

CFQ & PP: Conjugated Molecules

Reading

Brown and Foote: Sections 5.1, 6.6, 19.8 and 23.1 – 23.3

Lecture Handouts

Ethylene MOs (<http://web.chem.ucla.edu/~harding/ethyleneorbitals.html>)

1,3-Butadiene MOs (<http://web.chem.ucla.edu/~harding/butadieneorbitals.html>)

Optional Web Site Reading

Orbitals (<http://www.colby.edu/chemistry/OChem/DEMOS/Orbitals.html>)

Suggested Text Exercises

Brown and Foote: Chapter 19: 14 – 17, 51, 52

Chapter 23: 1, 2, 4 – 6, 11, 12, 21 – 34, 37

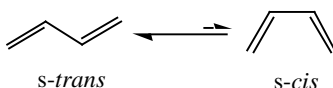
Optional Interactive Organic Chemistry CD and Workbook

Mechanisms: 1,2- and 1,4-Addition to a Conjugated Diene (p. 17)

Michael Reaction (p. 28)

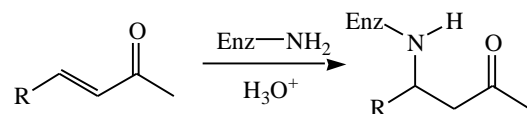
Concept Focus Questions

1. Define the following terms:
 - (a) Antibonding molecular orbital
 - (b) Barrier to rotation
 - (c) Bonding molecular orbital
 - (d) Conjugate addition
 - (e) Conjugated molecule
 - (f) HOMO
 - (g) LUMO
 - (h) Molecular orbital
 - (i) Node
2. Draw three resonance contributors and the resonance hybrid for 1,3-butadiene.
3. 1,3-Butadiene exists as a 95:5 equilibrium mixture of the *s-trans* and *s-cis* conformations. No other conformation is significantly populated.



- (a) Why is *s-trans* preferred over *s-cis*?
 - (b) Why does the molecule have a strong preference to be planar?
4. The barrier to rotation between the *s-cis* and *s-trans* conformations of 1,3-butadiene is about 1.5 kcal mol⁻¹ higher than the similar rotation for butane. Why?
 5. Estimate the C2-C3 bond length of 1,3-butadiene.

- Using a molecular orbital diagram, explain why H_2 is a stable molecule while He_2 is not.
- Using a molecular orbital diagram, briefly discuss the bonding in a simple alkene such as ethylene.
- Using a molecular orbital diagram, briefly discuss the bonding in a simple conjugated molecule such as 1,3-butadiene.
- Consider the addition reaction of an enzymatic amine to an enone (, α -unsaturated ketone).



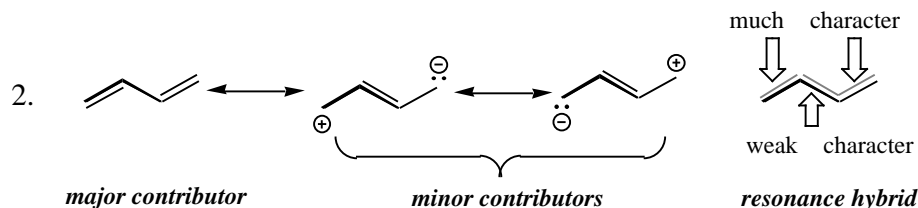
- Alkenes are normally nucleophiles, but in this reaction the alkene is functioning as an electrophile. Why?
 - Write a mechanism for this reaction.
- Describe in words the nature of the Diels-Alder reaction, and provide a clear example. Include the mechanism and all transition states.

Concept Focus Questions Solutions

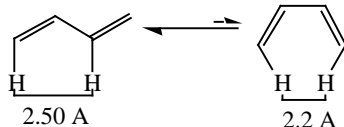
- Antibonding molecular orbital:** A molecular orbital in which electrons have higher energy than they would in isolated atomic orbitals.
 - Barrier to rotation:** The energy difference between the lowest and highest energy structures that result from rotation around a bond.
 - Bonding molecular orbital:** A molecular orbital in which electrons have lower energy than they would in isolated atomic orbitals.
 - Conjugate addition:** An addition reaction in which a new bond is formed at the end of a conjugated molecule.
 - Conjugated molecule:** A molecule containing two coplanar bonds separated by one bond.
 - HOMO (Highest Occupied Molecular Orbital):** The highest energy molecular orbital that contains a pair of electrons.
 - LUMO (Lowest Unoccupied Molecular Orbital):** The lowest energy molecular orbital that contains no electrons.

(h) **Molecular orbital**: A mathematical description of a region of space about a molecule in which there is a high probability (90-95%) of finding an electron or electron pair of a certain energy. (Molecular orbitals belong to a molecule as a whole and not to individual atoms.)

(i) **Node**: Plane of zero electron density.



3. (a) In the *s-cis* conformation, two terminal hydrogen atoms are fairly close together, causing van der Waals repulsion. The nonbonding interactions in the *s-trans* conformation are less severe because the hydrogen atoms are always further away. Thus the *s-trans* conformation has lower energy than the *s-cis* conformation.

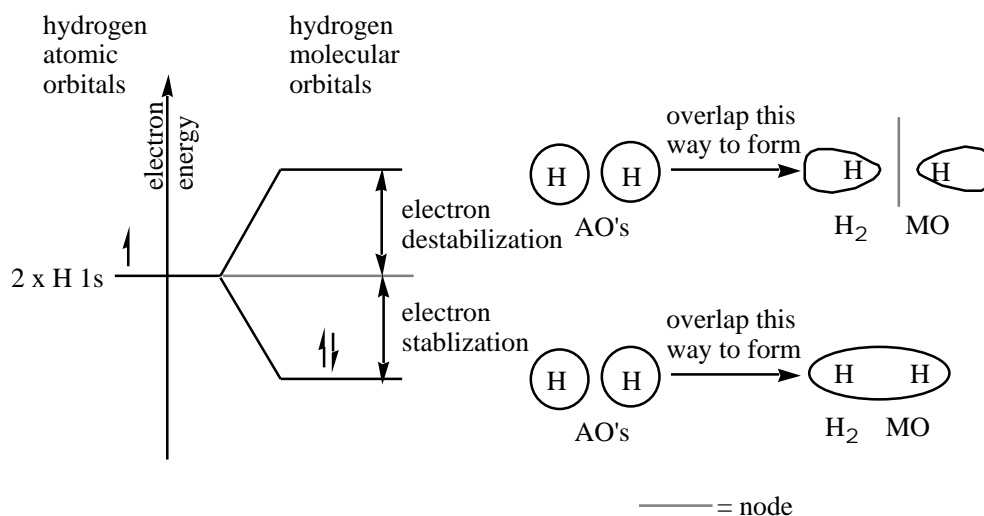


(b) All four carbons of 1,3-butadiene are sp^2 hybridized. Each carbon thus has a p_z orbital. The π bond between C1 and C2 as well as between C3 and C4 is strongest when these p_z orbitals have the greatest overlap. This occurs when the p_z orbitals are perfectly parallel. Bond rotation carries the p_z orbitals away from being parallel, weakening the π bond, and raising the energy of the molecule. The p_z orbitals of C2 and C3 can overlap as well, although the resulting π bond is not as strong as the C1-C2 or C3-C4 π bond. This can be seen on the resonance hybrid in question 2. For all four p_z orbitals to achieve maximum overlap, 1,3-butadiene must be planar. The extra π bonding between C2 and C3 provides enough extra stabilization to overcome the destabilizing eclipsing interactions that occur in the planar conformation.

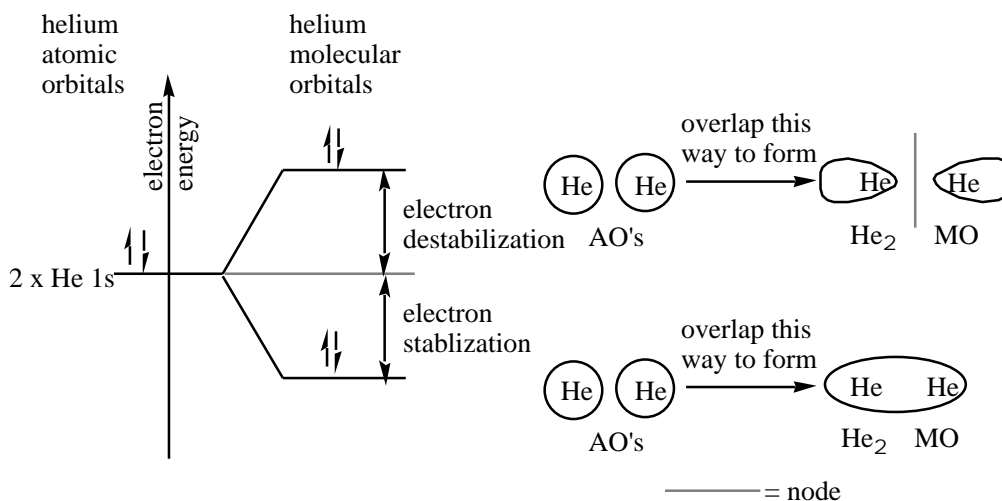
4. Rotation around the C2-C3 bond reduces the overlap between the p_z orbitals on these carbons. This in turn weakens the C2-C3 π bond, thus decreasing molecular stability. This decrease in stability is the origin of the barrier to rotation. Butane has no C2-C3 π bond, and therefore a lower barrier to rotation.

5. The resonance hybrid for 1,3-butadiene suggests that the C2-C3 bond has some character, but is not a full π bond. Thus we expect the C2-C3 bond length of 1,3-butadiene to be longer than a full π bond, but shorter than a normal σ bond.

6. Overlap of two hydrogen 1s orbitals yields two hydrogen molecular orbitals. Because the total energy of the molecular orbitals must be equal to the total energy of the atomic orbitals from which they are derived, there is one H_2 molecular orbital that is lower in energy than the starting 1s atomic orbital, and one higher in energy. (If the molecular orbitals were of the same energy as the atomic orbitals, there would be no electronic stabilization when bonding occurs, and hence no reason for bonding at all.) Electrons are placed into molecular orbitals using the same rules that apply to atomic orbitals. Each hydrogen atom contributes one electron. This electron pair fills the H_2 molecular orbital. Because the H_2 molecular orbital is lower in energy than the hydrogen 1s atomic orbitals, the electrons are stabilized. This stabilization is the bond energy.



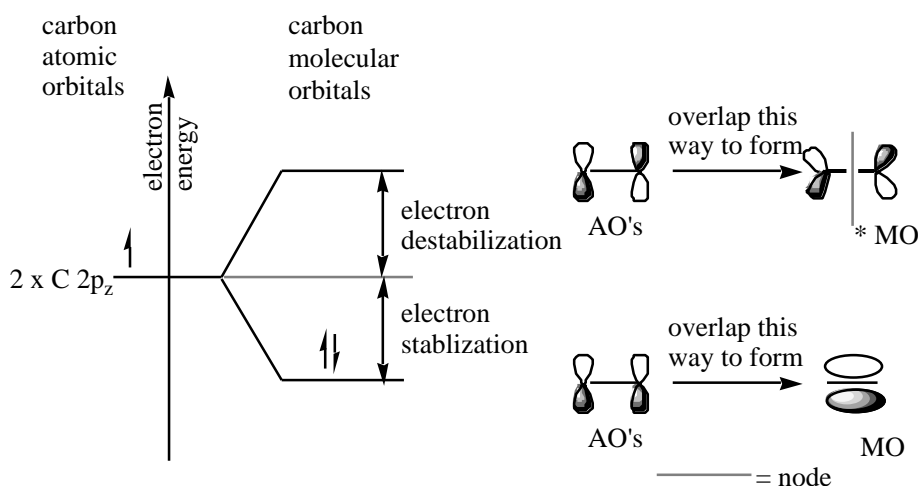
Helium also would use 1s orbitals to make a He-He bond, so the molecular orbital diagram looks very much like the H_2 molecular orbital diagram.



Each helium atom contributes two electrons to the molecular orbitals of He_2 . The diagram shows that the stability gained by a pair of electrons in the He_2 orbital is canceled out by the destabilization of the electron pair in the He_2^* orbital. There is no extra stability gained by bringing two helium nuclei within bonding distance. At this distance, the nuclear repulsion dominates, and He_2 flies apart.

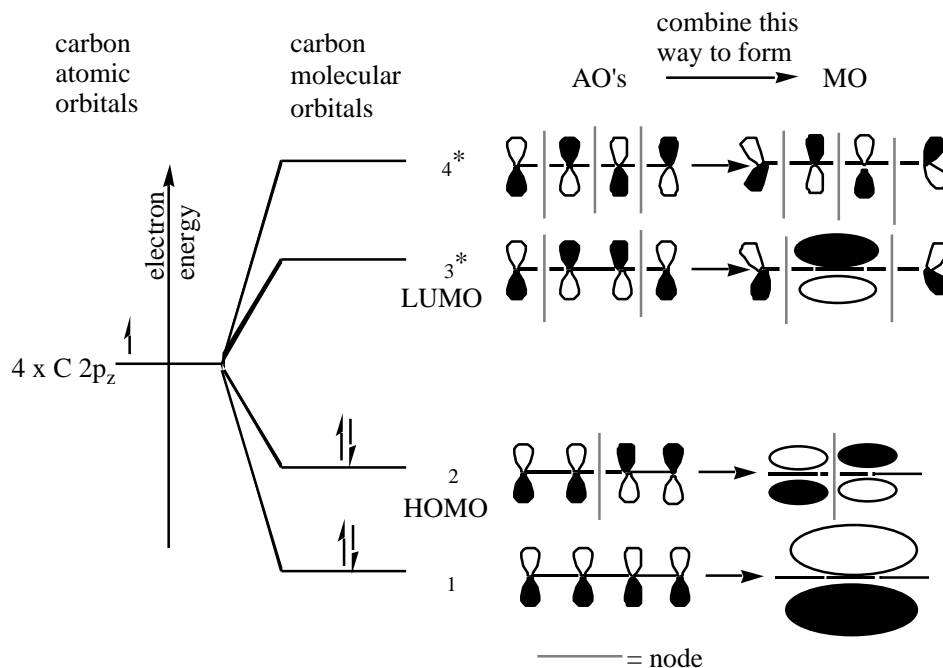
Alternate (and perhaps more rigorous viewpoint): Atomic orbitals are merely mathematical constructs that can be combined in different ways to form new mathematical constructs called molecular orbitals. This is the LCAO (Linear Combination of Atomic Orbitals) viewpoint. In this viewpoint, we consider various combinations of atomic orbitals that lead to the molecular orbitals.

7. The picture looks very much like the H_2 molecular orbital case, but a π bond is formed instead of a σ bond.



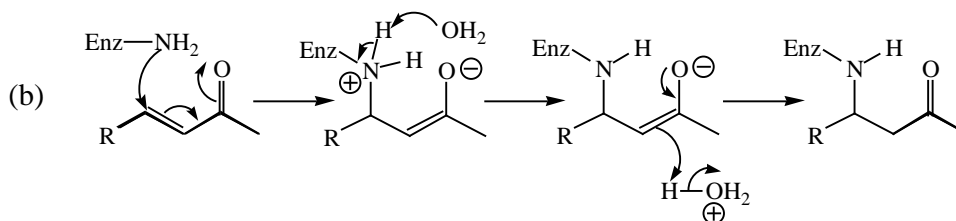
The ethylene orbital is bonding, and thus must have electron density between the two carbon atoms to hold them together. The orbital looks like a cloud of electron density between the two carbon atoms, with a planar node between. (Imagine a sandwich, with the orbital lobes as bread and the ethylene as cheese.) The ethylene * orbital is antibonding, so there is no electron density between the carbon atoms. A lack of electron density between atoms means that nuclear repulsion is more important when considering the bonding and stability of this orbital, and its contributions to molecular structure.

8. Using a molecular orbital diagram, and the same kinds of arguments used for H_2 and $\text{H}_2\text{C}=\text{CH}_2$, we can see that 1,3-butadiene has two occupied molecular orbitals. Only molecular orbitals that are occupied can have a significant effect on electronic and molecular structure.

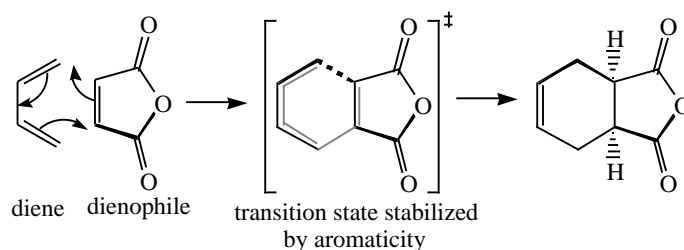


The π bond structure will be combination of ψ_1 and ψ_2 . The ψ_1 molecular orbital has electron density shared by all four carbons. In ψ_2 , the electron density is between C1-C2 and C3-C4, with a node between C2 and C3. Putting the two orbitals together, we see that 1,3-butadiene has π electron density across all four carbons, but this π electron density is greatest between C1-C2 and C3-C4. This is consistent with the resonance description of this molecule in question 5 above. Compare this the molecular orbitals of 1,3-butadiene lecture handout.

9. (a) We can tell the alkene is an electrophile because the amine is a nucleophile. The alkene can accept electrons (i.e., be an electrophile) because it is attached to the electron-withdrawing carbonyl, and because the negative charge of the intermediate is stabilized by resonance (enolate).

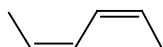


10. The Diels-Alder reaction is a cycloaddition between a single bond (such as an alkene, alkyne or one bond of a conjugated molecule), and a conjugated pair of bonds. In the basic Diels-Alder reaction, the isolated bond is an alkene and is termed the dienophile. The conjugated component is a 1,3-diene. Reaction of an alkene and 1,3-diene is a concerted reaction, affording a new cyclohexene derivative.



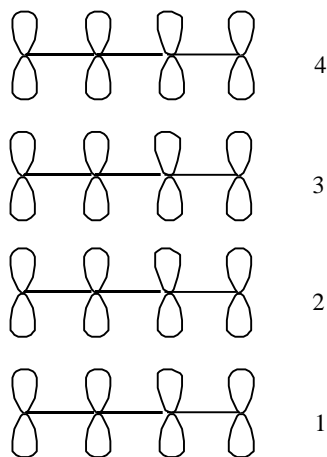
Practice Problems

Questions 1 - 5 refer to (*Z,Z*)-2,4-hexadiene. This molecule exists almost exclusively in the planar, *s-trans* conformation shown below.



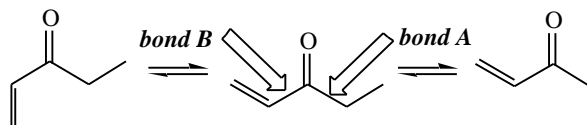
1. Draw an isomer of this molecule that is not conjugated.
2. Write the *s-trans*/*s-cis* equilibrium for this molecule.
3. Why is this molecule planar?
4. Why is *s-trans* the dominate conformation of this molecule?
5. Estimate the C3-C4 bond length of this molecule.

Questions 6 - 10 refer to the following incomplete molecular orbital picture of 1,3-butadiene.

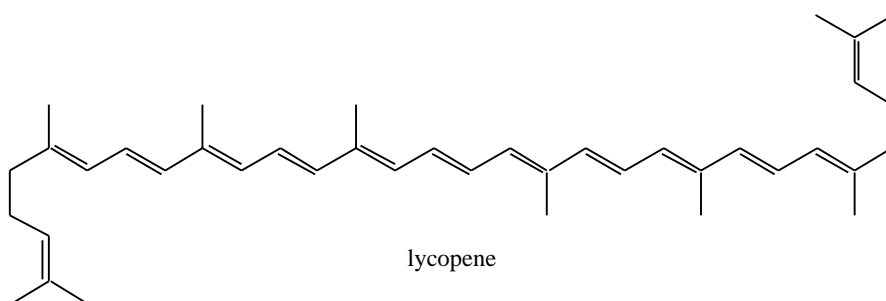


6. Complete the diagram by supplying the phases of all the p_z orbital lobes, and distributing the electrons. Label all the important features of your diagram.
7. Briefly explain how the HOMO and LUMO are involved when a molecule functions as a nucleophile (electron source) or electrophile (electron acceptor).

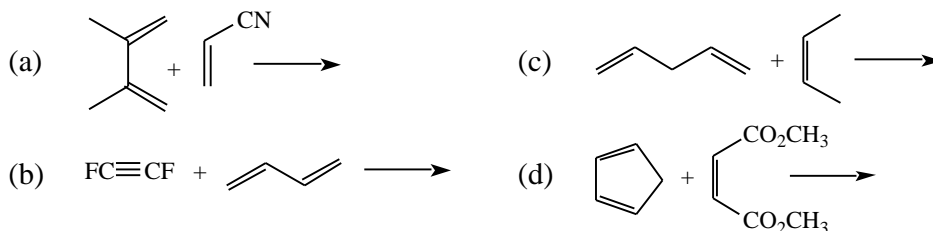
8. Which molecular orbital of 1,3-butadiene has two nodes?
9. In which molecular orbital are electrons most stable?
10. Briefly describe why conjugation leads to an increased barrier to rotation about a bond connecting two sp^2 -hybridized carbon atoms.
11. Why is the barrier to rotation for bond **A** lower than the barrier to rotation for bond **B**?



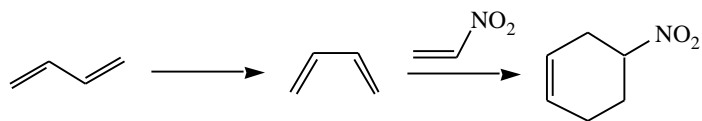
12. Very briefly explain how the arrangement of molecular orbitals is responsible for the special stability of a conjugated structure such as lycopene, the molecule that gives tomatoes their red color. "Resonance" is not a sufficiently detailed answer.



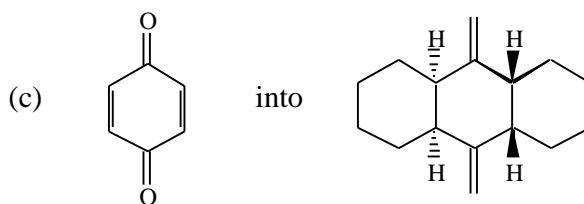
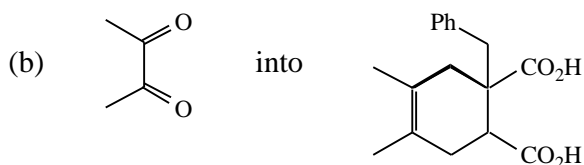
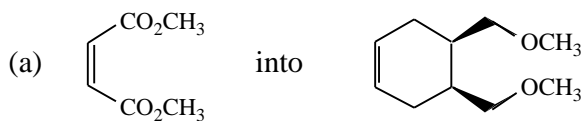
13. Provide products. If no reaction occurs explain why.



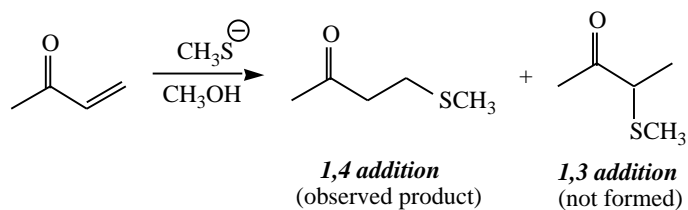
14. Briefly explain why a Diels-Alder dienophile must be in an s-cis conformation, even though this conformation is less stable than the s-trans conformation.
15. Give a dienophile that (a) is always s-cis, and (b) is always s-trans.
16. Draw an energy profile for the process shown below. Include both transition states. Assume the overall process is exothermic.



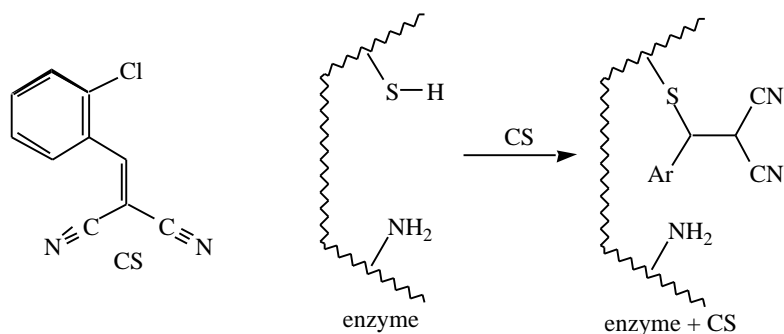
17. Suggest reactions to carry out each transformation. Each case requires more than one step, and is most effectively achieved with a Diels-Alder reaction.



18. An α, β -unsaturated ketone (an enone) reacts with a nucleophile to give the 1,4 addition product, not the 1,3 addition product. Explain this regioselectivity.



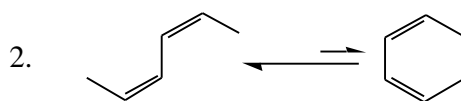
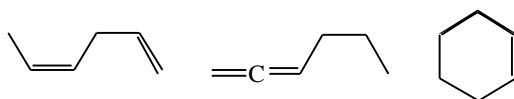
19. Consider the chemistry of CS, a component of tear gas that causes pain and burning in the eyes and skin by reacting with free sulfhydryl (SH) groups in various enzymes. "Ar" is an abbreviation for the benzene ring of CS.



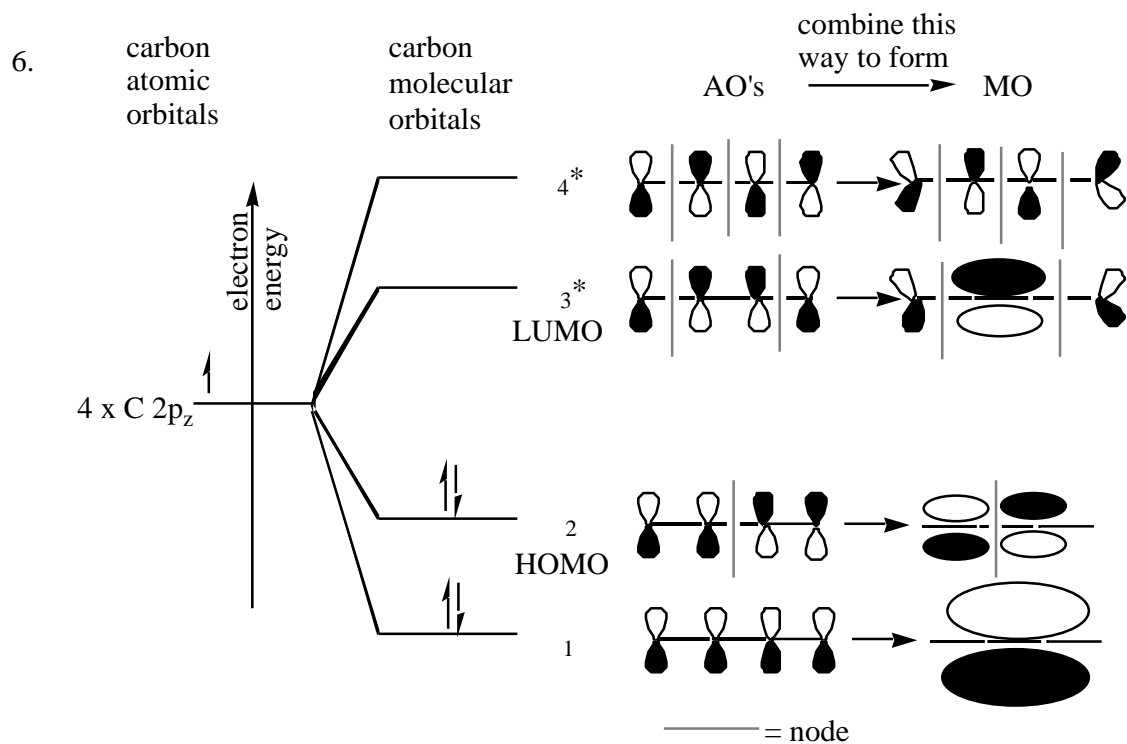
- (a) Alkenes normally react as nucleophiles, but in this reaction the alkene is an electrophile. Briefly explain why the alkene of CS is electrophilic.
- (b) Provide a mechanism to show how CS reacts with the enzyme.

Practice Problems Solutions

1. An isomer without conjugation lacks the planar alternating π bond arrangement. There are a number of possibilities, three of which are shown here.

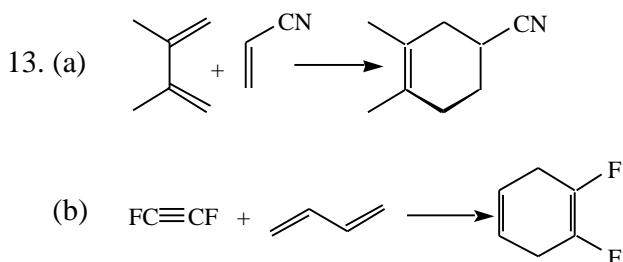


3. There is a partial π bond formed by the overlap of p_z orbitals on C3 and C4. This extra bonding imparts additional stability to the molecule. The maximum amount of p_z overlap (affording the maximum bond strength and thus maximum stabilization) occur when the two p_z orbitals are parallel. The molecule must be planar for the p_z orbitals to be parallel.
4. The p_z overlap mentioned in the previous answer forces the molecule to be planar. There are two fully planar conformations: *s-cis* and *s-trans*. In the *s-cis* conformation, the two terminal methyl groups are brought into close proximity, resulting in significant repulsion. In the *s-trans* conformation, the nearest groups to these terminal methyls are hydrogen atoms. Since hydrogen is smaller than methyl, a H-CH₃ repulsion is not as severe as a CH₃-CH₃ repulsion. Make a model and measure interatomic distances at closest approach to verify this. Calculations with Spartan (a molecular modeling program) suggest that the CH₃-CH₃ interaction is so severe in this molecule that it twists out of planarity to avoid it!
5. The partial π character of the C3-C4 bond will make it shorter than a typical C-C bond, but longer than a full C=C bond.

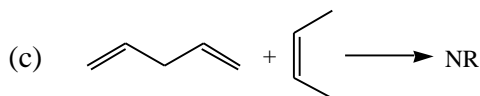


7. The HOMO (**H**ighest **O**ccupied **M**olecular **O**rbital) contains the electrons in the highest energy orbital. These electrons are the most easily lost by the molecule. If a molecule functions as a nucleophile, the electrons come from this orbital. The LUMO (**L**owest **U**noccupied **M**olecular **O**rbital). This is the lowest energy orbital that contains no electrons. This is the lowest energy orbital available to accept electrons. If the molecule functions as an electrophile, the new electrons go into this orbital.
8. There is a small inconsistency in counting nodes must be addressed first. A node is defined as "any point where the value of the solution of the wave equation is zero" or "a region of zero electron density." An isolated p_z orbital therefore has a node at the nucleus, between the two lobes. When p_z orbitals are combined to create a molecular orbital, the nuclear nodes become a nodal plane. Imagine the molecular orbitals of butadiene as a sandwich: electron bread, and carbon cheese. The cheese is a node. All the molecular orbitals of 1,3-butadiene have this node. Our interest in node counting stems from the fact that increasing the number of nodes increases the MO energy. Since all MOs have the nuclear nodal plane, it does not influence their relative energies, and so it is frequently ignored. Thus, the ψ_1 orbital has zero nodes, ψ_2 has one, ψ_3 has two, and ψ_4 has three nodes. (Alternately, the nuclear node can be counted, but then it must be counted for all MOs. If counted in the butadiene case, ψ_1 has one node, ψ_2 has two nodes, etc.)
9. The electrons are most stable in the lowest energy orbital, ψ_1 .

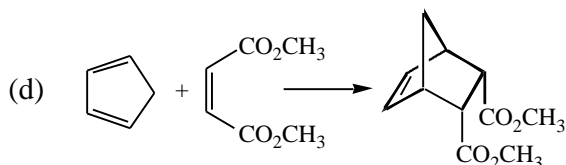
10. A π bond connecting two sp^2 -hybridized carbon atoms has a partial σ bond character. The partial σ bond results from overlap of p_z orbitals on adjacent carbons. The partial σ bond is strongest when orbital overlap is greatest. This occurs when the two p_z orbitals are parallel. Rotation around the π bond reduces p orbital overlap, weakening the partial σ bond, and reducing molecular stability. The resistance to this rotation (and subsequent loss of stability) is the reason why rotation around a π bond joining two sp^2 -hybridized carbon atoms is greater than for rotation about a σ bond joining two sp^3 -hybridized carbon atoms.
11. Both of the carbons that make up bond **B** have p orbitals. Overlap of these p orbitals gives bond **B** partial σ character. Rotation around bond **B** would result in loss of p orbital overlap, a process that reduces bonding and thus reduces molecular stability. This loss of stability contributes to barrier to rotation for bond **B**. Bond **A** has no such σ character because one of the two carbons of bond **A** is sp^3 . It is because bond **B** has partial σ character whereas bond **A** does not that bond **A** has a lower barrier to rotation.
12. That a molecule with conjugated π bonds is more stable than a nonconjugated isomer is related to the π electron and molecular orbital energies. If the molecule is conjugated, the total stabilization of π electrons relative to isolated π electrons is greater than if the molecule is not conjugated. Thus, the special stability associated with conjugation (or aromaticity) is a function of the electron distribution in the molecular orbitals. (Any sort of resonance or delocalization explanation is not completely adequate because it does not explain every feature of a conjugated system. Resonance fails to explain why the planar conformation of 1,3-butadiene is more stable than a nonplanar conformation. Science strives to adopt a theory that explains as many facts of as many systems as possible. The molecular orbital rationale presented above explains more of the features of a conjugated system than does the resonance rationale. On an exam the more rigorous molecular orbital rationale would receive more credit than the less rigorous resonance rationale.)



The diene must rotate into an s-cis conformation before the cycloaddition can occur. Recall that molecules are dynamic so even though 1,3-butadiene is shown here in the s-trans conformation, it is in fact interconverting between s-cis and s-trans many times per second.

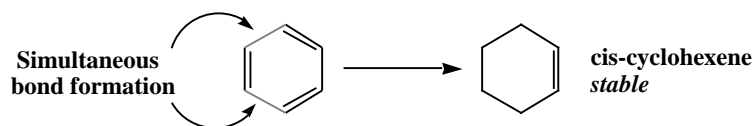


No reaction occurs because the diene is not conjugated. In addition, the basic Diels-Alder dienophile must be electron deficient. This alkene is electron-rich, as it bears two electron-donating methyl groups.

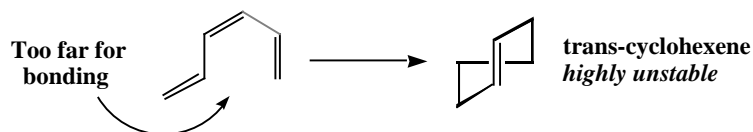


14. In the Diels-Alder reaction transition state, two new carbon-carbon bonds are being formed between the terminal sp^2 carbons of the diene and dienophile. The reaction is concerted (all bond making and bond breaking occurs in a single transition state), so both new bonds form simultaneously. This requires both sets of terminal carbons to be within bonding distance at the same time. This can be achieved when the diene is s-cis, but when the diene is s-trans the termini are too far apart. (Verify this by examining molecular models.) In addition, an s-trans diene would lead to a trans-cyclohexene, a molecule with exceptionally high strain. (Trans-cyclohexene is so unstable that it has never been isolated.)

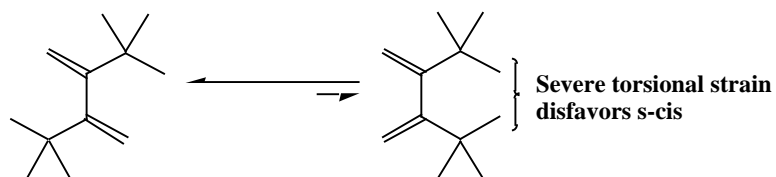
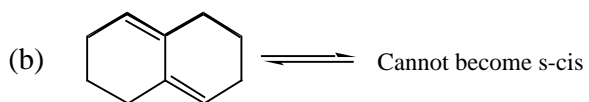
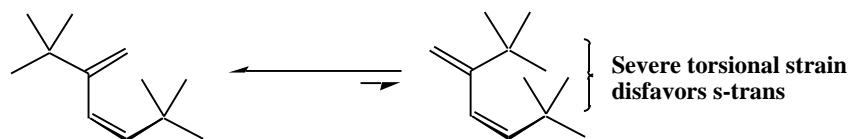
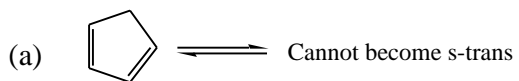
s-Cis diene transition state allows simultaneous bond formation and leads to cis-cyclohexene product:



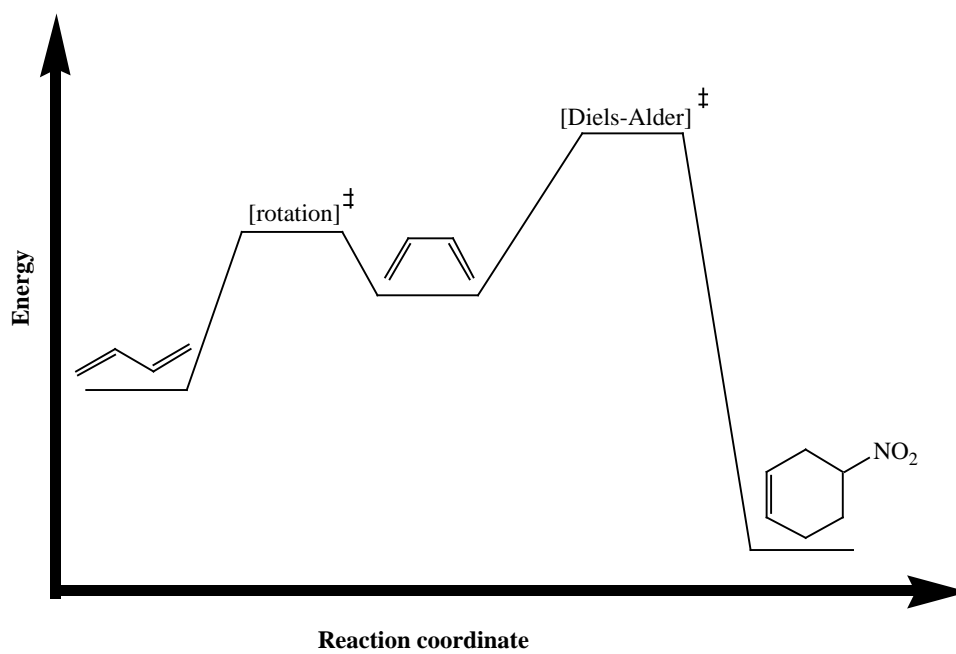
s-Trans diene transition state forbids simultaneous bond formation and leads to trans-cyclohexene product:



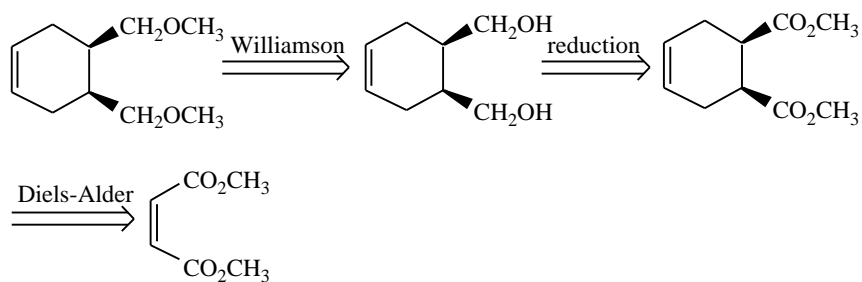
15. Interconversion between the s-cis and s-trans conformations might be prevented because the rotation around the bond connecting the conjugated bonds cannot occur without breaking other bonds. Alternately, the molecule may have free rotation but the energy difference between the two conformations may be so large that the equilibrium significantly favors one conformation over the other. Examples illustrating both of these features are given.



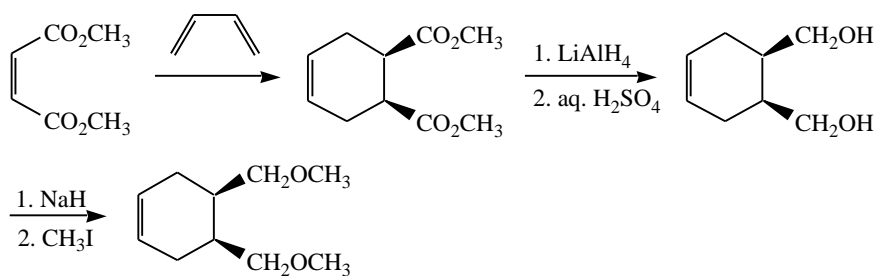
16.



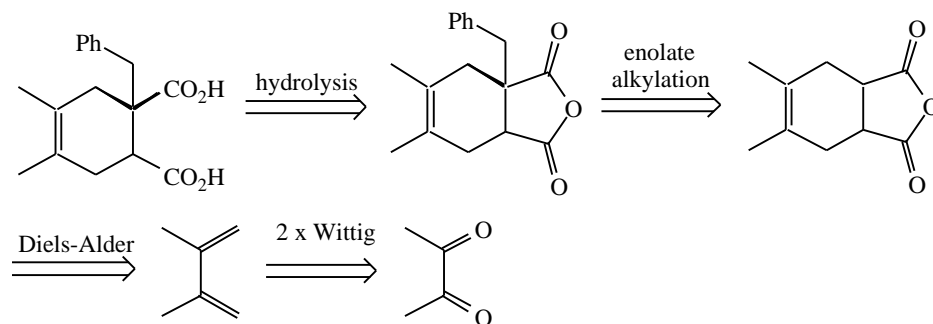
17. (a) Retrosynthesis:



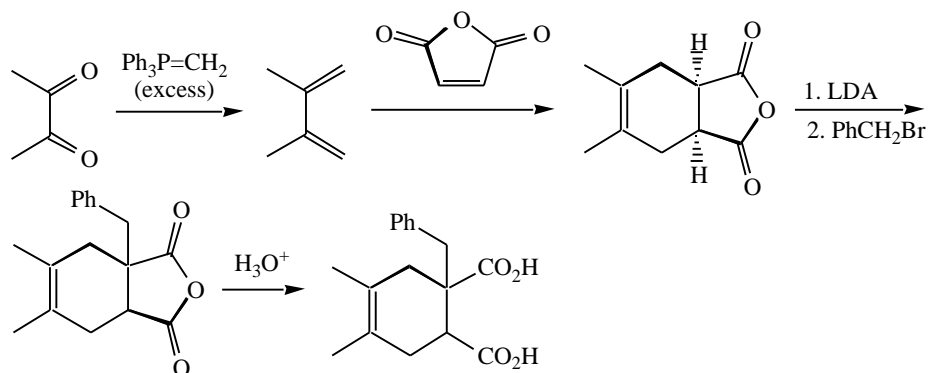
Forward direction:



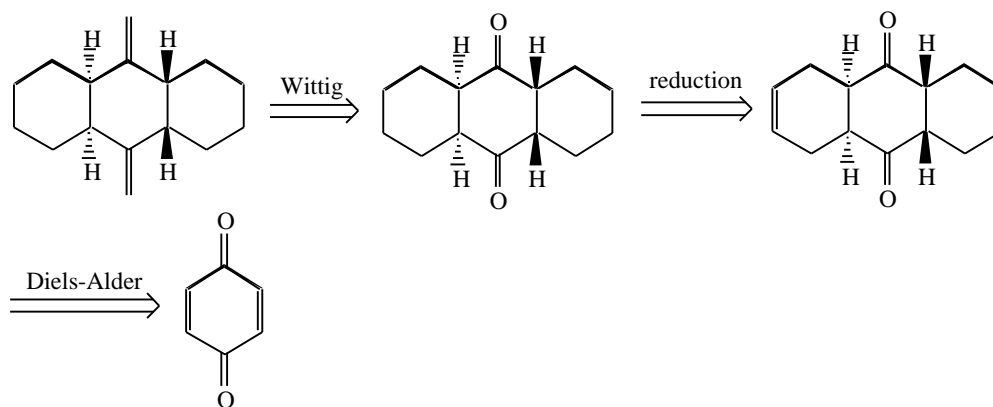
(b) Retrosynthesis:



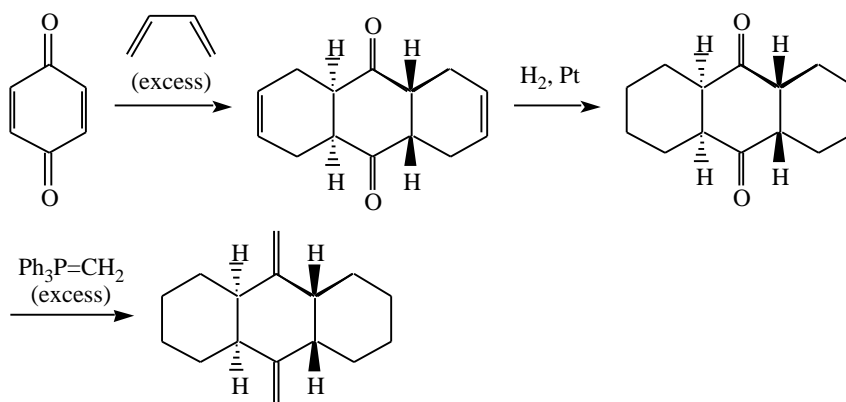
Forward direction:



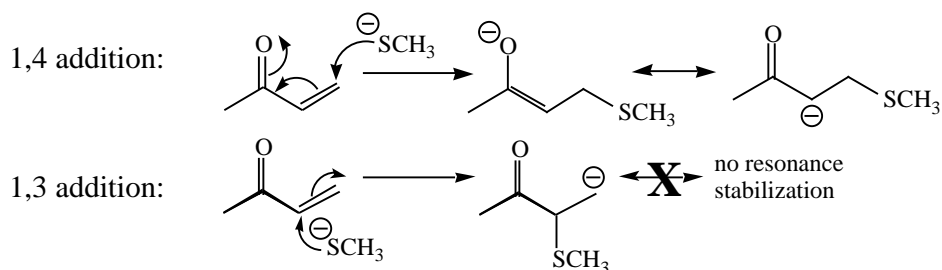
(c) Retrosynthesis:



Forward direction:



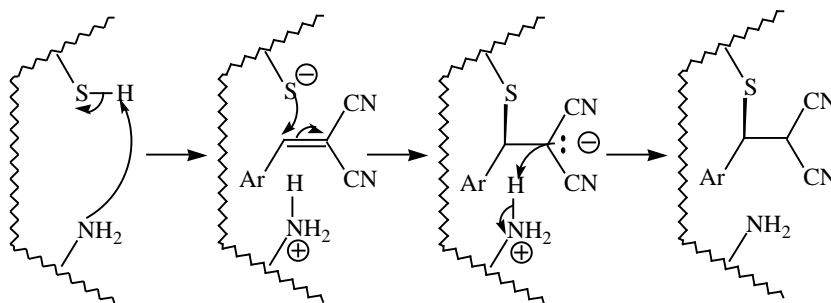
18. The mechanism step that controls which product isomer is formed is the step in which the methanethiolate ion (CH_3S^-) attacks the alkene.



Any time a reactive intermediate such as a carbanion can be formed in a mechanism step, the most stable intermediate is preferred. (There are some cases where choice of the most stable intermediate may not be obvious; all factors must be considered.) In this nucleophilic attack, two anions are formed. The anion resulting from 1,4 addition enjoys resonance stabilization (it is an enolate), whereas the anion resulting from 1,3 addition does not. Thus 1,4 addition is favored over 1,3 addition.

19. (a) Alkenes normally react as nucleophiles by sharing their π electrons. The two electron withdrawing nitrile groups make the alkene electron poor, and hence electrophilic. Alternate answer: Alkenes normally cannot function as electrophiles because addition of an extra electron pair results in an unstabilized carbanion. The nitrile groups allow stabilization of this carbanion through resonance, so an alkene bearing one or more nitrile groups may accept electron density and function as an electrophile.

(b) "Ar" is a common abbreviation for an aromatic ring.



There are several alternate mechanisms, depending upon the sequence of steps and assumptions made. Any of these alternate mechanisms are acceptable as long as they do not violate any chemical common sense.