



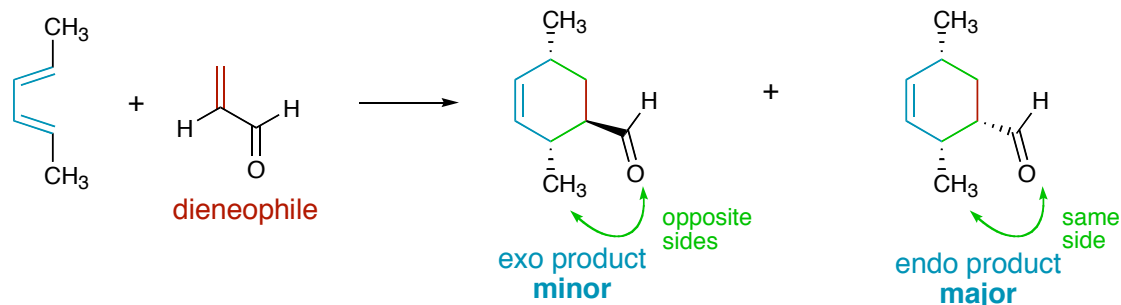
Chem 342 • Organic Chemistry II

Lecture Summary 07 - 30 Jan 2009

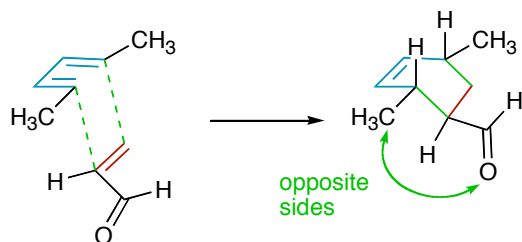
Chapter 14 - Conjugated Dienes and Ultraviolet Spectroscopy

Diels Alder Stereochemistry

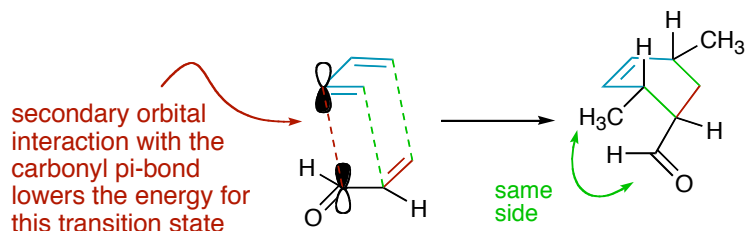
The Diels-Alder cycloaddition prefers to place the electron withdrawing group underneath the diene because the carbonyl pi-bond can interact with the diene pi-system. This gives rise to the endo product as the major product in the reaction.



exo transition state

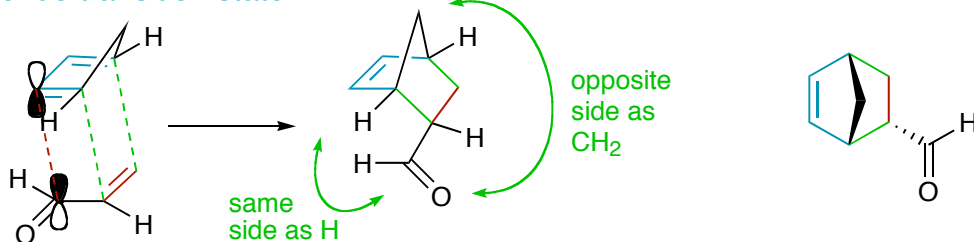


endo transition state



Note that if the groups on the diene are pointing in, they will end up on opposite sides in the ENDO transition state. For example, look at cyclopentadiene shown below.

endo transition state



If you always draw the reaction with dienophile approaching from the bottom and looking at the product from the top - you can use these simple rules for the stereochemistry for ENDO:

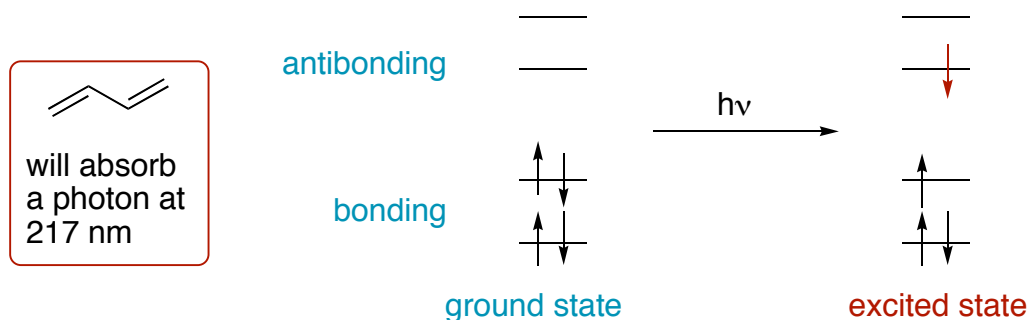
The EWG will always be on the same

Groups on the end of the diene pointing out will be down in the product

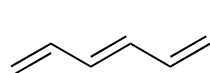
Groups on the end of the diene pointing in will be up in the product

Ultraviolet - Visible Spectroscopy

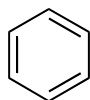
The energy required to push an electron from a bonding orbital in the ground state to an antibonding orbital (excited state) lies in the range of UV-visible light. The most easily excited photons are those in pi bonds. The more conjugated the pi-system is, the lower the energy required to excite the electron. Thus, UV-vis spectroscopy can give us information about the extent of conjugation. The property of light absorption by conjugated molecules is important in biology and for dyes.



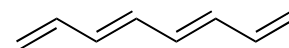
Several examples of conjugated molecules are shown below with the wavelength where absorption is maximum. Anything above 400 nm or so absorbs Visible light and should be colored.



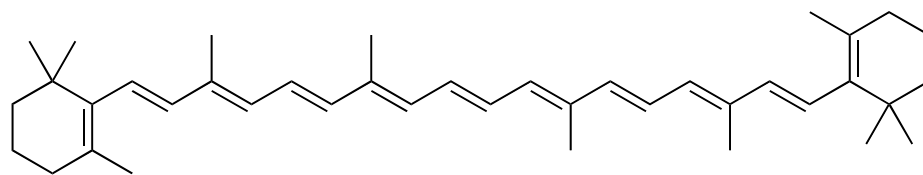
$$\lambda_{\max} = 258$$



$$\lambda_{\max} = 254$$



$$\lambda_{\max} = 290$$



β -carotene (orange color of carrots, squash, etc.) $\lambda_{\max} = 455$ (absorbs blue light)

An example of how conjugation affects color due to changing wavelengths of absorption is shown below. The picture on the left shows a cylinder filled with Tomato Juice. Notice the orange red color due to lycopene. When a solution of bromine (Br_2) is added, the red color disappears and blue/green colors appear. This is caused by bromination of the double bonds of lycopene reducing the amount of conjugation. Thus, the wavelength that is absorbed by the molecule changes to higher energy.

Daily Quiz

Q: What is the major product of the following Diels-Alder Reaction?

<input type="checkbox"/> 1:	
<input type="checkbox"/> 2:	
<input checked="" type="checkbox"/> 3:	
<input type="checkbox"/> 4:	