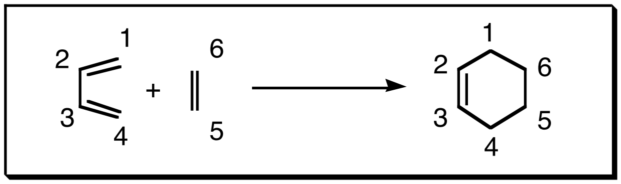
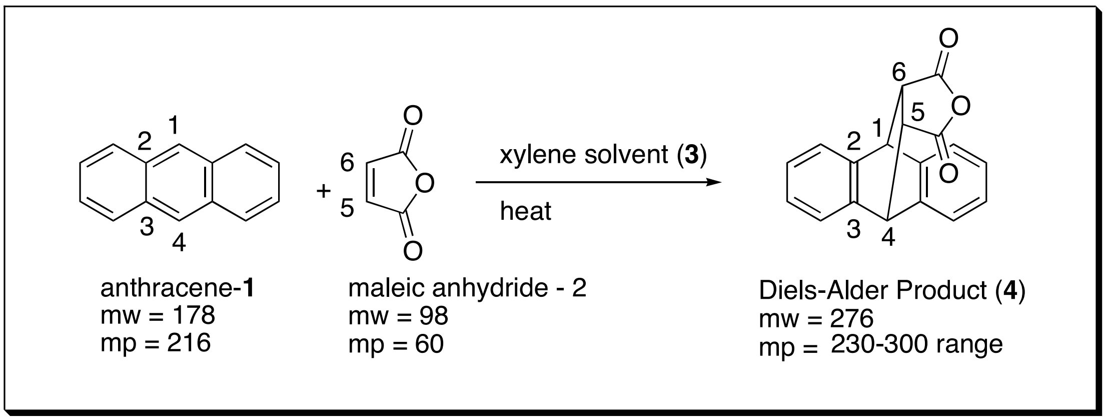
Diels-Alder Reaction

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: When you first get into lab, set up a heating mantle/sand bath and begin to warm it to 180-200ºC. Use a small heating mantle, and fill it about half-way with sand. Plug it into one of the bottom two outlet plugs. Put a 300º-type thermometer into the sand bath; the thermometer should be supported by a steel ring so it doesn't tip over and break! A power setting of somewhere in the 35-50 range may eventually sustain your bath temperature in the 180-200º range, but this will vary with different heating mantles. Keep an eye on the thermometer temperature so that it doesn't get too hot.

Flame dry a 25-mL round-bottomed 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.

Reaction Conditions: Bury your round-bottom flask into your sand bath. It may be helpful to use a spatula to move some of the sand aside so that you can get the flask in. Heat the reaction mixture in a heating mantle to “reflux” (until it boils steadily). If it isn’t boiling, either bury it deeper into the sand, or increase the temperature of the bath. Note: it is not necessary that the bath be hot prior to putting the reaction mixture in. The ideal temperature should be around 185-200˚C, and the thermometer should give you an idea of what you are actually working at. But the real key is to be hot enough for things to boil; if it’s hot enough to boil, things should work. Reflux the solution for 30 minutes, during which time the yellow color of the reaction mixture should lighten. (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. Make up a mixture of 4 mL ethyl acetate and 4 mL of hexane in a grad cylinder. Disconnect the aspirator, add half of the ethyl acetate/hexane mixture, and reconnect the aspirator. Repeat this sequence again with the other half. Vacuum dry for at least 8-10 minutes before weighing the product for a yield calculation and taking the melting point.

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)

- Draw the chemical equation
- Write down each chemical used and the quantity.
- 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).
- Identify the limiting reactant, and calculate the theoretical yield.
- 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.
- Report the observed melting point
- Report the observed mass yield.
- Calculate the actual percent yield.

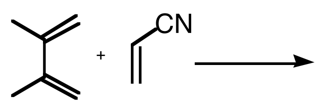
Name:

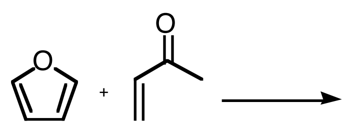
Questions:

1. Maleic Anhydride is an exceptionally reactive dienophile. Why?

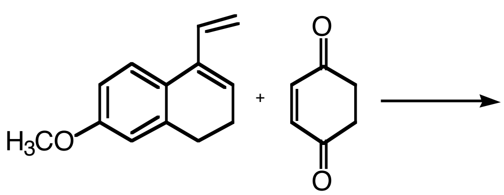
2. Anthracene is an unusually unreactive diene. Explain why? (Two factors, actually…)

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?