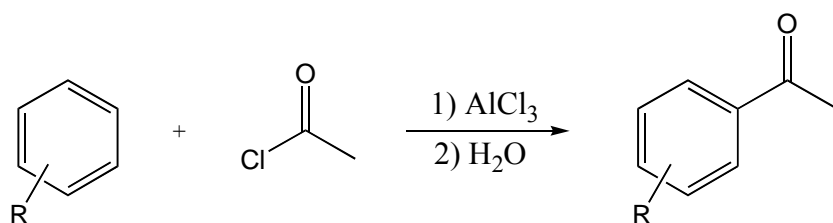


The Friedel-Crafts Acylation

The Friedel-Crafts acylation is an example of an electrophilic aromatic substitution (EAS) reaction. It is an excellent way to introduce a carbon chain to an aromatic ring, and is thus of great synthetic value.

In this experiment, you will perform a Friedel-Crafts acylation of an unknown substituted benzene (C_8H_{10}) using acetyl chloride. You will then determine the identity of your product, and (by reasoning) your starting unknown, using IR and 1H -NMR spectroscopies.



Safety:

- Acetyl chloride, aluminum chloride and concentrated HCl are very corrosive. **Handle with gloves!**

Required Reading:

Padías:

Proton NMR (pp. 77 – 96)

IR (pp. 66 – 76)

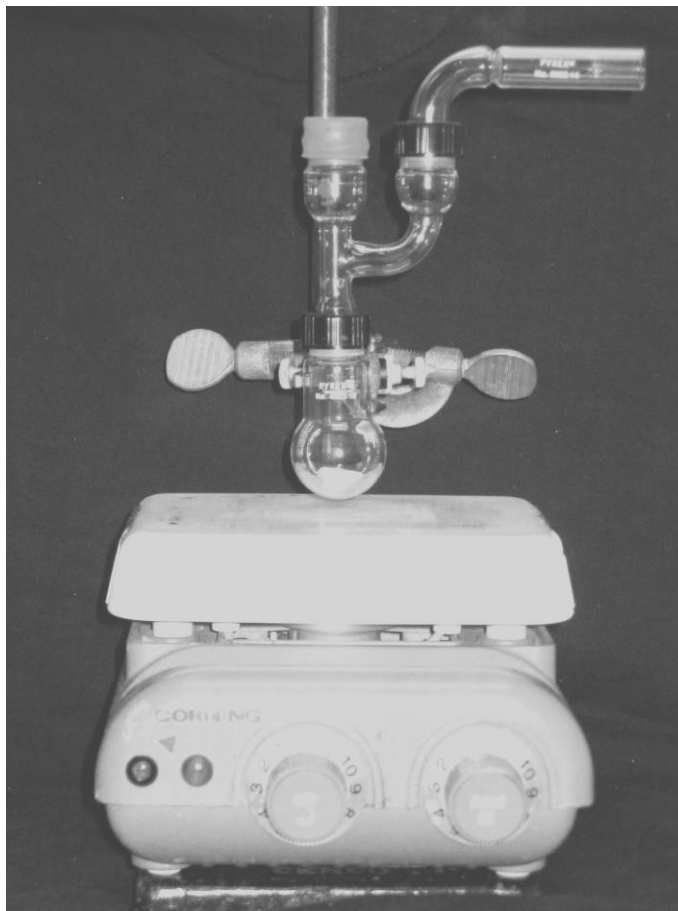
Percent Yield (p. 14 – 16)

Procedure:

CAUTION! Acetyl chloride, aluminum chloride and concentrated HCl are very corrosive. Handle with gloves!

Place 800 mg of AlCl₃ into a 10 mL round bottom flask with a spin vane. Add 2 mL of dichloromethane and add a Claisen adapter, rubber septum and drying tube as shown below. Place the assembly under the hood and add 0.5 mL of acetyl chloride dropwise via syringe with stirring. In a 3 mL conical vial, weigh out 425 mg of your unknown. Add the unknown to your reaction flask dropwise via syringe, and stir for 30 minutes. Add 4 mL of ice water dropwise (add slowly!) via syringe and remove the septum. Add 4 mL of concentrated HCl using a pipet, and stir until the solids dissolve. Transfer the mixture to a separatory funnel, rinsing with 1 mL of dichloromethane. Drain the lower organic layer into a small Erlenmeyer flask and remove the aqueous layer. Return the


organic layer to the separatory funnel and wash with 1 mL of 5% sodium bicarbonate (vent frequently!). Drain the organic layer into a 5 mL conical vial, and dry the solution over Na_2SO_4 . Transfer the solution to a small pre-weighed beaker and evaporate the solvent by warming gently under the hood. Determine the weight of your product, and obtain IR and $^1\text{H-NMR}$ spectra.



Lab Report:

Interpret your IR spectrum. Use the $^1\text{H-NMR}$ to determine the structure of your product. Discuss how the NMR signal positions, integrations, and multiplicities are consistent with your proposed product. Determine the identity of your starting material from the structure of your product. Calculate the percent yield (show the calculation) of your product.

Questions:

1. The Friedel-Crafts acylation of benzene gives only the monosubstituted product, even when an excess of catalyst and acyl chloride are used. Explain why.
2. The Friedel-Crafts acylation of benzene with phosgene and aluminum chloride gives a product with the formula $C_{13}H_{10}O$. What is the structure of the product? Explain how this product is formed.
3. Using Spartan, model the Highest Occupied Molecular Orbital (HOMO) of *o*-nitrotoluene:
 - a) Construct a model of *o*-nitrotoluene (to attach a nitro group, select “nitro” from the “Groups” dropdown box). Minimize the energy by clicking on the  button.
 - b) Select “Setup” “Calculation.” In the “calculate” box, choose “Equilibrium Geometry” at the “Ground” state with “Semi-Empirical” “AM1” model. Click “OK.” Do not submit the calculation at this time.
 - c) Select “Setup” “Surfaces.” Click “Add” and from the “Surface” dropdown box select “HOMO.” Check the “Fixed” box next to “Isovalue” and enter 0.11 in the field, click “OK”. Leave the surfaces dialog box open.
 - d) Select “Setup” “Submit” to submit the calculation. Click “Save” when the “Save as” dialog box appears.
 - e) When the calculation is completed, check the box next to “homo” in the surfaces dialog box. The orbital lobes of the HOMO for *o*-nitrotoluene will be superimposed on the molecule.

Knowing that an electrophile will prefer to attack the atom where the HOMO has its largest lobe, where is the most likely site of attack? Is this consistent with what you know about substituent directing effects in EAS? Be sure to include a printout of the model (showing the HOMO) in your report.