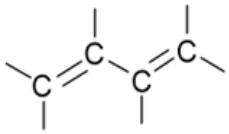
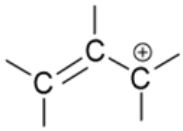
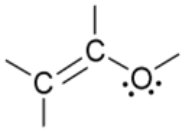
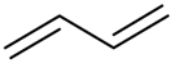
Conjugated Systems

Background

Conjugation occurs whenever p orbitals or lone pair orbitals can overlap on three or more adjacent atoms. Overlapping orbitals in conjugated systems have a stabilizing effect because electron density is delocalized. Examples of conjugated atoms are shown below.

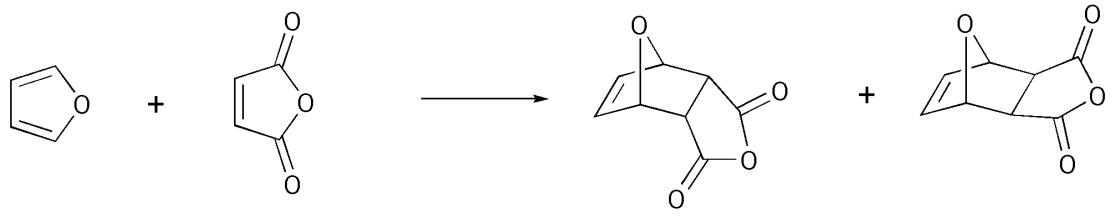
Conjugated alkenes have a double, single, double bond pattern. Tetrahedral carbons do not have lone pairs or p orbitals and therefore are not part of conjugated systems. Alkenes separated by tetrahedral carbons or other groups that cannot overlap with the orbital system are known as isolated alkenes.


conjugated diene


isolated diene

<u>The Diels-Alder Reaction</u>

Conjugated alkenes undergo different reactions than isolated alkenes. In Part 1 of the experiment you will Perform a Diels- Alder reaction which occurs with conjugated dienes. Furan and maleic anhydride react to form a bicyclic Diels-Alder adduct. The bicyclic product can have either endo or exo stereochemistry.



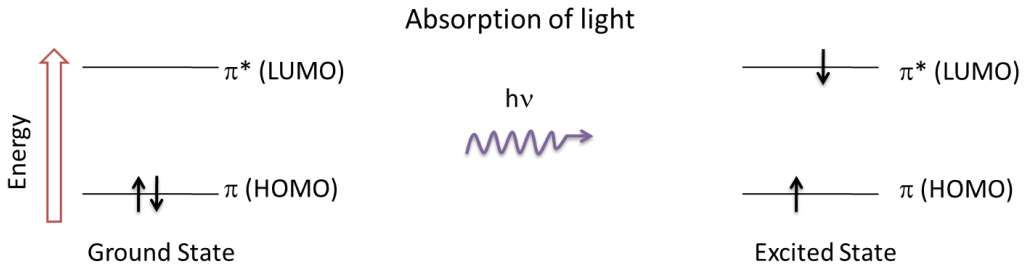
furan maleic anhydride endo product exo product

In Diels-Alder reactions the endo product forms faster - it has a lower energy transition state due to favorable pi orbital overlap. If the endo product forms the reaction is said to be under kinetic control. Exo products are generally more stable than endo products because they are less sterically hindered. If the exo product forms the reaction is said to be under thermodynamic control.

After forming and purifying the Diels-Alder product, you will take the melting point and determine if kinetic or the thermodynamic product was formed. The melting point of the endo product is 81^{o}C and the melting point of the exo product is 114^{o}C.

<u>Sunscreens and UV Absorption</u>

π bonds absorb photons of light as electrons get promoted from the highest unoccupied molecular orbital (HOMO or the π molecular orbital) to the lowest unoccupied molecular orbital (LUMO or the π* molecular orbital). In other words, an electron absorbs light energy to go from the ground state an excited state.



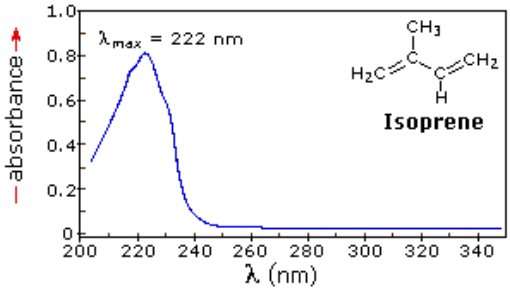
The energy of the photon absorbed is equal to the energy gap between the HOMO and LUMO. For isolated alkenes, the wavelength of this photon is in the UV region (~170 nm). As conjugation increases, the HOMO/LUMO gap gets smaller so the wavelength absorbed gets longer. The peak wavelength absorbed shifts from UV wavelengths (200 – 400nm) to longer visible wavelengths (400 – 800 nm) as molecules become more conjugated. Additionally, the absorptions of conjugated systems are usually stronger.

Sunscreens contain molecules that absorb UV radiation before it reaches the skin. Most of the molecules are conjugated organics. Titanium dioxide and zinc oxide are also used which both absorb and scatter UV light. Some sunscreens contain more than one molecule to protect in different regions of the spectrum. The UVA region is 315 – 400 nm, and the higher energy UVB region is 280 – 315 nm. SPF measures of how much UVB radiation will reach the skin.

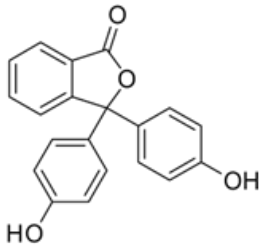
In this lab you will investigate various sunscreens using TLC plates and a shortwave/longwave UV lamp. TLC plates contain molecules that absorb UV light and reemit it at a lower energy visible wavelength (green). If the sunscreen blocks the UV rays before it hits the plate, it will appear dark – no visible light will be emitted if no UV light was absorbed.

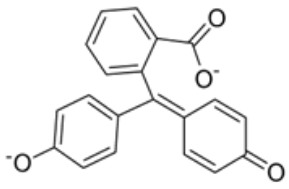
<u>UV-Vis Spectroscopy</u>

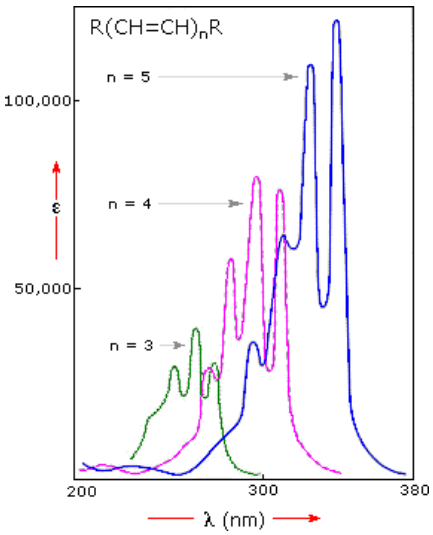
UV-Vis spectra are plotted with wavelength increasing on the x-axis and absorbance increasing on the y-axis. The peak wavelength absorbance (λ_{max}) is used to compare conjugated systems. The longer the peak wavelength, the more conjugated the molecule is.



In this lab you will use UV-Vis Spectroscopy to investigate a pH indicator. pH indicators are molecules that go from colorless to colored or from one color to a different color in a specific pH range. For instance, phenolphthalein goes from colorless to fuchsia around pH 8.5. The color change corresponds to a change in the amount of conjugation in the molecule. Different forms of the molecule are favored at different pH values. Below are the two forms of phenolphthalein. Based on their structure, can you tell which form is favored at high pH?







If a solution appears colorless, the conjugated molecule absorbs only in the UV region, not in the visible. If a solution appears colored, the molecule absorbs visible light. The color absorbed is roughly opposite on the color wheel from the color it appears – we only see the color that is <u>not</u> absorbed. For instance if a molecule appears red, it is absorbing green light.

Spectra are from the Virtual Textbook of Organic Chemistry, William Reusch.

Procedure

Part 1 – The Diels Alder Reaction

Reaction Set-up

Put 1.20 g of maleic anhydride and 10 mL of ether in a test tube. Heat the mixture in a warm (not boiling) water bath until all the anhydride has dissolved under a fume hood. Stir with a glass stirring rod if needed. Add more ether to replace any that evaporates. (**Caution** - Ether has a low boiling point and a tendency to quicky boil over when heated to excess. As soon as bubbles form, remove the test tube from the water bath). When the solution has cooled to room temperature, add 1.00 mL of furan. Stopper the test tube and cover the seal with paraffin to prevent evaporation. (Caution - Ether has a low boiling point - stoppering a warm test tube will generate pressure and could lead to an explosion) Label with your group's name and allow the test tube to stand in the designated test tube rack for several days at room temperature.

Isolation and Purification

Collect the solid product with vacuum filtration. Recrystallize the product by dissolving it in hexanes and heating in a hot water bath until it just begins boiling then, while stirring with a glass rod, add enough hot ethyl acetate to just dissolve the product (may take 5 to 10 mL or more). Allow the solution to cool to room temperature then cool in an ice bath. Collect the product with vacuum filtration and wash with 5 mL of cold hexanes. Allow air to pass through the filter for several minutes until the product is dry. Once dry, weigh the product.

Characterization

The product tends to decompose near its melting point, therefore, get a rough estimate of the melting point by heating a first sample at a rapid rate, then retake the measurement at a slower rate, inserting the second sample when the melting point apparatus has reached the approximate melting point. Determine if your product is endo or exo and propose an explanation for your result. Since this is the first time you are using your group's thermometer this semester, you may want to calibrate it with benzoic acid.

Part 2 – Sunscreens

Obtain three commercial sunscreens and a TLC plate. Observe the TLC plate under a UV lamp, switching between long wave and shortwave, noting its appearance. (**Caution** - do not look directly at the UV light.) Then spread a small amount of each sunscreen thinly on separate regions of the TLC plate, removing any excess sunscreen. Place the TLC plate under a UV lamp again, switching between long wave and short wave, and observe the effect of the sunscreens on the TLC plate. Note any similarities and differences between the appearance of the sunscreens. Also take note of at least one organic ingredient in each sunscreen (not inorganic compounds like zinc oxide), as well as its SPF rating and whether it is rated for UVA or UVB protection.

Part 3–UV-Vis Spectroscopy

1. Obtain two clean cuvettes and two clean test tubes. Add 5 mL of 0.1 M NaOH to one test tube and 5 mL of 1.0 M HCl to the other. Add three drops of 0.04% bromophenol blue solution to each test tube. Fill each cuvette to the line with one of the solutions.

2. Note if your cuvette has four clear sides, or two clear sides and two frosted. If all sides are clear, it does not matter how it is placed in the machine's slots. If it has two frosted sides, be sure that the beam will pass through the clear sides – clear sides go on the sides where there are holes for the light beam.

3. *[This step should be done once per machine at the beginning of the lab class, it may be done by your instructor]* Fill a clean cuvette with water. Wipe the sides of the cuvette with a kimwipe. Place the cuvette in slot B. Use arrow buttons to navigate to Scanning mode and hit enter. Enter 350 nm and 800nm as your scanning wavelengths then start the test. Choose collect baseline.

4. Wipe the sides of the first cuvette with a kimwipe. Place it in slot one. Choose measure sample.

5. Choose edit graph>math>peaks > turn on peaks, set features to 1. (The number of features is the number of peaks the program will look for. Record the top number (wavelength). The bottom number is the absorbance.

6. Remove the first cuvette from slot 1 and replace it with the second cuvette. Repeat steps 4 & 5 for the second sample.

You may dispose of solutions from the UV-VIS part of the lab in the sink.

Chemicals:

furan	maleic anhydride	diethyl ether	hexanes
ethyl acetate	bromophenol blue (aq)	1.0 M HCl	0.10 M NaOH
Benzoic acid for calibration.			

Equipment:

50 mL Erlenmeyer flask	beaker	stirring rod	rubber stopper
side arm flask	rubber adapter	Buchner funnel	vacuum hose
melting point tubes	melting point apparatus	TLC plates	sunscreens
UV lamp	plastic pipettes	2x50 mL Beakers	3 cuvettes
Genesys UV-Vis spectrophotometer			

Waste Disposal: Filtrate and recrystallization liquids - liquid organic waste
Diels Alder product – solid organic waste
TLC plates – regular waste bin
UV-Vis samples - sink