CH 2280 HYDROGENATION OF DISUBSTITUTED CHALCONES
(Adapted from a procedure by J. R. Mohrig, C. N. Hammond, and P. F. Schatz.)

Materials

From the Chemicals Hood:  From the Stockroom (Blue Bin):
Ammonium formate  ½” “pea-sized” stir bar  Stirbar retriever
10% Palladium on carbon Small metal clamp
Methanol  (2) Wire clips
Diethyl ether  Separatory funnel with stopcock
Magnesium sulfate  Glass stopper
Kimwipes© 100 mL round-bottom flask

SAFETY INFORMATION

Wear gloves while conducting this experiment.

Keep palladium on activated carbon (Pd/C) away from heat and sources of ignition. Do not breathe the dust.
If dry Pd/C comes into contact with methanol vapor, it can ignite the methanol solvent.
Be sure to add the Pd/C to your reaction flask before adding the methanol. Be sure to clean up any spilled catalyst with a wet Kimwipe© and then discard it in the “Palladium Waste” bottle in the hood.

Ammonium formate is an irritant. Avoid contact with skin, eyes and clothing.
Ammonia is an irritant.
Methanol is flammable and toxic. Use it in the hood.
Hydrogen gas is generated in the reaction. Hydrogen is an extremely flammable gas. It may form explosive mixtures with air.
Diethyl ether is extremely volatile and flammable. Use it in the hood.

This reaction involves a transfer of hydrogen from ammonium formate to the chalcone.
Ammonium formate is an efficient source of hydrogen, in that it readily decomposes into hydrogen, carbon dioxide and ammonia in the presence of the catalyst, palladium on carbon (Pd/C).

\[
\begin{align*}
\text{H}&\text{O}^neg\text{NH}_4^+\overset{\text{Pd/C}}{\longrightarrow} \text{CO}_2 + \text{H}_2 + \text{NH}_3 \\
\text{ammonium formate}
\end{align*}
\]

Formation of CO\(_2\) provides a substantial driving force to the reactivity of ammonium formate as a hydrogen donor. Some of the hydrogen gas can be adsorbed onto the surface of the palladium metal and react with the chalcone. Alternatively, the ammonium formate could react with the palladium and directly transfer hydrogen to the chalcone. The exact mechanism is not known.

Catalytic hydrogenation of chalcones could take place at a number of functional groups. For example, the alkene double bond could be reduced.

\[
\begin{align*}
\text{\text{-}}&\text{\text{-}} + \text{H}_2 \overset{\text{Pd/C}}{\longrightarrow} \text{\text{-}}&\text{\text{-}}
\end{align*}
\]

In addition, activated single bonds to heteroatoms can be cleaved in a process called hydrogenolysis; the heteroatom is replaced by hydrogen.

\[
\begin{align*}
\text{C-X} + \text{H}_2 \overset{\text{Pd/C}}{\longrightarrow} \text{C-H} + \text{HX}
\end{align*}
\]

**Procedure**

Place 1.0 g of the chalcone and 7.5 mmol of ammonium formate *per mmol of chalcone* in a 100-mL round-bottomed flask. If you do not have 1.0 g of your chalcone, we may have some in the stockroom, ask if you need some.

Prepare a water-cooled reflux condenser (See Figure 1 below, on page 4) before adding any reagents to your round-bottom flask. Hook up the tubing and start the water flowing *(NOT TOO FAST!)* at this time.

Weigh 0.10 g of 10% palladium on carbon on a weighing paper or plastic weigh boat and add the Pd/C carefully to the flask so that it does not adhere to the ground-glass joint. Use the powder funnel (the one with the wide bore) for this. If some of the black powder does end up on the interior neck of the flask, wipe it off with a Kimwipe© and place the Kimwipe© in the “Palladium Waste” bottle in the hood. Swirl the flask to coat the surface of the black catalyst with the other reagents. *(Safety precaution: Add the methanol only after swirling the solid reagents together in the flask. Failure to do so can result in fire and a burned hand!)* Add 20 mL of methanol (by pouring it down the side of the round-bottom flask) and again swirl the flask to mix the contents. The reaction mixture will start bubbling even before it refluxes, due to the gas produced in the decomposition of ammonium formate. Attach the water-cooled reflux condenser to the flask and place the flask in a sand bath. Begin heating the flask (turn the digital setting on the hot
plate/stirrer to 200 °C). (Reminder: Do not begin to time the reflux period until the methanol is boiling and recondensing from the condenser).

Heat the mixture at reflux for 15 minutes. Shorter heating can leave unreacted chalcone and longer heating can produce complex product mixtures.

**Recovery of the Product**

At the end of the reflux period, cool the flask containing the reaction mixture in an ice-water bath for 5 min. Pack a small plug of cotton into the stem of a funnel, then add fluted filter paper and filter the reaction mixture into a clean 125 mL Erlenmeyer flask. Rinse the black solid with 5 mL of methanol, add a wooden stick to the Erlenmeyer and evaporate the solvent by placing the flask IN the steam bath. An oily residue should result.

Add 5 mL of water and 15 mL of ether to the crude product in the flask. Swirl the flask to mix its contents and then transfer the mixture to a separatory funnel. Mix the two phases to produce an efficient extraction and then drain the aqueous phase into a flask. Pour the ether layer into another Erlenmeyer flask. Extract the aqueous phase again with an additional 10 mL of ether. Combine the two ether solutions in the separatory funnel and wash this ether with 10 mL of water. Drain the aqueous phase and pour the ether solution into a clean, dry, 50-mL Erlenmeyer flask. Dry the ether solution with anhydrous magnesium sulfate for 15 min, swirling occasionally.

**Isolation and Spectroscopic Analysis of the Product Mixture**

Filter by gravity (fluted filter paper) or decant the dried ether/product solution into a clean, dry, tared 50-mL Erlenmeyer flask. Evaporate the ether on a steam bath (add a wooden stick). The product may be either oil or a solid. Record the mass of your product. Analyze your product by NMR and IR. Compare your spectra to those of the chalcone itself. Predict the structure of your product, based on its spectra.

**Cleanup:** Place the Pd/C catalyst-containing filter paper and any other materials containing Pd into the waste container designated “Palladium Waste” in the hood. Place the spent drying agent and the aqueous layer remaining from the extractions into a container for inorganic waste.
Figure 1. Reflux Apparatus for Hydrogenation of Chalcones