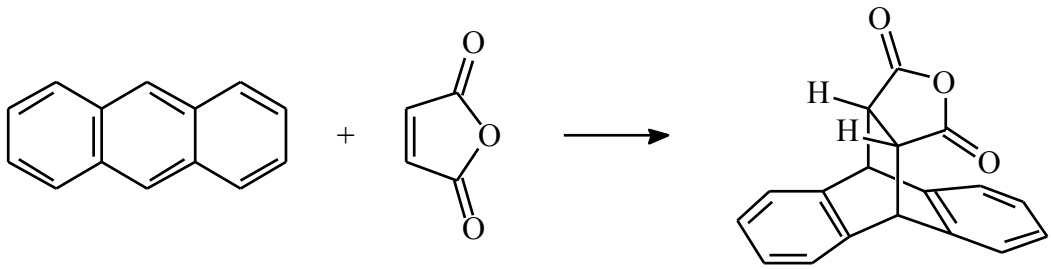
# 20 A Diels-Alder Reaction

The Diels-Alder reaction is an important synthetic tool because it produces new six-membered rings with a high degree of stereoselectivity. The assigned readings cover the theory and background of the reaction. In our experiment, the diene is anthracene, the dienophile is maleic anhydride, and the product is 9, 10-dihydroanthracene-9, 10-α,β-succinic acid anhydride, also referred to simply as product.

The reaction will be carried out in refluxing xylene. The products will be isolated by vacuum filtration and analyzed by TLC.




**PRE-EXPERIMENT ASSIGNMENT**

Study this chapter of the manual, section 17.7 in Klein and the lecture notes on the Chemistry Department web site. Be sure to review the procedures and theory relating to TLC analyses from 2230L. Do the first 7 parts of your notebook write-up.

**A student who has prepared for the Diels-Alder experiment should be able to:**

1. Define, recognize, and explain the following: Diels-Alder reaction, concerted reaction, diene, dienophile, adduct, *s-cis*, *s-trans*, *exo*, *endo*, anhydride (and give an example of the last of these).
2. Give the equation for the reaction between anthracene and maleic acid.
3. Calculate the theoretical yield and the percent yield for this and similar experiments given the necessary data, and perform any of the intermediate calculations required by this process.
4. Draw the structure given the name, or give the name from the structure, of the compounds used in the day's experiment, and give the role of each (reactant, solvent, catalyst, etc.).
5. Identify and explain safety considerations for this experiment.
6. Be able to explain the theory and practical aspects of analyzing materials using TLC. (Review sections from 2230L)
7. Perform the day's experiments safely and successfully.

Quizzes given after the experiment has been performed may also include:

7. Explain and interpret features of the experiment, including: The disappearance of the yellow color during the reaction, the consequences of failure to dry the product completely, the formation of the solid after cooling solution.
8. Correctly interpret TLC results. Calculate Rf values.
9. Given the structures of two of the compounds involved in a Diels-Alder reaction (diene, dienophile, adduct), predict the third.
9. Predict the relative rates of reactions of given dienes and dienophiles. Important considerations include: Endo products are favored over exo, though this is not an absolute preference. Diels-Alder reactions are faster when: a) The starting diene is conjugated and in the s-*cis* conformation (otherwise they don't work at all). b) Either the diene has electron-releasing (usually alkyl) groups attached to it and the dienophile has electron-withdrawing groups attached to it; or c) the diene has electron-withdrawing groups and the dienophile has electron-releasing groups. (Note: Using method c is less common and the starting materials are unusual.)
10. Define and/or explain *[4+2]-cycloaddition*.

**Safety Precautions**

Xylene is a flammable organic solvent. Do not have any open flames or sparking devices in the vicinity of the reaction. Do not allow the reflux ring to move too far up the neck of the test tube or boiling flammable xylene will overflow. Xylene vapors are a central nervous system (CNS) depressant. Keep vapors to a minimum. Heat test tubes in chemical fume hood. Maleic anhydride is a skin irritant. Wash skin if contact is made. Maleic anhydride is toxic when inhaled or ingested. Do not eat or breathe. Anthracene may cause irritation to eyes, skin and respiratory tract.

The test tube will contain very hot liquid. Handle with care. Let test tube cool to room temperature before handling.

**The Reaction**

Turn your sand bath on and set it to about 40. Obtain about 0.08 g of anthracene, 0.06 g of maleic anhydride, about 1 mL of xylene, and a boiling chip and add them to a large test tube. (Remember to not waste time getting exact target amounts, but to record exactly how much material was obtained directly in notebook.) Clamp the tube to a ring stand and heat the reaction mixture for 40 minutes.

The liquid in the bottom of the test tube will boil, but the vapors formed will condense in the cooler portion of the test tube and the liquid will return to the bottom. This is known as refluxing. Make sure that the reflux ring, the region where the vapors are condensing, stays below the middle of the test tube at all times. During this time the yellow color of the mixture usually becomes lighter. (Why should the reflux ring be kept below the middle of the test tube?)

A thermometer is not needed during the reflux, yet the temperature remains at a constant. Why? What temperature is the solution?

After 40 minutes have passed, allow the reaction mixture to cool to room temperature. Then cool it in ice for ten minutes to complete the crystallization of the product.

**The Workup**

Set up an apparatus for suction filtration using the 25 mL filter flask and the Hirsch funnel from your kit. (Make sure that there is a frit in the funnel before you put in the filter paper.) Be sure to clamp the apparatus so it won't tip over. Apply the vacuum and pour your reaction mixture into the funnel. Once the solvent has passed through the funnel, add 12 drops of cold ethyl acetate to rinse the test tube, and then transfer it to the crystals on the filter paper. The vacuum will remove the ethyl acetate. Repeat the washing with a second portion of ethyl acetate. Continue to run the vacuum for a few minutes longer to air-dry the crystals. Weigh the product and calculate percent yield.

**The Analysis: TLC**

Obtain a TLC plate. Dissolve a small amount of product in a shell vial in about 10 drops of acetone. Cap the shell vial and shake for a full minute. Spot the TLC plate with 1) an authentic maleic anhydride sample 2) and authentic anthracene sample and 3) product. Develop the TLC sample using provided 80:20 hexane: ethyl acetate solvent. The spots are not visible by the naked eye. Observe spots under UV light. Circle each spot and place a small dot in the center of each. Note the appearance of the spots. Calculate the Rf value of each.

**CLEANUP**

Used and excess solvents are placed in the non-halogenated liquid waste bottle in the hood. The Diels-Alder adduct is placed in the non-halogenated solid waste bottle. Used Pasteur pipettes and melting-point capillaries are placed in the broken glass box.

**POST-EXPERIMENT ASSIGNMENT**

Write the lab report and have it ready to turn in by the beginning of the next lab. Your Calculations section should show how you calculated the theoretical and percent yields. Your Conclusions section should state whether you successfully made the adduct and the percent yield. If your percent yield was not 100%, you should explain where the missing material might have gone (or where extra material might have come from). Explain the TLC results and the observed purity of the product. Prepare for the Diels-Alder portion of the next quiz.