

16: CONJUGATED SYSTEMS, ORBITAL SYMMETRY, AND ULTRAVIOLET SPECTROSCOPY



CHAPTER OVERVIEW

16: CONJUGATED SYSTEMS, ORBITAL SYMMETRY, AND ULTRAVIOLET SPECTROSCOPY

Learning Objectives

After reading this chapter and completing ALL the exercises, a student can be able to

- construct & interpret MO diagrams of ethene, butadiene and allylic systems (refer to section 16.1)
- recognize reactions that are enhanced by resonance stabilization of the allylic intermediate (refer to section 16.2)
- predict the products and specify the reagents for electrophilic addition reactions (EAR) of conjugated dienes (refer to section 16.3)
- specify reaction conditions to promote thermodynamic or kinetic control of the reaction mechanism; correlate these conditions to reaction energy diagrams (section 16.4)
- predict the products and specify the reagents for bimolecular substitution reactions (S_N2) of allylic halides (refer to section 16.5)
- predict the products of Diels-Alder reactions with stereochemistry, including the orientation of cycloaddition with asymmetrical reagents (refer to sections 16.6 and 16.7)
- develop mechanisms to explain the observed products of 1,2- & 1,4- addition reactions, including the resonance forms of the stabilized intermediates (refer to section 16.6)
- use MO theory to predict whether cycloaddition reactions will be thermally or photochemically allowed (refer to section 16.6 and 16.7)
- recognize the effect of conjugation on UV absorption (refer to section 16.9 and 16.10)
- use Beer's Law in UV absorption calculations (refer to section 16.9 and 16.10)
- explain how light, the conjugation of double bonds, and the stereochemistry of double bonds contribute to visualizing color

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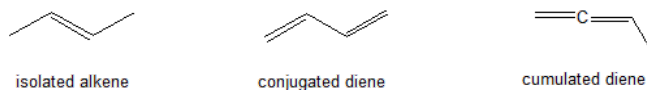
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16.1: STABILITY OF CONJUGATED DIENES - MOLECULAR ORBITAL THEORY

INTRODUCTION

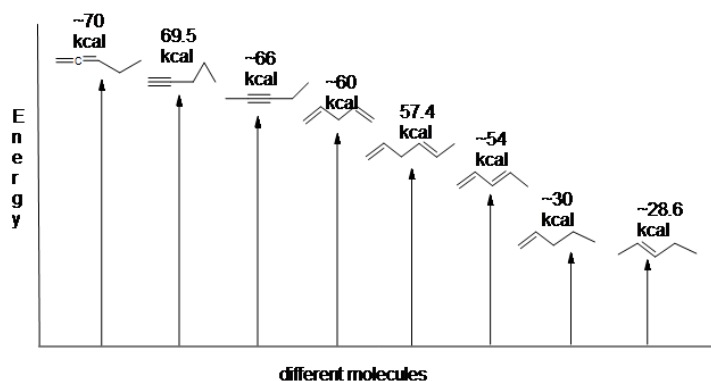
Conjugated dienes are characterized by alternating carbon-carbon double bonds separated by carbon-carbon single bonds. Cumulated dienes are characterized by adjacent carbon-carbon double bonds. While conjugated dienes are energetically more stable than isolated double bonds. Cumulated double bonds are unstable. The chemistry of cumulated double bonds can be explored in advance organic chemistry courses. The chemistry of isolated alkenes is covered in Chapters 8 and 9 of this LibreText. The chemistry of conjugated double bonds is the focus of this chapter.



CONJUGATED DIENE STABILITY

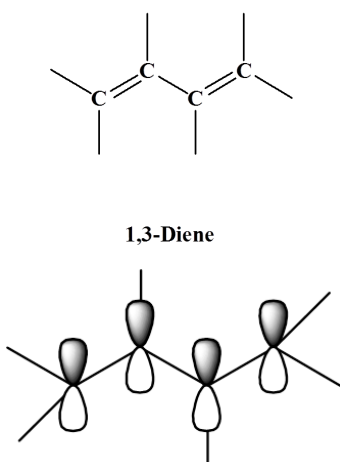
Conjugated dienes are more stable than non conjugated dienes (both isolated and cumulated) due to factors such as delocalization of charge through resonance and hybridization energy. This stability can be seen in the differences in the energies of hydrogenation between isolated and conjugated alkenes. Since the higher the heat of hydrogenation the less stable the compound, it is shown below that conjugated dienes (~54 kcal) have a lower heat of hydrogenation than their isolated (~60 kcal) and cumulated diene (~70 kcal) counterparts.

Here is an energy diagram comparing different types of bonds with their heats of hydrogenation to show relative stability of each molecule:

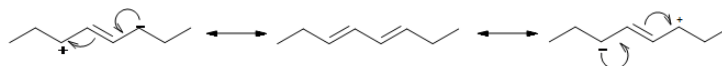


STABILITY OF CONJUGATED DIENES - THE RESONANCE EXPLANATION

Conjugated double bonds are separated by a single bond. 1,3-dienes are an excellent example of a conjugated system. Each carbon in 1,3-dienes is sp^2 hybridized and therefore has one p orbital. The four p orbitals in 1,3-butadiene overlap to form a conjugated system.

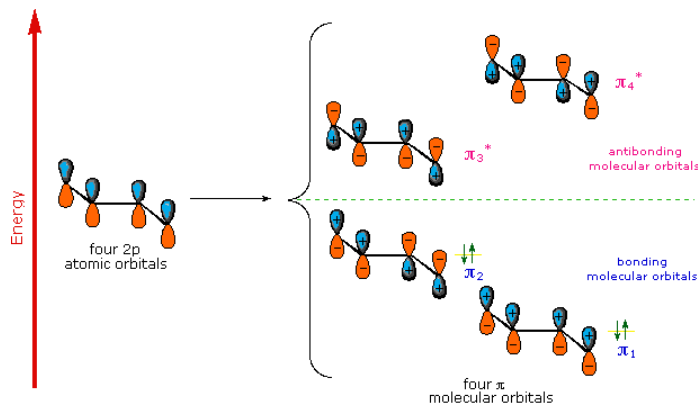


The resonance structure shown below gives a good understanding of how the pi electrons are delocalized across the four carbons in this conjugated diene. This delocalization of electrons stabilizes the conjugated diene:



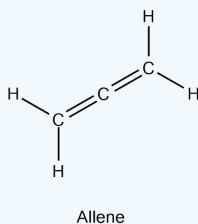
STABILITY OF CONJUGATED DIENES - THE MOLECULAR ORBITALS EXPLANATION

A molecular orbital model for 1,3-butadiene is shown below. Note that the lobes of the four p-orbital components in each pi-orbital are colored differently and carry a plus or minus sign. This distinction refers to different phases, defined by the mathematical wave equations for such orbitals. Regions in which adjacent orbital lobes undergo a phase change are called **nodes**. Orbital electron density is zero in such regions. Thus a single p-orbital has a node at the nucleus, and all the pi-orbitals shown here have a nodal plane that is defined by the atoms of the diene. This is the only nodal surface in the lowest energy pi-orbital, π_1 . Higher energy pi-orbitals have an increasing number of nodes. Since 1,3-butadiene has four pi electrons. The two bonding molecular orbitals are filled to explain the measurable stability of conjugated double bonds.



Exercise

1. The heat of hydrogenation for allene is about 300 kJ/mol. Order a conjugated diene, a non-conjugated diene, and allene in increasing stability.



Answer

1. allene < non-conjugated diene < conjugated diene (most stable)

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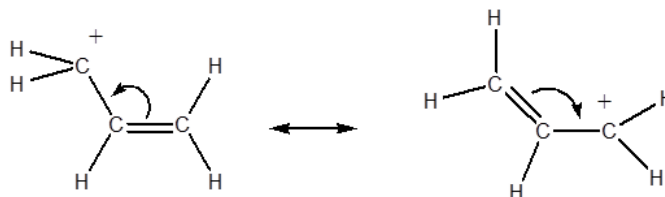
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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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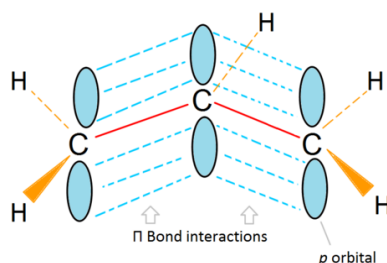
16.2: ALLYLIC CATIONS

RESONANCE AND ALLYLIC CARBOCATION STABILITY

Conjugation occurs when p orbital on three or more adjacent atoms can overlap. Conjugation tends to stabilize molecules. Allylic carbocations are a common conjugated system. The resonance structures below help explain the stability of allylic carbocations. The true structure of the conjugated allyl carbocation is a hybrid of the two resonance structure so the positive charge is delocalized over the two terminal carbons. This delocalization stabilizes the allyl carbocation making it more stable than a normal primary carbocation.



The positive charge of a carbocation is contained in a p orbital of a sp^2 hybridized carbon. This allows for overlap with double bonds. The positive charge is more stable because it is spread over 2 carbons.



MOLECULAR ORBITALS AND ALLYLIC CARBOCATION STABILITY

The stability of the carbocation of propene is due to a conjugated π electron system. A "double bond" doesn't really exist. Instead, it is a group of 3 adjacent, overlapping, non-hybridized p orbitals we call a **conjugated π electron system**. You can clearly see the interactions between all three of the p orbitals from the three carbons resulting in a really stable cation. It all comes down to where the location of the electron-deficient carbon is.

Molecular orbital descriptions can explain allylic stability in yet another way using 2-propenyl. Fig.6

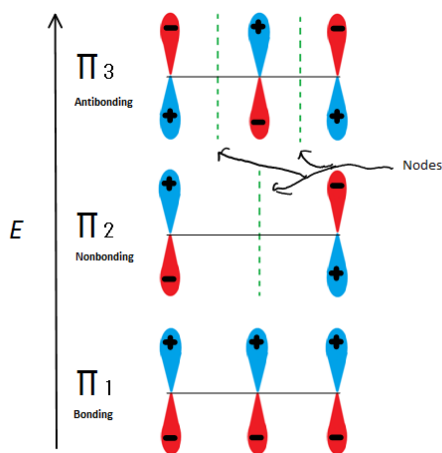


Figure: The 3 possible Molecular orbitals of 2-propenyl

If we just take the π molecular orbital and not any of the s, we get three of them. π_1 is bonding with no nodes, π_2 is nonbonding (In other words, the same energy as a regular p-orbital) with a node, and π_3 is antibonding with 2 nodes (none of the orbitals are interacting). The first

two electrons will go into the π_1 molecular orbital, regardless of whether it is a cation, radical, or anion. If it is a radical or anion, the next electron goes into the π_2 molecular orbital. The last anion electron goes into the nonbonding orbital also. So no matter what kind of carbon center exists, no electron will ever go into the antibonding orbital.

The Bonding orbitals are the lowest energy orbitals and are favorable, which is why they are filled first. Even though the nonbonding orbitals can be filled, the overall energy of the system is still lower and more stable due to the filled bonding molecular orbitals.

This figure also shows that π_2 is the only molecular orbital where the electron differs, and it is also where a single node passes through the middle. Because of this, the charges of the molecule are mainly on the two terminal carbons and not the middle carbon.

This molecular orbital description can also illustrate the stability of allylic carbon centers in figure 7.

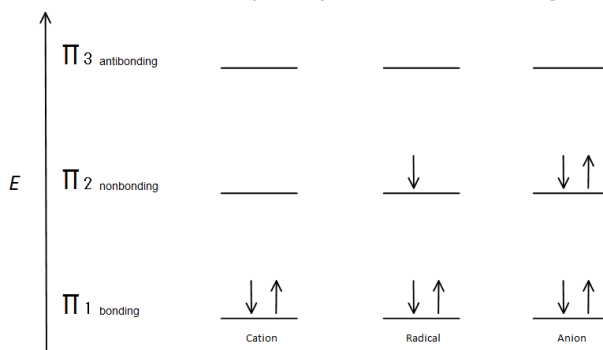
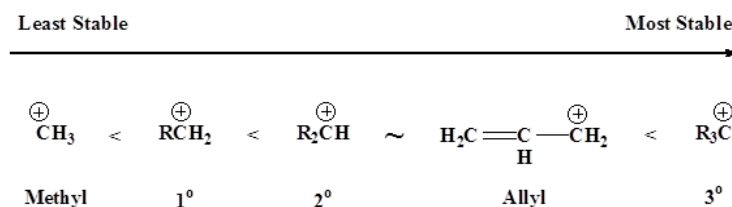


Figure: Diagram showing how the electrons fill based on the Aufbau principle.

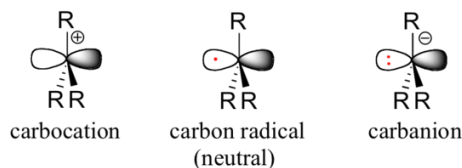
The π bonding orbital is lower in energy than the nonbonding p orbital. Since every carbon center shown has two electrons in the lower energy, bonding π orbitals, the energy of each system is lowered overall (and thus more stable), regardless of cation, radical, or anion.

RELATIVE STABILITIES OF CARBOCATIONS

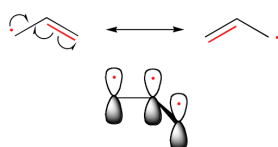


ALLYLIC RADICALS

As organic chemists, we are particularly interested in radical intermediates in which the unpaired electron resides on a carbon atom. Experimental evidence indicates that the three bonds in a carbon radical have trigonal planar geometry, and therefore the carbon is considered to be sp^2 -hybridized with the unpaired electron occupying the perpendicular, unhybridized $2p_z$ orbital. Contrast this picture with carbocation and carbanion intermediates, which are both also trigonal planar but whose $2p_z$ orbitals contain zero or two electrons, respectively.



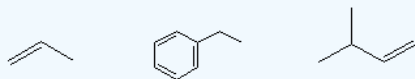
The trend in the stability of carbon radicals parallels that of carbocations (section 8.4B): tertiary radicals, for example, are more stable than secondary radicals, followed by primary and methyl radicals. This should make intuitive sense, because radicals, like carbocations, can be considered to be electron deficient, and thus are stabilized by the electron-donating effects of nearby alkyl groups. Benzylic and allylic radicals are more stable than alkyl radicals due to resonance effects - an unpaired electron can be delocalized over a system of conjugated π bonds. An allylic radical, for example, can be pictured as a system of three parallel $2p_z$ orbitals sharing three electrons.



This can also explain why [allylic radicals](#) are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.

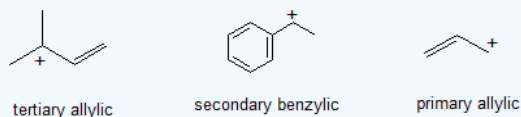
Exercise

2. Draw the bond-line structure for the most stable carbocation that can be formed from each hydrocarbon below. Arrange the carbocations in order of decreasing stability.



Answer

2. Carbocations in order of decreasing stability.



CONTRIBUTORS AND ATTRIBUTIONS

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- Jim Clark ([Chemguide.co.uk](#))
- Jeffrey Hu

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16.3: ELECTROPHILIC ADDITIONS TO CONJUGATED DIENES

OBJECTIVES

- After completing this section, you should be able to
- write an equation for the addition of one or two mole equivalents of a halogen or a hydrogen halide to a nonconjugated diene.
- write an equation for the addition of one or two mole equivalents of a halogen or a hydrogen halide to a conjugated diene.
- write the mechanism for the addition of one mole equivalent of hydrogen halide to a conjugated diene, and hence account for the formation of 1,2- and 1,4-addition products.
- explain the stability of allylic carbocations in terms of resonance.
- draw the resonance contributors for a given allylic carbocation.
- predict the products formed from the reaction of a given conjugated diene with one mole equivalent of halogen or hydrogen halide.
- predict which of the possible 1,2- and 1,4-addition products is likely to predominate when one mole equivalent of a hydrogen halide is reacted with a given conjugated diene.
- use the concept of carbocation stability to explain the ratio of the products obtained when a given conjugated diene is reacted with one mole equivalent of hydrogen halide.

KEY TERMS

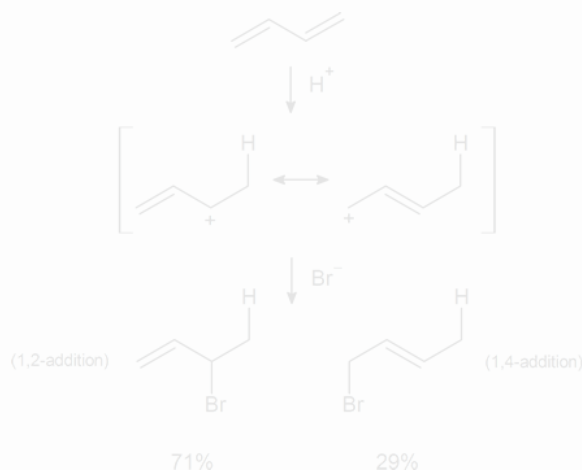
- Make certain that you can define, and use in context, the key terms below.
- 1,2-addition
- 1,4-addition

STUDY NOTES

Notice that the numbers used in the expressions 1,2-addition and 1,4-addition do *not* refer to the positions of the carbon atoms in the diene molecule. Here, 1,2 indicates two neighbouring carbon atoms, while 1,4 indicates two carbon atoms which are separated in the carbon chain by two additional carbon atoms. Thus in 1,2- and 1,4-additions to 2,4-hexadiene, the additions actually occur at carbons 2 and 3, and 2 and 5, respectively.

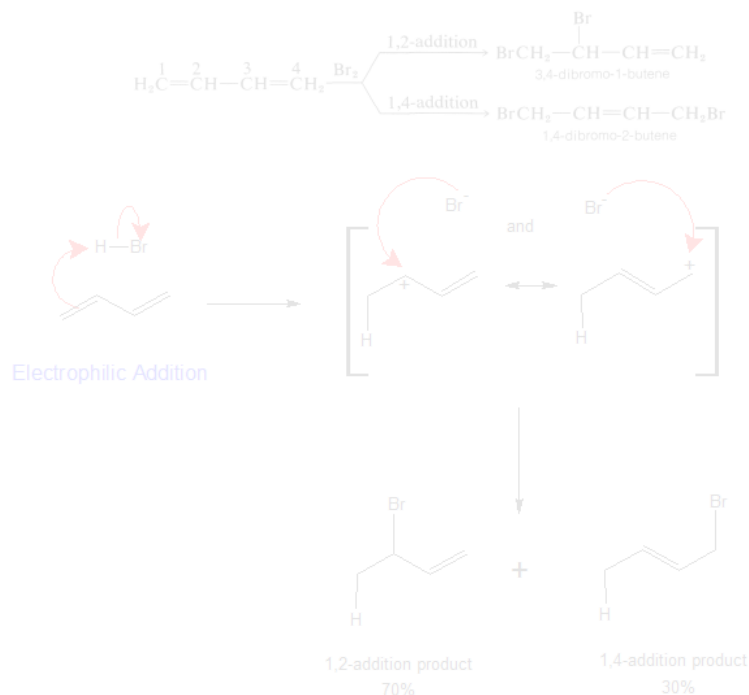
The term “monoadduct” should be interpreted as meaning the product or products formed when one mole of reagent adds to one mole of substrate. In the objectives above, this process is referred to as the addition of one mole equivalent (or one mol equiv).

In Section 7.9 we saw that electrophilic addition to a simple alkene would follow Markovnikov’s rule, where the stability of the carbocation intermediate would increase: primary < secondary < tertiary. With conjugated dienes the allylic carbocation intermediately generated has different resonance forms. The following scheme represents the mechanism for the addition of HBr to 1,3-butadiene (at 0°C). Note the resonance contributors for the allylic carbocation intermediate and that the product resulting from the secondary cation is generated in higher yield than from the primary cation as you might expect from our discussions until now. However, in the next section you will see that the resulting product ratio can be drastically affected by a number of reaction conditions, including temperature.



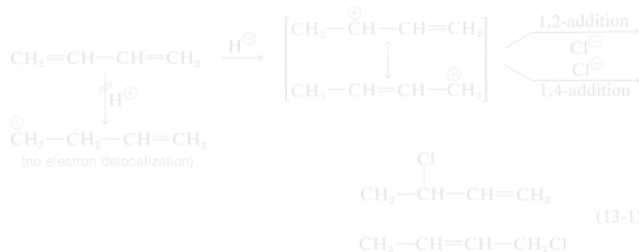
The reactions of 1,3-butadiene are reasonably typical of conjugated dienes. The compound undergoes the usual reactions of alkenes, such as catalytic hydrogenation or radical and polar additions, but it does so *more readily* than most alkenes or dienes that have isolated double

bonds. Furthermore, the products frequently are those of 1,2 and 1,4 addition:



The 1,2-addition product is favored because its secondary allylic carbocation intermediate is more stable.

Formation of both 1,2- and 1,4-addition products occurs not only with halogens, but also with other electrophiles such as the hydrogen halides. The mechanistic course of the reaction of 1,3-butadiene with hydrogen chloride is shown in Equation 13-1. The first step, as with alkenes, is formation of a carbocation. However, with 1,3-butadiene, if the proton is added to C1C1 (but not C2C2), the resulting cation has a substantial delocalization energy, with the charge distributed over two carbons (review Sections 6-5 and 6-5C if this is not clear to you). Attack of Cl^- as a nucleophile at one or the other of the positive carbons yields the 1,2- or the 1,4- addition product:



An important feature of reactions in which 1,2 and 1,4 additions occur in competition with one another is that the ratio of the products can depend on the temperature, the solvent, and also on the *total time of reaction*.

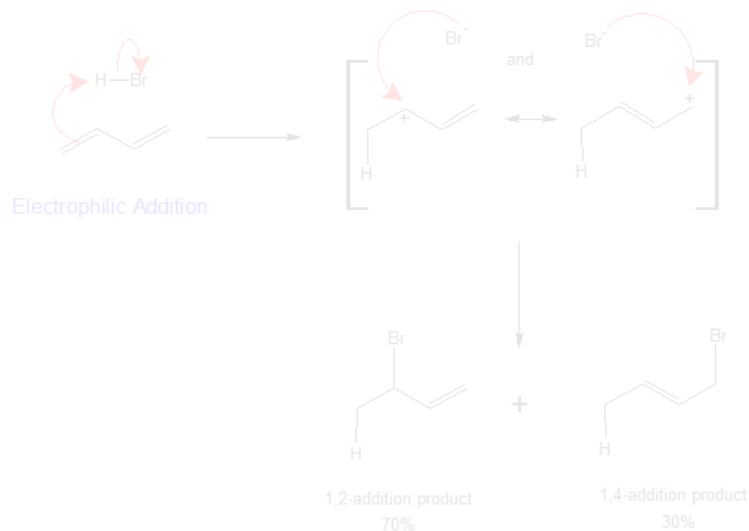
DIRECT VS CONJUGATE ADDITION

The description of direct versus conjugate addition uses numbers localized within the conjugate system and have nothing to do with the numbering system used to determine the IUPAC name for a conjugated diene. The reactions of 1,3-butadiene are reasonably typical of conjugated dienes and illustrate the difference in the numbering system to describe the reaction versus the IUPAC nomenclature numbers.



MECHANISM FOR THE ELECTROPHILIC ADDITION TO CONJUGATE DIENES

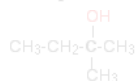
The mechanism below explains the formation and distribution of addition products to conjugated dienes using 1,3-butadiene as an example. The first step, as with isolated alkenes, is the formation of a carbocation. For 1,3-butadiene, the proton is added to form the allylic, resonance stabilized carbocation intermediate. The resulting cation has a substantial delocalization energy, with the charge distributed over two carbons. The nucleophile reacts with both carbons, but favors the carbon bearing the larger partial positive charge. The reaction yields both the 1,2- or the 1,4- addition products. The more stable the intermediate produces the greater the percentage of the final products as shown in the mechanism below.



The 1,2-addition product is favored because its secondary allylic carbocation intermediate is more stable.

Formation of both 1,2- and 1,4-addition products occurs not only with hydrohalic acids, but with halogens, catalytic hydrogenation or radical, and other polar additions associated with the electrophilic addition reactions of isolated alkenes.

In a tertiary (3°) alcohol, the carbon atom holding the $-OH$ group is bonded directly to three alkyl groups, which may be any combination of same or different. Examples:



2-methylpropan-2-ol

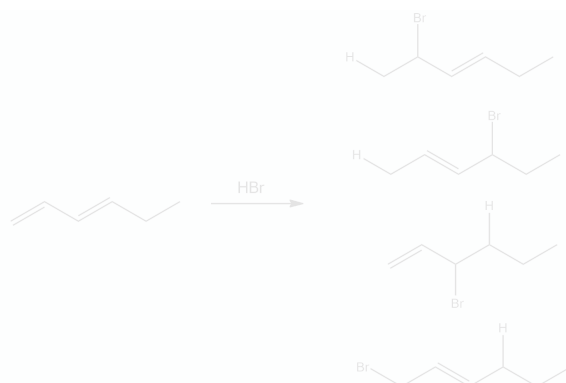
2-methylbutan-2-ol

Exercise

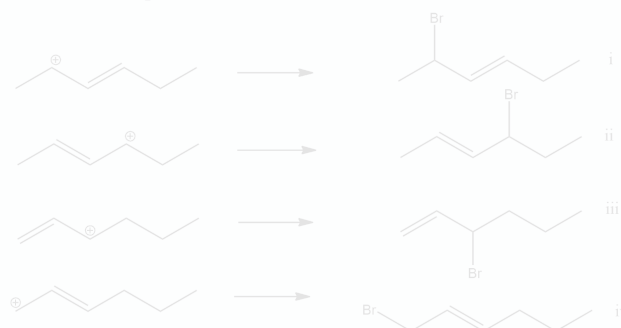
- Give the 1,2 and the 1,4 products of the addition of one equivalent of HBr to 1,3-hexa-diene.
- Look at the previous addition reaction of HBr with a diene. Consider the transition states, predict which of them would be the major products and which will be the minor.

Answer

3.



4. The products i-iii all show a secondary cation intermediate which is more stable than primary. Therefore those would be major products and the iv product would be the minor product.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition*. W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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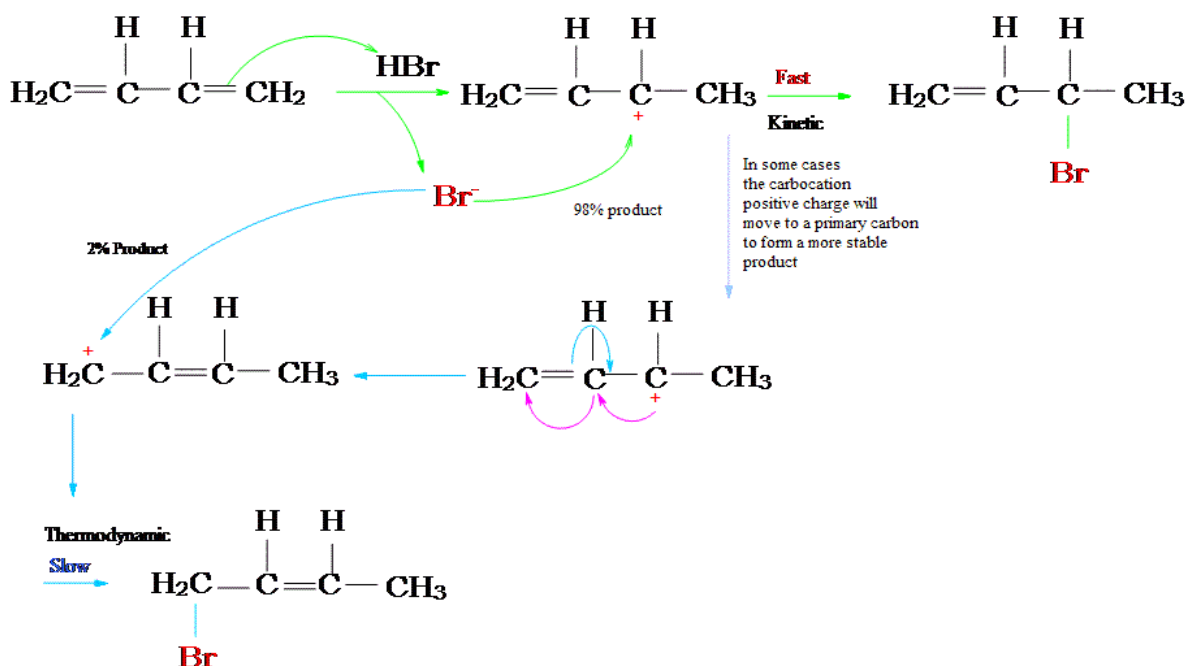
16.4: KINETIC VERSUS THERMODYNAMIC CONTROL

THERMODYNAMIC VS KINETIC CONTROL

Upon electrophilic addition, the conjugated diene forms a mixture of two products—the kinetic product and the thermodynamic product—whose ratio is determined by the conditions of the reaction. A reaction yielding more thermodynamic product is under thermodynamic control, and likewise, a reaction that yields more kinetic product is under kinetic control. The reaction of one equivalent of hydrogen bromide with 1,3-butadiene gives different ratios of products under different reaction conditions to illustrate the difference between thermodynamic and kinetic control.

The green mechanism arrows show the formation of the kinetically favored 1,2-addition product. As shown in the reaction energy diagram below the reaction, the 1,2-addition reaction has a smaller activation energy and faster reaction rate. This faster reaction rate is what led to the term "kinetic control". This reaction is favored by low temperatures where the activation energy becomes the primary barrier to chemical reactivity.

The blue mechanism arrows show the formation of the 1,4-addition product, the thermodynamically favored product. As shown in the reaction energy diagram below the reaction, the product of the 1,4-addition reaction is lower in potential energy. Its formation is favored by reactions at high temperatures where there is adequate thermodynamic energy to overcome all of the activation energy barriers. This reaction is favored by elevated temperatures which led to the term "thermodynamic control".



The table below summarizes the empirically derived reactivity patterns for conjugated dienes at four different reaction conditions. Becoming familiar with the reactivity data and patterns in this table helps us build wisdom for determining the optimum reaction conditions when competing mechanisms are possible.

Table : Conjugated Dienes: Kinetic vs. Thermodynamic Conditions

Temperature	Kinetic or Thermodynamically Controlled	Speed of Reaction	1,2-adduct : 1,4-adduct Ratio
-15 °C	Kinetic	Fast	70:30
0 °C	Kinetic	Fast	60:40
40 °C	Thermodynamic	Slow	15:85
60 °C	Thermodynamic	Slow	10:90

A Warning: Not every reaction has different thermodynamic and kinetic products!

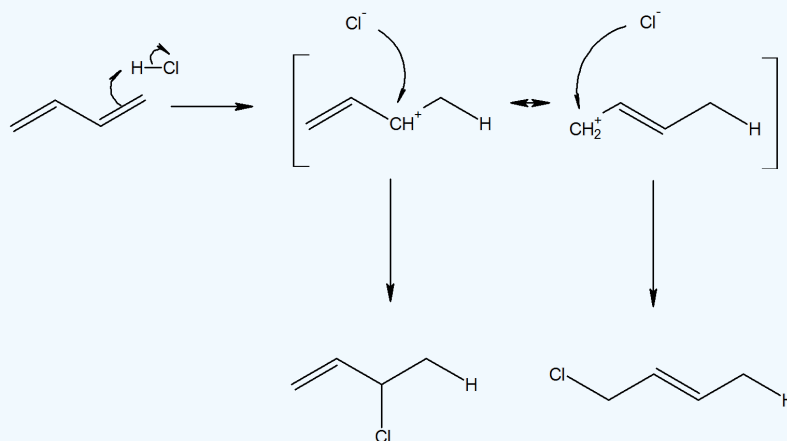
Note that not every reaction has an energy profile diagram like Figure 16.4.1, and not every reaction has different thermodynamic and kinetic products! If the transition states leading to the formation of C (e.g., T_{C1} , and T_{C2}) were to be higher in energy than that leading to B (e.g., T_{B1} , and T_{B2}), then B would simultaneously be both the thermodynamic and kinetic product. There are plenty of reactions in which the more stable product (*thermodynamic*) is also formed faster (*kinetic*).

Exercise

5. Consider the reaction with 1,3-butadiene reacting with HCl. Propose a mechanism for the reaction.

Answer

5.



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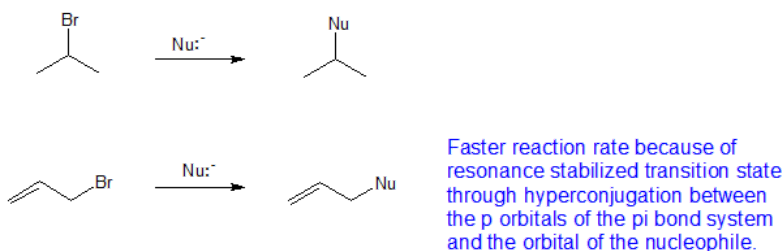
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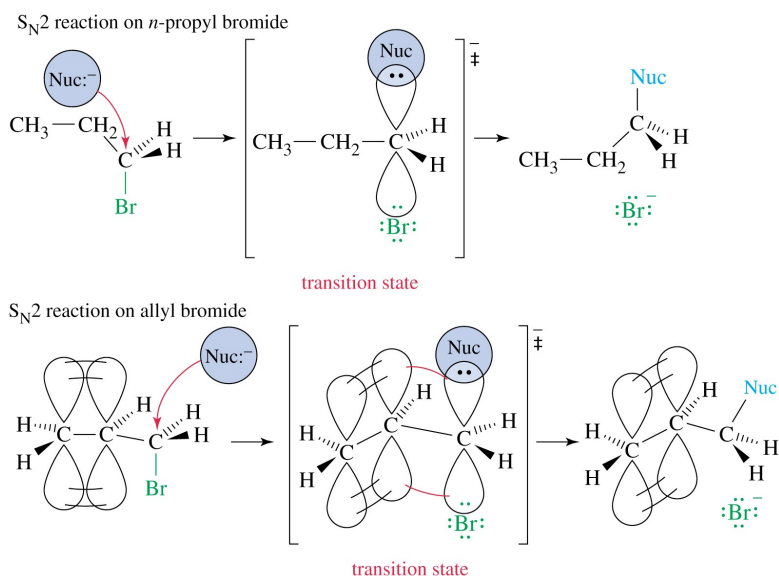
16.5: S_N2 REACTIONS OF ALLYLIC HALIDES AND TOSYLATES

S_N2 REACTIONS OF ALLYLIC HALIDES AND TOSYLATES

Allylic halides and tosylates are excellent electrophiles for bimolecular nucleophilic substitution reactions (S_N2).



They exhibit faster S_N2 reactivity than secondary alkyl halides because the bimolecular transition state is stabilized by hyperconjugation between the orbital of the nucleophile and the conjugated pi bond of the allylic group as shown in the diagram below.

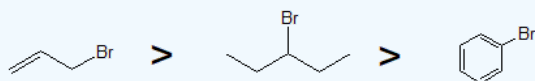


Exercise

6. Arrange the compounds 3-bromopentane, bromobenzene, and 3-bromo-1-propene in order of decreasing S_N2 reactivity using their bond-line structures.

Answer

6.



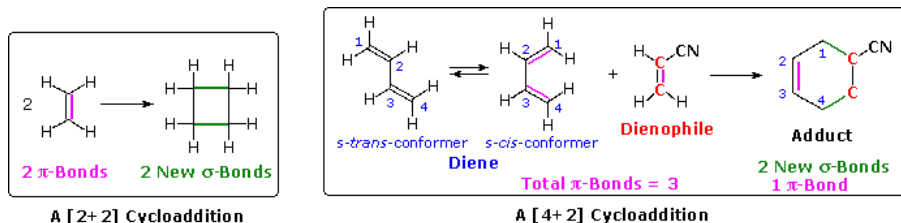
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16.6: THE DIELS-ALDER (4 + 2) CYCLOADDITION REACTION

THE DIELS-ALDER (4+2) CYCLOADDITION REACTION

A cycloaddition reaction is the concerted bonding together of two independent pi-electron systems to form a new ring of atoms. When this occurs, two pi-bonds are converted to two sigma-bonds, the simplest example being the hypothetical combination of two ethene molecules to give cyclobutane. This does not occur under normal conditions, but the cycloaddition of 1,3-butadiene to cyanoethene (acrylonitrile) does, and this is an example of the Diels-Alder reaction. The following diagram illustrates two cycloadditions, and introduces several terms that are useful in discussing reactions of this kind.

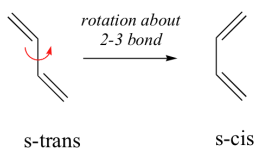


In the hypothetical ethylene dimerization on the left, each reactant molecule has a pi-bond (colored orange) occupied by two electrons. The cycloaddition converts these pi-bonds into new sigma-bonds (colored green), and this transformation is then designated a [2+2] cycloaddition, to enumerate the reactant pi-electrons that change their bonding location.

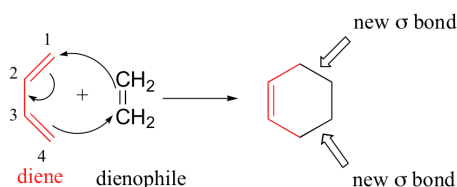
The Diels-Alder reaction is an important and widely used method for making six-membered rings, as shown on the right. The reactants used in such reactions are a conjugated diene, simply referred to as the **diene**, and a double or triple bond co-reactant called the **dienophile**, because it combines with (has an affinity for) the diene. The Diels-Alder cycloaddition is classified as a [4+2] process because the diene has four pi-electrons that shift position in the reaction and the dienophile has two.

DIELS-ALDER MECHANISM

The Diels-Alder reaction is a single step process, so the diene component must adopt an *s-cis* conformation in order for the end carbon atoms (#1 & #4) to bond simultaneously to the dienophile. For many acyclic dienes the *s-trans* conformer is more stable than the *s-cis* conformer (due to steric crowding of the end groups), but the two are generally in rapid equilibrium, permitting the use of all but the most hindered dienes as reactants in Diels-Alder reactions. In order for a Diels-Alder reaction to occur, the diene molecule must adopt what is called the ***s-cis* conformation**:

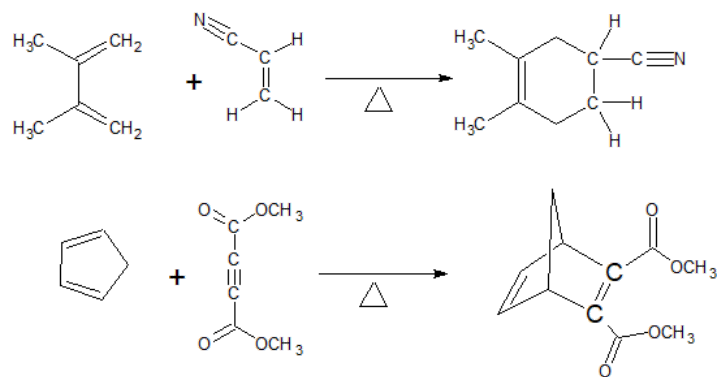


In its usual form, the diene component is electron rich, and the best dienophiles are electron poor due to electron withdrawing substituents such as CN, C=O & NO₂. The initial bonding interaction reflects this electron imbalance, with the two new sigma-bonds being formed simultaneously, but not necessarily at equal rates. Essentially, this process involves overlap of the 2p orbitals on carbons 1 and 4 of the diene with the two 2p orbitals on the sp²-hybridized carbons of the dienophile. Both of these new overlaps form new sigma bonds, and a new pi bond is formed between carbon 2 and 3 of the diene.



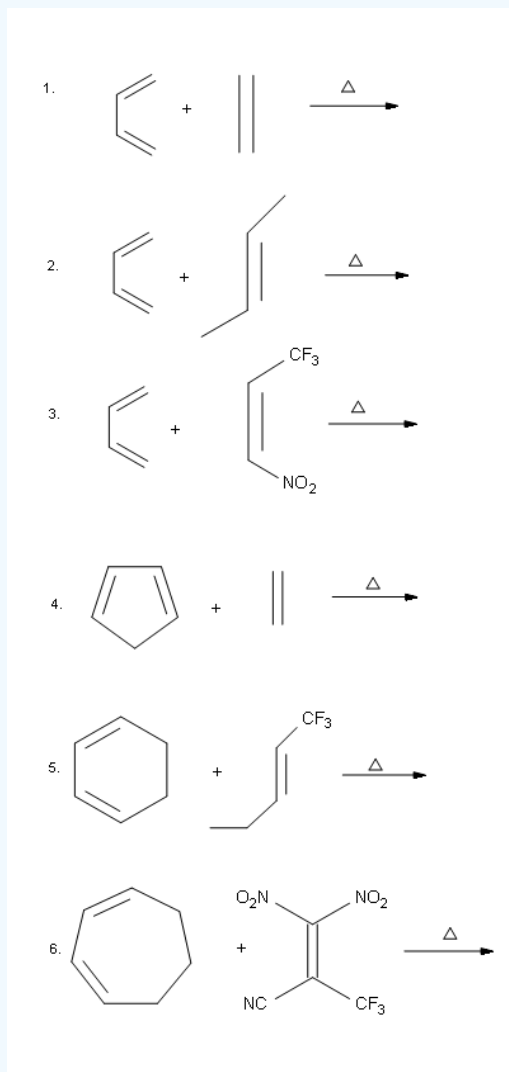
One of the most important things to understand about this process is that it is *concerted* – all of the electron rearrangement takes place at once, with no carbocation intermediates.

Since the diene takes the role of the nucleophile, electron donating groups increase the reactivity of the diene. While the dienophile takes the role of the electrophile, electron withdrawing groups increase the reactivity of the dienophile. The reactions below are examples of the Diels-Alder reaction.



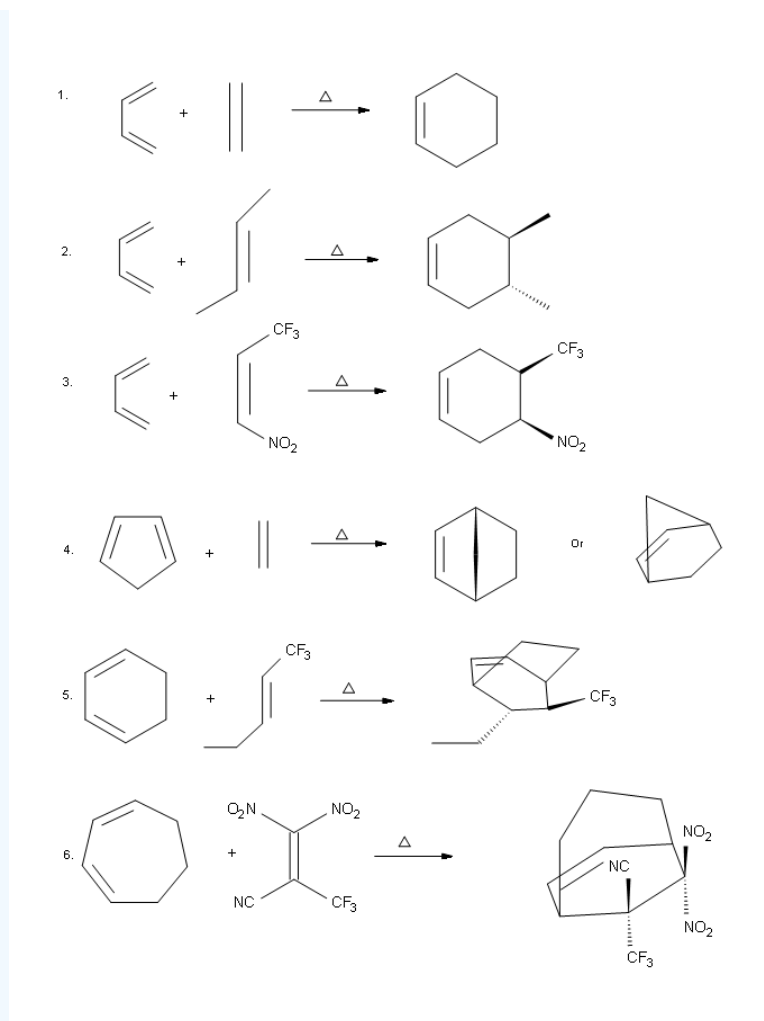
Exercise

7. Draw the bond-line structures for the reactions below.



Answer

7.



CONTRIBUTORS AND ATTRIBUTIONS

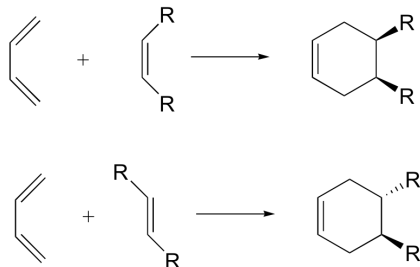
- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- [Prof. Steven Farmer](#) ([Sonoma State University](#))
- [William Reusch](#), Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
- [Amar Patel](#) (UCD)

16.6: The Diels-Alder (4 + 2) Cycloaddition Reaction is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

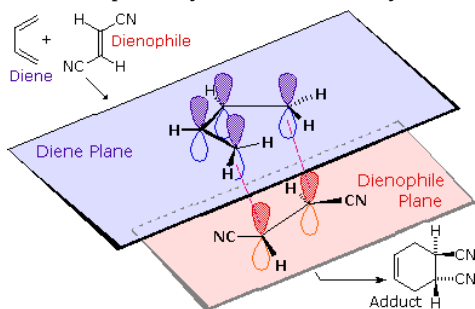
16.7: DIELS-ALDER STEREOCHEMISTRY

DIELS-ALDER REACTIONS ARE STEREOSPECIFIC

The Diels-Alder reaction is enormously useful for synthetic organic chemists, not only because ring-forming reactions are useful in general but also because in many cases two new stereocenters are formed, and the reaction is inherently stereospecific. A *cis* dienophile will generate a ring with *cis* substitution, while a *trans* dienophile will generate a ring with *trans* substitution:

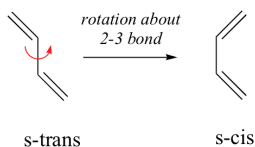


We noted earlier that addition reactions of alkenes often exhibited stereoselectivity, in that the reagent elements in some cases added syn and in other cases anti to the the plane of the double bond. Both reactants in the Diels-Alder reaction may demonstrate stereoisomerism, and when they do it is found that the relative configurations of the reactants are preserved in the product (the adduct). The following drawing illustrates this fact for the reaction of 1,3-butadiene with (*E*)-dicyanoethene. The *trans* relationship of the cyano groups in the dienophile is preserved in the six-membered ring of the adduct. Likewise, if the terminal carbons of the diene bear substituents, their relative configuration will be retained in the adduct. Using the earlier terminology, we could say that bonding to both the diene and the dienophile is syn. An alternative description, however, refers to the planar nature of both reactants and terms the bonding in each case to be **suprafacial** (i.e. to or from the same face of each plane). This stereospecificity also confirms the synchronous nature of the 1,4-bonding that takes place.

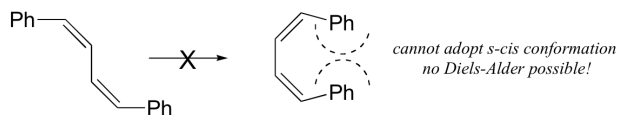


DIENE SUBSTITUENTS AND DIELS-ALDER REACTIVITY

In order for a Diels-Alder reaction to occur, the diene molecule must adopt what is called the **s-cis conformation**:



The s-cis conformation is higher in energy than the s-trans conformation, due to steric hindrance. For some dienes, extreme steric hindrance causes the s-cis conformation to be highly strained, and for this reason such dienes do not readily undergo Diels-Alder reactions.

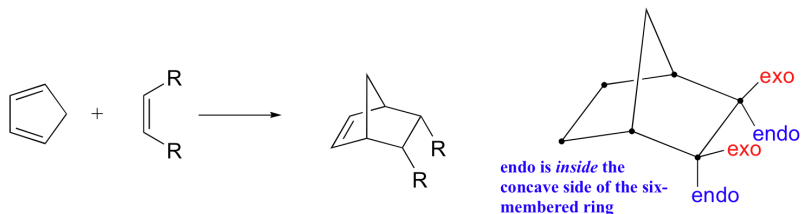


BICYCLIC RING FORMATION AND THE EXO- AND ENDO- POSITIONS

Cyclic dienes that are 'locked' in the s-cis conformation are especially reactive. The result of a Diels-Alder reaction involving a cyclic diene is a **bicyclic** structure:

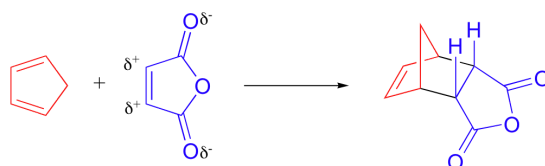


Here, we see another element of stereospecificity: Diels-Alder reactions with cyclic dienes favor the formation of bicyclic structures in which substituents are in the **endo position**.



The endo position on a bicyclic structure refers to the position that is *inside* the concave shape of the larger (six-membered) ring. As you might predict, the **exo position** refers to the *outside* position.

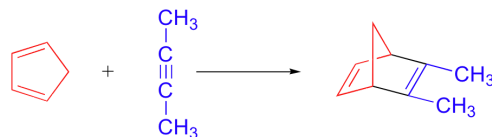
The rate at which a Diels-Alder reaction takes place depends on electronic as well as steric factors. A particularly rapid Diels-Alder reaction takes place between cyclopentadiene and maleic anhydride.



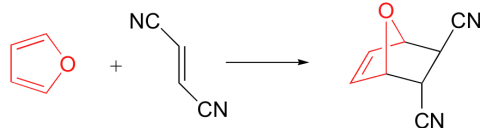
We already know that cyclopentadiene is a good diene because of its inherent *s-cis* conformation. Maleic anhydride is also a very good dienophile, because the electron-withdrawing effect of the carbonyl groups causes the two alkene carbons to be electron-poor, and thus a good target for reaction with the pi electrons in the diene.

In general, Diels-Alder reactions proceed fastest with electron-donating groups on the diene (eg. alkyl groups) and electron-withdrawing groups on the dienophile.

Alkynes can also serve as dienophiles in Diels-Alder reactions:

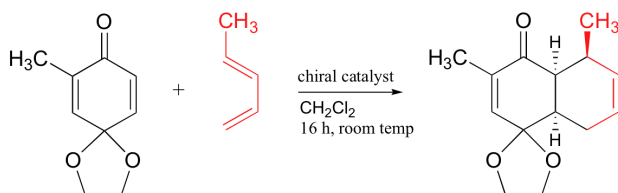


Below are three examples of Diels-Alder reactions that have been reported in recent years:



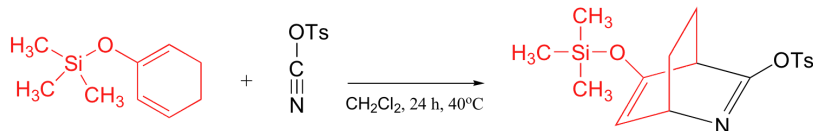
J. Med. Chem. **2008**, *51*, 424

[link](#)



Org. Lett. **2001**, *3*, 1559

[link](#)



J. Org. Chem. **2003**, *68*, 8256

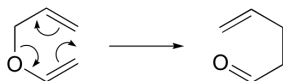
[link](#)

OTHER PERICYCLIC REACTIONS

The Diels-Alder reaction is just one example of a **pericyclic** reaction: this is a general term that refers to concerted rearrangements that proceed through cyclic transition states. Two well-studied intramolecular pericyclic reactions are known as the Cope rearrangement . . .

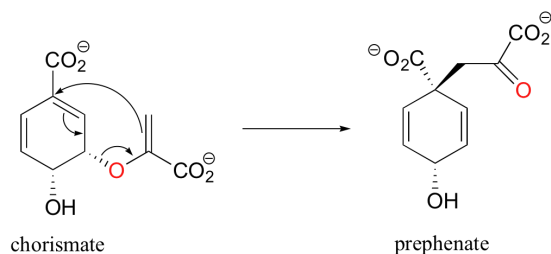


. . .and the Claisen rearrangement (when an oxygen is involved):



Notice that the both of these reactions require compounds in which two double bonds are separated by three single bonds.

Pericyclic reactions are rare in biological chemistry, but here is one example: the Claisen rearrangement catalyzed by chorismate mutase in the aromatic amino acid biosynthetic pathway.



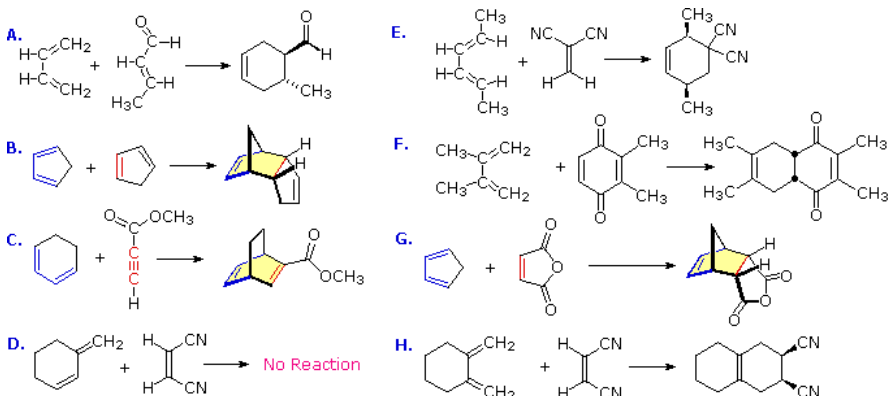
The study of pericyclic reactions is an area of physical organic chemistry that blossomed in the mid-1960s, due mainly to the work of R.B. Woodward, Roald Hoffman, and Kenichi Fukui. The **Woodward-Hoffman rules** for pericyclic reactions (and a simplified version introduced by Fukui) use molecular orbital theory to explain why some pericyclic processes take place and others do not. A full discussion is beyond the scope of this text, but if you go on to study organic chemistry at the advanced undergraduate or graduate level you are sure to be introduced to this fascinating area of inquiry.

DIELS-ALDER REACTION SUMMARY

The essential characteristics of the Diels-Alder cycloaddition reaction may be summarized as follows:

1. The reaction always creates a new six-membered ring. When intramolecular, another ring may also be formed.
2. The diene component must be able to assume a s-cis conformation.
3. Electron withdrawing groups on the dienophile facilitate reaction.
4. Electron donating groups on the diene facilitate reaction.
5. Steric hindrance at the bonding sites may inhibit or prevent reaction.
6. The reaction is stereospecific with respect to substituent configuration in both the dienophile and the diene.

These features are illustrated by the following eight examples, one of which does not give a Diels-Alder cycloaddition.

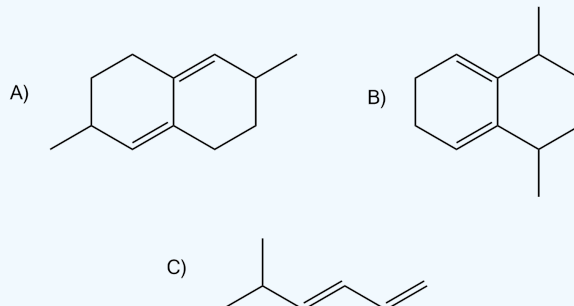


There is no reaction in example **D** because this diene cannot adopt an s-cis orientation. In examples **B**, **C**, **F**, **G** & **H** at least one of the reactants is cyclic so that the product has more than one ring, but the newly formed ring is always six-membered. In example **B** the same cyclic compound acts as both the diene (colored blue) and the dienophile (colored red). The adduct has three rings, two of which are the five-membered rings present in the reactant, and the third is the new six-membered ring (shaded light yellow). Example **C** has an alkyne as a dienophile (colored red), so the adduct retains a double bond at that location. This double bond could still serve as a dienophile, but in the

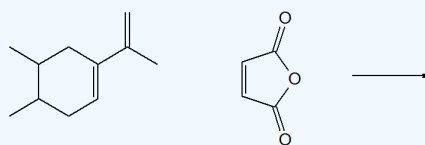
present case the diene is sufficiently hindered to retard a second cycloaddition. The quinone dienophile in reaction **F** has two dienophilic double bonds. However, the double bond with two methyl substituents is less reactive than the unsubstituted dienophile due in part to the electron donating properties of the methyl groups and in part to steric hindrance. The stereospecificity of the Diels-Alder reaction is demonstrated by examples **A**, **E** & **H**. In **A** & **H** the stereogenic centers lie on the dienophile, whereas in **E** these centers are on the diene. In all cases the configuration of the reactant is preserved in the adduct.

Exercise

8. Of the following dienes, which are *S*-trans and which are *s*-cis? Of those that are *s*-trans, are they able to rotate to become *s*-cis?



9. Predict the product of the following reaction.



Answer

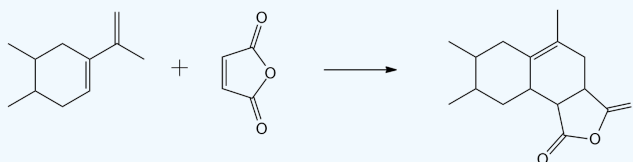
8.

A) *s*-trans, unable to rotate to become *s*-cis

B) *s*-cis

C) *s*-trans, can rotate to become *s*-cis.

9.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

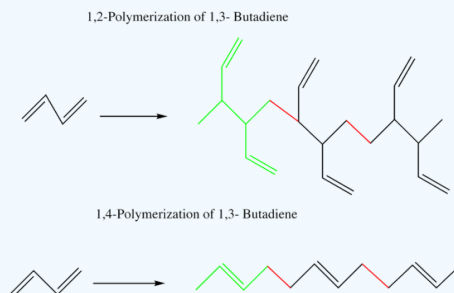
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16.8: DIENE POLYMERS - NATURAL AND SYNTHETIC RUBBERS

Conjugated dienes (alkenes with two double bonds and a single bond in between) can be polymerized to form important compounds like rubber. This takes place, in different forms, both in nature and in the laboratory. Interactions between double bonds on multiple chains leads to cross-linkage which creates elasticity within the compound.

POLYMERIZATION OF 1,3-BUTADIENE

For rubber compounds to be synthesized, 1,3-butadiene must be polymerized. Below is a simple illustration of how this compound is formed into a chain. The 1,4 polymerization is much more useful to polymerization reactions.



Above, the green structures represent the base units of the polymers that are synthesized and the red represents the bonds between these units which form these polymers. Whether the 1,3 product or the 1,4 product is formed depends on whether the reaction is thermally or kinetically controlled.

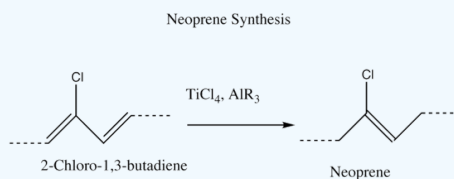
NATURAL RUBBER

Natural rubber is an addition polymer that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene), which is a conjugated diene hydrocarbon as mentioned above. In natural rubber, most of the double bonds formed in the polymer chain have the Z configuration, resulting in natural rubber's elastomer qualities.

Charles Goodyear accidentally discovered that by mixing sulfur and rubber, the properties of the rubber improved in being tougher, resistant to heat and cold, and increased in elasticity. This process was later called vulcanization after the Roman god of fire. Vulcanization causes shorter chains to cross link through the sulfur to longer chains. The development of vulcanized rubber for automobile tires greatly aided this industry.

SYNTHETIC RUBBER

The most important synthetic rubber is Neoprene which is produced by the polymerization of 2-chloro-1,3-butadiene.



In this illustration, the dashed lines represent repetition of the same base units, so both the products and reactants are polymers. The reaction proceeds with a mechanism similar to the Friedel-Crafts mechanism. Cross-linkage between the chlorine atom of one chain and the double bond of another contributes to the overall elasticity of neoprene. This cross-linkage occurs as the chains lie next to each other at random angles, and the attractions between double bonds prevent them from sliding back and forth.

OUTSIDE LINKS

- "Dienes," <http://en.Wikipedia.org/wiki/Diene>
- "Rubber," <http://en.Wikipedia.org/wiki/Rubber>
- "Neoprene," en.Wikipedia.org/wiki/Neoprene

REFERENCES

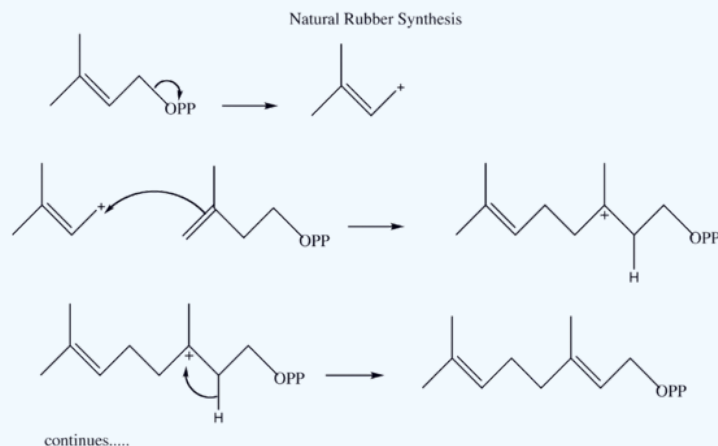
1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. New York: W. H. Freeman & Company, 2007.
2. Buehr, Walter. Rubber: Natural and Synthetic. Morrow, 1964.

Exercise

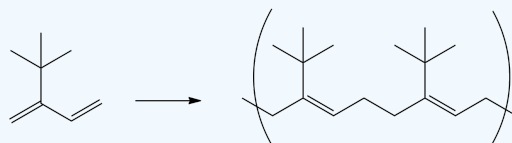
10. Draw out the mechanism for the natural synthesis of rubber from 3-methyl-3-butenyl pyrophosphate and 2-methyl-1,3-butadiene. Show the movement of electrons with arrows.
11. Draw a segment for the polymer that may be made from 2-*tert*-butyl-1,3-butadiene.
12. Propose the mechanism for the acid catalyzed polymerization of 2-methyl-1,3-butadiene.

Answer

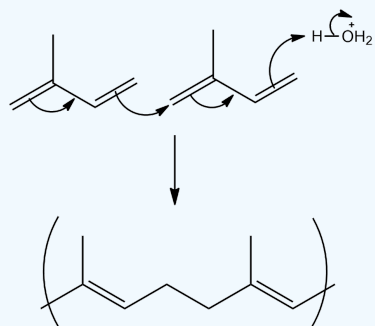
10.



11.



12. The initial step is an addition of a hydrogen from the acid, followed by the polymerization.



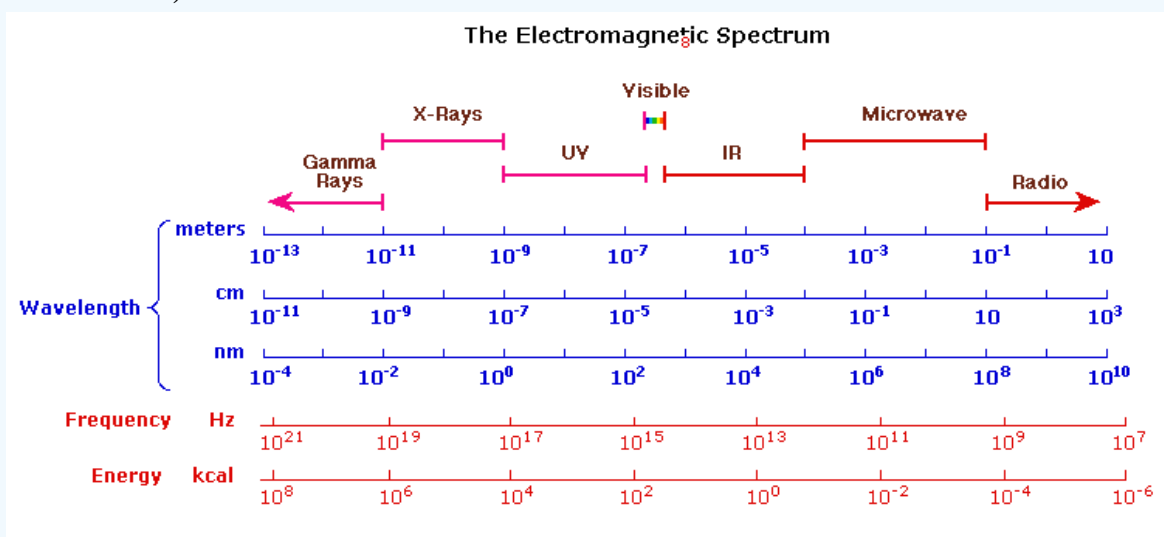
CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

16.9: STRUCTURE DETERMINATION IN CONJUGATED SYSTEMS - ULTRAVIOLET SPECTROSCOPY

THE ELECTROMAGNETIC SPECTRUM

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency (shown in the top equation below the chart).

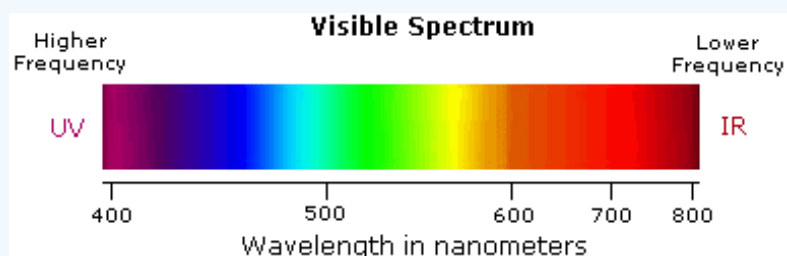
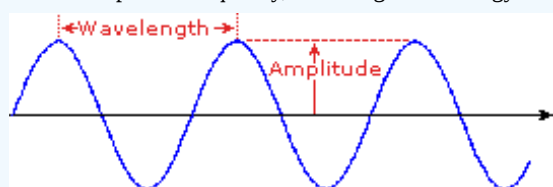


The energy associated with a given segment of the spectrum is proportional to its frequency. The bottom equation describes this relationship, which provides the energy carried by a photon of a given wavelength of radiation.

$$v = c/\lambda \quad v = \text{frequency, } \lambda = \text{wavelength, } c = \text{velocity of light (} c = 3 \cdot 10^{10} \text{ cm/sec)}$$

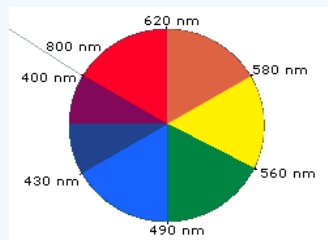
$$\Delta E = h\nu \quad E = \text{energy, } \nu = \text{frequency, } h = \text{Planck's constant (} h = 6.6 \cdot 10^{-27} \text{ erg sec)}$$

To obtain specific frequency, wavelength and energy values use this calculator.



- **Indigo:** 420 - 440 nm
- **Green:** 490 - 570 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

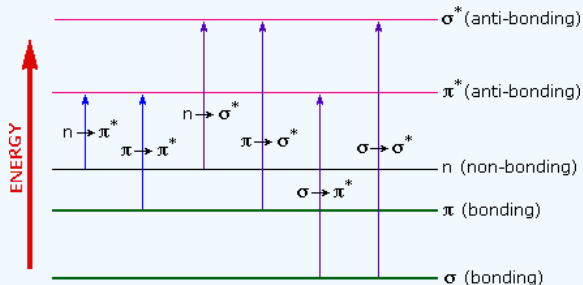


Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. The deep orange hydrocarbon carotene is widely distributed in plants, but is not sufficiently stable to be used as permanent pigment, other than for food coloring. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated π -electrons**.

UV-VISIBLE ABSORPTION SPECTRA

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

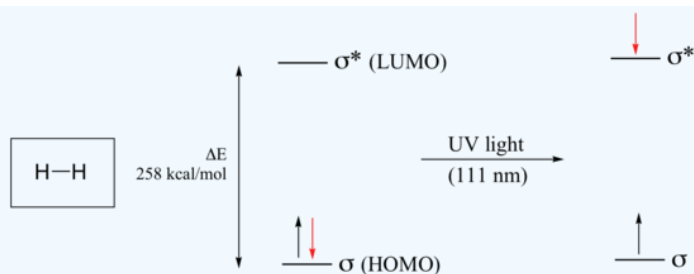


The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an **excited state**.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

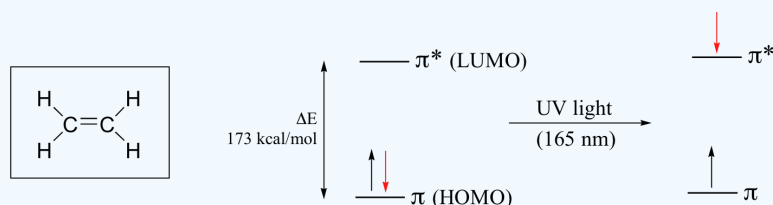
ELECTRONIC TRANSITIONS

Let's take as our first example the simple case of molecular hydrogen, H_2 . As you may recall from section 2.1A, the molecular orbital picture for the hydrogen molecule consists of one bonding σ MO, and a higher energy antibonding σ^* MO. When the molecule is in the ground state, both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The antibonding σ^* orbital, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).



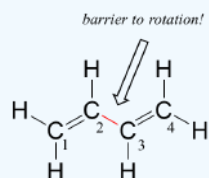
If the molecule is exposed to light of a wavelength with energy equal to ΔE , the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO – in other words, from the σ to the σ^* orbital. This is referred to as a $\sigma - \sigma^*$ **transition**. ΔE for this electronic transition is 258 kcal/mol, corresponding to light with a wavelength of 111 nm.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a $\pi - \pi^*$ **transition**. Because $\pi - \pi^*$ energy gaps are narrower than $\sigma - \sigma^*$ gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



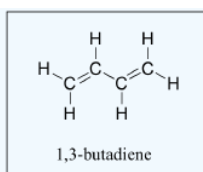
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated pi systems. In these groups, the energy gap for $\pi - \pi^*$ transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

Next, we'll consider the 1,3-butadiene molecule. From valence orbital theory alone we might expect that the C_2-C_3 bond in this molecule, because it is a sigma bond, would be able to rotate freely.

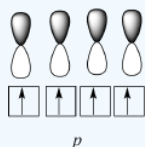


Experimentally, however, it is observed that there is a significant barrier to rotation about the C_2-C_3 bond, and that the entire molecule is planar. In addition, the C_2-C_3 bond is 148 pm long, shorter than a typical carbon-carbon single bond (about 154 pm), though longer than a typical double bond (about 134 pm).

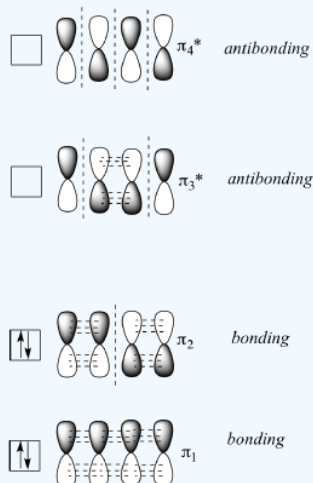
Molecular orbital theory accounts for these observations with the concept of **delocalized π bonds**. In this picture, the four p atomic orbitals combine mathematically to form four pi molecular orbitals of increasing energy. Two of these - the bonding pi orbitals - are lower in energy than the p atomic orbitals from which they are formed, while two - the antibonding pi orbitals - are higher in energy.



atomic orbitals

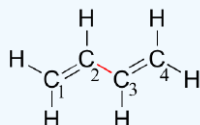


molecular orbitals



The lowest energy molecular orbital, π_1 , has only constructive interaction and zero nodes. Higher in energy, but still lower than the isolated p orbitals, the π_2 orbital has one node but two constructive interactions - thus it is still a bonding orbital overall. Looking at the two antibonding orbitals, π_3^* has two nodes and one constructive interaction, while π_4^* has three nodes and zero constructive interactions.

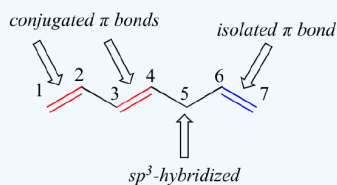
By the *aufbau* principle, the four electrons from the isolated $2p_z$ atomic orbitals are placed in the bonding π_1 and π_2 MO's. Because π_1 includes constructive interaction between C_2 and C_3 , there is a degree, in the 1,3-butadiene molecule, of pi-bonding interaction between these two carbons, which accounts for its shorter length and the barrier to rotation. The valence bond picture of 1,3-butadiene shows the two pi bonds as being isolated from one another, with each pair of pi electrons 'stuck' in its own pi bond. However, molecular orbital theory predicts (accurately) that the four pi electrons are to some extent delocalized, or 'spread out', over the whole pi system.



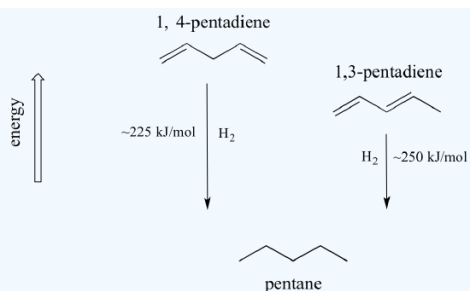
1,3-butadiene

space-filling view

1,3-butadiene is the simplest example of a system of **conjugated pi bonds**. To be considered conjugated, two or more pi bonds must be separated by only one single bond - in other words, there cannot be an intervening sp^3 -hybridized carbon, because this would break up the overlapping system of parallel p orbitals. In the compound below, for example, the C_1 - C_2 and C_3 - C_4 double bonds are conjugated, while the C_6 - C_7 double bond is **isolated** from the other two pi bonds by sp^3 -hybridized C_5 .

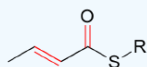


A very important concept to keep in mind is that *there is an inherent thermodynamic stability associated with conjugation*. This stability can be measured experimentally by comparing the **heat of hydrogenation** of two different dienes. (Hydrogenation is a reaction type that we will learn much more about in chapter 15: essentially, it is the process of adding a hydrogen molecule - two protons and two electrons - to a pi bond). When the two *conjugated* double bonds of 1,3-pentadiene are 'hydrogenated' to produce pentane, about 225 kJ is released per mole of pentane formed. Compare that to the approximately 250 kJ/mol released when the two *isolated* double bonds in 1,4-pentadiene are hydrogenated, also forming pentane.

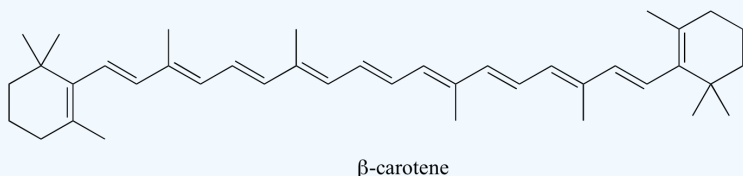


The conjugated diene is lower in energy: in other words, it is more stable. In general, conjugated pi bonds are more stable than isolated pi bonds.

Conjugated pi systems can involve oxygen and nitrogen atoms as well as carbon. In the metabolism of fat molecules, some of the key reactions involve alkenes that are conjugated to carbonyl groups.

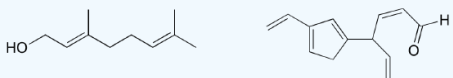


In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather than the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region – to be transmitted. This is why carrots are orange.

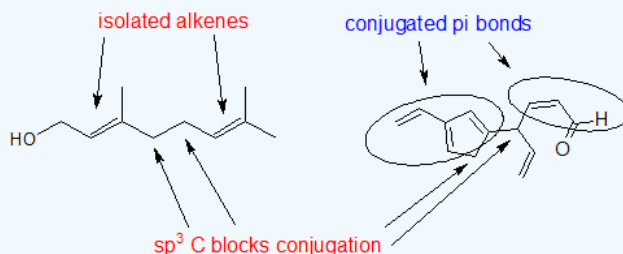


EXAMPLE 1

Identify all conjugated and isolated double bonds in the structures below. For each conjugated pi system, specify the number of overlapping *p* orbitals, and how many pi electrons are shared among them.

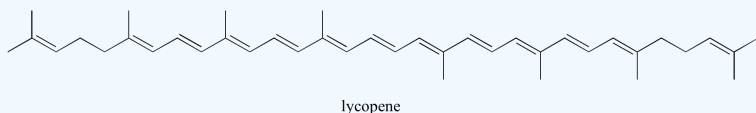


Solution: Look for sp^3 hybridized carbons to find disruptions in conjugation.

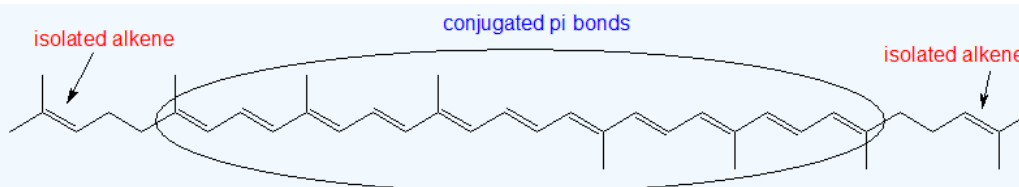


EXAMPLE 2

Identify all isolated and conjugated pi bonds in lycopene, the red-colored compound in tomatoes. How many pi electrons are contained in the conjugated pi system?



Solution: There are 11 conjugated pi bonds for a total of 22 pi electrons and 2 isolated pi bonds.



Exercise

13. What is the energy range for 300 nm to 500 nm in the ultraviolet spectrum? How does this compare to energy values from NMR and IR spectroscopy?

Answer

13.

$$E = hc/\lambda$$

$$E = (6.62 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})/(3.00 \times 10^{-7} \text{ m})$$

$$E = 6.62 \times 10^{-19} \text{ J}$$

The range of 3.972×10^{-19} to 6.62×10^{-19} joules. This energy range is greater in energy than the in NMR and IR.

CONTRIBUTORS

- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

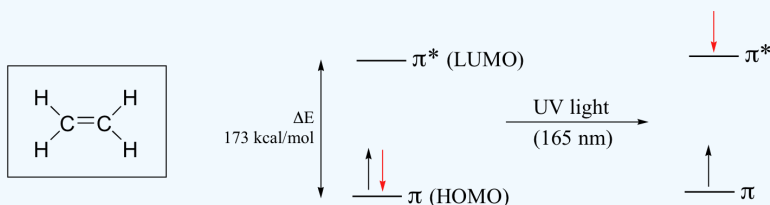
16.9: Structure Determination in Conjugated Systems - Ultraviolet Spectroscopy is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

16.10: INTERPRETING ULTRAVIOLET SPECTRA - THE EFFECT OF CONJUGATION

UV SPECTROSCOPY AND π ELECTRON TRANSITIONS BETWEEN THE HOMO AND LUMO

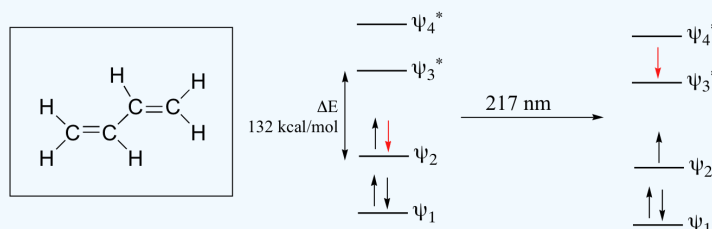
The ultraviolet absorption maximum of a conjugated molecule is dependent upon the extent of conjugation. As the conjugation increases, the Molecular Orbital energy decreases so that the π electron transitions occur in the UV and visible regions of the electromagnetic spectrum. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a $\pi - \pi^*$ transition. Because $\pi - \pi^*$ energy gaps are narrower than $\sigma - \sigma^*$ gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



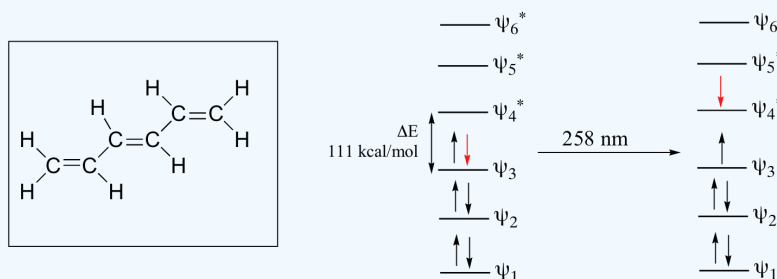
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated π systems. In these groups, the energy gap for $\pi - \pi^*$ transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer.

Let's revisit the MO picture for 1,3-butadiene, the simplest conjugated system. Recall that we can draw a diagram showing the four π MO's that result from combining the four $2p_z$ atomic orbitals. The lower two orbitals are bonding, while the upper two are anti-bonding.

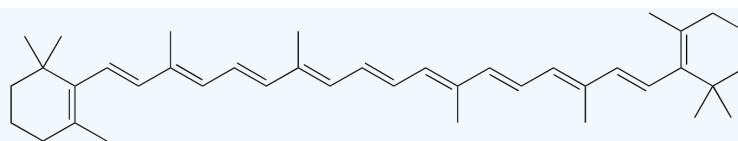


Comparing this MO picture to that of ethene, our isolated π -bond example, we see that the HOMO-LUMO energy gap is indeed smaller for the conjugated system. 1,3-butadiene absorbs UV light with a wavelength of 217 nm.

As conjugated π systems become larger, the energy gap for a $\pi - \pi^*$ transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the $\pi - \pi^*$ transition in 1,3,5-hexatriene, for example, occurs at 258 nm, corresponding to a ΔE of 111 kcal/mol.

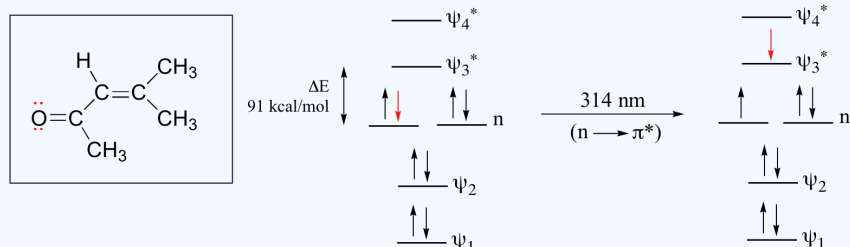


In molecules with extended π systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather than the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



β -carotene

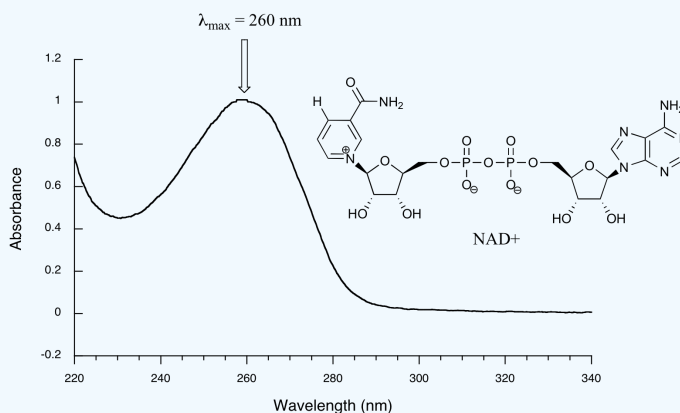
The conjugated pi system in 4-methyl-3-penten-2-one gives rise to a strong UV absorbance at 236 nm due to a $\pi - \pi^*$ transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π^* antibonding MO:



This is referred to as an **$n - \pi^*$ transition**. The nonbonding (n) MO's are higher in energy than the highest bonding p orbitals, so the energy gap for an $n - \pi^*$ transition is smaller than that of a $\pi - \pi^*$ transition – and thus the $n - \pi^*$ peak is at a longer wavelength. In general, $n - \pi^*$ transitions are weaker (less light absorbed) than those due to $\pi - \pi^*$ transitions.

LOOKING AT UV-VIS SPECTRA

We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is the same as for IR spectroscopy: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred. Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+ (we'll learn what it does in [section 16.4](#)) This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.



You'll notice that this UV spectrum is much simpler than the IR spectra we saw earlier: this one has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm) rather than in cm^{-1} as is the convention in IR spectroscopy.

Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum.. The first is λ_{max} , which is the wavelength at maximal light absorbance. As you can see, NAD^+ has $\lambda_{\text{max}} = 260 \text{ nm}$. We also want to record how much light is absorbed at λ_{max} . Here we use a unitless number called **absorbance**, abbreviated 'A'. This contains the same information as the 'percent transmittance' number used in IR spectroscopy, just expressed in slightly different terms. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength *before* it passes through the sample (I_0), divides this value by the intensity of the same wavelength *after* it passes through the sample (I), then takes the \log_{10} of that number:

$$A = \log I_0/I$$

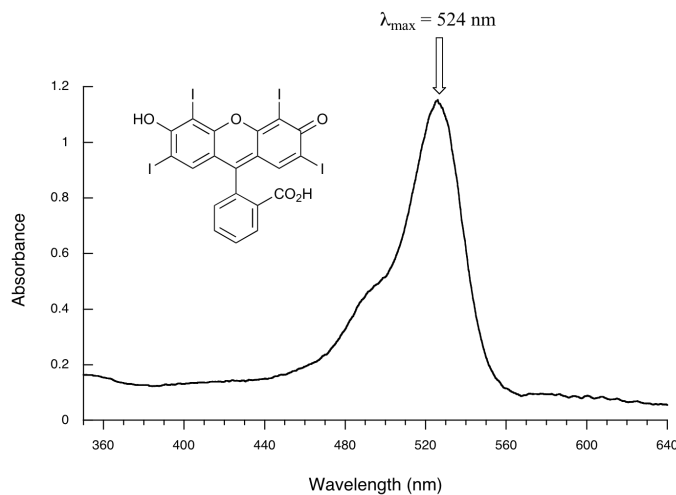
You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

Exercise

14. Express $A = 1.0$ in terms of percent transmittance (%T, the unit usually used in IR spectroscopy (and sometimes in UV-vis as well)).

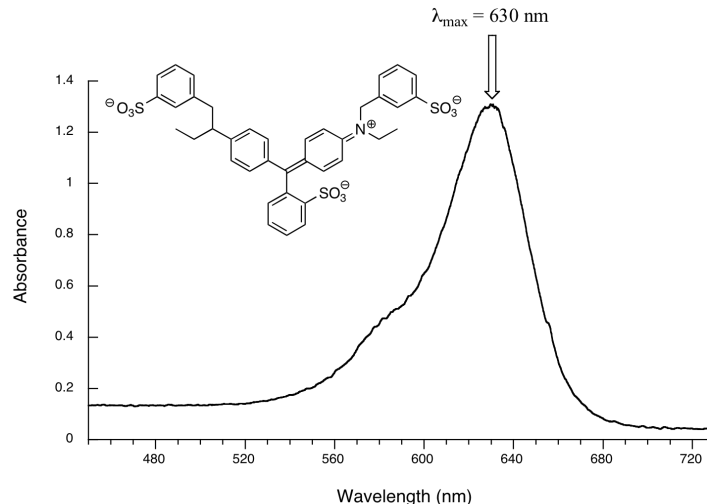
[Solution](#)

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes.

Now, take a look at the spectrum of another food coloring, Blue #1:



Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

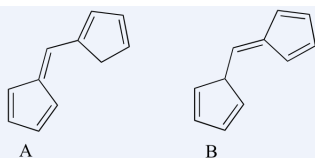
Exercise

15. How large is the $\pi - \pi^*$ transition in 4-methyl-3-penten-2-one?

[Solution](#)

Exercise

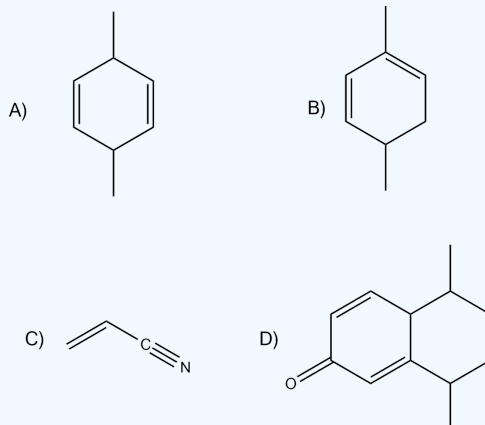
16. Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.



Solution

Exercise

17. Which of the following would show UV absorptions in the 200-300 nm range?



Answer

17. B would be the only one to show in that range.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

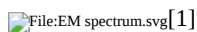
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16.11: CONJUGATION, COLOR, AND THE CHEMISTRY OF VISION

INTRODUCTION

Light is one of the most important resources for civilization, it provides energy as it pass along by the sun. Light influence our everyday live. Living organisms sense light from the environment by photoreceptors. Light, as waves carry energy, contains energy by different wavelength. In vision, light is the stimulus input. Light energy goes into the eye and stimulates its photoreceptors.

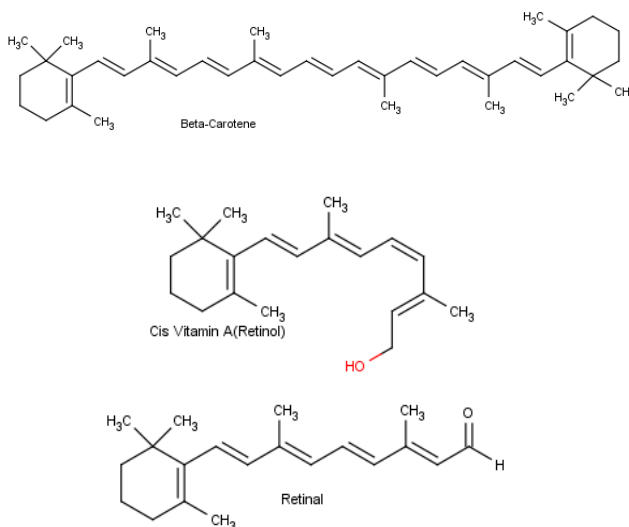
PHYSICAL CHARACTERISTICS OF LIGHT



The energy of light can be determined from its wavelength. The energy of light increases from long wavelength to short wavelength. The visible spectrum ranges from 400 nm to 700 nm.

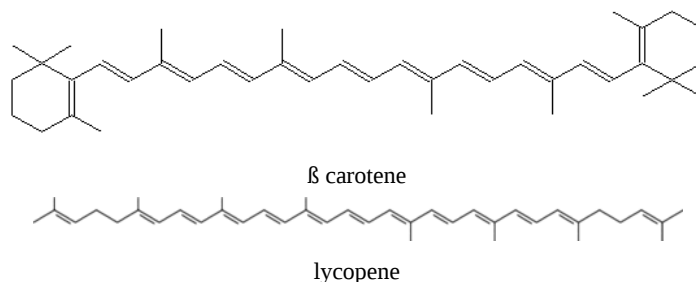
ENERGY CONVERTING CHEMICALS

Light energy can convert chemical to other forms. Vitamin A, also known as retinol, anti-dry eye vitamins, is a required nutrition for human health. The predecessor of vitamin A is present in the variety of plant carotene. Vitamin A is critical for vision because it is needed by the retina of eye. Retinol can be convert to retinal, and retinal is a chemical necessary for rhodopsin. As light enters the eye, the 11-*cis*-retinal is isomerized to the all-*trans* form.



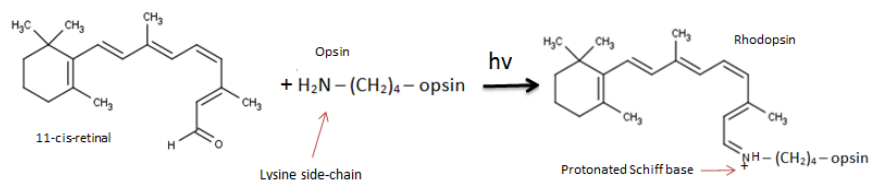
COLORED MOLECULES

The conjugated double bonds in beta-carotene produce the orange color in carrots. The conjugated double bonds in lycopene produce the red color in tomatoes.



MECHANISM OF VISION

We now know in rhodopsin, there is protein and retinal. The large protein is called opsin. Opsin does not absorb visible light, but when it bonded with 11-*cis*-retinal by its lysine side-chain to form rhodopsin, the new molecule has a very broad absorption band in the visible region of the spectrum.[2][3]

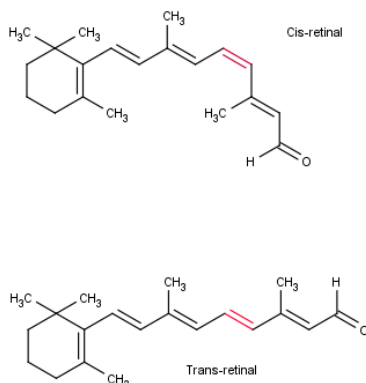


The reaction above shows Lysine side-chain from the opsin react with 11-cis-retinal when stimulated. By removing the oxygen atom from the retinal and two hydrogen atom from the free amino group of the lysine, the linkage show on the picture above is formed, and it is called Schiff base.

SIGNAL TRANSDUCTION PATHWAY

In human eyes, rod and cones react to light stimulation, and a series of chemical reactions happen in cells. These cells receive light, and pass on signals to other receiver cells. This chain of process is class signal transduction pathway. Signal transduction pathway is a mechanism that describe the ways cells react and response to stimulation.

The molecule cis-retinal can absorb light at a specific wavelength. When visible light hits the cis-retinal, the cis-retinal undergoes an [isomerization](#), or change in molecular arrangement, to all-trans-retinal. The new form of trans-retinal does not fit as well into the protein, and so a series of geometry changes in the protein begins. The resulting complex is referred to a bathrhodopsin (there are other intermediates in this process, but we'll ignore them for now).



As the protein changes its geometry, it initiates a cascade of biochemical reactions that results in changes in charge so that a large potential difference builds up across the plasma membrane. This potential difference is passed along to an adjoining nerve cell as an electrical impulse. The nerve cell carries this impulse to the brain, where the visual information is interpreted.

REFERENCES

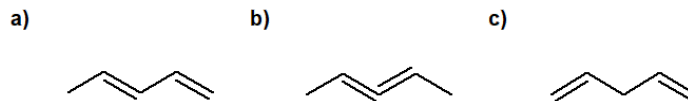
1. Biochemistry, L. Stryer (W.H. Freeman and Co, San Francisco, 1975).
2. *The Cambridge Guide to the Material World*, Rodney Cotterill (Cambridge University Press, Cambridge, 1985)

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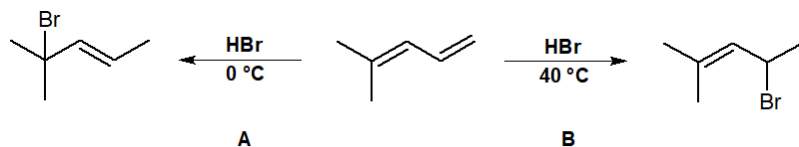
16.12: ADDITIONAL EXERCISES

General Review

16-1 Identify which of the following dienes are isolated, conjugated, or cumulated.



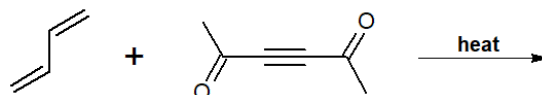
16-2 Identify which pathway gives the thermodynamic or the kinetic product and provide a reason for your answer.



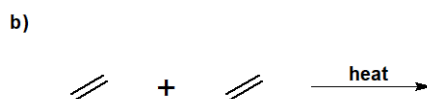
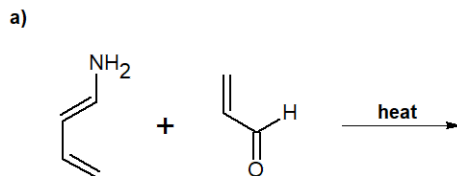
16-3 Draw the resonance structures of the following molecule.



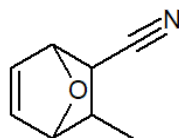
16-4 Provide the final product of the following reaction.



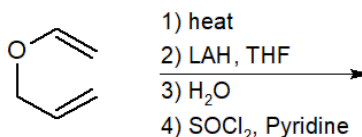
16-5 Predict the final product for the following reactions.



16-6 For the following compound, predict which bonds could be broken to give the most probable Diels-Alder dienes that reacted to make the compound. Provide the resulting dienes from the prediction.



16-7 Give the final product of the following reaction chain..



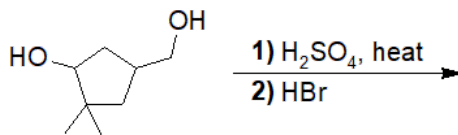
1,2- and 1,4-Addition to Conjugated Dienes

16-8 Predict all possible products of the following reaction.



16-9 Identify the kinetic and thermodynamic products of the previous problem, 16-8.

16-10 Predict the kinetic product(s) of the following reaction and provide proper IUPAC nomenclature.

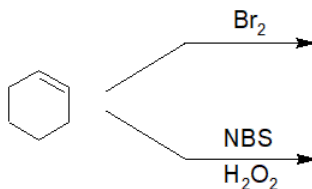


Allylic Radicals

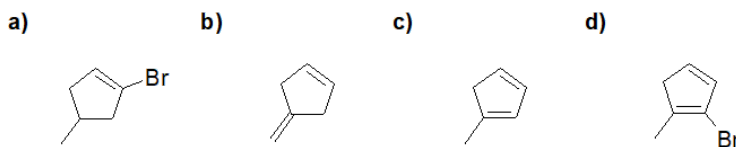
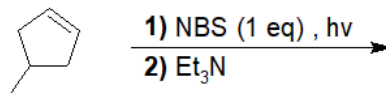
16-11 Draw arrows to show the movement of electrons in the following allylic radical.



16-12 Show the products of the following reactions.

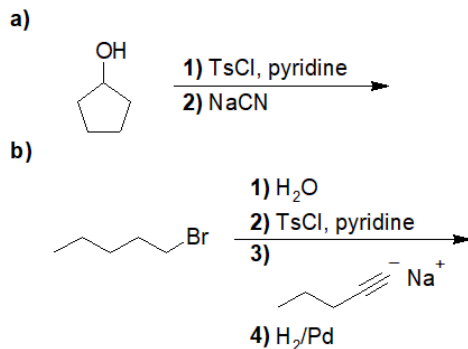


16-13 Choose the correct answer of the following reaction.

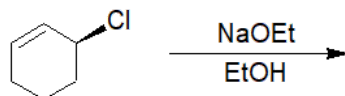


$\text{S}_{\text{N}}2$ Displacement Reactions of Allylic Halides and Tosylates

16-14 Predict the products of the following reactions.

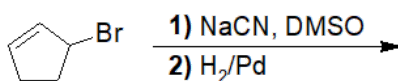


16-15 Choose the correct IUPAC nomenclature of the product of the following reaction and provide its structure.



- a) (3R)-3-ethoxycyclohex-1-ene
- b) (3S)-3-ethoxycyclohex-1-ene
- c) ethoxycyclohexane
- d) cyclohexa-1,3-diene

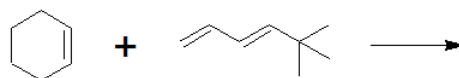
16-16 Predict the product of the following reaction.



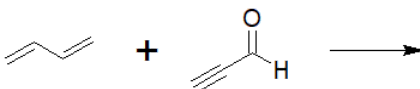
Diels-Alder Reactions

16-17 Predict the products of the following Diels-Alder reactions.

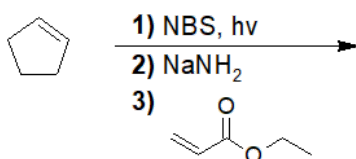
a)



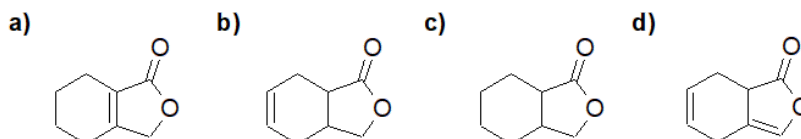
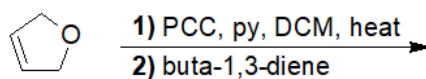
b)



16-18 Predict the product of the following reaction.



16-19 Choose the correct answer.



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16.13: SOLUTIONS TO ADDITIONAL EXERCISES

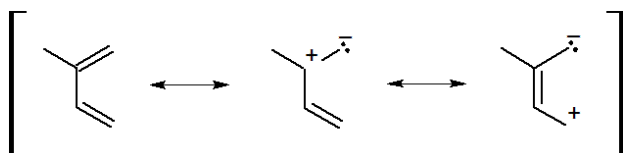
General Review

16-1

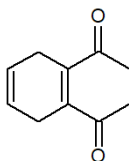
1. Conjugated
2. Cumulated
3. Isolated

16-2 Pathway A leads to the kinetic product. Since the intermediate formed during this pathway is the most stable intermediate, it forms the fastest and will always give the kinetic product. Pathway B forms the thermodynamic product, which is the most stable final product.

16-3

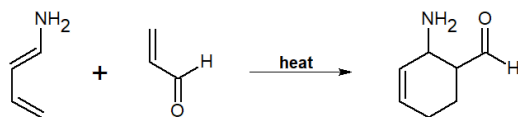


16-4

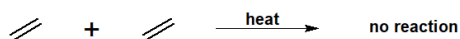


16-5

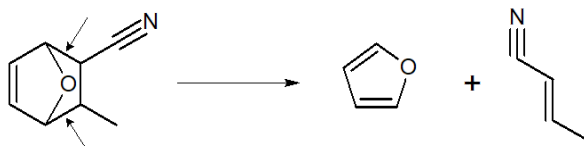
a)



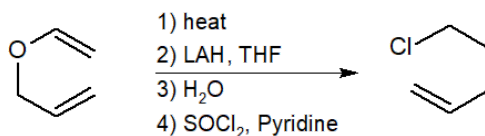
b)



16-6

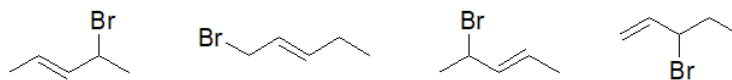


16-7



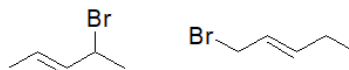
1,2- and 1,4-Addition to Conjugated Dienes

16-8:



16-9:

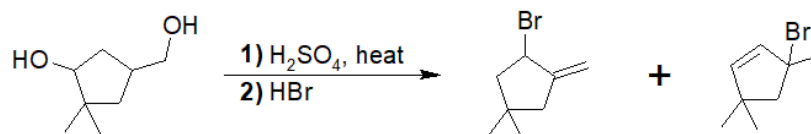
Thermodynamic:



Kinetic:

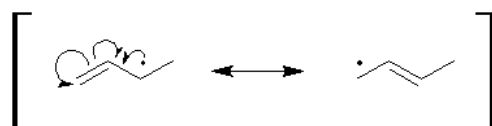


16-10:

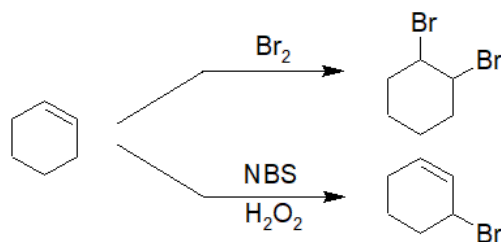


Allylic Radicals

16-11:



16-12:

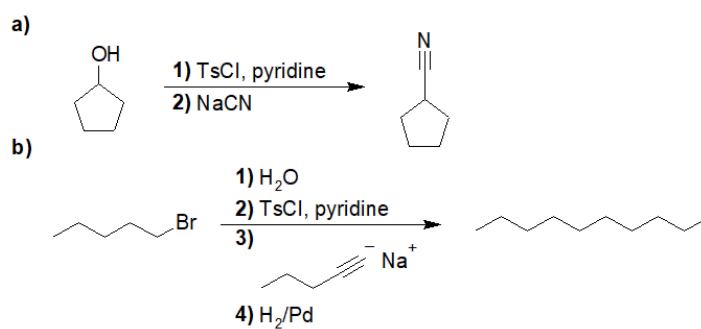


16-13:

Answer: C

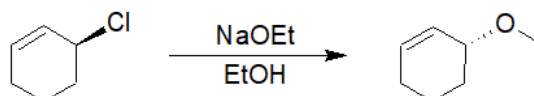
S_N2 Displacement Reactions of Allylic Halides and Tosylates

16-14:

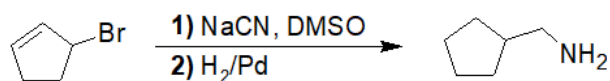


16-15:

Answer:

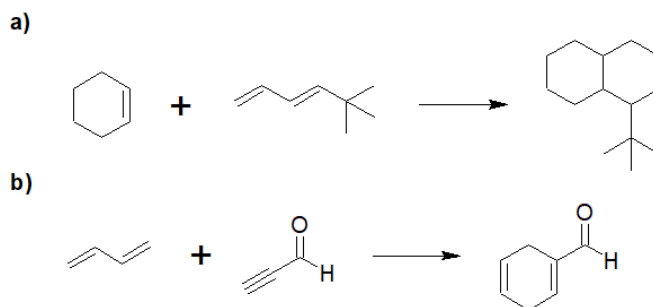


16-16:

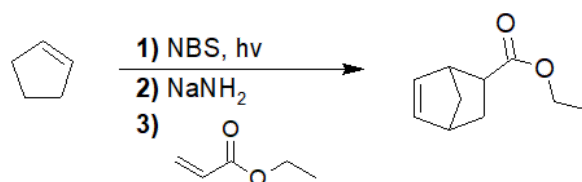


Diels-Alder Reactions

16-17:



16-18:



16-19:

Answer: B

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