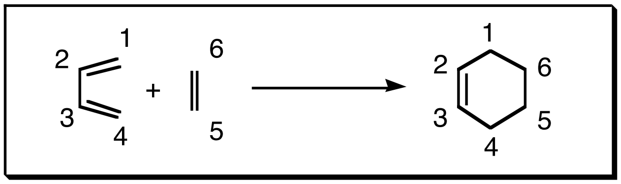
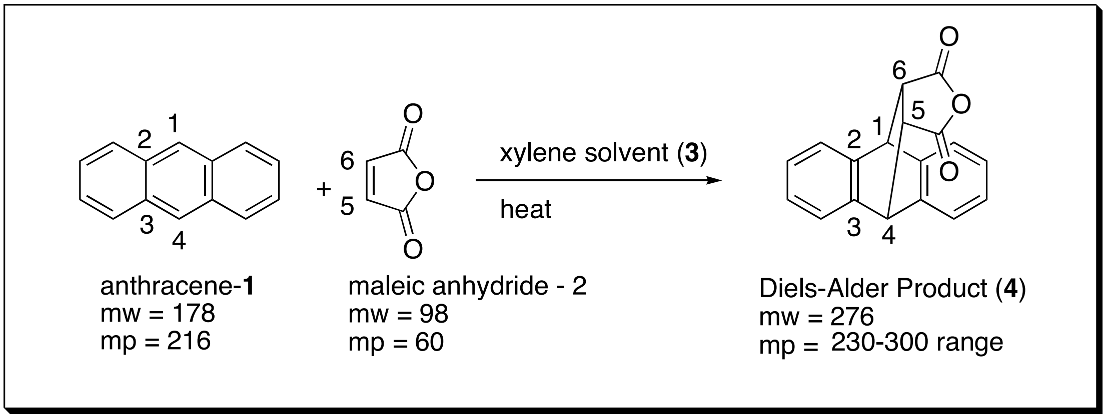
Diels-Alder Reaction

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: Use a dry a 25-mL round-bottomed flask with a small stir bar. Clamp the flask very securely above a hot-plate/stir-plate near a sink. Weigh out 0.80g of anthracene and 0.40g of maleic anhydride (both are solids) and add them to the flask. Add 10mL of xylene via syringe. (The xylene will be in the liquids-dispensing hood. Return the xylene syringe after injecting, so that other students can use it!) Attach a reflux condenser to your flask, 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. The water should enter the bottom connector; the hose from the top connecter should flow into the sink.)

Reaction Conditions: Turn the magnetic stirrer on, then warm the solution to "reflux" (until it boils steadily) by setting your hot plate to setting 8 (for the heater). Note: the boiling point for the xylene solvent is 138º; the actual temperature is actually somewhat hotter than that, because the dissolved solutes elevate the boiling point to some degree. 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 for 10 minutes, 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. Try to crush any chunks. 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)

- Note: the "Standard Synthesis Layout" used a different reaction as an example.
- Adapt your report to the actual reaction you're doing today. This obviously will involve showing the reactants and products involved in the actual reaction!
- 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.

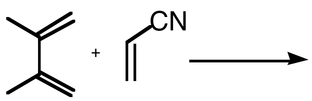
Name:

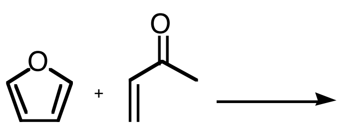
Questions:

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

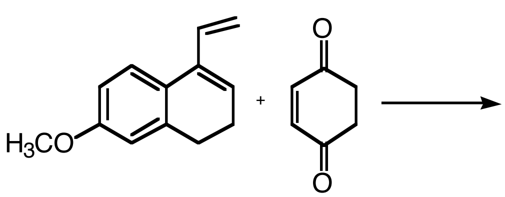
2. Anthracene is an unusually unreactive diene. Explain why? (Two factors, actually…)

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

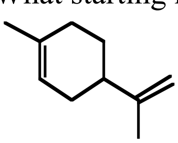




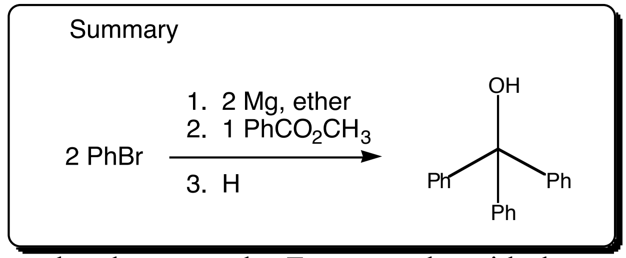
4. Draw the product of the following Diels-Alder reaction. Note: One can imagine the left reactant potentially providing more than one "diene" group. You may wish to consider why one diene group might be more reactive than any others (or conversely why other diene groups might be less reactive …).



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



Standard Synthesis Laboratory Report Format: The following layout is standard for a "synthesis reaction" report. Provide the parts and information in the sequence specified.



1. Title = Reaction Summary
For an organic reaction, there is no point in having a Worded Title: The chemical reaction is the best title summary of what you did!

2. Listing of all Chemicals Used
- This should include all chemicals used, including solvents.
- For each chemical, you should include the actual quantity used and measured. For example, with the methyl benzoate you measured a volume by syringe, rather than by weighing on a balance. So you should list the volume you actually used rather than just the weight.
- For reactants that might possibly be limiting reactants and might possibly factor into calculation of the theoretical yield, you must include more than just the quantity of chemical used. You should also include a conversion from what you measured into the number of moles used.
- In some cases, there may be considerable roundoff (you needn't keep precise record of the quantity of solvent that was used, for example, or of sodium sulfate drying agent…)
- If a person was later to repeat your experiment, they should be able to look at this list and know all the chemicals they'd need to have on hand and in what quantities, in order to complete the experiment.

3. Calculation of Theoretical Yield
- Specify which chemical is the limiting reactant
- Given moles of limiting reactant, calculate theoretical moles of product
- Given moles of product, calculate theoretical grams of product.
- Note: Why do this so early in report?
    - First, because it fits in near your mole calculations above.
    - Second, if calculated in advance. as with most research, you know which chemical is limiting and thus must be measured most carefully, but you also know which are in excess and thus need not be measured with equal precision.
    - Third, it's nice to know approximately how much material is expected, so you can recognize whether your actual results are reasonable or problematic.

4. Writeup of Actual Procedure.
- For this particular experiment, the "procedure" section will be by far the biggest portion of your report.
- This should be a concise but detailed description of things, including:
    - What you actually did (even if not recommended or not from recipe)
    - All observations should be included. These include all observed changes, such as:
        - Changes in **color**
        - Changes in **solubility** (formation of precipitate or cloudiness…)
        - Changes in **temperature** (like, reaction became hot…)
        - Formation of **bubbles**
    - Time and temperature details:
        - Whenever you heat something or cool something, the procedure should specify
        - Specify times. Whether you boiled for 5 minutes or 5 hours matters!
- Writing details: As a record of what actually happened, the report must be written in **past tense**, not **command tense**. (Rather than "Add this", should read "I added this", or "I dropped that…")
    - Use of personal pronouns is accepted in this class. You may use "I" or "we" to simplify writing.

5. Product Analysis
- Any NMR, mp, bp, TLC information. For this report, mp and TLC information must be included.
- Final yield and percent yield information.

6. Discussion/Summary. Need not be long, but any conclusions or excuses would go here…

7. Answers to any assigned Questions