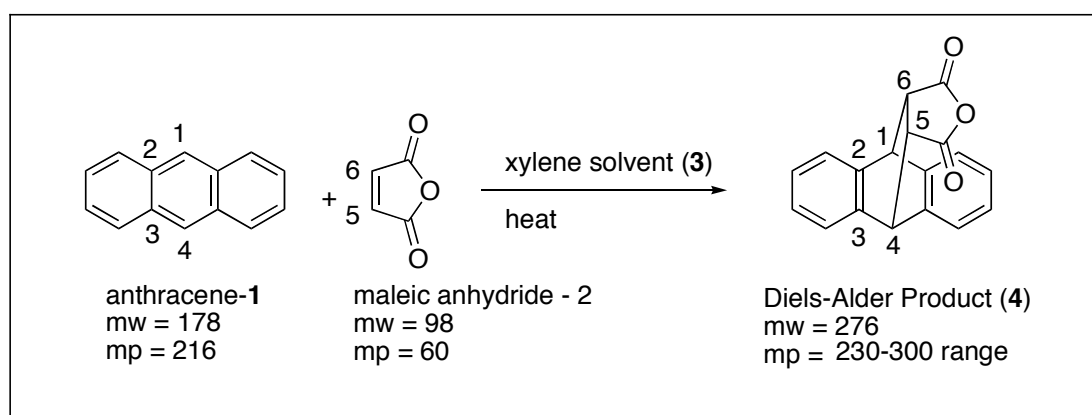
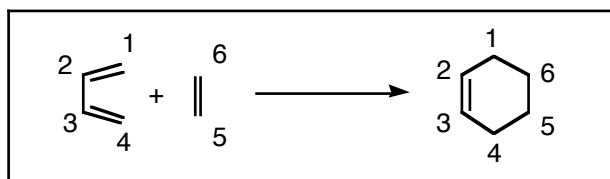


Diels-Alder Reaction

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.

Reaction Setup: Flame dry a 25-mL round-bottomed flask with a small stir bar. (The maleic anhydride is slightly water sensitive). Weigh out 0.80g of anthracene and 0.40g of maleic anhydride (both are solids). Add the two solids into the flask. (Be sure the flask has cooled for at least two minutes before adding the solids, or they will melt.) Carry the round-bottomed flask to the hood (carefully), and add 10mL of xylene via buret. Carry the mixture back to your hood, and clamp the flask very securely above a hot-plate/stir-plate near a sink. Attach a reflux condenser, and tubing so that water can flow through the condenser. (The array needs to be set up near a sink so that the tubes will reach.)

Reaction Conditions: Turn the magnetic stirrer on, then warm the solution to “reflux” (until it boils steadily) by initially setting your hot plate to setting 8 (for the heater, not the stirrer). Note: the boiling point for the xylene solvent is 138°; the actual temperature is actually somewhat

hotter than that, because the dissolved solutes elevate the boiling point to some degree. Once the solution has begun to reflux, reduce the heat setting to 5, or whatever it takes to maintain a gentle boil. Reflux the solution for 30 minutes. (Write up your report while you wait! Be sure to include observational details, including colors and color changes and solubilities and solubility changes.) 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.

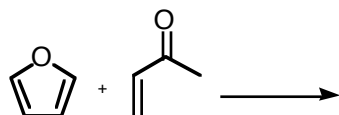
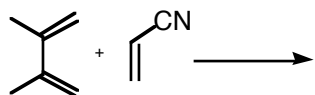
Lab Report: Should follow the standard synthesis layout. (See website and/or handout)

- 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.

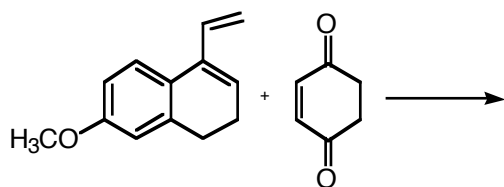
Name:

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?

