6. Friedel-Crafts Alkylation: 1,4-Dimethoxybenzene and Biphenyl

M. Jones: Friedel-Crafts Alkylation, 14.5, pp 688-692.
Disubstituted Benzenes: *ortho, meta,* and *para* Substitution, 14.9, pp 704-717.

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

The purpose of this experiment is to perform a Friedel-Crafts alkylation using two different methods on two different aromatic compounds. A Friedel-Crafts alkylation involves the substitution of an aromatic ring with an alkyl group using a strong Lewis acid catalyst. This reaction belongs in the reaction category of electrophilic aromatic substitution. The dimethoxybenzene contains two activating methoxy groups, which are *ortho, para* directors. Normal substitution of an aromatic ring does not occur because of the stability of the ring. It does not act like a normal alkene. In fact, addition of HBr will not occur like it would in the case of an alkene or a diene. A catalyst is required to "convince" the arene ring to undergo substitution and lose its aromaticity for a short time.

There are basically three different steps in this reaction: formation of the electrophile, followed by nucleophilic attack of the arene, and rearomatization of the ring. The overall reaction is given in Figure 1 and the mechanism is depicted in Figure 2.

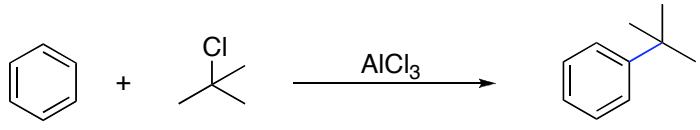

Figure 1. The general reaction for Friedel-Crafts alkylation of benzene.

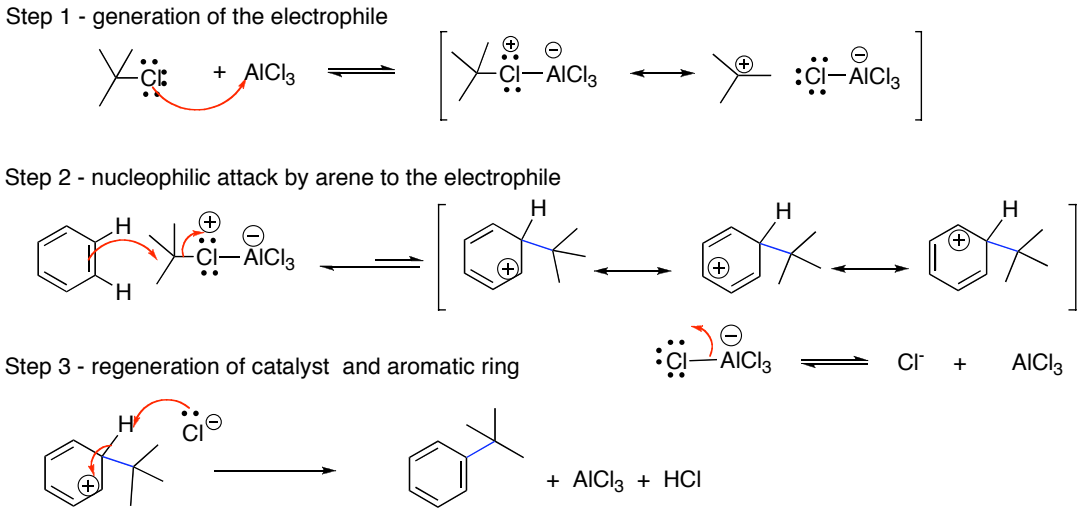

Figure 2. The general mechanism for Friedel-Crafts alkylation of benzene.

The electrophile wants electrons. It is formed because the chloride has an affinity for the metal (which has an empty *p* orbital). In the second step, the arene attacks the electrophile forming a resonance-stabilized intermediate. In the final step, there is an equilibrium, which generates the chloride as a base. It pulls off a proton to regenerate the aromatic product. These reactions are known to be extremely exothermic due to the reactivity of the Lewis Acid.

You will be performing two different Friedel-Crafts reactions using two different substrates and two different catalysts. The two overall reactions are depicted below in Figure 3.

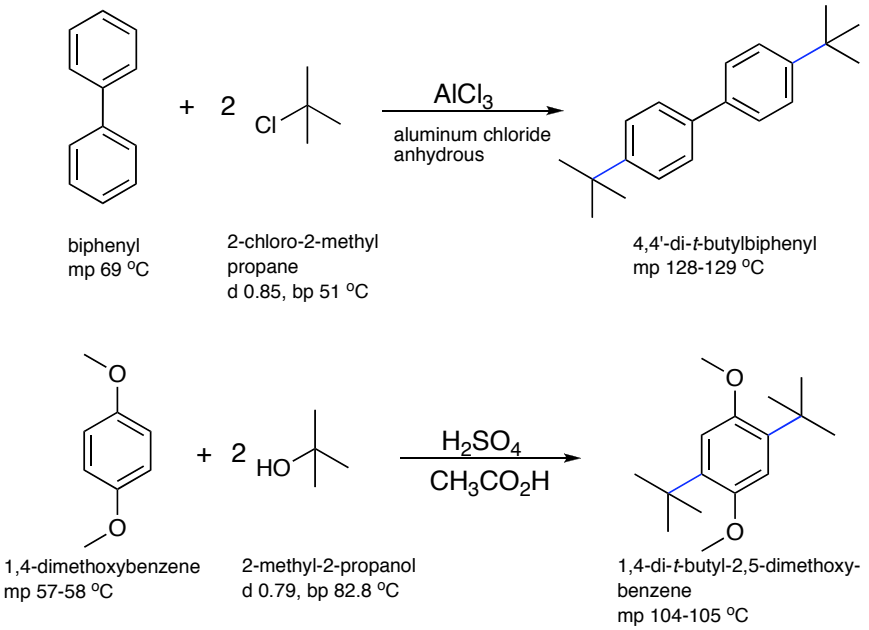

Figure 3. The overall reactions for the alkylation of *p*-dimethoxybenzene and biphenyl.

Cautions:

-Take extra care when handling the acetic and sulfuric acid.

-Make sure to use a clean spatula, filter flask, and reaction tube. The reaction tubes should be cleaned with soap, water and a brush first, rinsed thoroughly, and dried (if needed rinse with acetone).

-Make sure to return the top to the bottles.

Experiment

There are two parts to this experiment.

Part A.

Fit a 25 mL filter flask with a hose. To the other end, fit the hose with a Büchner funnel and immerse into a 400 mL beaker of water. This will be your "water trap" to capture any gases produced during the reaction. Add 0.75 g of biphenyl, 4 mL of nitromethane, and a spatula tip of aluminum chloride (0.25 g) to the flask. Then, fit the flask with a rubber septum. With a syringe, add 1.25 mL *t*-butylchloride through the septum over a four-minute period. Make sure the addition does not generate too much heat. The reaction should not get warmer than room temperature. After the addition is complete, swirl the flask for another 15 minutes. Add 8 mL of ice water to the flask with stirring. Place the flask in an ice water bath and add 4 mL of methanol. A solid should form. Vacuum filter the resulting solid, wash with ice water, and then wash with 5 mL of ice-cold methanol. Recrystallize the solid from toluene/methanol. Record the melting point of the product.

Part B.

In a large reaction tube, dissolve 500 mg of *p*-dimethoxybenzene in 2 mL of glacial acetic acid. Add 1 mL of *t*-butyl alcohol and place the tube in an ice-bath. You may have to heat the vial of *t*-butyl alcohol in a hot water bath to aid in this transfer. In small aliquots, add 1.6 mL of concentrated sulfuric acid with stirring after each addition. After addition is complete, let the reaction stand at room temperature for 15 minutes. Place the tube back into the ice bath and add 10 mL of water in small aliquots. When addition is complete, add an additional 10 mL of water. Vacuum filter and recrystallize solid in methanol and record the melting point of the product.