapted and scaled to deliver 35 mmol of purified product. **Remember:** the targeted amounts are deliverable quantities. You will need to adjust all starting materials to allow for losses and make some assumptions about percent yields. Write an individual pre-lab in your lab notebooks for your respective reaction that includes an exact sketch of the apparatus, which you plan to use, and calculations for amounts of reagents including a statement of your assumptions. Highlight the calculated starting material quantities. Do not proceed until you have Dr. R's signature approving the proposal.

Phase Three (Implementation, Analysis and Reporting.)

Execute and complete all work. Consult the course Web calendar for due dates. Write up a journal style report in the format of the publication draft used in your previous peer review analysis. Your group's final report should include a short abstract, which the draft does not, and also include structural characterization data (NMR/IR) as in the draft. Refer to the course Web assignment page for a list of questions that are to be answered, typed and attached to the final report.

Generic example of an abstract:

Polymer Journal
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Electrophilic Aromatic Acylation Synthesis of Wholly Aromatic Polyketones Composed of 2,2'-Dimethoxybiphenylene Units

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ABSTRACT: Wholly aromatic polyketones have been successfully synthesized via AlCl_3 -mediated Friedel-Crafts acylation polymerization and P_2O_5 - MsOH mediated direct condensation polymerization between 2,2'-dimethoxybiphenyl (1a), an excellent acyl-acceptant monomer for electrophilic aromatic acylation polymerization, and arenedicarboxylic acid derivatives.

KEY WORDS Aromatic Polyketones/ Noncrystal Polymers/ Friedel-Crafts Acylation/ Wholly Aromatic Polyketones

Acylation

Electrophilic aromatic substitution reactions begin with the interaction of nucleophilic π electrons of an aromatic ring with a strong electrophile. The intermediate carbocation rapidly loses H^+ to reform the aromatic system. In the case of Friedel-Crafts acylation, the electrophile is an acylium ion, formed by the reaction of an acid chloride with aluminum chloride. The mechanism is shown in Figure 1.

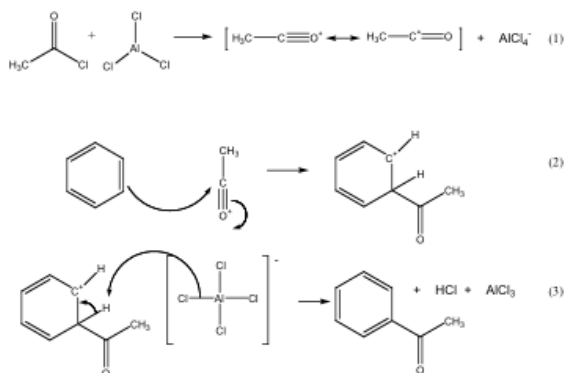


Figure 1: Mechanism for Friedel-Crafts Acylation

A typical procedure and apparatus follows:

NOTE: Aluminum chloride is water sensitive, an irritant, and corrosive. It will react with the moisture on your skin to liberate HCl. Handle it with care, weigh out only what is necessary, and work quickly but safely. Acetyl chloride is corrosive. Keep materials in a hood. Keep all reagent bottles tightly capped.

Anhydrous aluminum chloride (0.055 mol, 1.1 equiv) and 15 mL of methylene chloride were placed in a 100-mL, round-bottomed (RB) flask with an addition funnel and drying tube, and a reflux condenser connected to a gas trap. **NOTE:** The system must be perfectly dry before adding any reagents. Do not wash the addition funnel between adding the acetyl chloride and the aromatic compound. The mixture was cooled to $\sim 0^\circ C$ in an ice/water bath. Acetyl chloride (0.055 mol, 1.1 equiv) as a solution in 10 mL of methylene chloride was added to the addition funnel and then dropwise to the aluminum chloride over 10 min.

After the addition was complete, the aromatic compound (0.050 mol) dissolved in 10 mL of methylene chloride was added in the same manner. The addition rate was adjusted so the solution did not boil excessively. After addition was complete, the ice bath was removed and the reaction was allowed to cool to room temperature. After stirring for an additional 15 minutes at room temperature, the reaction mixture was poured carefully and very slowly, with stirring, into about 25 g of ice and 15 mL of concentrated HCl in a beaker. The mixture was transferred to a separatory funnel and the organic layer collected. The aqueous layer was extracted with 20 mL of methylene chloride. The combined organic layers were extracted with two portions of saturated sodium bicarbonate and dried over anhydrous $MgSO_4$. The drying agent was gravity filtered. The methylene chloride was removed by rotary evaporation. The crude product was weighed and distilled. Samples of distilled product were analyzed by IR and NMR spectroscopy.

