

Chapter 17

Conjugated Pi Systems and Pericyclic Reactions

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 17. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

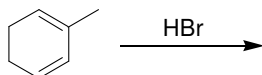
- Conjugated dienes experience free-rotation about the C2-C3 bond, giving rise to two important conformations: *s*-_____ and *s*-_____. The *s-trans* conformation is lower in energy.
- The HOMO and LUMO are referred to as _____ orbitals, and the reactivity of conjugated polyenes can be explained with **frontier orbital theory**.
- An _____ state is produced when a π electron in the HOMO absorbs a photon of light bearing the appropriate energy necessary to promote the electron to a higher energy orbital.
- Reactions induced by light are called _____ reactions.
- When butadiene is treated with HBr, two major products are observed, resulting from _____-addition and _____-addition.
- Conjugated dienes that undergo addition at low temperature are said to be under _____ control. Conjugated dienes that undergo addition at elevated temperature are said to be under _____ control.
- _____ reactions proceed via a concerted process with a cyclic transition state, and they are classified as **cycloaddition reactions**, _____ reactions, and **sigmatropic rearrangements**.
- The Diels–Alder reaction is a [_____] **cycloaddition** in which two C-C bonds are formed simultaneously.
- High temperatures can often be used to achieve the reverse of a Diels–Alder reaction, called a _____ **Diels–Alder**.
- The starting materials for a Diels–Alder reaction are a diene, and a _____.
- The Diels–Alder reaction only occurs when the diene is in an _____ conformation.
- When cyclopentadiene is used as the starting diene, a bridged bicyclic compound is obtained, and the _____ cycloadduct is favored over the _____ cycloadduct.
- Conservation of orbital symmetry determines whether an electrocyclic reaction occurs in a _____ fashion or a _____ fashion.
- A [_____] sigmatropic rearrangement is called a **Cope rearrangement** when all six atoms of the cyclic transition state are carbon atoms.
- Compounds that possess a conjugated π system will absorb UV or visible light to promote an electronic excitation called a _____ transition.
- The most important feature of the absorption spectrum is the _____, which indicates the wavelength of maximum absorption.
- When a compound exhibits a λ_{max} above 400 nm, the compound will absorb _____ light, rather than UV light.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 17. The answers appear in the section entitled *SkillBuilder Review*.

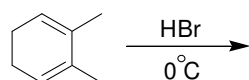
17.1 Proposing the Mechanism and Predicting the Products of Electrophilic Addition to Conjugated Dienes

IN THE SPACE PROVIDED, DRAW THE MECHANISM OF THE REACTION THAT IS EXPECTED TO OCCUR WHEN THE FOLLOWING COMPOUND IS TREATED WITH HBr. MAKE SURE TO DRAW ALL POSSIBLE PRODUCTS.



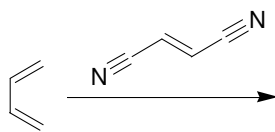
17.2 Predicting the Major Product of an Electrophilic Addition to Conjugated Dienes

DRAW THE MAJOR PRODUCTS OF THE FOLLOWING REACTION:



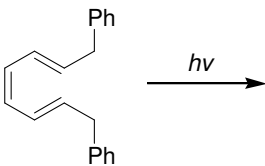
17.3 Predicting the Product of a Diels–Alder Reaction

DRAW THE MAJOR PRODUCTS OF THE FOLLOWING REACTION:

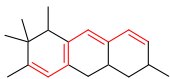


17.4 Predicting the Product of an Electrocyclic Reaction

DRAW THE MAJOR PRODUCTS OF THE FOLLOWING REACTION:

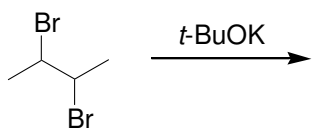
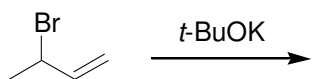
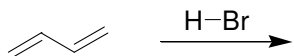
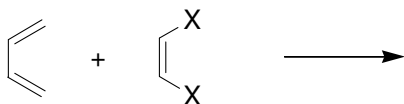
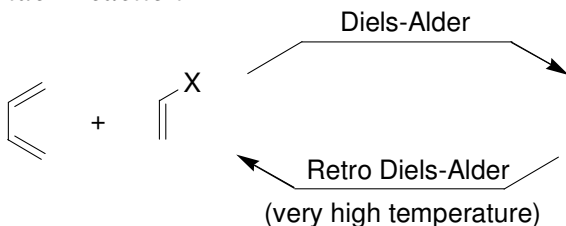


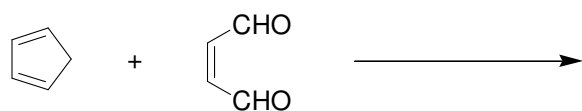
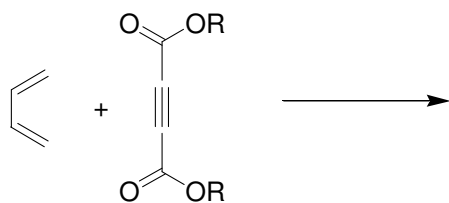
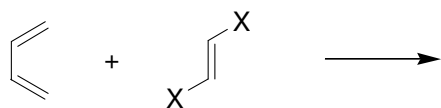
17.5 Using Woodward–Fieser Rules to Estimate λ_{\max}

<p>USE WOODWARD-FIESER RULES TO ESTIMATE λ_{\max} FOR THE FOLLOWING COMPOUND:</p> 	<p>BASE VALUE = <input type="text"/></p> <p>ADDITIONAL DOUBLE BONDS = <input type="text"/></p> <p>AUXOCHROMIC ALKYL GROUPS = <input type="text"/></p> <p>EXOCYCLIC DOUBLE BOND = <input type="text"/></p> <p>HOMOANNULAR DIENE = <input type="text"/></p> <hr/> <p>TOTAL = <input type="text"/></p>
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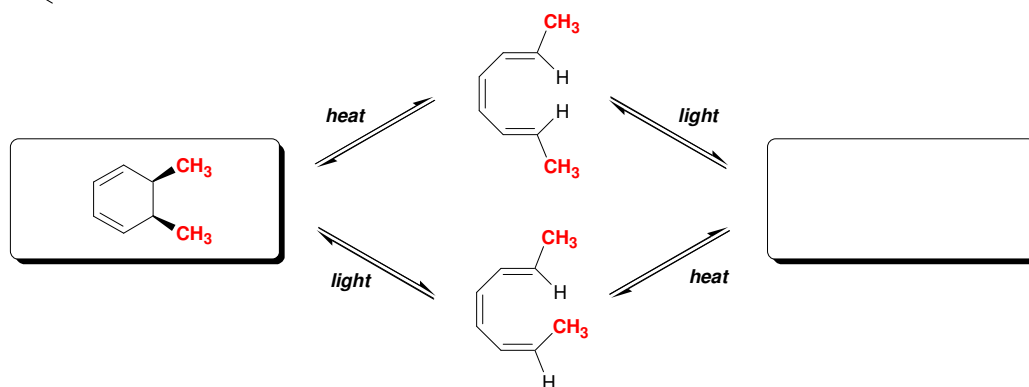
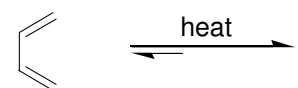
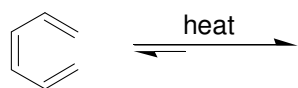
Review of Reactions

Predict the Products for each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 17. The answers appear in the section entitled *Review of Reactions*.

Preparation of Dienes**Electrophilic Addition****Diels–Alder Reaction**



Electrocyclic Reactions

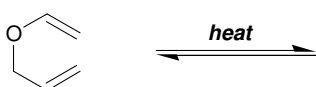


Sigmatropic Rearrangements

Cope Rearrangement

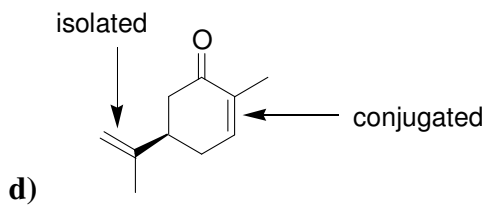
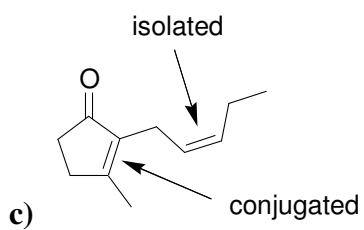
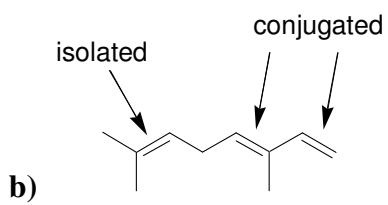
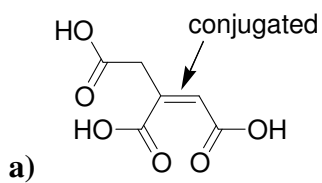


Claisen Rearrangement

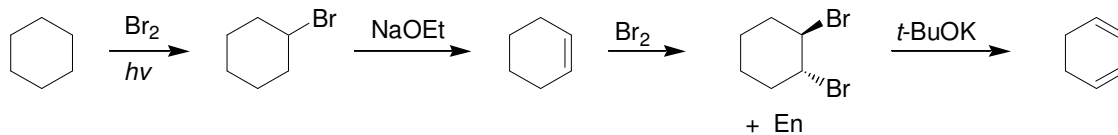


Solutions

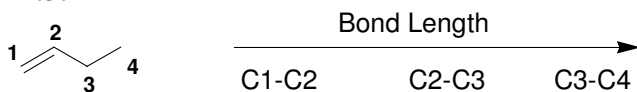
17.1.



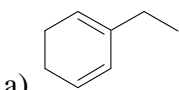
17.2.



17.3.

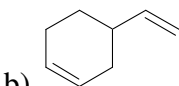


17.4.



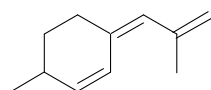
a)

The conjugated diene will liberate the least heat because it is the most stable of the three compounds.

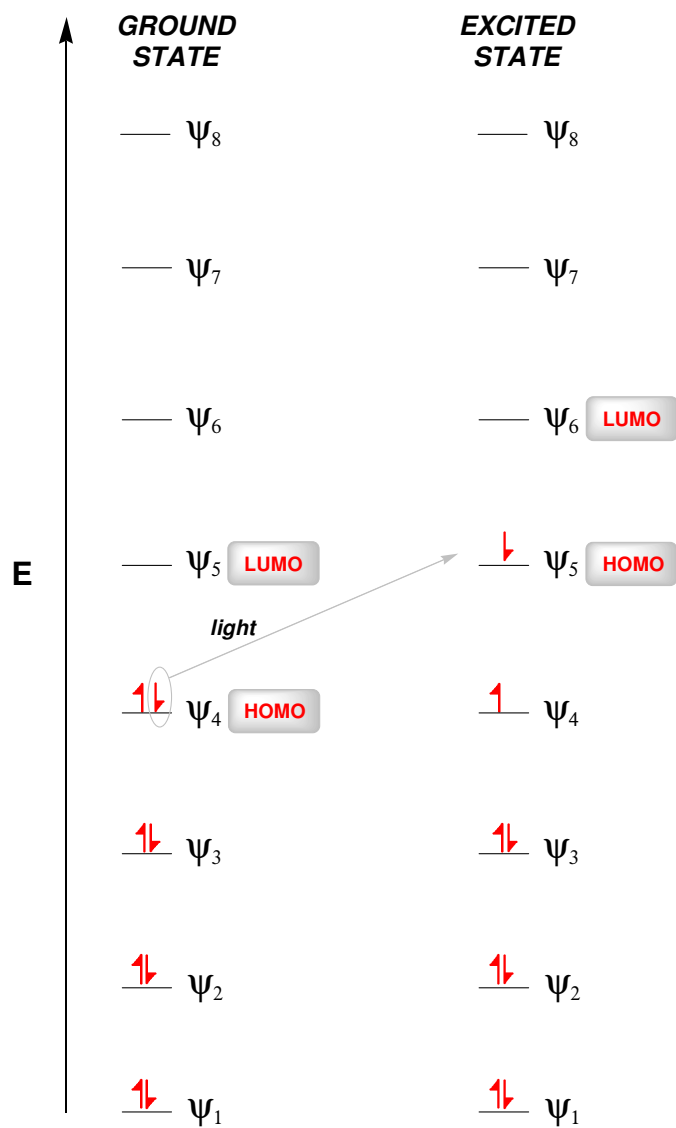


b)

This isolated diene will liberate more heat than the other isolated diene, because the π bonds in this compound are not highly substituted (one π bond is monosubstituted and the other is disubstituted). In the other isolated diene, the π bonds are disubstituted and trisubstituted (and therefore more stable).

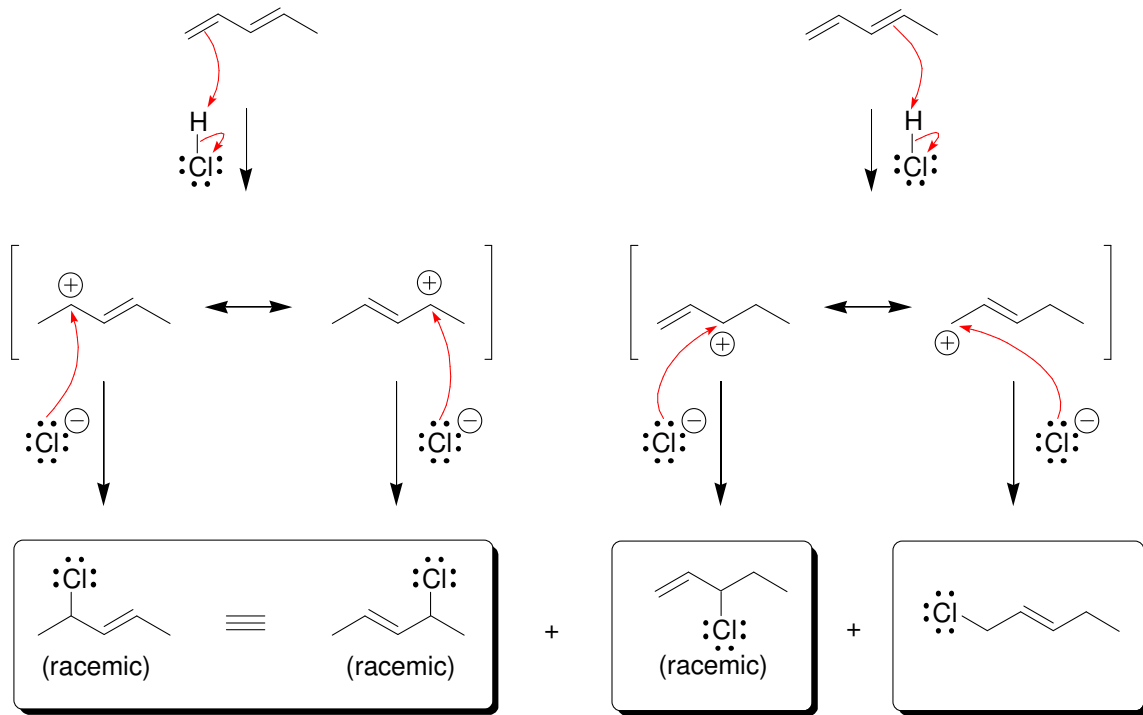
17.5. In the compound below, all three π bonds are conjugated:

17.6.

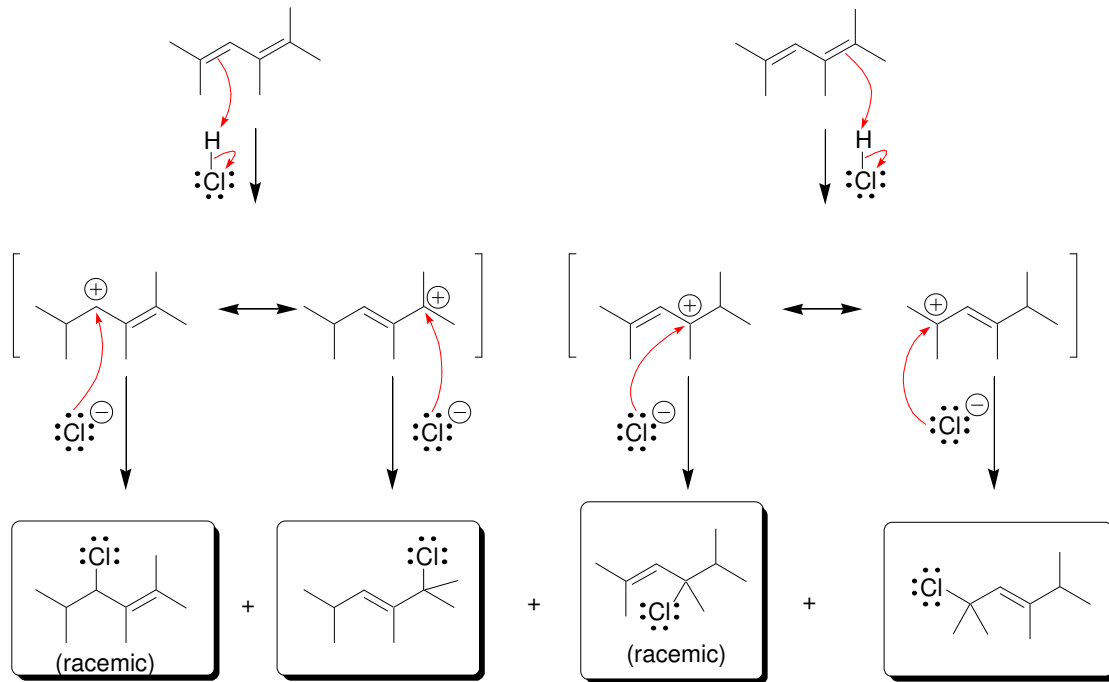


17.7.

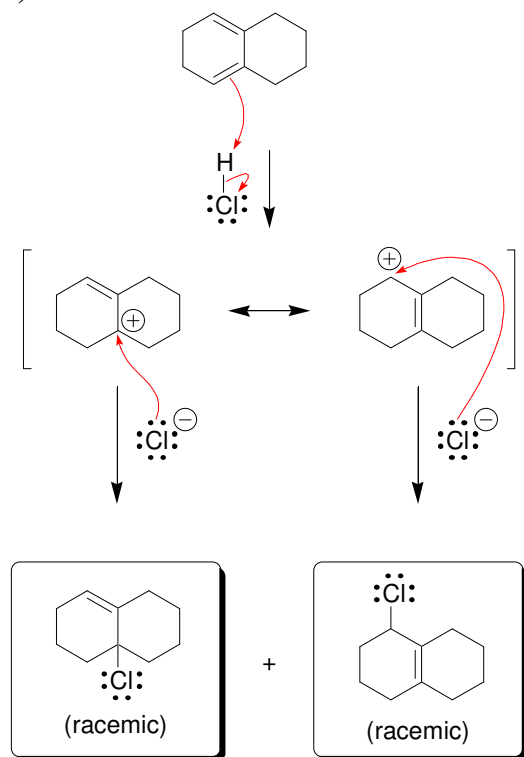
a)



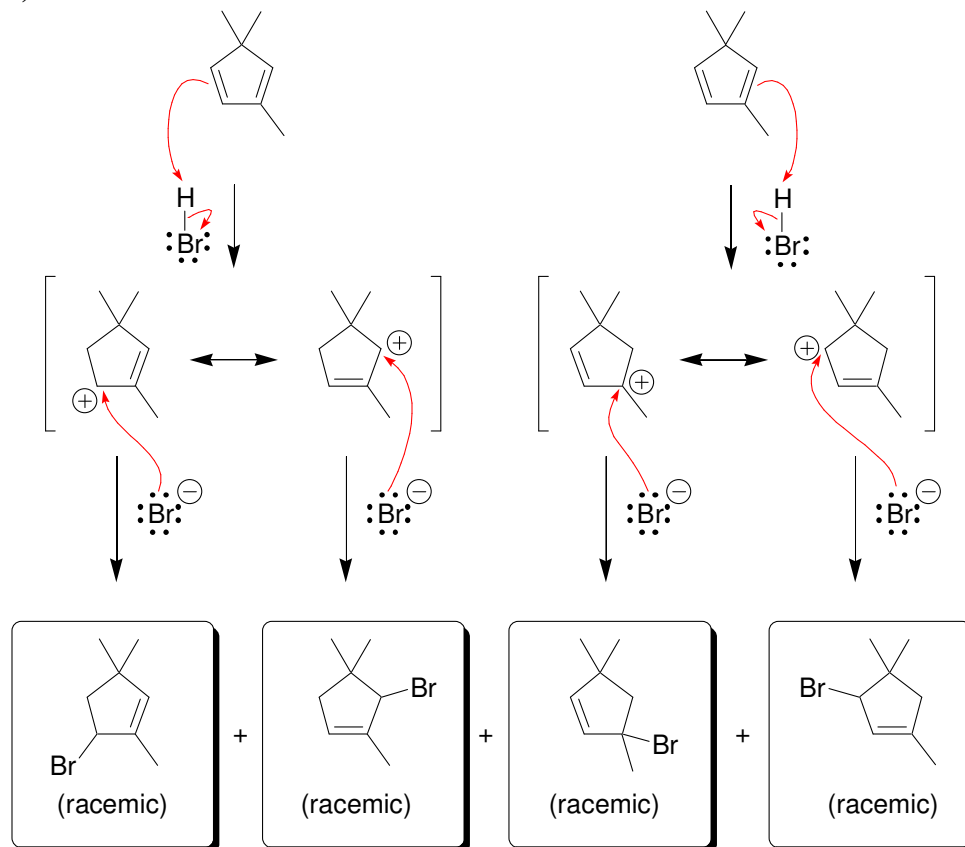
b)



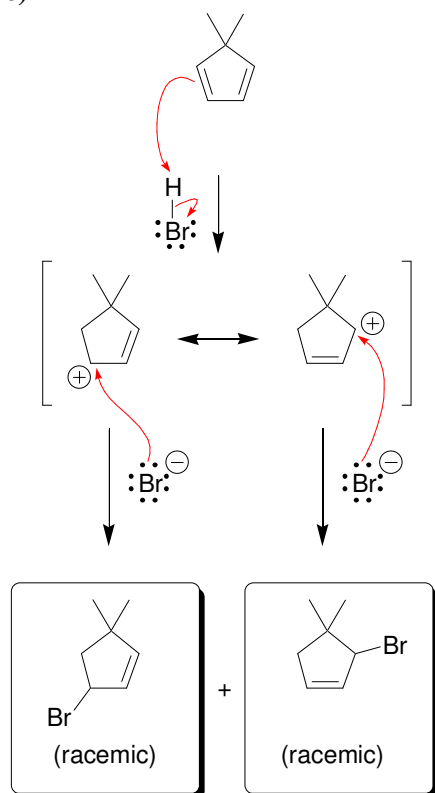
c)



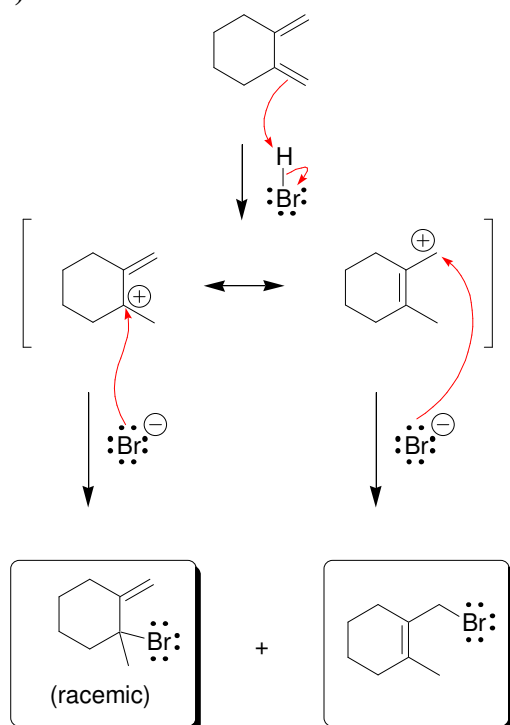
d)



e)

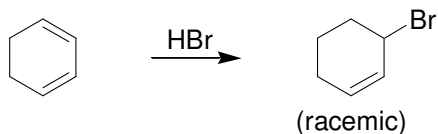


f)



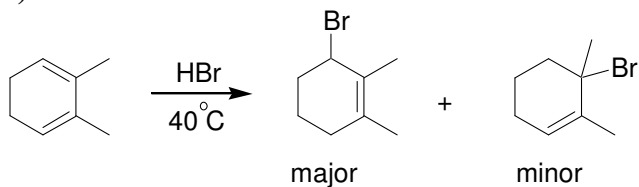
17.8. The first diene can be protonated either at C1 or at C4. Each of these pathways produces a resonance stabilized carbocation. And each of these carbocations can be attacked in two positions, giving rise to four possible products. In contrast, the second diene yields the same carbocation regardless of whether protonation occurs at C1 or at C4. This resonance-stabilized carbocation can be attacked in two positions, giving rise to two products.

17.9.

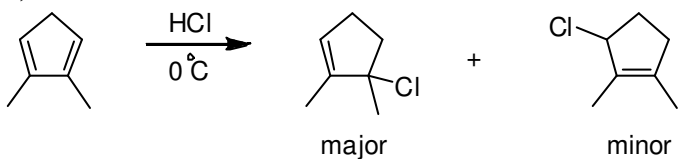


17.10.

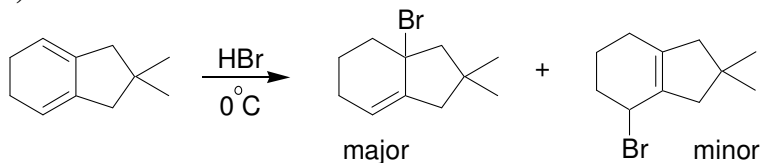
a)



b)

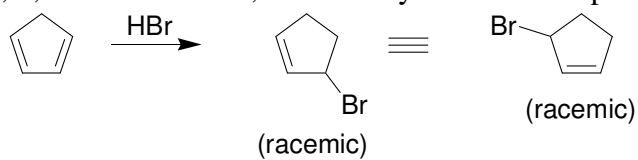


c)

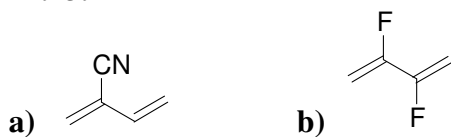


17.11. In this case, the π bond in the 1,2-adduct is more substituted than the π bond in the 1,4-adduct (trisubstituted rather than disubstituted). As a result, the 1,2-adduct predominates at either low temperature or high temperature.

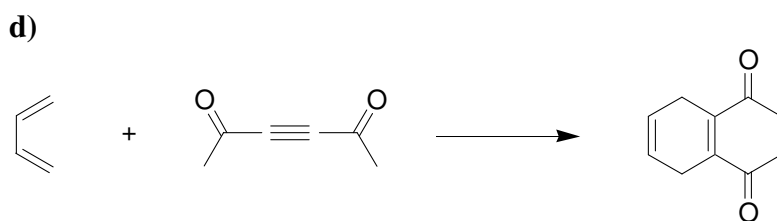
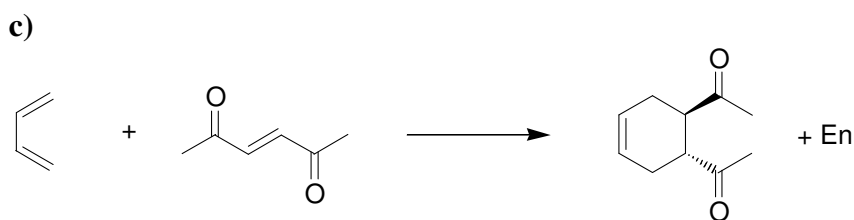
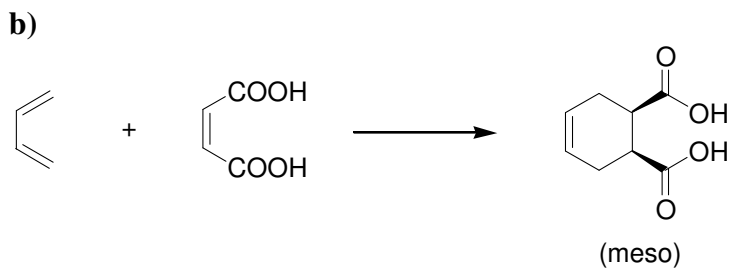
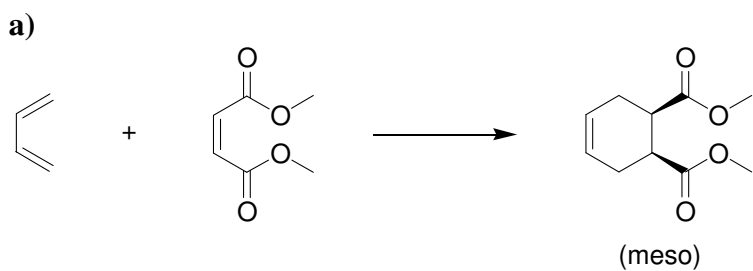
17.12. In this case, 1,2-addition and 1,4-addition yield the same product.



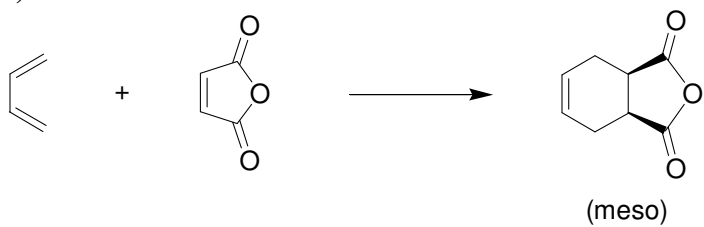
17.13.



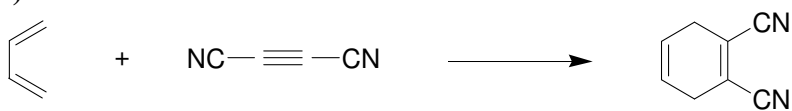
17.14.



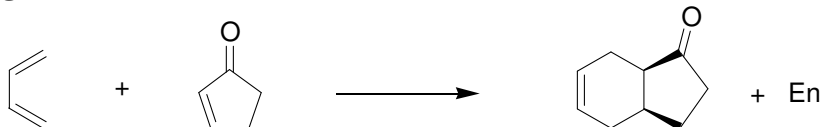
e)



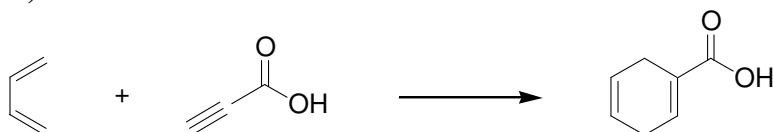
f)



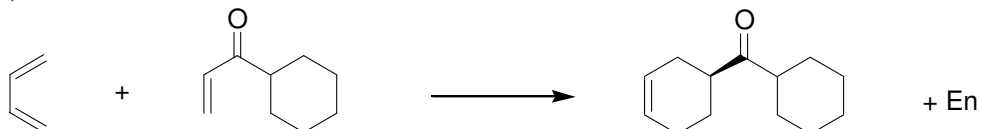
g)



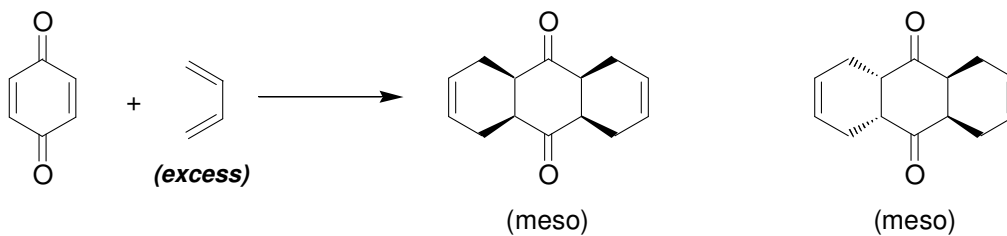
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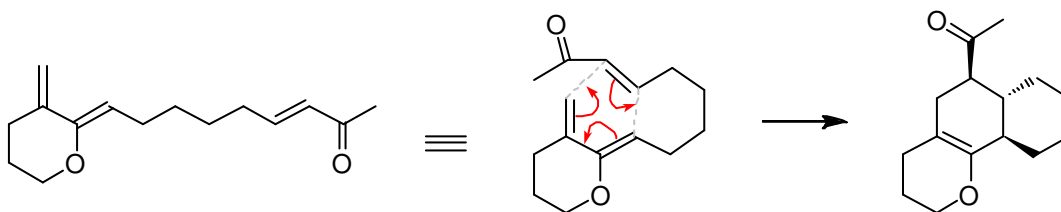
i)



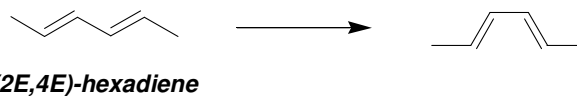
17.15.



17.16.



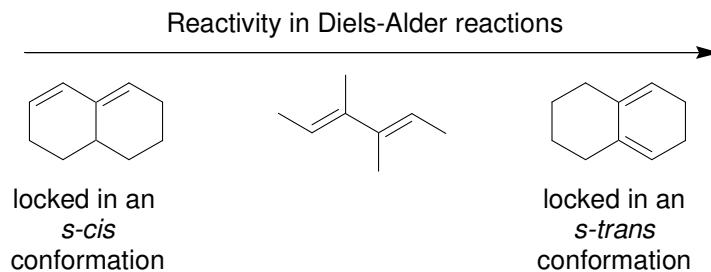
17.17. The $2E,4E$ isomer is expected to react more rapidly as a diene in a Diels–Alder reaction, because it can readily adopt an s -*trans* conformation.



In contrast, the $2Z,4Z$ isomer is expected to react more slowly as a diene in a Diels–Alder reaction, because it cannot readily adopt an s -*trans* conformation, as a result of steric hindrance.

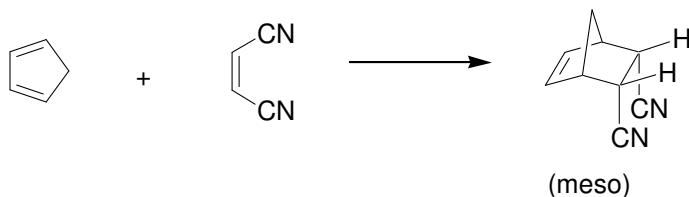


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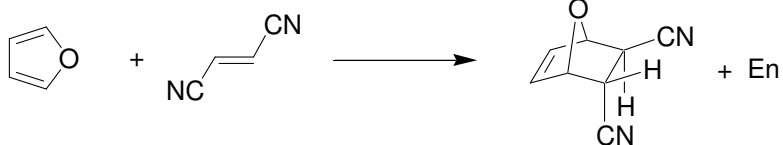


17.19.

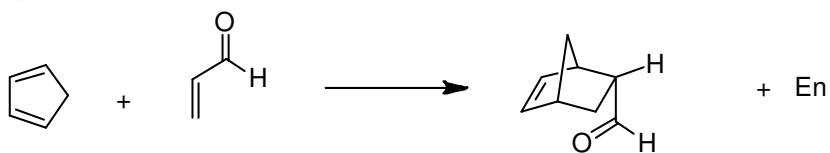
a)



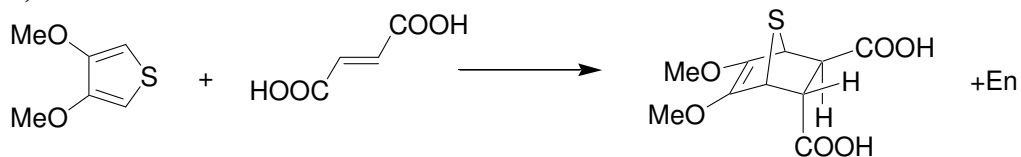
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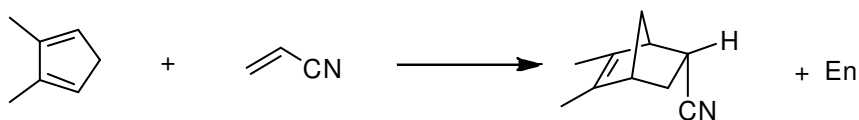
c)



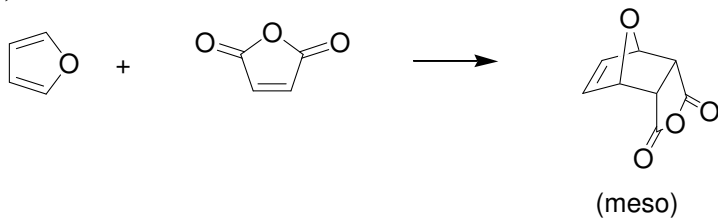
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e)

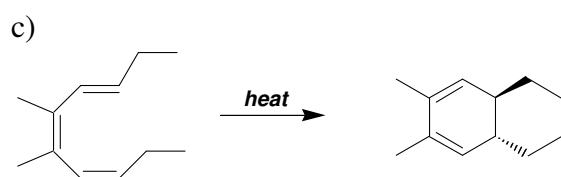
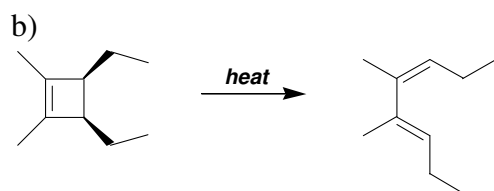
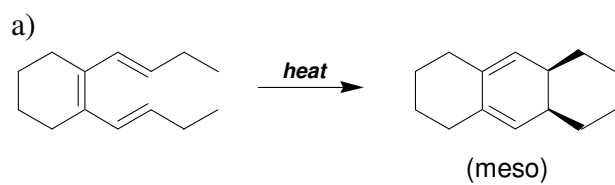


f)

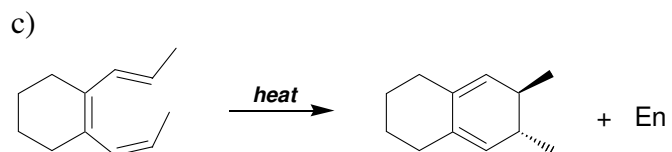
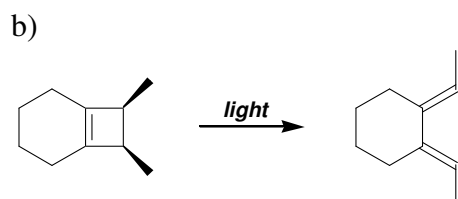
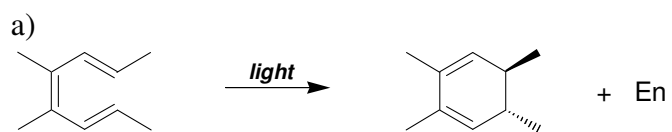


17.20. We first consider the HOMO of one molecule of butadiene and the LUMO of another molecule of butadiene. The phases of these MOs do not align, so a thermal reaction is symmetry-forbidden. However, if one molecule is photochemically excited, the HOMO and LUMO of that molecule are redefined. The phases of the frontier orbitals will align under these conditions, so the reaction is expected to occur photochemically.

17.21.

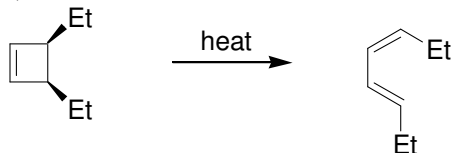


17.22.

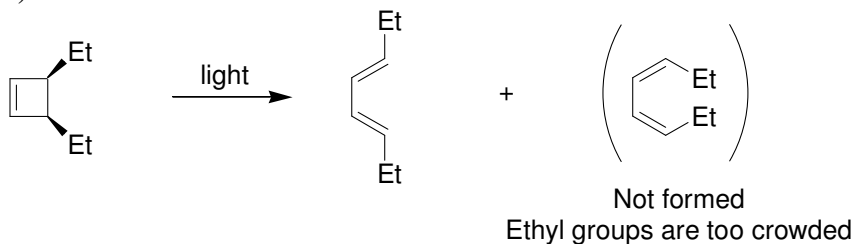


17.23.

a)



b)



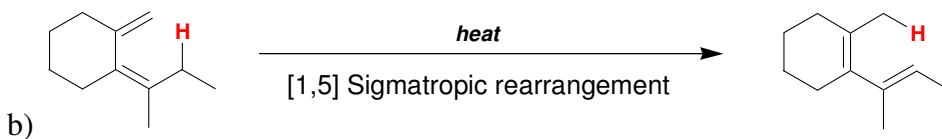
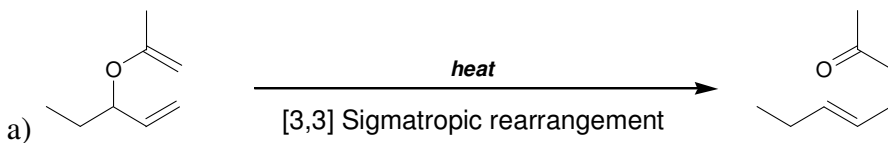
17.24.

a) a meso compound

b) a pair of enantiomers

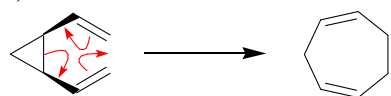
c) a pair of enantiomers

17.25.



17.26.

a)

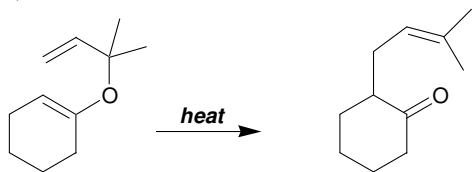


b) [3,3] Sigmatropic rearrangement

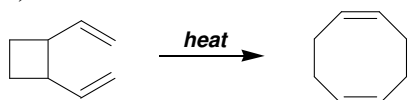
c) The ring strain associated with the three-membered ring is alleviated. The reverse process would involve forming a high-energy, three-membered ring. The equilibrium disfavors the reverse process.

17.27.

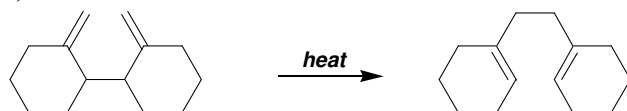
a)



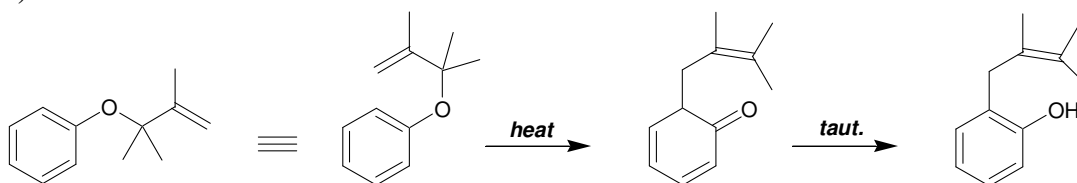
b)



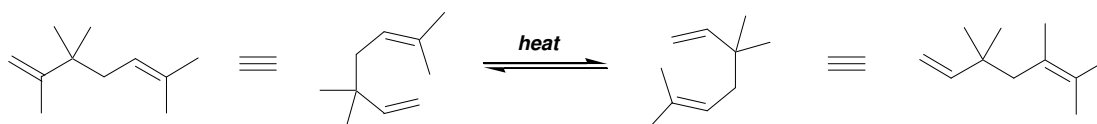
c)



d)



17.28.



17.29.

a)

Base	=	217
Additional double bonds	=	0
Auxochromic alkyl groups	=	+25
Exocyclic double bond	=	+5
<u>Homoannular diene</u>	=	<u>0</u>
Total	=	247 nm

b)

$$\begin{array}{rcl}
 \text{Base} & = & 217 \\
 \text{Additional double bonds} & = & +30 \\
 \text{Auxochromic alkyl groups} & = & +25 \\
 \text{Exocyclic double bond} & = & +5 \\
 \text{Homoannular diene} & = & \underline{0} \\
 \text{Total} & = & 277 \text{ nm}
 \end{array}$$

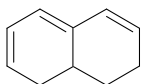
c)

$$\begin{array}{rcl}
 \text{Base} & = & 217 \\
 \text{Additional double bonds} & = & +30 \\
 \text{Auxochromic alkyl groups} & = & +30 \\
 \text{Exocyclic double bonds} & = & +15 \\
 \text{Homoannular diene} & = & \underline{0} \\
 \text{Total} & = & 292 \text{ nm}
 \end{array}$$

d)

$$\begin{array}{rcl}
 \text{Base} & = & 217 \\
 \text{Additional double bonds} & = & +30 \\
 \text{Auxochromic alkyl groups} & = & +35 \\
 \text{Exocyclic double bonds} & = & +5 \\
 \text{Homoannular diene} & = & \underline{+39} \\
 \text{Total} & = & 326 \text{ nm}
 \end{array}$$

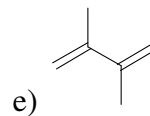
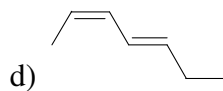
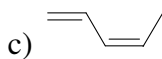
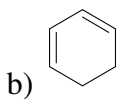
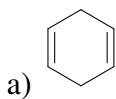
17.30



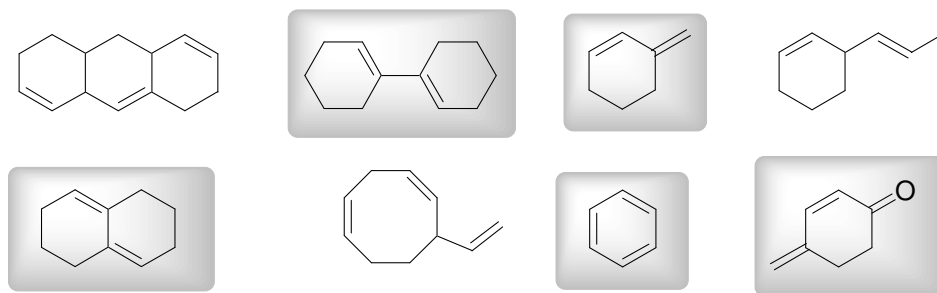
17.31.

- a) Blue.
- b) Red-Orange.
- c) Blue-violet.

17.32.



17.33.



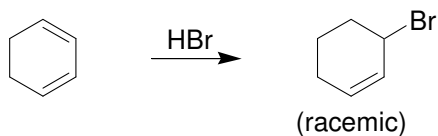
17.34.

a) These drawings represent two different conformations of the same compound: the *s-cis* conformation and the *s-trans* conformation. These two conformations are in equilibrium at room temperature.

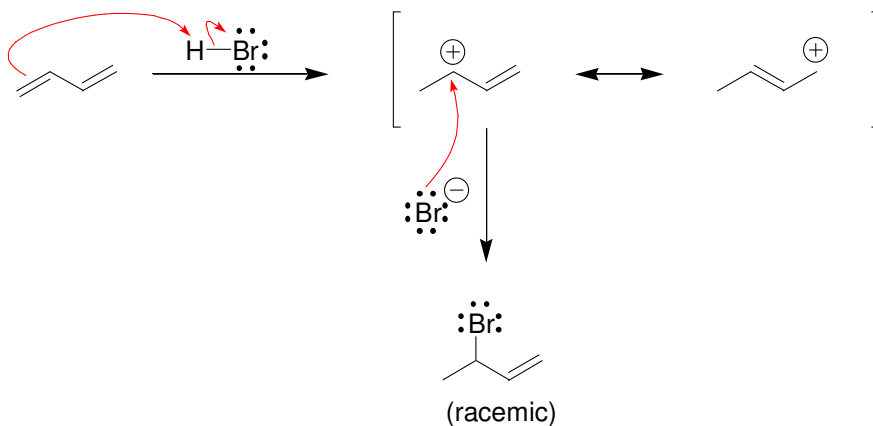
b) These drawings represent two different compounds: (*Z*)-1,3,5-hexatriene and (*E*)-1,3,5-hexatriene. These compounds are diastereomers and can be isolated from one another.

c) These drawings represent two different conformations of the same compound: the *s-cis* conformation and the *s-trans* conformation. These two conformations are in equilibrium at room temperature.

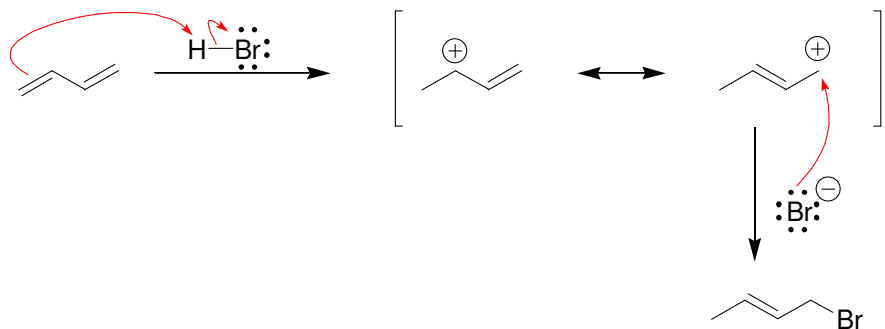
17.35.



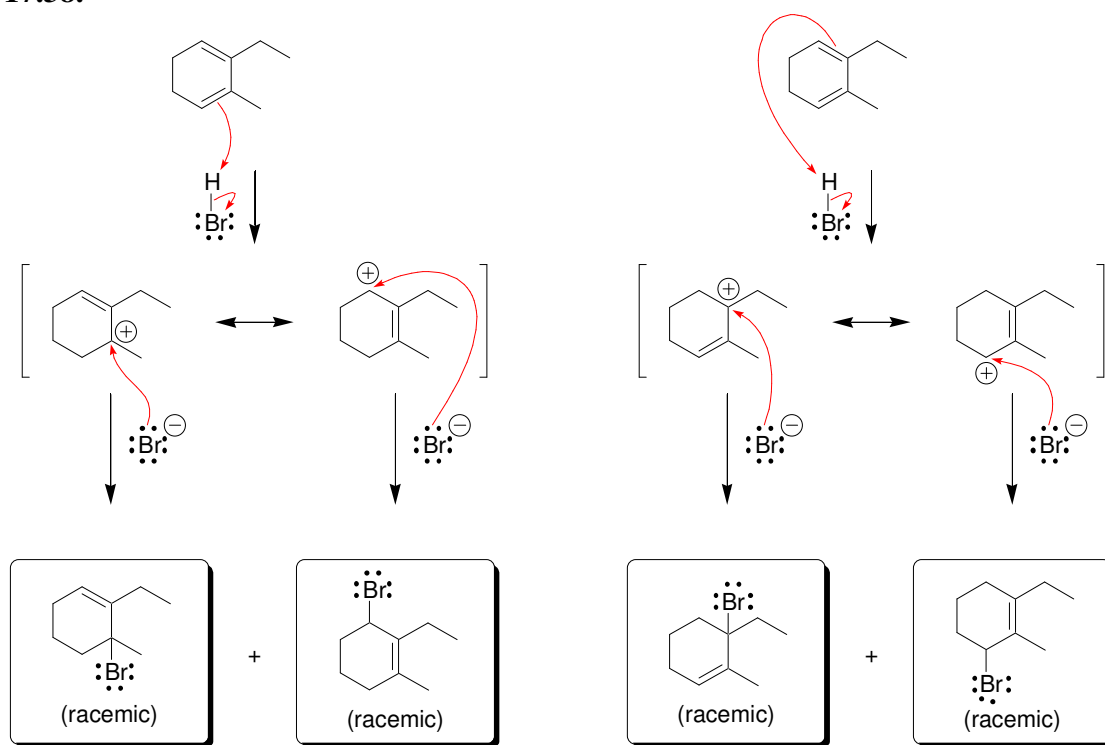
17.36.



17.37.



17.38.



17.39. An increase in temperature allowed the system to reach equilibrium concentrations, which are determined by the relative stability of each product. Under these conditions, the 1,4-adducts predominate. Once at equilibrium, lowering the temperature will not cause a decrease in the concentration of the 1,4-adducts.

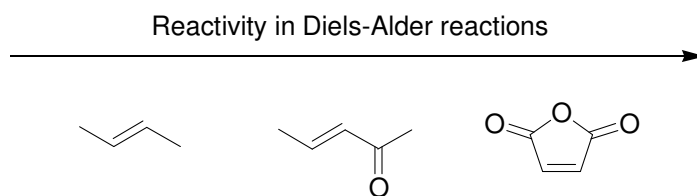
17.40.

a) The *tert*-butyl groups provide significant steric hinderance that prevents the compound from adopting an *s-cis* conformation.

b) This diene is not conjugated.

c) The methyl groups provide significant steric hinderance that prevents the compound from adopting an *s-cis* conformation.

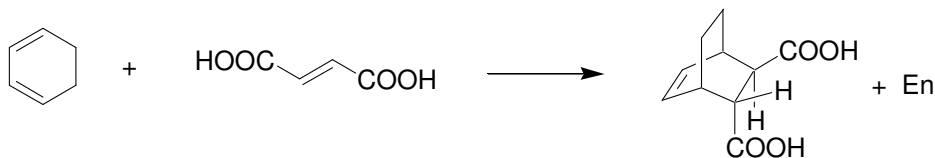
d) This diene cannot adopt an *s-cis* conformation

17.41.

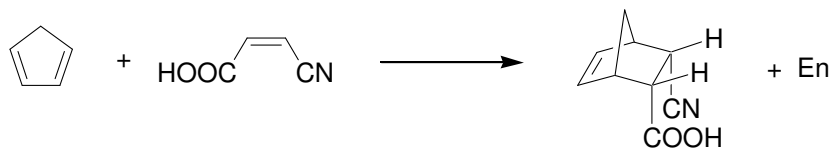
17.42. The π bonds in 1,2-butadiene are not conjugated, and λ_{\max} is therefore lower than 217 nm. In fact, it is below 200 nm, which is beyond the range used by most UV-VIS spectrometers.

17.43.

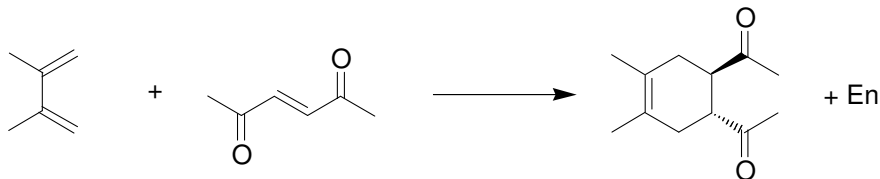
a)



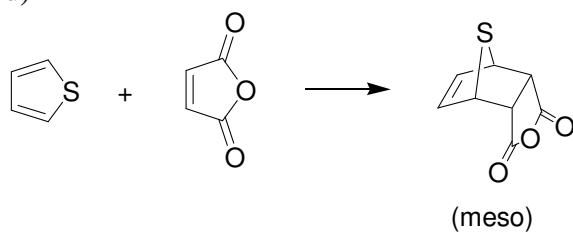
b)



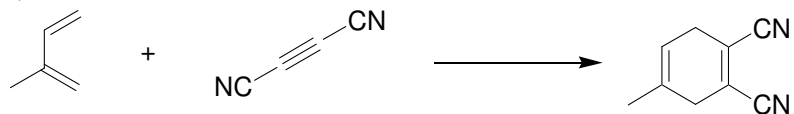
c)



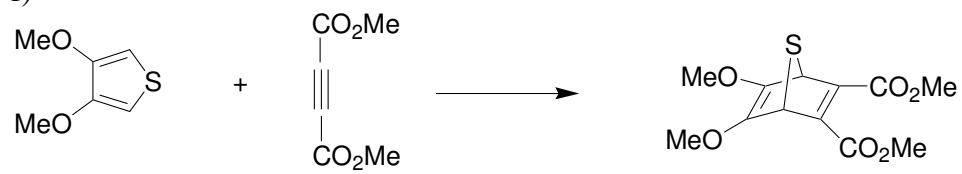
d)



e)



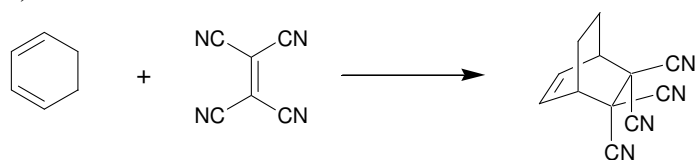
f)

**17.44.**

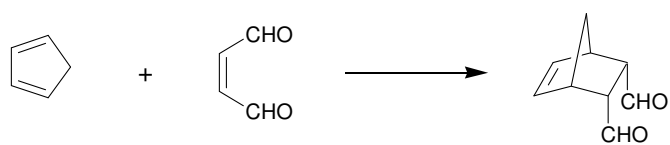
a)



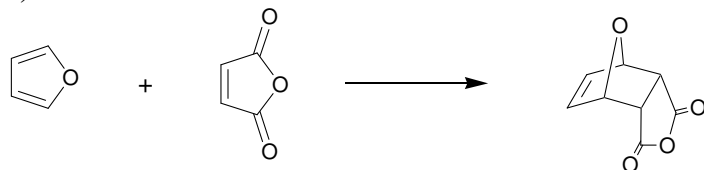
b)

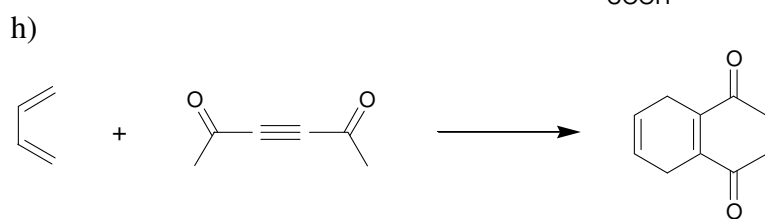
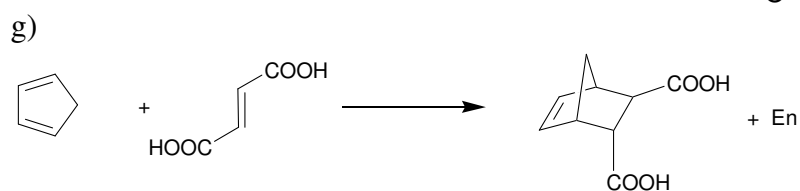
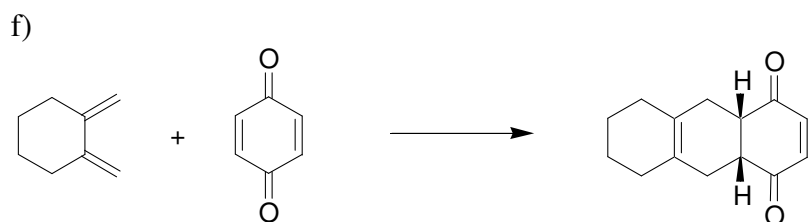
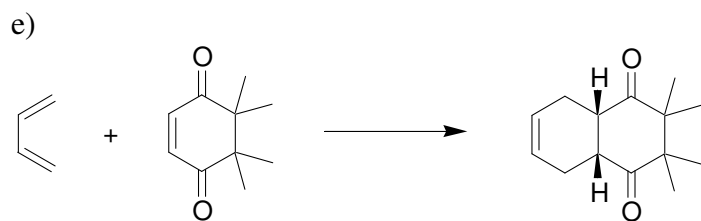
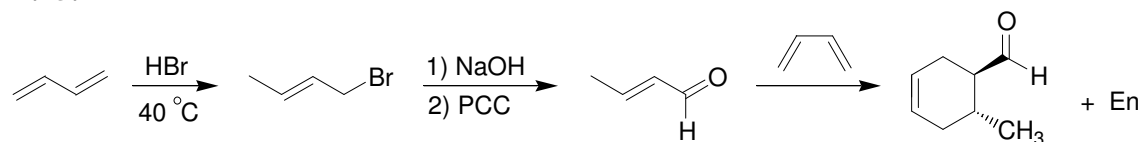
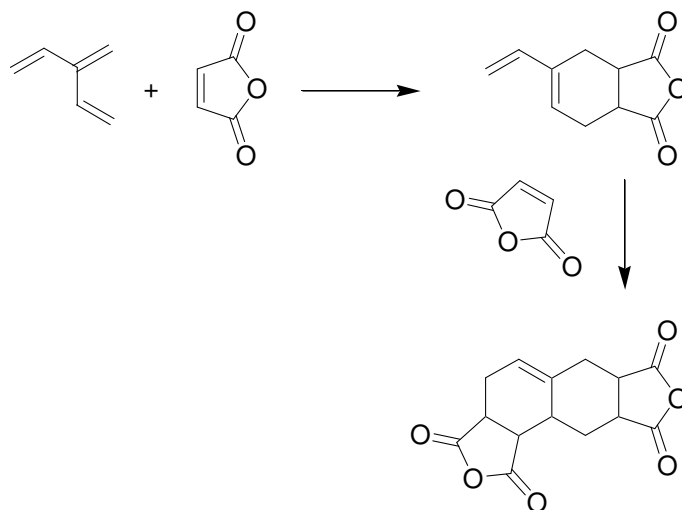


c)

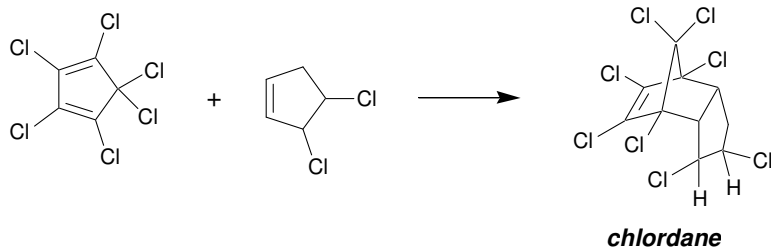


d)




17.45.

17.46.


17.47.

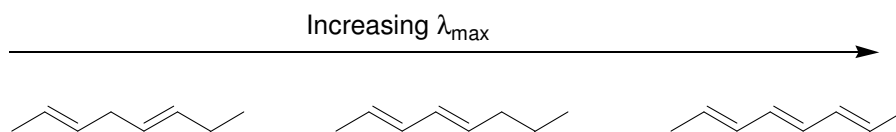


17.48. The two ends of the conjugated system are much farther apart in a seven-membered ring than they are in a five-membered ring.

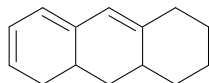
17.49.



17.50.



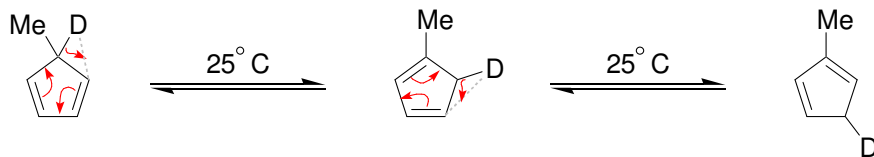
17.51. Two of the π bonds are homoannular in this compound, which adds +39 nm according to Woodward-Fieser rules.



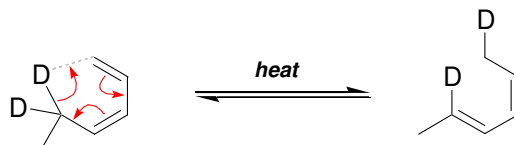
17.52.

Base	=	217
Additional double bonds	=	+60
Auxochromic alkyl groups	=	+35
Exocyclic double bonds	=	+5
<u>Homoannular diene</u>	=	<u>+39</u>
Total	=	356 nm

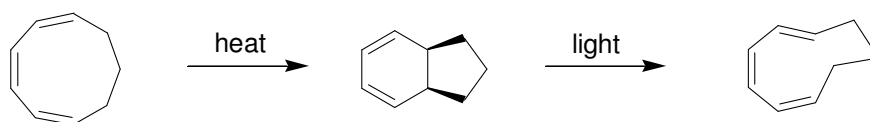
17.53. Each of these transformations can be explained with a [1,5] sigmatropic rearrangement:



17.54. This transformation can be explained with a [1,5] sigmatropic rearrangement:

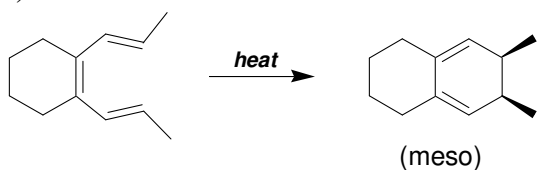


17.55.

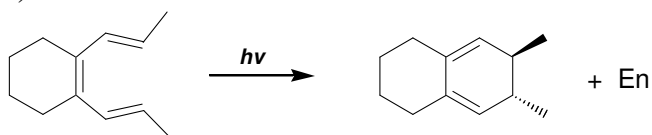


17.56.

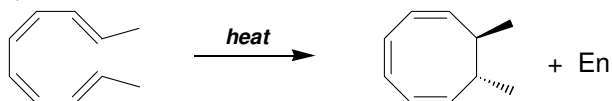
a)



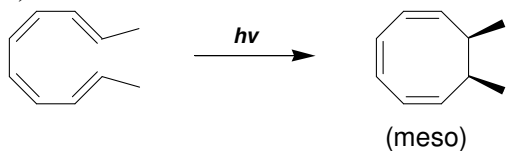
b)



c)

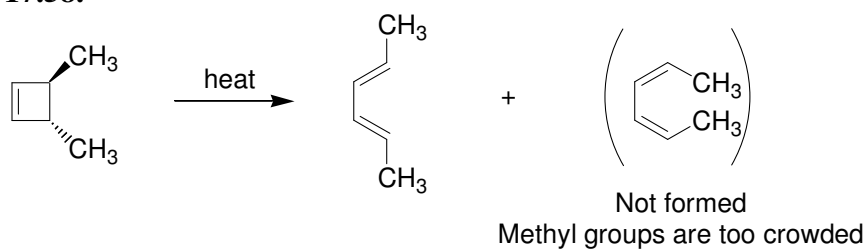


d)

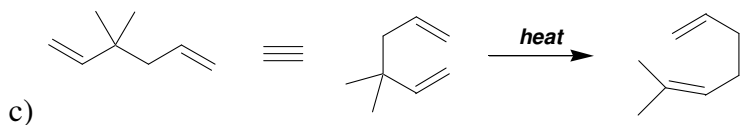
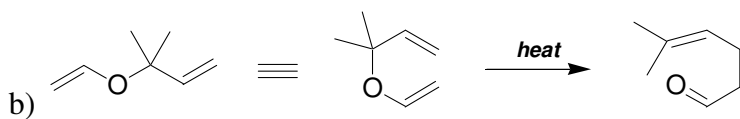
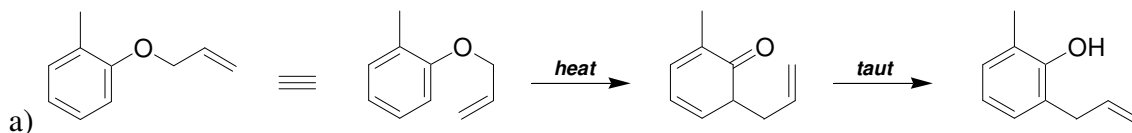


17.57. The compound on the right has a π bond in conjugation with the aromatic ring, while the compound on the left does not. Therefore, the compound on the right side of the equilibrium is expected to be more stable, and the equilibrium will favor the compound that is lower in energy.

17.58.

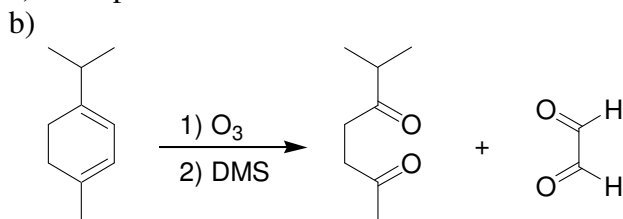


17.59.

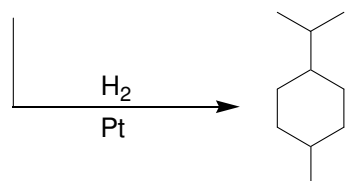


17.60.

a) α -Terpinene has two double bonds.



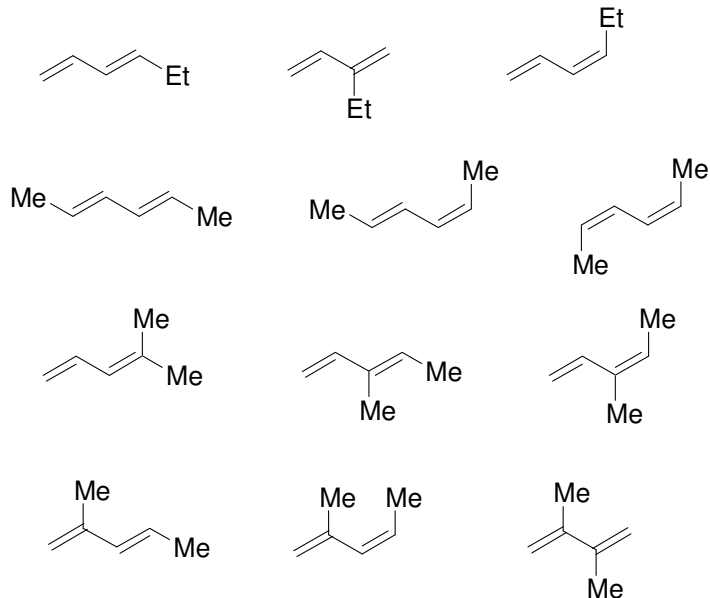
α -terpinene



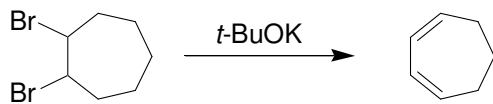
c)

Base	=	217
Additional double bonds	=	0
Auxochromic alkyl groups	=	+20
Exocyclic double bonds	=	0
<u>Homoannular diene</u>	=	<u>+39</u>
Total	=	276 nm

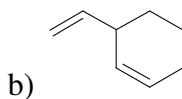
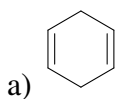
17.61.



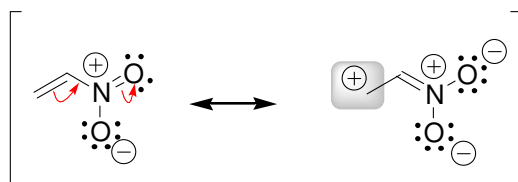
17.62.



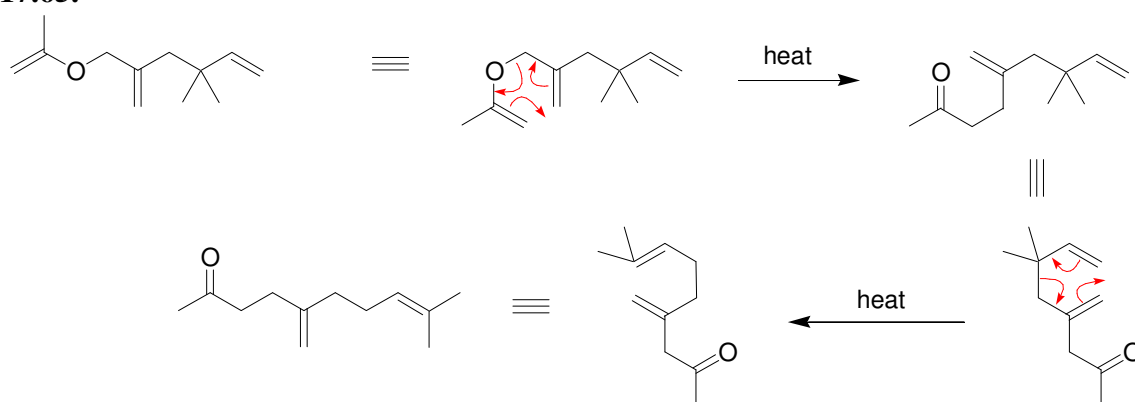
17.63. In each case, the non-conjugated isomer will be higher in energy:



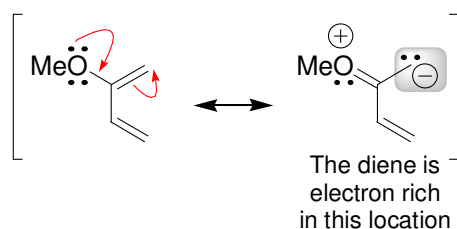
17.64. Nitroethylene should be more reactive than ethylene in a Diels–Alder reaction, because the nitro group is electron-withdrawing, via resonance:



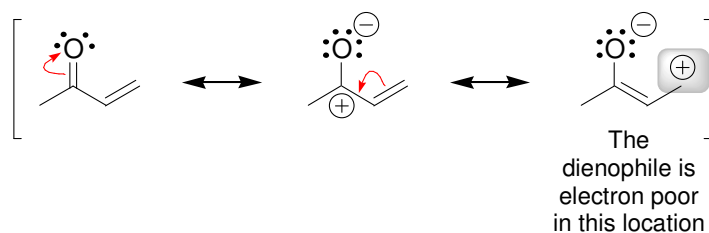
17.65.



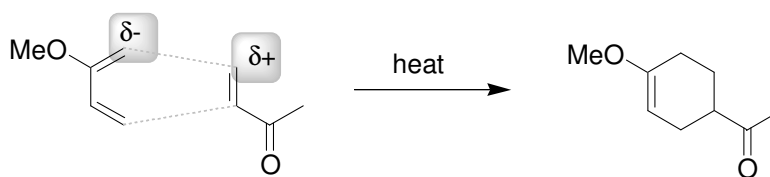
17.66. The diene is electron-rich in one specific location, as seen in the second resonance structure below:



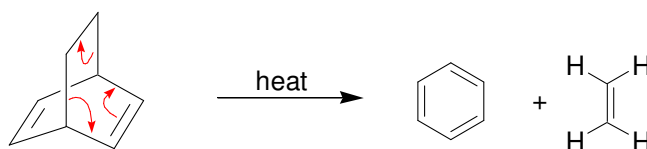
The dienophile is electron-poor in one specific location, as seen in the third resonance structure below:



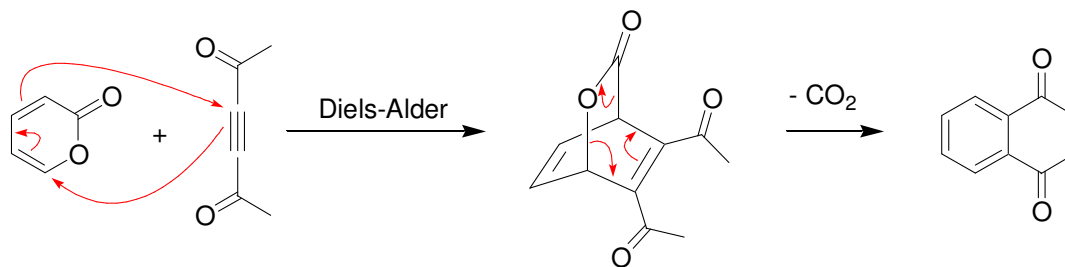
These two compounds will join in such a way that the electron-poor center lines up with the electron-rich center:



17.67.



17.68.



17.69. The nitrogen atom in divinyl amine is sp^2 hybridized. The lone pair is delocalized, and joins the two neighboring π bonds into one conjugated system. As such, the compound absorbs light above 200 nm (UV light). In contrast, 1,4-pentadiene has two isolated double bonds and therefore does not absorb UV light in the region between 200 and 400 nm.