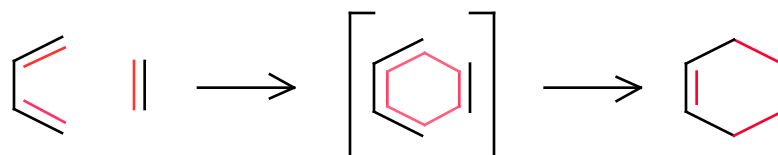


Reminder: These notes are meant to supplement, not replace, the textbook and laboratory manual.

A Diels-Alder Reaction

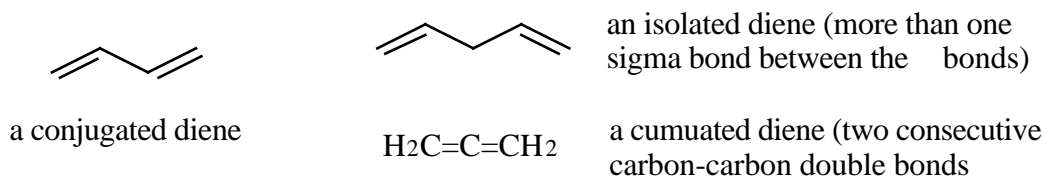
1. The Diels-Alder reaction is a member of a class of reactions called cycloadditions. In all Diels-Alder reactions, three bonds, two in a diene and one in a dienophile, reorganize to give a six-membered ring containing one bond and two new sigma bonds. The illustration shows the bonds that change in red. The structure in the center is the transition state.



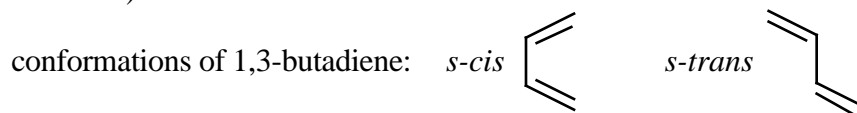
Some terminology related to the Diels-Alder reaction:

A *concerted reaction* is one in which all of the electrons move at the same time. The Diels-Alder reaction is a concerted reaction. Other examples: S_N2 and E2 reactions are concerted. In contrast, S_N1 and E1 reactions are not, because they involve the formation of an intermediate (a carbocation).

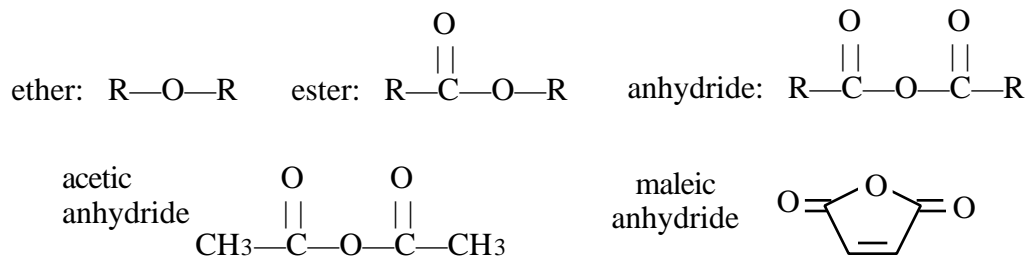
In a Diels-Alder reaction, a *conjugated diene* (a compound in which a carbon-carbon double bond is followed by a carbon-carbon single bond and then another carbon-carbon double bond) reacts with a *dienophile* (a compound containing a bond that reacts with a diene) to give a product called an *adduct*.



Many dienes can assume more than one conformation; that is, they have forms that can change from one to the other by rotation around single bonds. In 1,3-butadiene (shown here), the *s-cis* conformation changes to the *s-trans* conformation by rotation of the single bond between the bonds. (Note: Dienes react to form Diels-Alder adducts only in the *s-cis* conformation.)

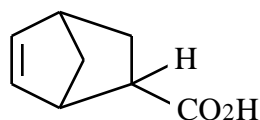


Anhydrides are compounds that have two acyl groups attached to an oxygen. They can be thought of as relatives of ethers and esters, as shown here. Anhydrides can be cyclic or not, as illustrated by the examples below.

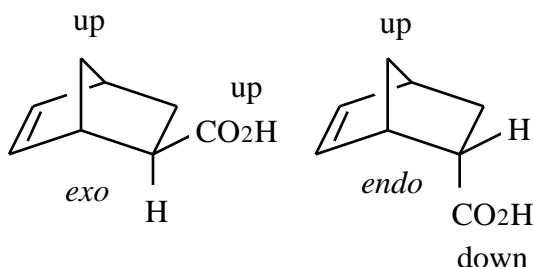


Many adducts have two stereoisomers, the *endo* and the *exo*. These are stereoisomers, not conformations, because bonds must be broken and formed to convert one to another.

top view of a
Diels-Alder
adduct

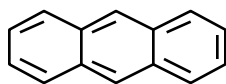


side views of
the same
compound

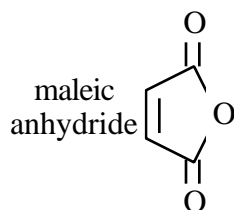


In an *exo* isomer, the group (CO_2H in this case) is on the same side of the central ring of the molecule as the shorter of the two bridges, as indicated above. In an *endo* isomer, the group is on the same side as the longer bridge.

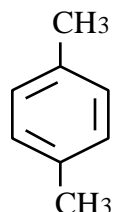
- The equation for the reaction between anthracene and maleic anhydride is given on page 82 of the lab manual (6th edition).
- It is necessary to calculate a percent yield for this experiment. For instructions and examples on how to do this, see the sample problems with solutions on this web site.
- Here are the structures of compounds involved in this experiment. Anthracene and maleic anhydride are reactants, xylene is a solvent, ethyl acetate is used to wash the crystals, and ethanol and acetone are often used to wash glassware. The compound at the bottom is the product of the reaction.



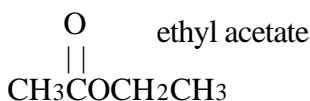
anthracene



maleic
anhydride



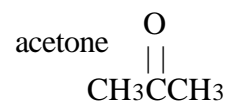
this is *p*-xylene,
one of three
xylene isomers



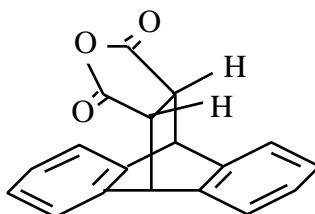
ethyl acetate



ethanol



acetone



9,10-dihydroanthracene-9,10- , -succinic acid anhydride

5. Safety considerations for this experiment include:

All of the compounds involved in this experiment are at least slightly toxic, and all four of the solvents are highly flammable. Handle them with the usual precautions.

You will be using a sand bath and a Mel-Temp apparatus during this experiment. As you know by now, portions of both of these pieces of equipment become very hot during normal use. Handle them with care, and don't touch the hot parts. They also use electricity; do not use water or other solvents carelessly around them. If the wires on any electrical apparatus are frayed, the shock and fire hazards are multiplied; do not use the apparatus.

Notes for topics that may be included in quizzes given after the experiment:

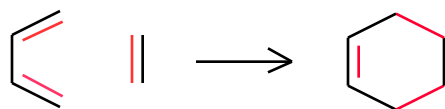
7. Some features of this experiment include:

If you fail to dry the product completely, it will include some solvent and water, and you will calculate a percent yield that is unrealistically high, possibly over 100%.

Leftover solvent is not likely to have an effect on the melting point range, since it will probably evaporate before the melting point (which should be over 250°) is reached.

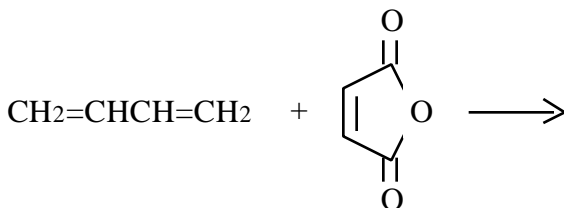
You are not responsible for explaining why the yellow color of the reaction disappears. That was included in the lab manual by accident.

8. In predicting the product of Diels-Alder reactions or devising syntheses using it, remember that all Diels-Alder reactions work this way:

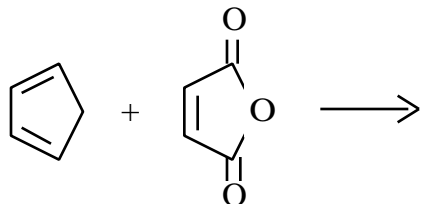
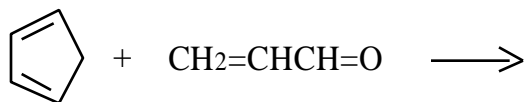


That is, the three pi bonds of the reactants move to give two sigma bonds and a pi bond in the cyclohexene ring of the product. Any group attached to the six carbons of the three rings is carried along for the ride. *Endo* products are formed rather than *exo* when there is a choice. Here are some sample problems; answers (with hints) will be given on a later page.

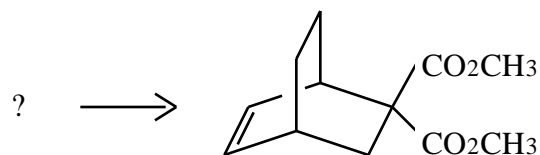
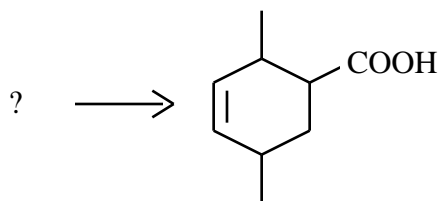
a) Predict the product of each of these reactions:



a) Predict the product, continued.



b) Identify the starting materials that can be used to produce the compounds shown using a Diels-Alder reaction..



9. To predict the relative rates of reaction of dienes, use these rules.

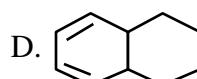
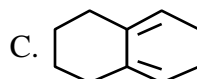
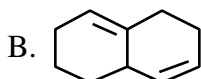
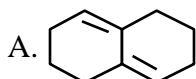
Only conjugated dienes react as dienes in Diels-Alder processes. Isolated and cumulated dienes may react as dienophiles, but they cannot react as dienes.

Dienes in the *s-trans* conformation do not react in Diels-Alder reactions. Acyclic dienes may rotate around a single bond to become *s-cis*, but some dienes are locked in the *s-trans* conformation in cyclic structures and cannot react.

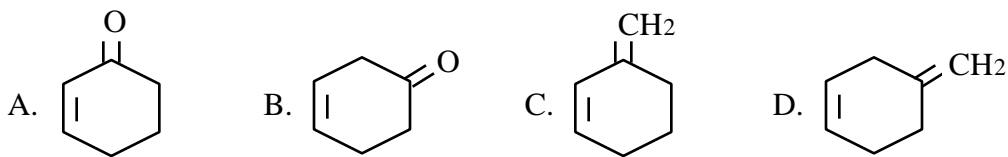
Dienes containing electron-releasing groups (usually alkyl groups) react faster, especially with dienophiles that contain electron-withdrawing groups (almost always groups that contain electronegative atoms). The opposite combination also gives relatively fast reactions, but the starting materials are unusual.

Here are some sample questions. Answers will be given on a later page.

a) Which of these dienes gives the FASTEST reaction with maleic anhydride?



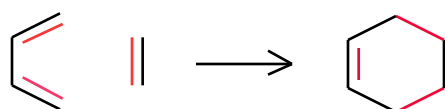
b) Which of these dienophiles gives the FASTEST reaction with cyclopentadiene?



10. A [4+2]-cycloaddition is a reaction in which a compound containing four electrons reacts with a compound containing two electrons to form a new cyclic compound. A Diels-Alder reaction is a [4+2]-cycloaddition.

ANSWERS TO QUESTIONS (with hints):

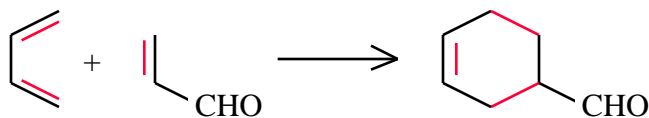
8. a) In predicting the products of reactions, remember the general reaction:



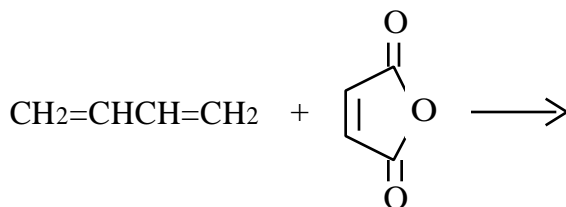
For the first problem, the $\text{CH}_2=\text{CHCH}=\text{CH}_2$ is the diene and the $\text{CH}_2=\text{CHCH}=\text{O}$ is the dienophile. Take the starting materials:



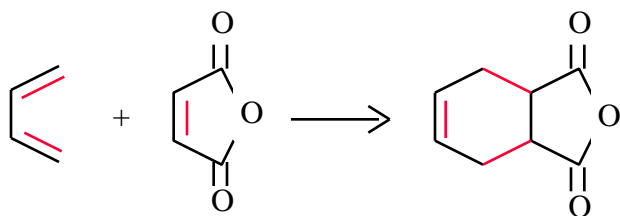
Write them as bond-line formulas to correspond with the ones in the general reaction. Move the electrons around to make a six-membered ring, and there's your product. There is only one ring, so there are no *endo* and *exo* isomers.



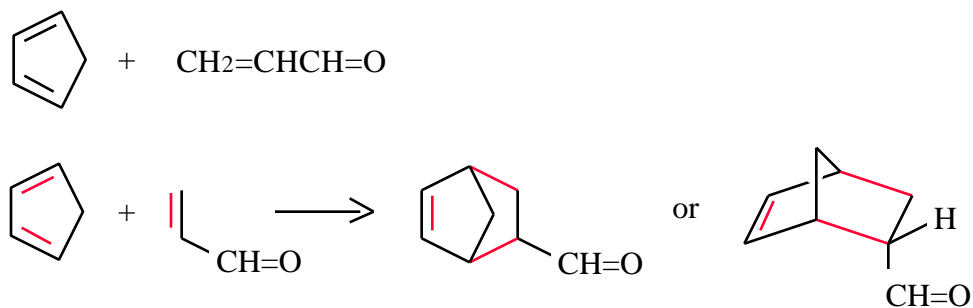
The starting diene in the second problem is the same as the one in the first problem. The dienophile is the familiar maleic anhydride.



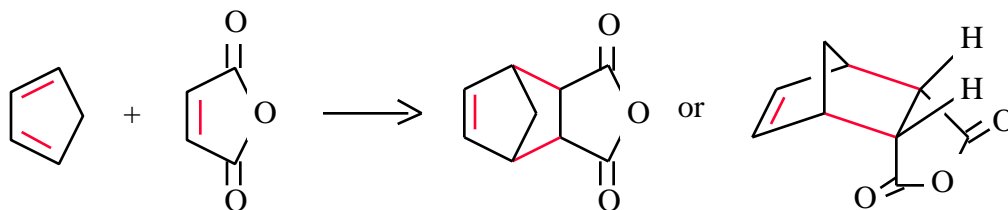
Write the diene structure as a bond-line formula and proceed as usual.



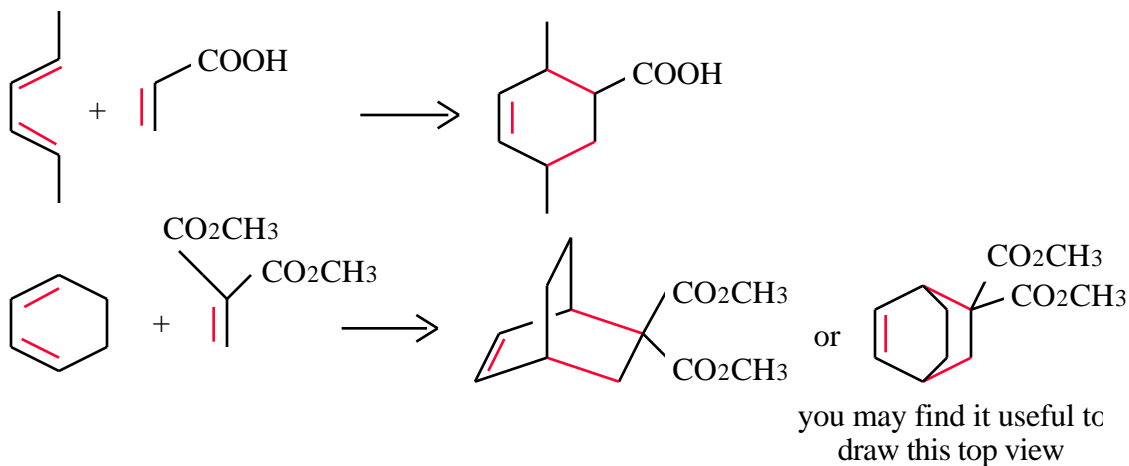
The starting dienophile in the third problem is the same as the one in the first problem. The starting diene is cyclopentadiene. Write the bond-line formula for the dienophile and proceed as usual. The CH₂ group in the cyclopentadiene just goes along for the ride. A side view of the product can be used to show that it is *endo*.



The starting dienophile in the fourth problem is the same as the one in the second problem. The starting diene is cyclopentadiene. The bond-line formulas are already written: Once again the side view shows that the product is *endo*.



b) To identify the starting materials, find the cyclohexene ring in the product and move its bonding electrons around to figure out what the starting materials were.



9. a) A is *s-trans*, and B is isolated; neither gives a Diels-Alder reaction. C has more electron-donating alkyl groups attached to its sp² carbons, and therefore reacts faster than D.
 b) A and B both contain electron-withdrawing carbonyl groups, and they'll therefore react faster than C and D. A has a carbonyl group closer to the carbon-carbon double bond that actually reacts, and is therefore the fastest-reacting dienophile.