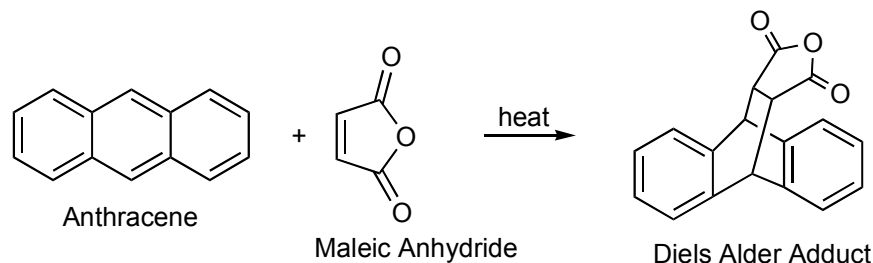


A Neat Diels-Alder Reaction: 9,10-dihydroanthracene-9,10- α,β -succinic acid anhydride

Revised 1/2019; Neat Procedure by Josh Hirner and Anne Moody

The Diels-Alder reaction is a concerted [4+2] cycloaddition between a diene and a dienophile (which is often an alkene). The reaction simultaneously forms two C-C single bonds. The reaction you will carry out is between anthracene (the diene) and maleic anhydride (the dienophile):



This particular example is a widely used reaction in organic teaching labs, but the traditional procedure calls for refluxing anthracene and maleic anhydride in a mixture of xylenes, an aromatic petroleum product; the xylenes also adhere to the final product, making the workup process lengthier. The procedure you will follow has eliminated the solvent entirely. The solvent-free ("neat") reaction helps cut down on waste and allows the reaction to proceed to completion much faster than the traditional method. (Why do you suppose that is so?) Carried out carefully, it has the added benefit of growing large crystals directly in your reaction vessel. (Again, why do you suppose that happens?)

Green Chemistry:

Green Chemistry is a relatively recent movement with the goal of making chemistry more environmentally benign, both in industry and academia. This exercise has been designed with the Twelve Principles of Green Chemistry in mind. You can read all the Principles online¹, but those that are most directly related to this experiment are as follows:

- Principle 1: Prevent waste.
By eliminating the use of a solvent for the reaction, we can cut down on the amount of hazardous waste that is generated.
- Principle 7: Maximize atom economy.
The Diels-Alder reaction incorporates *all* of the reactant atoms into the final product, so the atom economy should be very close to 100%.
- Principle 8: Use safer solvents and reaction conditions.
Xylenes are derived from petroleum, so by removing this non-renewable resource from the procedure, we are left with a synthesis that is both better for the environment and without the strong fumes from this solvent.

A pre-lab note:

- The CAS registry number for this product (9,10-dihydroanthracene-9,10- α,β -succinic acid anhydride) is 5443-16-3. Even with this number, physical data on this may be hard to find; its MW is 276.2861 g/mol and its mp is 261-262°C.

¹ <http://www.epa.gov/greenchemistry/pubs/principles.html>

Experimental:

Temperature control is an important aspect of this procedure. At the beginning of lab period, set your hotplate on your lab jack, add an aluminum heat block, and turn the hotplate to about setting 6. We are trying to regulate the temperature to 210-260 °C. We will monitor the temperature with a thermometer in the aluminum block.

Anhydrides are readily hydrolyzed at high temperatures in the presence of atmospheric water vapor. To prevent this, prepare a drying tube by inserting a small amount of cotton, some CaCl₂, and some more cotton to seal the end.

Weigh out 0.240 g anthracene and 0.120 g of maleic anhydride; mix these solids gently but thoroughly on a weighing paper. Using a paper funnel and/or your flat spatula, slide these solids into your 4 or 5 mL conical vial trying to avoid coating the vial sides.

Attach the conical vial to a water cooled condenser with the prepared drying tube at the top. The condenser is present simply to ensure that the top of the conical vial is sufficiently cool. Turn on the water for the condenser to keep the glassware cooled.

Once all the glassware is assembled together and clamped to the monkey bars, raise the hotplate on the lab jack and begin heating. A 1:1 molar mixture of anthracene and maleic anhydride usually melts at approximately 210 °C, so if your sample does not melt, very slowly increase the setting of the hotplate until it does melt some. (It may not completely liquefy.) Note that heating the reaction mixture beyond ~260 °C increases your likelihood of obtaining unwanted oxidized side products, so take your time and increase the temperature slowly.

Once the temperature is somewhere between 210-260 °C, the reaction will proceed very quickly and should be complete within 15 minutes at most. Watch as the walls of the conical vial become cloudy with crystal formation.

After the reaction is complete, lower and remove the hotplate, and allow the conical vial to cool slowly to RT. When it is cool enough to touch, remove the vial and examine the crystals, noting the different layers of crystals that may have formed. If you have distinct layers, the highest layer in the vial should be white and highly crystalline; this should be your product -- 9,10-dihydroanthracene-9,10- α,β -succinic acid anhydride in relatively pure form. The remaining solid in the vial is likely to be yellow-green to dark green in color and is *also* mostly 9,10-dihydroanthracene-9,10- α,β -succinic acid anhydride. Small amounts of oxidized anthracene give it its color.

Recrystallize all of the product (all of the various shades of green together!) from ethyl acetate. To do so, use hot ethyl acetate to transfer the solid to a 25 or 50 mL Erlenmeyer flask; you will likely need close to 15 or 20 mL of the solvent. Heat the mixture to dissolve as much solid as possible, adding a bit more ethyl acetate if needed; you may have a small amount of solid that will not dissolve. Decolorize with a tiny amount of decolorizing carbon as part of the process. (The decolorizing agent has a strong affinity for most organics, including your product, so don't use too much!) Use a hot gravity filtration to remove the spent decolorizing agent from the reaction mixture, and then allow the product to crystallize from the solution. These crystals will probably be noticeably smaller than your first crop from the conical vial, if you had nice crystals in the top layer.

When the sample is dry, determine the mass of the product, and calculate theoretical and percent yields. Measure the melting point of your sample, and run IR, ¹H NMR, and/or ¹³C NMR spectra, as required by your professor.

Clean-Up

The nonhazardous CaCl₂ drying agent can go in the regular trash can. From the recrystallization, the ethyl acetate should be put into the liquid organic hazardous waste, and the filtered solid impurities should go in the solid hazardous waste.