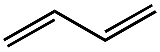
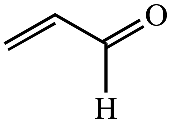
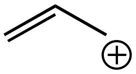
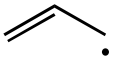
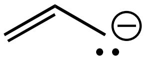
Lecture Notes
Chem 51B
S. King

Chapter 16 Conjugation, Resonance, and Dienes

I. Conjugation

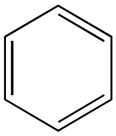
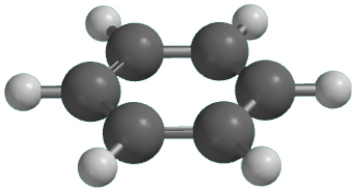
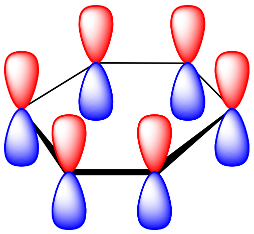
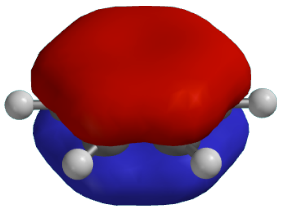
Conjugation occurs whenever *p*-orbitals can overlap on three or more adjacent atoms.

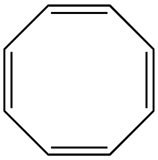
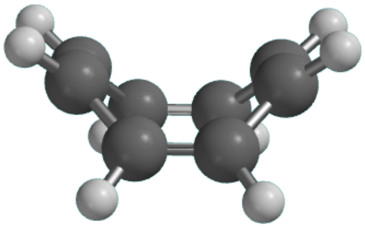
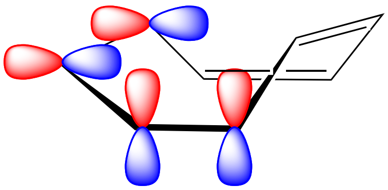



- Conjugated systems are more stable than non-conjugated systems because they are resonance stabilized.
- When *p*-orbitals overlap, the e^- density in each of the π-bonds is spread over a larger volume. This lowers the energy and stabilizes the molecule.
- To delocalize non-bonded electrons, or electrons in π-bonds, there must be *p*-orbitals that can overlap. This may mean that the hybridization of an atom is different that would have been predicted using the rules outlined in chapter 1.
- Conjugated systems must be planar to allow overlap of adjacent *p*-orbitals.

Compare:

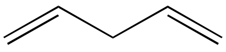





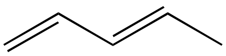
A. Relative Stabilities of Conjugated Dienes

Experimental heats of hydrogenation of isomeric dienes can be used to compare their relative stabilites. When hydrogenation gives the same alkane from two different dienes, the *more stable* diene has the *smaller* heat of hydrogenation

Compare:



$$+ \; H_2 \xrightarrow[\text{catalyst}]{\text{Pt}} CH_3CH_2CH_2CH_2CH_3 \qquad \Delta H^\circ = -61 \; \frac{\text{kcal}}{\text{mole}}$$

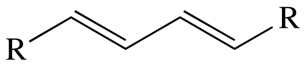


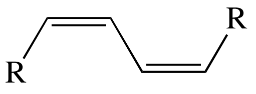
$$+ \; H_2 \xrightarrow[\text{catalyst}]{\text{Pt}} CH_3CH_2CH_2CH_2CH_3 \qquad \Delta H^\circ = -54 \; \frac{\text{kcal}}{\text{mole}}$$

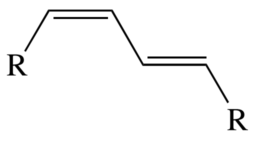
Shown graphically:

B. Conformations of Conjugated Dienes

There are three possible stereoisomers for a conjugated diene:



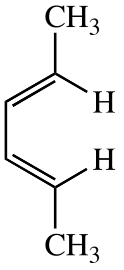


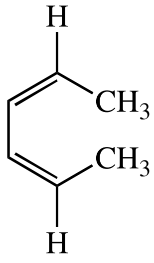


There are two possible conformations that result from free rotation about the C–C single bond *(remember: double bonds cannot rotate!)*

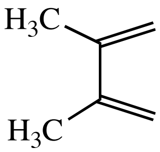
s-trans conformation: Double bonds are *trans* about the single bond.

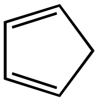
s-cis conformation: Double bonds are *cis* about the single bond.





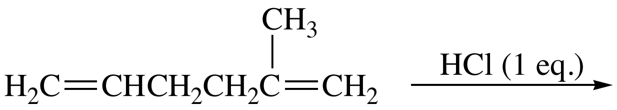
Most conjugated dienes prefer the ***s*-trans conformation.** *Some exceptions:*



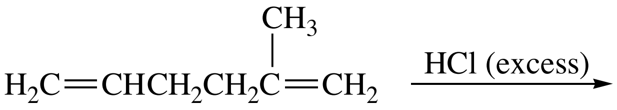


II. Electrophilic Addition Reactions of Isolated Dienes

Isolated dienes react exactly like alkenes. If an excess of electrophilic reagent is used, two independent addition reactions will occur. If only one equivalent of electrophilic reagent is added, it will add to the more reactive double bond.



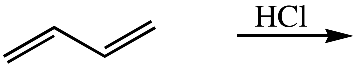
$$H_2C{=}CHCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \xrightarrow{\text{HCl (1 eq.)}}$$



$$H_2C{=}CHCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \xrightarrow{\text{HCl (excess)}}$$

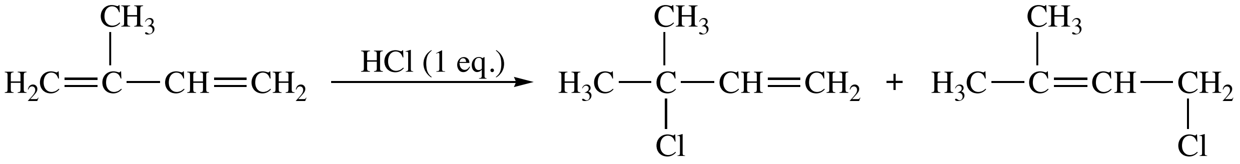
III. Electrophilic Addition Reactions of Conjugated Dienes: 1,2 and 1,4 Addition

Addition of one equivalent of HCl to a conjugated diene gives two products:



Mechanism:

☛ If the conjugated diene is not symmetrical, the major products of the reaction result from addition to the most reactive double bond *(the one that forms the more stable carbocation.)*



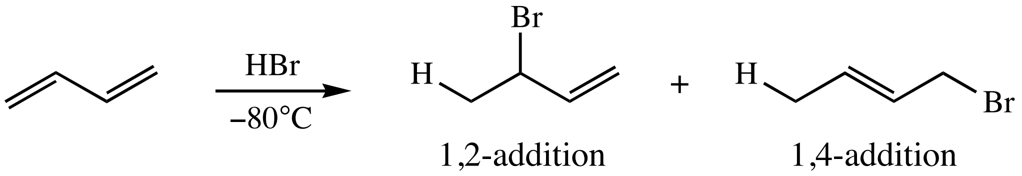
$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2 \xrightarrow{\text{HCl (1 eq.)}} H_3C{-}\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH{=}CH_2 + H_3C{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH{-}\underset{\underset{\displaystyle Cl}{|}}{CH_2}$$

A. Kinetic *vs.* Thermodynamic Products

When a reaction produces more than one product, the product that is formed more rapidly is the **kinetic product**, and the product that is the most stable is the **thermodynamic product**.

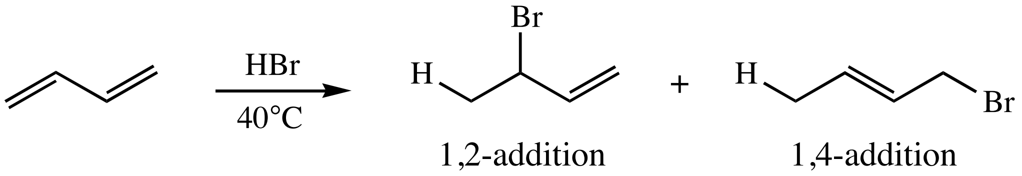
- ✦ *The product that is formed faster is called the* kinetic product.
- ✦ *The product that predominates at equilibrium is called the* thermodynamic product. *It is the most stable product.*

For many organic reactions, the most stable product ***is*** the one that is formed more rapidly – that is, the kinetic and thermodynamic product are the ***same***. For electrophilic addition of HX to a conjugated diene, however, the most stable product is formed ***more slowly*** – that is, the kinetic and thermodynamic product are ***different***.



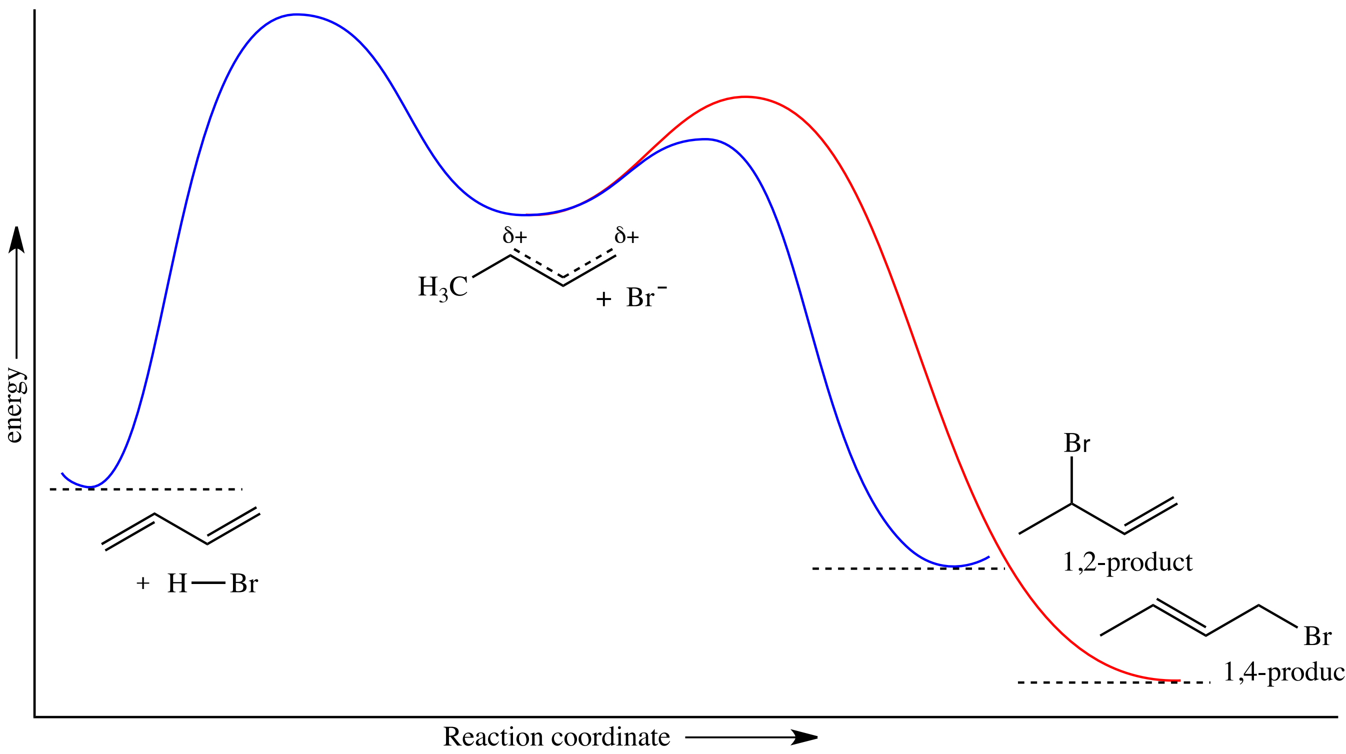
Look **at the effect of temperature**:

If you allow the reaction mixture to warm up to 40°C, or if you run the reaction at 40°C, you get a different product distribution:



Q. Why does the product distribution change?

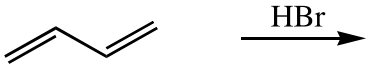
A. Look @ the energy diagram:



- At –80°C, there is not enough energy for the reverse reaction to occur, ∴ the product that forms fastest *(the one with the smallest E_a)* will predominate.
- At 40°C, there is enough energy for the reverse reaction to take place (the products can revert back to the **common intermediate.**) The products can now interconvert to form a thermodynamic mixture.
- The thermodynamic product reverses less readily because it has a larger energy barrier that the kinetic product.
- Thus, when a reaction is *irreversible* under the conditions of the reaction, it is said to be under **kinetic control**, and the relative amounts of the products formed will depend on the rates at which they are formed.

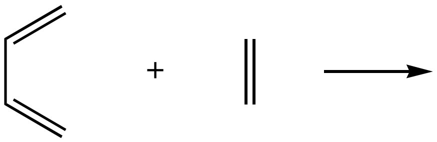
- A reaction is under **thermodynamic control** when there is sufficient energy to allow it to be reversible. The relative amounts of the products formed will depend on their stabilities.

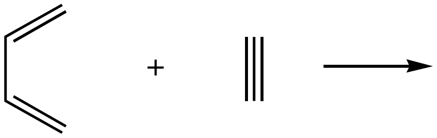
Why is the 1,2 product formed more rapidly?



IV. The Diels-Alder Reaction

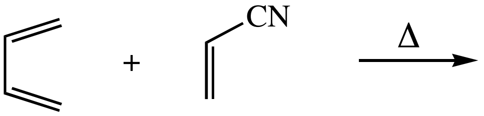
Alkenes and alkynes add to conjugated dienes to form 6-membered rings:

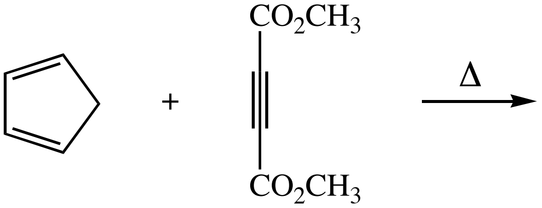




- The alkene or alkyne is called a **dienophile** *(lover of dienes)*
- The reaction is a **[4 + 2] cycloaddition** because a ring is formed by the interaction of 4π e^-‘s in the diene with 2π e^-‘s in the alkene or alkyne.

Examples:





Characteristics of the Diels-Alder Reaction:

A. Mechanism:

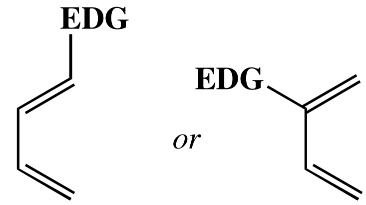
This is a concerted reaction:

- Reactant bonds are broken & product bonds are formed at the same time.
- The mechanism does not involve radical or ionic intermediates.

B. Substituent effects:

The most reactive dienophiles are electron poor and the most reactive dienes are electron rich.

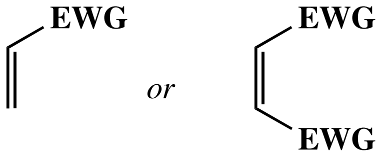
Reactive dienes:



EDG = electron donating group

Examples:

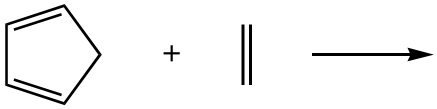
Reactive Dienophiles:

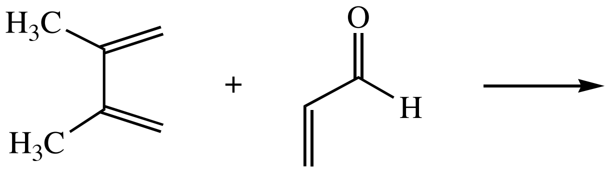


EWG = Electron withdrawing group

Examples:

Compare:

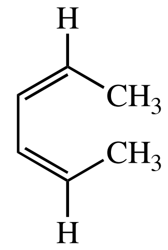
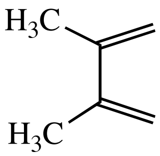
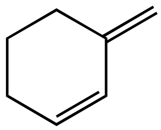
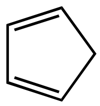




C. Stereochemistry:

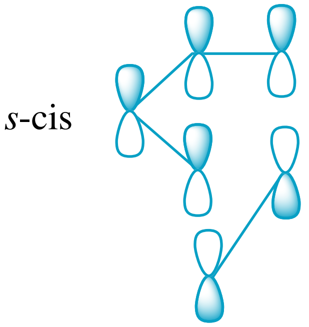
1. Diene: must be in *s*-cis conformation.

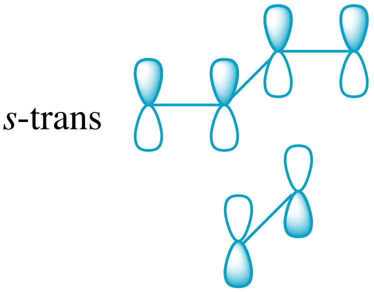
✦ Dienes that easily adopt the *s*-cis conformation undergo the Diels-Alder reaction more readily.

Diene	Diels-Alder rate, *(compared with 1,3 butadiene)*
	
	
	
	

Q. Why does the diene have to be in the *s*-cis conformation?

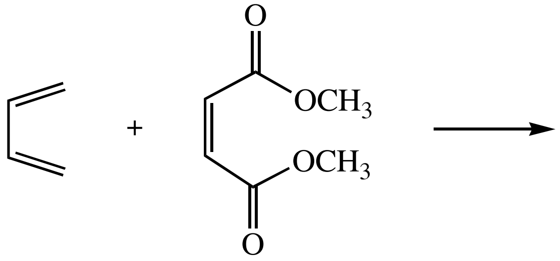
A.

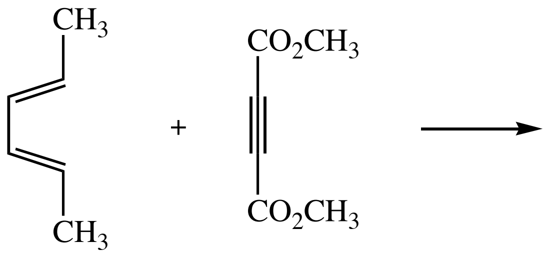




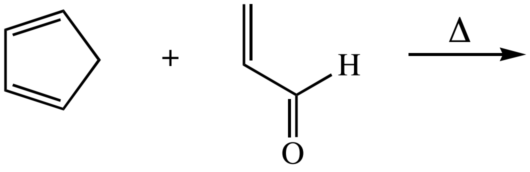
2. The Diels-Alder Reaction is Stereospecific:

Substituents on the same side of the diene or dienophile will be *cis* on the newly formed ring.



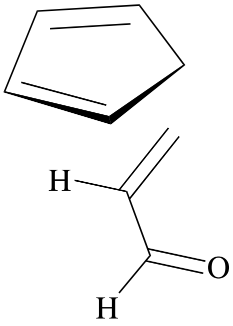


3. The endo rule:

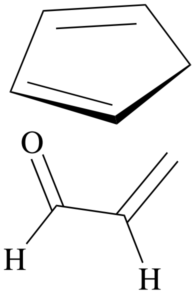


The dienophile can orient in two ways:

EWG
turned *away*
from diene

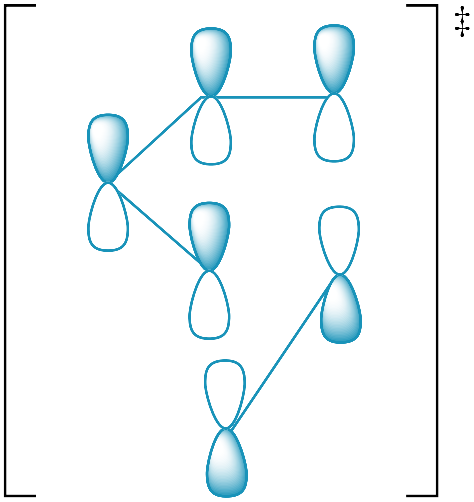


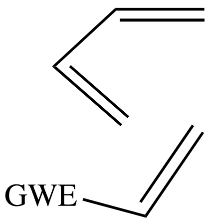
EWG
tucked *under*
the diene



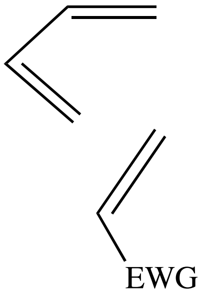
- ***endo*** products are preferred! This is the opposite of the result predicted by sterics.

Reason: **Secondary overlap**! (overlap of the p-orbitals of the EWG with the p-orbitals of C2 & C3 of the diene. This stabilizes the transition state)



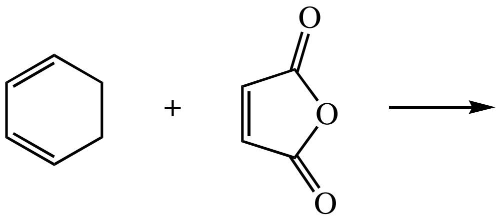


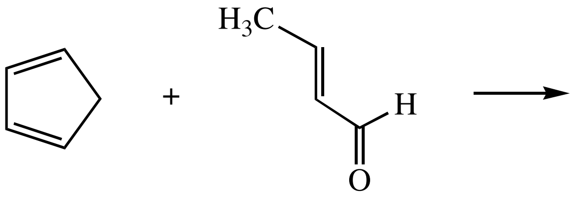
not



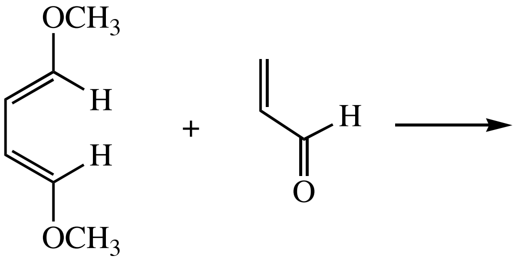
Examples: Use the endo rule to predict the major product of the following cycloaddition reactions:

a. ***Cyclic diene***

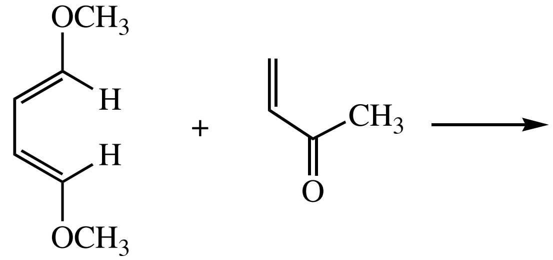




b. ***Acyclic diene:*** *The endo rule applies to acyclic dienes also!*



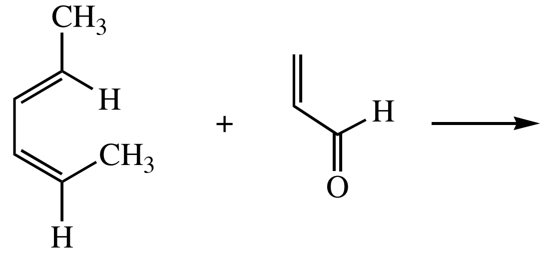
EZ way to determine stereochemistry for acyclic dienes:



General Rule:

Outside substituents on the diene ***and*** EWG on the dienophile are on the ***same*** side of the ring in the product.

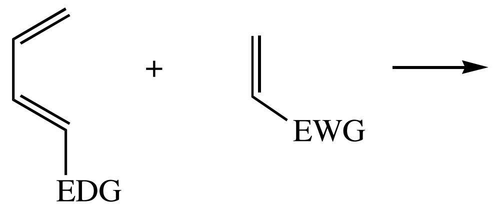
Example:

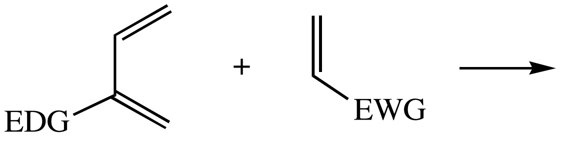


NOTE: The enantiomer has the opposite relative orientation!

4. Regioselectivity: The Diels-Alder reaction is regioselective.

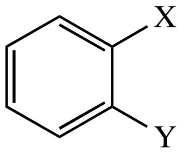
With unsymmetrical dienes and dienophiles there are 2 possible orientations:

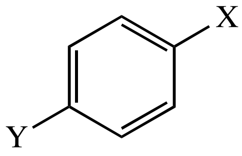


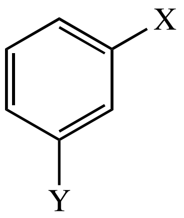


the ortho-para rule: The substituents tend to end up in a 1,2 or 1,4 relationship on the 6-membered ring (*ortho* or *para*).

Nomenclature comes from benzene chemistry:

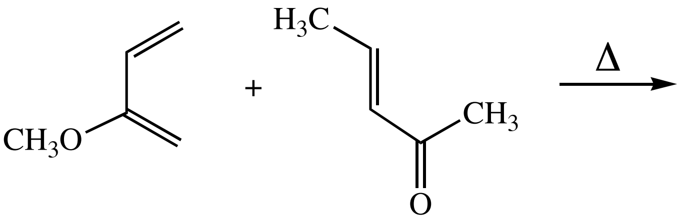




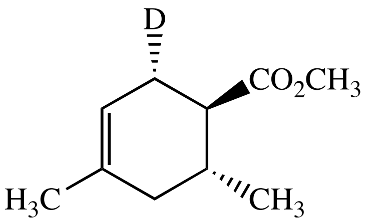


D. Synthesis using the Diels-Alder Reaction

Example 1: Predict the product in the following reaction:



Example 2: What diene & dienophile are needed to make the following product?



Steps:

1. Draw three arrows around ring, starting with π-bond.
2. Draw reagents, maintaining stereochemistry in diene and dienophile.