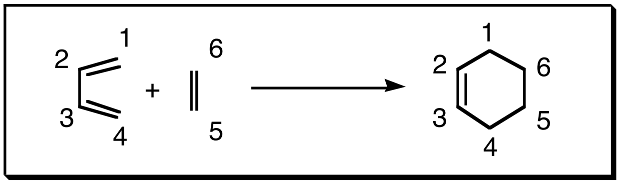
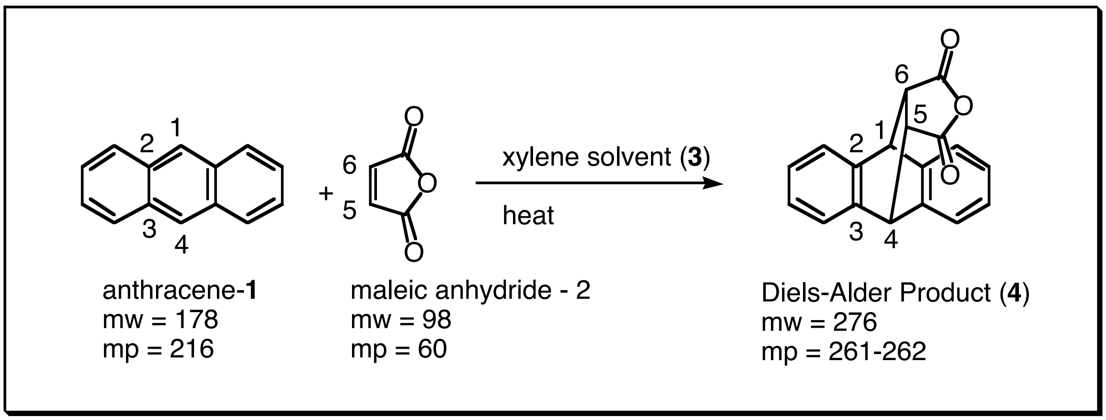
Diels-Alder Reaction

General Diels-Alder Reaction: A conjugated "diene" reacts with a "dienophile" to produce a cyclohexene ring. The "dienophile" is activated by electron-withdrawing substituents (carbonyls). The diene must be in a "cisoid" conformation in order to react. Attachments to the reactants remain attached as spectator atoms.





Overview of Actual Reaction: Anthracene (1) will serve as a student-friendly low-smell Diels-Alder diene, with the labeled carbons functioning as the reactive diene. Maleic anhydride (2) will function as the dienophile. Xylene (dimethylbenzene) is used as a high-boiling solvent so that the reaction will work fast enough to complete conveniently. In terms of activation, notice that maleic anhydride is a highly reactive dienophile, due to the presence of two electron-withdrawing carbonyl substituents. Anthracene, however, is an unusually unreactive diene. This is due to both steric effects, but more importantly because the "diene" is really part of an aromatic ring system and is thus stabilized. This stabilization in the reactant reduces the reactivity (stability/reactivity principle). The "cyclohexene" ring produced in every Diels-Alder reaction is hard to visualize, but consists of the six labeled atoms in the product.

Reagents and Equipment: Add boiling chips to a 25-mL round-bottomed flask. Flame dry the flask. Weigh and place 0.80g of anthracene and 0.40g of maleic anhydride into the flask (both are solids). Attach a reflux condenser, and attach a drying column on top to exclude wet air (similar to what was done in the Grignard experiment). Carry the apparatus to the hood (carefully), remove the reflux condenser/drying column, add 10mL of xylene via buret to the round-bottomed flask, and immediately place the reflux condenser/drying column back onto the flask. Return the system to your bench, and clamp it securely at the neck of the flask.

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Reaction Conditions: Heat the reaction mixture in a heating mantle or in a heating mantle/sand bath to "reflux" (until it boils steadily). This should be around 185-200˚C. If you use a sand bath, it will be helpful to begin heating this and trying to establish a steady temperature as soon as you enter the lab; sticking a thermometer into the sand will help you measure how hot it is. Reflux the solution for 30 minutes, during which time the yellow color of the reaction mixture should gradually disappear. (Write up your report while you wait!) Allow the solution to cool to room temperature, then place it in an ice bath for 10 minutes to complete the crystallization of the product.

Isolation of the Product: Collect the crystals by vacuum filtration using a Buchner funnel. Wash twice by the following sequence: disconnect the aspirator, add 3 mL of ethyl acetate, and reconnect the aspirator. Let dry for at least one day before taking the melting point and weighing the product for a yield calculation.

Caution: Xylene and ethyl acetate are both strong smelling chemicals. Be very careful to rinse them out only in the hood. And be very careful to keep them covered to reduce fumes.

Lab Report: Should follow the standard synthesis layout. (See website and/or handout)
1) Draw the chemical equation
2) Write down each chemical used and the quantity.
3) For the diene and the dienophile, determine the numbers of moles used. (One or both of these will be the limiting reactant, and thus their moles factor into yield calculations). Neither the original solvent nor any wash solvents need any mole calculations. (These are not limiting, so they have no yield impact).
4) Identify the limiting reactant, and calculate the theoretical yield.
5) Write up the procedure followed, including descriptive information (times, temperatures, color changes). This should be in past tense: what you actually did, and what you saw.
6) Report the observed melting point
7) Report the observed mass yield.
8) Calculate the actual percent yield.

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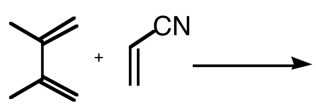
Name:

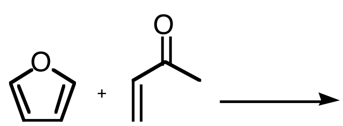
<u>Questions:</u>

1. Maleic Anhydride is an <u>exceptionally reactive</u> dienophile. Why?

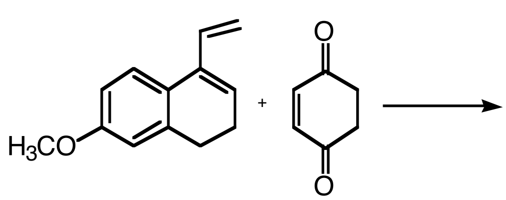
2. Anthracene is an <u>unusually unreactive diene</u>. Explain why? (Two factors, actually…)

3. Draw the products of the following Diels-Alder reactions.





4. Draw the product of the following Diels-Alder reaction. Note: One can imagine the left reactant potentially providing more than one "diene" group. You may wish to consider why one diene group might be more reactive than any others (or conversely why other diene groups might be less reactive …).



5. What starting materials would be used to prepare the following compound by the Diels-Alder reaction?