

Organic Chemistry
Notes Part 19

UV/Vis Spectroscopy (8th edition, Chapter 13.23, 9th edition, same)

Ultraviolet/Visible spectroscopy tells you about _____. The more conjugation in your molecule, the _____ the wavelength of light. Let us first cover colors briefly. Color has to do with organic or inorganic molecules absorbing light.

What are the three primary colors? _____

See <http://www.cbu.edu/~ddawson/212/Handouts/Primary-colors.jpg> This is a scan of the color wheel in the Chemistry 115 lab and was scanned by Dr. Mike Condren.

An item that is red absorbs which colors? _____

An item that is green absorbs which colors? _____

An item that is blue absorbs which colors? _____

An item that is cyan absorbs which color? _____

An item that is magenta absorbs which color? _____

An item that is yellow absorbs which color? _____

Your clothes are turning yellow over time. How would you make them look whiter?

What is a dye? _____

What is a lake? _____

What is chlorine bleach? _____

What is non-chlorine bleach? _____

How do bleaches work? _____

Why is the sky blue? According to Wikipedia http://en.wikipedia.org/wiki/Diffuse_sky_radiation "The sunlit sky appears blue because air scatters short-wavelength light more than longer wavelengths. Since blue light is at the short wavelength end of the visible spectrum, it is more strongly scattered in the atmosphere than long wavelength red light. The result is that the human eye perceives blue when looking toward parts of the sky other than the sun. "

Homo/Lumo

UV spectroscopy converts an electron from a HOMO to a LUMO. Some possible transformations for this step are given below.

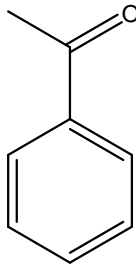
σ to σ^* - happens when only single bonds and no lone pairs are present.

π to π^* - happens when you have double bonds and no lone pairs are present.

n to π^* - happens when you have a lone pair of electrons and double bonds are present also.

n to σ^* - happens when you have a lone pair of electrons and no double bonds.

Can a molecule undergo more than one transition? _____. An example is shown below with acetophenone.

<u>Molecule</u>	<u>λ_{\max}</u>	<u>ϵ</u>	<u>Assignment</u>
	244 nm	12,600	π to π^*
	280	1,600	π to π^*
	317	60	n to π^*

λ_{\max} and ϵ (8th edition, pg. 582, 9th edition, pg. 553)

λ_{\max} is defined as the tallest point on a peak in the spectrum. ϵ is defined as the molar absorptivity. Given below is an example of a UV spectrum. Absorbance is on the Y axis and wavelength in nanometers is on the X axis

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Molar absorptivity is how well the transition reacts to the wavelength of light. The π to π^* at 244 nm above reacts well with the wavelength of light while the peak at 317 does not react very well.

Molar absorptivity is calculated using the Beer-Lambert Law which is shown below.

$$\epsilon = MA/cl$$

M = molecular weight, c = concentration (in grams/liter)

A = absorption, l = path length thru the sample in centimeters

Given below is a table with some λ_{\max} values and absorptivities.

572 SPECTROSCOPIC METHODS OF STRUCTURE DETERMINATION

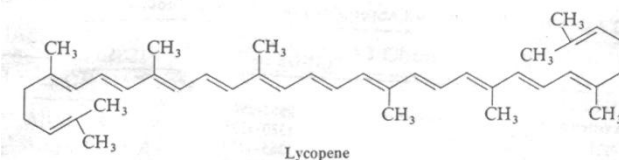


Table 13.1 gives the values of λ_{\max} for a number of unsaturated compounds.

TABLE 13.1 Long-wavelength absorption maxima of unsaturated hydrocarbons

COMPOUND	STRUCTURE	λ_{\max} (nm)	ϵ_{\max}
Ethene	$\text{CH}_2=\text{CH}_2$	171	15,530
<i>trans</i> -3-Hexene	$\begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{CH}_3 \end{array}$	184	10,000
Cyclohexene		182	7,600
1-Octene	$\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}_2$	177	12,600
1-Octyne	$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CH}$	185	2,000
1,3-Butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	217	21,000
<i>cis</i> -1,3-Pentadiene	$\begin{array}{c} \text{CH}_3 \quad \text{CH}=\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	223	22,600
<i>trans</i> -1,3-Pentadiene	$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}=\text{CH}_2 \end{array}$	223.5	23,000
1-Buten-3-yne	$\text{CH}_2=\text{CHC}\equiv\text{CH}$	228	7,800
1,4-Pentadiene	$\text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2$	178	17,000
1,3-Cyclopentadiene		239	3,400
1,3-Cyclohexadiene		256	8,000
<i>trans</i> -1,3,5-Hexatriene	$\begin{array}{c} \text{CH}_2=\text{CH} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}=\text{CH}_2 \end{array}$	274	50,000

Solvents are important and can change the _____. The transition of acetone occurs at 279 nm in n-hexane, at 270 nm in ethanol and at 265 in water.

Take home lesson: The more conjugation you have in your molecule, the closer the HOMO and LUMO will be to each other and the longer the wavelength of light that is required.

(8th edition Problem 13.25, 9th edition, same) λ_{\max} for the π to π^* transition in ethylene is 170 nm. Is the HOMO-LUMO energy difference in ethylene greater than or less than that of cis,trans-1,3-cyclooctadiene (230 nm)?

(8th edition, Problem 13.26, 9th edition, same) Which one of the C_5H_8 isomers has its λ_{\max} at the longest wavelength? 2-methyl-1,3-butadiene, 1,4-pentadiene, or cyclopentene?

Advanced Spectroscopy (8th edition, Chapter 13.19, 9th edition, same)

So far we have talked about 1D NMR. Advanced spectroscopy includes 2D, 3D and 4D NMR. An example of 2D NMR is given in your book in section 13.19 (both editions). 2D NMRs have two frequency axis and are used to correlate the two items represented by the axis.

Some examples of 2D NMR

1) <u>Name</u>	<u>Long Name</u>	<u>Use</u>
COSY	Correlated Spectroscopy,	correlates protons with protons

How to Read

Cosy has the same proton spectrum on each axis. Cosy also has a diagonal going from the bottom left to top right of the spectrum.

Identify a peak in the 1H NMR on the Y axis. Extend to the right in a straight line towards the other Y axis. When you reach a cross point, go up to the X axis. The peak you picked in the Y axis and the one on the X axis are CORRELATED. It is possible for a peak on the Y axis to be correlated to more than one peak.

Example: (8th edition, Figure 13.31, 9th edition, Figure 13.30)

2) <u>Name</u>	<u>Long Name</u>	<u>Use</u>
Hetcor	Heteronuclear chemical shift correlation	correlates protons with carbons

How to Read

The proton spectrum is on the Y axis and the carbon is on the X axis Identify a peak in the 1H NMR and trace vertically until you reach a cross peak. Trace horizontally to the ^{13}C NMR. The protons causing the signal you identified in the 1H NMR are on the carbon that gives the peak in the ^{13}C with the cross peak.

Example: (8th edition, Figure 13.32, 9th edition, Figure 13.31)

3) <u>Name</u>	<u>Long Name</u>	<u>Use</u>
HMQC	Heteronuclear Multiple Quantum Coherence	correlates protons with carbons

How to Read

Very similar to # 2 except proton is on the X axis and carbon is on the Y axis. This is called the proton or inverse detected version. The advantage is at least an eightfold increase in sensitivity which saves you substantial time required to obtain the spectrum.

<u>4) Name</u>	<u>Long Name</u>	<u>Use</u>
Inadequate	Incredible Natural Abundance Double Quantum Transfer Experiment	correlates carbon to carbon

How to Read

Carbon spectrum is on the X axis. Frequency in Hz is on the Y axis. Identify a peak in the ^{13}C NMR. Go down vertically until you reach a cross point. From this cross point, trace horizontally until you reach another cross point. From this second cross point, trace vertically back to the ^{13}C NMR. These two ^{13}C NMR peaks are directly attached. Continue from this peak around the molecule.

<u>5) Name</u>	<u>Long Name</u>	<u>Use</u>
HMBC	Heteronuclear Multiple Bond Coherence	shows long range proton carbon couplings

How to Read

The Carbon NMR is on the Y axis and the proton is on the X axis. The HMBC is very similar to the HMQC except that the one bond couplings are gone while there are two and three bond couplings present. HMBC spectra are more difficult to read and more detail can be obtained from advanced spectroscopy books.

OTHER 2D NMR Techniques

<u>Name</u>	<u>Long Name</u>	<u>Use</u>
TOCSY	Totally Correlated Spectroscopy	not directly coupled nuclei but in the same spin system

<u>Name</u>	<u>Long Name</u>	<u>Use</u>
NOESY	Nuclear Overhauser Effect	Uses NOE to correlate protons (in peptides)

<u>Name</u>	<u>Long Name</u>	<u>Use</u>
ROESY	Rotating Frame Overhauser Effect Spectroscopy	Through space correlations

New Types of NMR

Gradient Field NMR, 3D NMR

NMR Time Scale (8th edition, Chapter 13.12, 13.13, 9th edition, same)

The NMR machine only “sees” slower chemical reactions. For example, 1,2,2,3,3,4,4,5,5,6,6-undecadeuterocyclohexane has one hydrogen in the ^1H NMR. This hydrogen can be in either the axial position or the equatorial position. At high temperatures, an average spectrum appears. At lower temperatures, it is possible to get a peak for the hydrogen in both the equatorial AND axial positions.

For ethanol, how many types of protons are there? It depends on the speed of the rotation and the speed of exchange for the OH peak.

Example 1 – High Purity Ethanol- Slow exchange speed for OH



The CH₃ shows up as a triplet, the CH₂ COUPLES to the OH and shows up as a pentet AND the alcohol proton shows up as a TRIPLET.

DMSO can also be added to alcohols to cause slow exchange of the hydrogens.

Example 2 – “Normal” Ethanol – Fast exchange speed of OH

CH₃CH₂OH

The CH₃ shows up as a triplet. The CH₂ shows up as a quartet and DOES NOT couple with the OH peak. The OH peak shows up as a broad peak and DOES NOT couple to the CH₂.

MRI- Magnetic resonance Imaging (8th edition, pgs. 564 – 565, 9th edition, pg. 535)

See page 564 or page 535 for an explanation.

Alcohol/Carboxylic acid\Amine\Amide peaks and D₂O (8th edition, pg. 564, 9th edition, pg. 534)

The addition of D₂O to any of the peaks above causes the peak to disappear since the NMR active hydrogen is replaced with deuterium which is not seen in the NMR at the same frequency as hydrogen. An example is shown below.

Conjugation in alkenes and allylic systems (8th edition, Chapter 10, 9th edition, same)

BAM!! (aka allyl) (8th edition, Chapter 10.1 – 10.7, 9th edition, Chapter 10.1 – 10.4)

When you have read or heard BAM, it makes you think of Emeril. Emeril likes to use garlic which is the root name of the _____ group. The _____ group can be a cation, an anion or a radical. Draw each one below.

Allyl cation

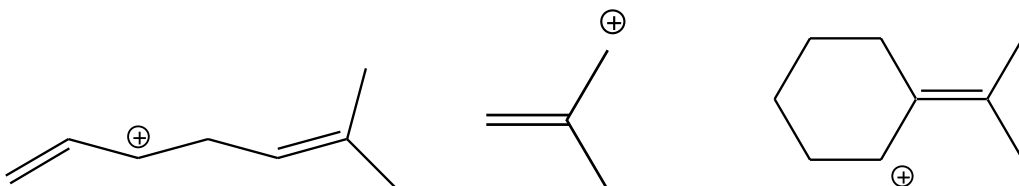
Allyl anion

Allyl radical

Allylic ions or radicals are very stable because they have more than one resonance contributor. This allows them to spread out the charge or radical which makes the ion or radical more stable. Pick any one of the drawings above and draw both resonance contributors below.

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(Problem 10.1, 8th edition) Write a second resonance structure for each of the following carbocations. Is the charge shared equally by both allylic carbons? If not, which one bears more of the charge?



Allyl $\text{S}_{\text{N}}1$ reactions (8th edition, Chapter 10.3, 9th edition, Chapter 10.2)

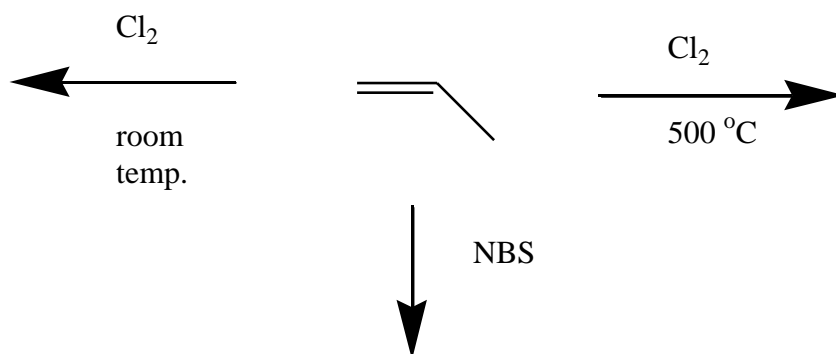
Tertiary allylic halides are more reactive in $\text{S}_{\text{N}}1$ reactions than tertiary halides. Which chloride below will undergo solvolysis in ethanol 100 times faster than the other chloride?



Allylic halogenation (8th edition, Chapter 10.6, 9th edition, Chapter 10.3)

The temperature is very important in deciding how some molecules or ions add to alkenes. At lower temperature, _____ of halides is the major reaction. However, at higher temp, _____ of hydrogen by halides is the major reaction. What is a high temperature? 500 °C will be used in class as an example of a high temperature reaction with _____. At this temperature, the mechanism is a free-radical version. For bromine, we will add _____

abbreviated _____ which gives a low concentration of bromine radical. Give the products of the following reactions.



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Classes of dienes (8th edition, Chapter 10.8, 9th edition, Chapter 10.5)

Dienes can be classified as _____, _____ or _____.

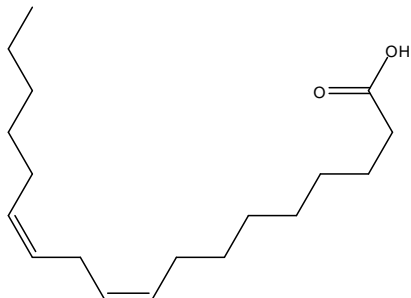
_____ - alkenes are next to each other.

_____ - alkenes alternate with single bonds. Double, single, double.

_____ - alkenes that are separated by two or more single bonds.

Linoleic acid

Given below is linoleic acid.



Conjugated linoleic acids (CLAs)

Conjugated linoleic acids are similar to linoleic acid but are _____. At least 13 isomers have been reported according to Wikipedia (http://en.wikipedia.org/wiki/Conjugated_linoleic_acid). Eight of the conjugated linoleic have the double bonds at the 9 and 11 positions or the 10 and 12 positions.

Give the four possible CLAs with the double bonds at the 9 and 11 position. Draw one of them.

Give the four possible CLAs with the double bonds at the 10 and 12 position. Draw one of them.

The major CLAs (according to Wikipedia) used for biochemical studies are the Z9,E11 and E10,Z12 isomers.

Are the CLAs that you circled above “trans fats”? _____. For nutritional labeling, these CLAs or any fats with conjugated double bonds are not considered trans fats. One of the purported benefits of “Organic” cows is that they produce more CLAs than cows fed grain.

Stabilities of dienes (8th edition, Chapter 10.9, 8th edition, Chapter 10.6)

Hydrogenation of an alkene to an alkane gives off heat or absorbs heat called the _____ of _____. Comparison of the heats of hydrogenation of different dienes that give the same product allows the stabilities of the different dienes to be determined. Three dienes that give the same product are 1,4-pentadiene, E-1,3-pentadiene and 1,2-pentadiene. All three of these dienes give pentane upon hydrogenation. 1,4-pentadiene is the _____ diene, 1,3-pentadiene is the _____ diene and 1,2-pentadiene is the _____ diene. 1-pentene has a heat of hydrogenation of 126 kJ/mol while 1,4-pentadiene has exactly double this value.

This means that _____ double bonds function as two separate dienes. 1,3-pentadiene has a heat of hydrogenation of 111 kJ/mol for removal of the first double bond. This means the conjugated double bond is _____ more stable than an isolated double bond.

This extra stability is called the delocalization energy, resonance energy, or conjugation energy.

1,2-pentadiene gives off more heat on removal of the first double bond than either diene above making cumulated dienes the _____ of the dienes.

(8th edition, Problem 10.10, 9th edition, Problem 10.12) Another way in which energies of isomers may be compared is by their heats of combustion. Match the heat of combustion with the appropriate diene.

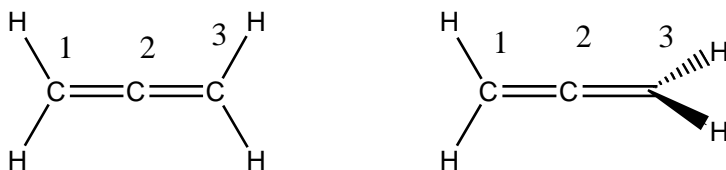
Dienes: 1,2-Pentadiene, (E)-1,3-pentadiene, 1,4-pentadiene

Heats of combustion: 3186 kJ/mol, 3217 kJ/mol, 3251 kJ/mol

Bonding in Allenes (8th edition, Chapter 10.11, 9th edition, Chapter 10.8)

Allene bonding was discussed very early in the semester. (Notes, part 2, bottom of page 3 and page 4). It is copied directly below.

Knowing what you know about hybrid orbitals, the drawing on the right is CORRECT.



Hybridization of atom 1 – sp^2

Hybridization of atom 2 – sp

Hybridization of atom 3 – sp^2

Orientation of p orbital in atom 1 for both structures – In/Out

LEFT STRUCTURE

Orientation of p orbital in atom 3 for left structure – In/Out

Orientation of p orbital in atom 2 for left structure for bond between atom 1 and 2 – In/Out

Orientation of p orbital in atom 2 for left structure for bond between atom 2 and 3 – In/Out

Problem: Orbitals on atom 2 can only overlap with orbital on EITHER Atom 1 or 3 but not BOTH.

RIGHT STRUCTURE

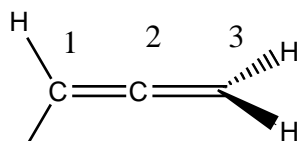
Orientation of p orbital in atom 3 for right structure – Up/Down

Orientation of p orbital in atom 2 for right structure for bond between atom 1 and 2 – In/Out

Orientation of p orbital in atom 2 for right structure for bond between atom 2 and 3 – Up/Down

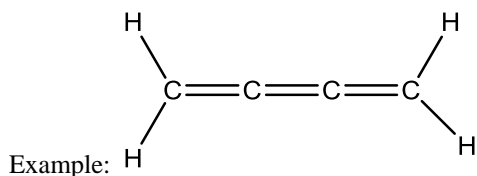
TAKE HOME LESSON:

IF DOUBLE BONDS ARE NEXT TO EACH OTHER, AN EVEN NUMBER OF ALKENES GIVES THE GROUPS ON THE END IN DIFFERENT PLANES.



Example: H

IF DOUBLE BONDS ARE NEXT TO EACH OTHER, AN ODD NUMBER OF ALKENES GIVES THE GROUPS ON THE END IN THE SAME PLANES.



As long as the groups on both ends of the diene are different, there is no plane of symmetry and therefore it is chiral.

Give an example of a chiral allene below.

(8th edition, Problem 10.11, 9th edition, Problem 10.14) Is 2-methyl-2,3-pentadiene chiral? What about 2-chloro-2,3-pentadiene?

Conformations of conjugated dienes (8th edition, pg. 403, 9th edition, pg. 384)

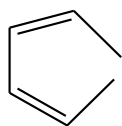
Conjugated dienes can exist in at least three conformations. These three conformations can be defined by the _____ angle between the double bond groups. The three conformations have dihedral angles of _____. _____, and _____ degrees. Two of these three conformations have conformations starting with a lowercase s. A lowercase s stands for single bond. These two conformations can be converted by rotation about a carbon-carbon single bond. The first conformation is called the _____ conformation and has the dihedral angle of 0 degrees.

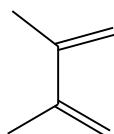
The second conformation is called the _____ conformation and has a dihedral angle of 180 degrees between the double bonds.

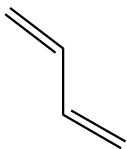
The conformation that has 90 degrees between the double bonds is the least stable due to no overlap between the two double bonds. Both the s-cis and s-trans conformations allow overlap between the two double bonds. The bond between the two double bonds has some double bond character. Show this with another resonance structure for 1,3-butadiene below.

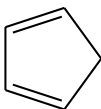
The _____ conformation is more stable than the _____ due to LESS van der Waals strain between the groups on the diene. The groups causing the strain can be on the 1 and 4 carbons of the conjugated diene or on the 2 and 3 carbons of the conjugated diene.

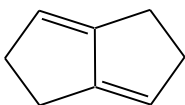
Indicate for the drawings below whether it is s-cis, s-trans or neither. If it is the s-cis conformer, draw the s-trans conformer. If it is the s-trans conformer, draw the s-cis. Which molecule(s) below can exist in only one conformation?







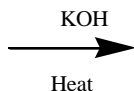
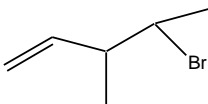
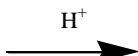
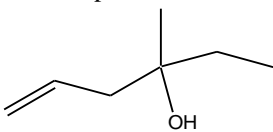




Synthesis of dienes (8th edition, Chapter 10.12, 9th edition, Chapter 10.9)

Formation of alkenes can generate either the Zaitsev product or the Hoffman product. The Zaitsev is the more stable alkene while the Hoffmann product is the least stable alkene. Dehydration of alkenes, which is an E₁ elimination, always forms the _____ product. Dehydrohalogenation of a halide, which is an E₂ elimination, can form either the Hoffman or Zaitsev alkene depending on the base used. Use of a _____ base like sodium methoxide gives the _____ product. Use of a _____ base like sodium tert-butoxide gives the _____ product. If an alkene is already present in a halide or alcohol, dehydration will always form the _____ diene, triene, etc. The most stable diene was seen above as the _____ diene.

Give the products of the following reactions.



Reaction Conditions

Conditions of a reaction can be changed to give different products. Some of the conditions that may be changed are given below.

Different solvent

Different _____ of reaction

Different length of time for reaction.

Different _____ procedure.

Different _____ like bases which may include different counter ions

We use different conditions to answer the two questions we ask about every reaction. _____ and _____. The _____ question leads to kinetic control while the _____ question leads to thermodynamic control.

The difference between kinetic and thermodynamic control can be shown on a potential energy diagram using a single compound. Draw the potential energy diagram below labeling each type of reaction control.

Kinetic control (8th edition, pg. 408, 9th edition, pg. 389)

Kinetic control of a reaction forms the product or products formed faster but that is (are) not as stable. Some conditions that are used for kinetic control are the following:

_____ - kinetically controlled reactions have a lower energy of activation and a lower heat gives less heat to the system. The less heat will not give as many molecules the energy to cross over the higher activation energy.

_____ - shorter reaction times will not allow molecules to equilibrate and less stable molecules to return to more stable molecules.

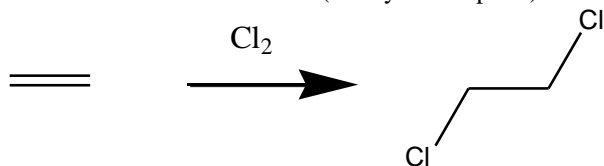
Thermodynamic control (8th edition, pg. 409, 9th edition, pg. 389)

Thermodynamic control of a reaction forms the product or products that are formed slower but that is (are) more stable. The conditions that are used for thermodynamic control are exactly the opposite of kinetic control. Longer reaction times are used to allow equilibration. Higher temperatures are used to allow more molecules to cross over the activation energy.

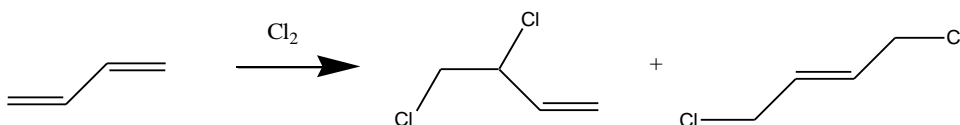
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Simple vs. Conjugate addition (8th edition, Chapter 10.13, 9th edition, Chapter 10.10)

Addition of chlorine (or any electrophile) to a single alkene is termed _____ or _____ addition. This is shown below.



With conjugated dienes, the situation is more difficult. Conjugated dienes can undergo both _____ addition as well as _____ or _____ addition. The two products are not equally stable.



(8th edition, Problem 10.14, 9th edition, Problem 10.17) Write structural formulas for the products of 1,2 and 1,4 addition of hydrogen chloride to 2,4-hexadiene.

Kinetic vs. Thermodynamic control in hydrogen halide addition to dienes (8th edition, Chapter 10.13, 9th edition, Chapter 10.10)

In most cases, conjugate addition products are more stable due to a _____ double bond. This is not always true but it is the case with butadiene. This means the conjugate addition product are under _____ control. The simple addition products are less stable but are formed at lower temperatures. This means they are under _____ control. They (kinetic products) are formed in higher yield at lower temperatures because the resonance contributor leading to the kinetic product makes more of a

contribution to the resonance hybrid. The resonance contributor leading to the thermodynamic product makes less of a contribution to the resonance hybrid. The simple and conjugate addition products interconvert at higher temperatures in the presence of the hydrogen halide.

Simple addition resonance contributor

Conjugate addition resonance contributor

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Halogen addition to dienes (8th edition, Chapter 10.14, 9th edition, Chapter 10.11)

Mixture of 1,2 and 1,4 addition products are formed when halides add to conjugated dienes. The double bond generated is almost always the E isomer.

(8th edition, Problem 10.15, 9th edition, Problem 10.18) Exclusive of stereoisomers, how many products are possible in the electrophilic addition of 1 mole of bromine to 2-methyl-1,3-butadiene?

More than 1, 4 addition

If the dienes have more than two conjugated double bonds, more products are possible. Work the example below. E-1,3,5-hexatriene has what types of additions possible? Show them below.

Questions:

- 1) What is a conjugated linoleic acid? Give an example.
- 2) Draw three dienes that give that same alkane upon hydrogenation.
- 3) Rank the dienes in question # 2 from most stable (=1) to least stable explaining your order.
- 4) Give an example of a molecule locked in an s-cis conformation.

5) Give an example of a molecule locked in an s-trans conformation.

7) Give conditions that will give you the kinetic product.

8) Give conditions that will give you the thermodynamic product.

9) What is meant by 1,4 addition?