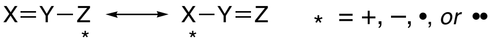
Chapter 16: Conjugation, Resonance, and Dienes

♦ Conjugation and delocalization of electron density

- The overlap of *p* orbitals on three or more adjacent atoms allows electron density to delocalize, thus adding stability (16.1).
- An allyl carbocation ($CH_2{=}CHCH_2^+$) is more stable than a 1° carbocation because of *p* orbital overlap (16.2).
- In any system X=Y–Z:, Z is sp^2 hybridized to allow the lone pair to occupy a *p* orbital, making the system conjugated (16.5).

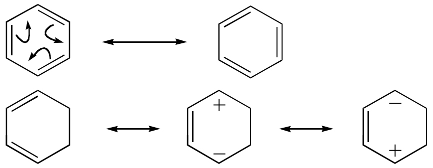
♦ Four common examples of resonance (16.3)

[1] The three atom "allyl" system:

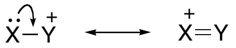


$X{=}Y{-}\underset{*}{Z} \longleftrightarrow \underset{*}{X}{-}Y{=}Z \qquad * = +, -, \bullet, \text{ or } \bullet\bullet$

[2] Conjugated double bonds:

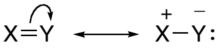


[3] Cations having a positive charge adjacent to a lone pair:



$\ddot{X}{-}\overset{+}{Y} \longleftrightarrow \overset{+}{X}{=}Y$

[4] Double bonds having one atom more electronegative than the other:

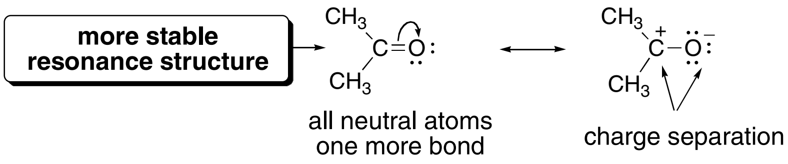


$X{=}Y \longleftrightarrow \overset{+}{X}{-}\overset{-}{Y}{:}$

[Electronegativity of Y > X]

♦ Rules on evaluating the relative "stability" of resonance structures (16.4)

[1] Structures with more bonds and fewer charges are more stable.

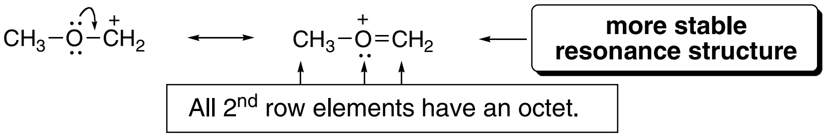


more stable resonance structure

all neutral atoms
one more bond

charge separation

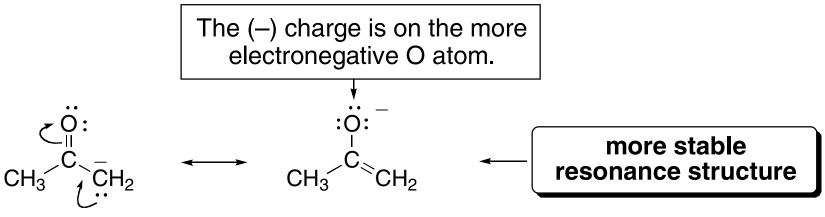
[2] Structures in which every atom has an octet are more stable.



more stable resonance structure

All 2nd row elements have an octet.

[3] Structures that place a negative charge on a more electronegative element are more stable.



The (–) charge is on the more electronegative O atom.

more stable resonance structure

♦ The unusual properties of conjugated dienes

[1] The C–C σ bond joining the two double bonds is unusually short (16.8).

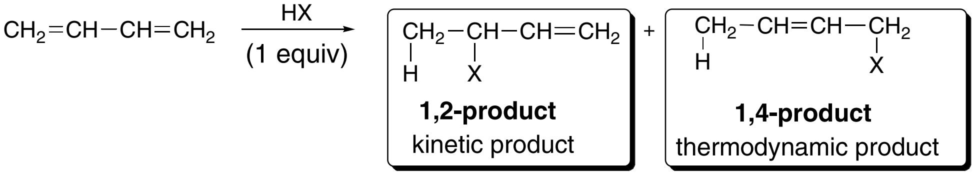
[2] Conjugated dienes are more stable than similar isolated dienes. ΔH^{o} of hydrogenation is smaller for a conjugated diene than for an isolated diene converted to the same product (16.9).

[3] The reactions are unusual:
- Electrophilic addition affords products of 1,2-addition and 1,4-addition (16.10, 16.11).
- Conjugated dienes undergo the Diels–Alder reaction, a reaction that does not occur with isolated dienes (16.12–16.14).

[4] Conjugated dienes absorb UV light in the 200–400 nm region. As the number of conjugated π bonds increases, the absorption shifts to longer wavelength (16.15).

♦ Reactions of conjugated dienes

[1] Electrophilic addition of HX (X = halogen) (16.10–16.11)



- The mechanism has two steps.
- Markovnikov's rule is followed. Addition of H^+ forms the more stable allylic carbocation.
- The 1,2-product is the kinetic product. When H^+ adds to the double bond, X^- adds to the end of the allylic carbocation to which it is closer (C2 not C4). The kinetic product is formed faster at low temperature.
- The thermodynamic product has the more substituted, more stable double bond. The thermodynamic product predominates at equilibrium. With 1,3-butadiene, the thermodynamic product is the 1,4-product.

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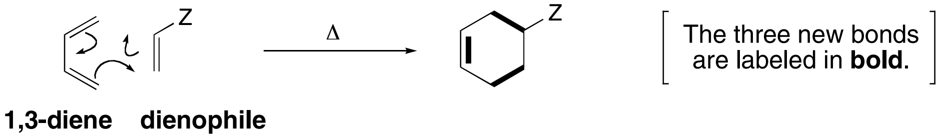
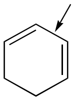
[2] Diels–Alder reaction (16.12–16.14)



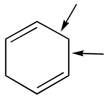
- The reaction forms two σ and one π bond in a six-membered ring.
- The reaction is initiated by heat.
- The mechanism is concerted: all bonds are broken and formed in a single step.
- The diene must react in the *s*-cis conformation (16.13A).
- Electron-withdrawing groups in the dienophile increase the reaction rate (16.13B).
- The stereochemistry of the dienophile is retained in the product (16.13C).
- Endo products are preferred (16.13D).

Chapter 16: Answers to Problems

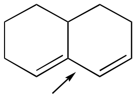
16.1 **Isolated dienes** have two double bonds separated by two or more σ bonds.
Conjugated dienes have two double bonds separated by only one σ bond.

a.


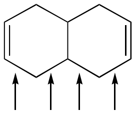
One σ bond separates two double bonds = **conjugated diene**

b.


Two σ bonds separate two double bonds = **isolated diene**

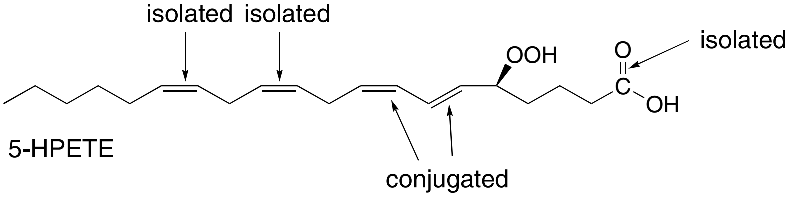
c.


One σ bond separates two double bonds = **conjugated diene**

d.


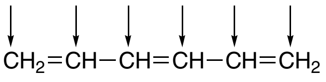
Four σ bonds separate two double bonds = **isolated diene**

16.2



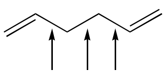
5-HPETE

16.3 **Conjugation** occurs when there are overlapping *p* orbitals on three or more adjacent atoms. Double bonds separated by 2 σ bonds are not conjugated.

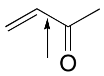
a.


$CH_2=CH-CH=CH-CH=CH_2$

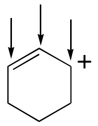
All of the carbon atoms are sp^2 hybridized. Each π bond is separated by only one σ bond. **conjugated**

b.


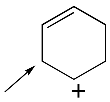
The two π bonds are separated by three σ bonds. **NOT conjugated**

c.


The two π bonds are separated by only one σ bond. **conjugated**

d.


Three adjacent carbon atoms are sp^2 hybridized and have an unhybridized *p* orbital. **conjugated**

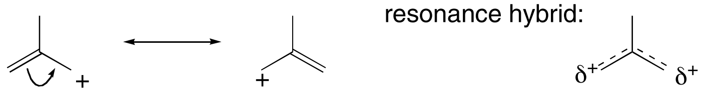
e.


This carbon is not sp^2 hybridized. **NOT conjugated**

16.4 Two resonance structures differ only in the placement of electrons. All σ bonds stay in the same place. Nonbonded electrons and π bonds can be moved. To draw the hybrid:

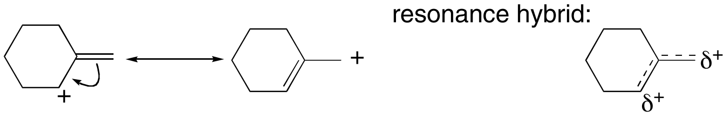
- Use a dashed line between atoms that have a π bond in one resonance structure and not the other.
- Use a δ symbol for atoms with a charge or radical in one structure but not the other.

a.



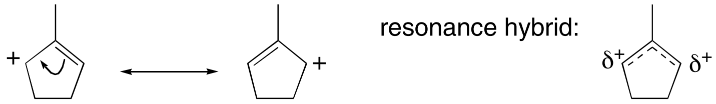
The + charge is delocalized on two carbons.

b.



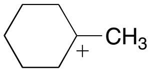
The + charge is delocalized on two carbons.

c.



The + charge is delocalized on two carbons.

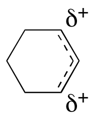
16.5 Each different kind of carbon atom will give a different ^{13}C signal. When a carbocation is delocalized as in structure **B,** carbons become equivalent.



A

5 different kinds of C

5 ^{13}C NMR signals



The two δ^+ carbons are identical.

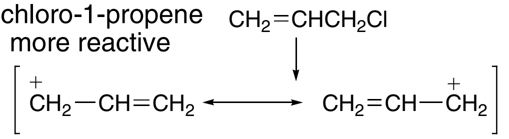
B

4 different kinds of C

4 ^{13}C NMR signals

16.6 S_N1 reactions proceed via a carbocation intermediate. Draw the carbocation formed on loss of Cl and compare. The more stable the carbocation, the faster the S_N1 reaction.

3-chloro-1-propene
more reactive

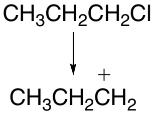


resonance-stabilized carbocation

Two resonance structures delocalize the positive charge on 2 C's making 3-chloro-1-propene more reactive.

$CH_3CH_2CH_2Cl$ is a 1° halide, which does not react by an S_N1 reaction because cleavage of the C–Cl bond forms a highly unstable 1° carbocation.

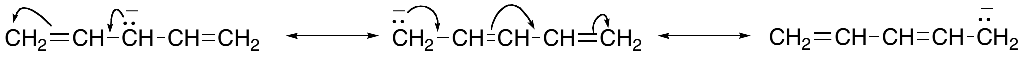
1-chloropropane
less reactive



only one Lewis structure
very unstable

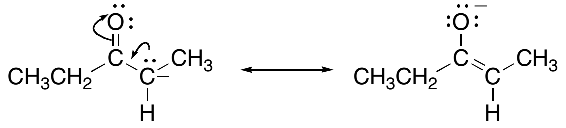
16.7

a.



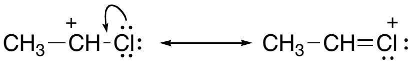
Move the charge
and the double bond.

b.



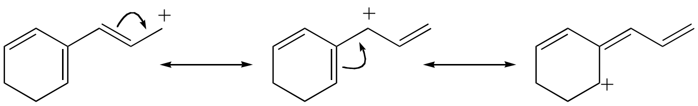
Move the charge
and the double bond.

c.



Move the lone pair.

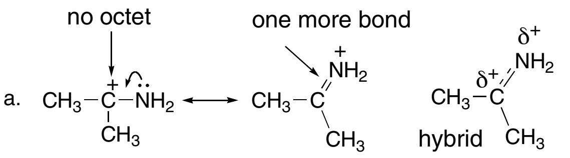
d.



Move the charge
and the double bond.

16.8 To compare the resonance structures remember:

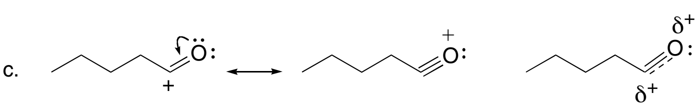
- Resonance structures with **more bonds** are better.
- Resonance structures in which **every atom has an octet** are better.
- Resonance structures with **neutral atoms** are better than those with charge separation.
- Resonance structures that place a **negative charge on a more electronegative atom** are better.



least stable

one more bond
All atoms have an octet.
better resonance structure
intermediate stability

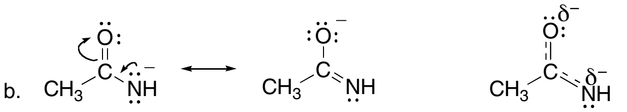
most stable



least stable

one more bond
better resonance structure
intermediate stability

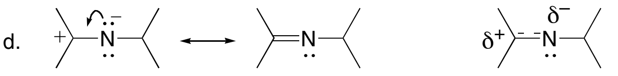
most stable



least stable

negative charge on the
more electronegative atom
better resonance structure
intermediate stability

hybrid
most stable

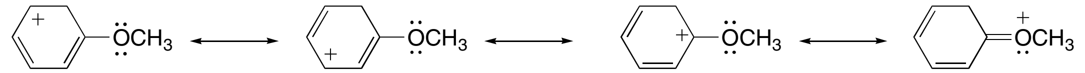


least stable

one more bond
better resonance structure
intermediate stability

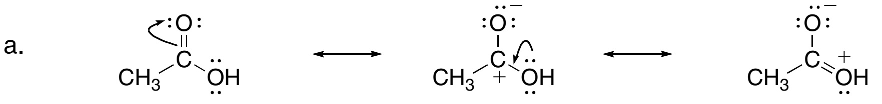
most stable

16.9



largest contribution
more bonds and all
atoms have octets

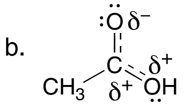
16.10



A
no charges
All atoms have an octet.
4 bonds (C–C + C–O)
most stable
lowest energy
resonance structure

B
2 charges
C does not have an octet.
3 bonds (C–C + C–O)
least stable
highest energy

C
2 charges
All atoms have an octet.
4 bonds (C–C + C–O)
intermediate stability
intermediate energy

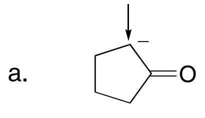


D

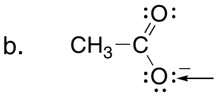
resonance hybrid
lower in energy
than any single
resonance form

c. In order of increasing energy: **D < A < C < B**

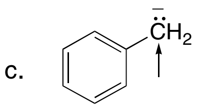
16.11 Remember that in any allyl system, there must be *p* orbitals to delocalize the lone pair.



sp^2 hybridized
trigonal planar geometry



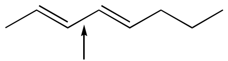
sp^2 hybridized
trigonal planar geometry



sp^2 hybridized
trigonal planar geometry

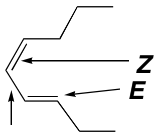
16.12 The ***s*-cis** conformation has two double bonds on the **same side** of the single bond.
The ***s*-trans** conformation has two double bonds on **opposite sides** of the single bond.

a. (2*E*,4*E*)-2,4-**octadiene** in the *s*-trans conformation



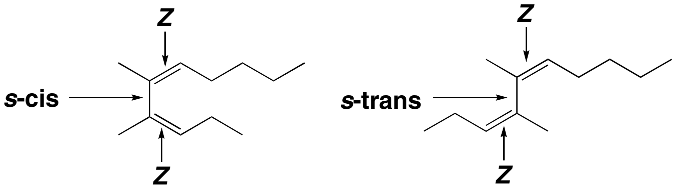
double bonds on opposite sides
***s*-trans**

b. (3*E*,5*Z*)- 3,5-**nonadiene** in the *s*-cis conformation

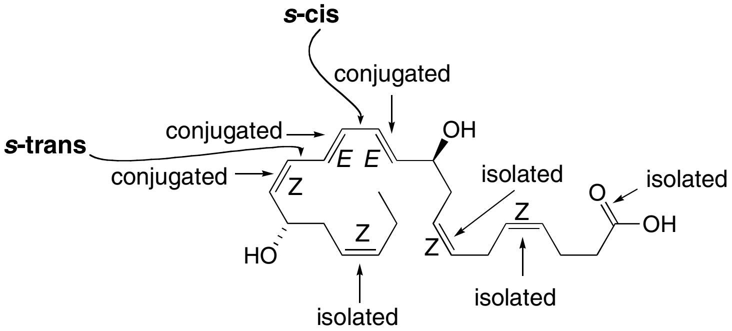


double bonds on the same side
***s*-cis**

c. (3*Z*,5*Z*)-4,5-dimethyl-3,5-**decadiene** in both the *s*-cis and *s*-trans conformations



16.13



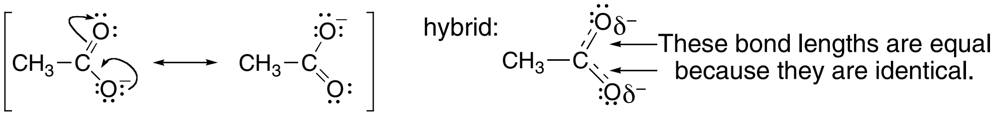
16.14 Bond length depends on hybridization and percent *s*-character. Bonds with a higher percent *s*-character have smaller orbitals and are shorter.

$HC\equiv C-C\equiv CH$
sp hybridized carbons
50% *s*-character
shortest bond

$CH_2=CH-CH=CH_2$
sp^2 hybridized carbons
33% *s*-character
intermediate length

CH_3-CH_3
sp^3 hybridized carbons
25% *s*-character
longest bond

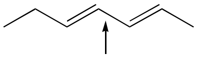
16.15 Two equivalent resonance structures delocalize the π bond and the negative charge.



These bond lengths are equal because they are identical.

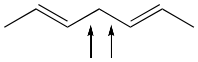
16.16 The **less stable** (higher energy) **diene** has the **larger heat of hydrogenation.** Isolated dienes are higher in energy than conjugated dienes, so they will have a larger heat of hydrogenation.

a.



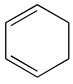
Double bonds separated by
one σ bond = **conjugated diene**
smaller heat of hydrogenation

or



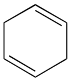
Double bonds separated by
two σ bonds = **isolated diene**
larger heat of hydrogenation

b.



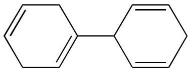
Double bonds separated by
one σ bond = **conjugated diene**
smaller heat of hydrogenation

or

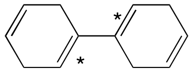


Double bonds separated by
two σ bonds = **isolated diene**
larger heat of hydrogenation

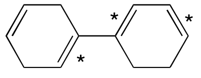
16.17 Isolated dienes are higher in energy than conjugated dienes. Compare the location of the double bonds in the compounds below.



0 conjugated double bonds
least stable



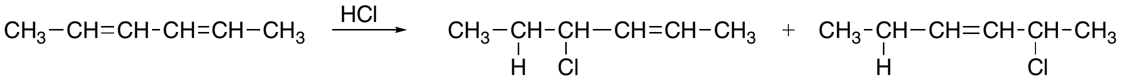
2 conjugated double bonds
intermediate stability



3 conjugated double bonds
most stable

16.18 Conjugated dienes react with HX to form 1,2- and 1,4-products.

a.

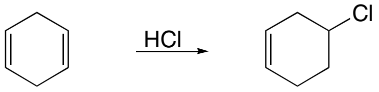


$$CH_3-CH=CH-CH=CH-CH_3 \xrightarrow{HCl} CH_3-\underset{H}{CH}-\underset{Cl}{CH}-CH=CH-CH_3 + CH_3-\underset{H}{CH}-CH=CH-\underset{Cl}{CH}-CH_3$$

1,2-product

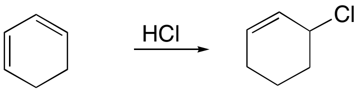
1,4-product

b.

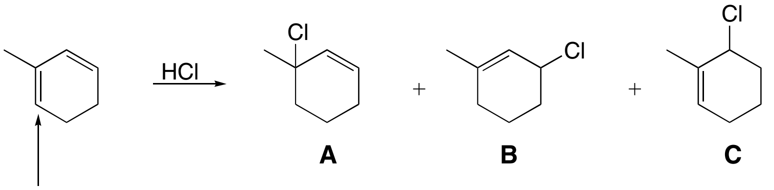


isolated diene

c.



d.

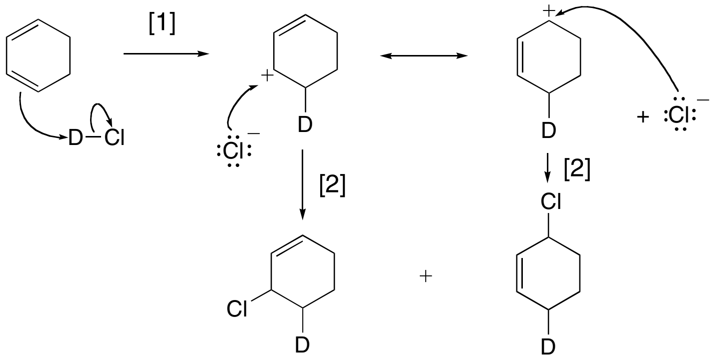


This double bond is more reactive, so **C** is probably a minor product
because it results from HCl addition to the less reactive double bond.

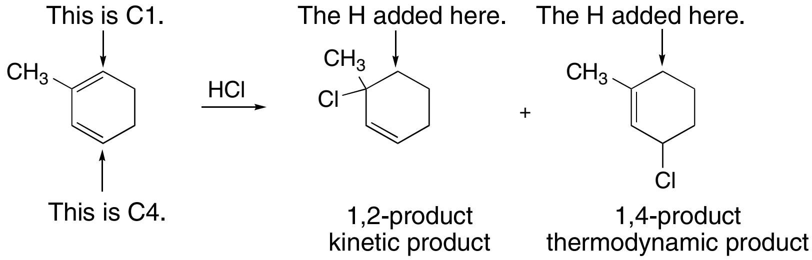
16.19 The mechanism for addition of DCl has two steps:

[1] **Addition of D^+** forms a resonance-stabilized carbocation.

[2] **Nucleophilic attack of Cl^-** forms 1,2- and 1,4-products.



16.20 Label the products as 1,2- or 1,4-products. The 1,2-product is the kinetic product, and the 1,4-product, which has the more substituted double bond, is the thermodynamic product.



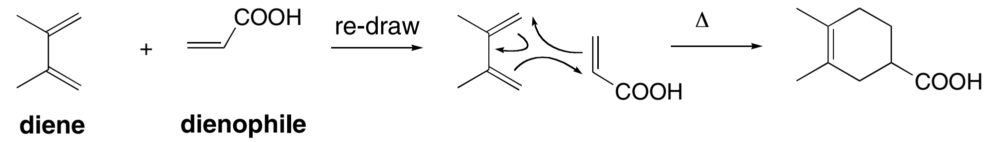
16.21 To draw the products of a Diels–Alder reaction:

[1] Find the 1,3-diene and the dienophile.

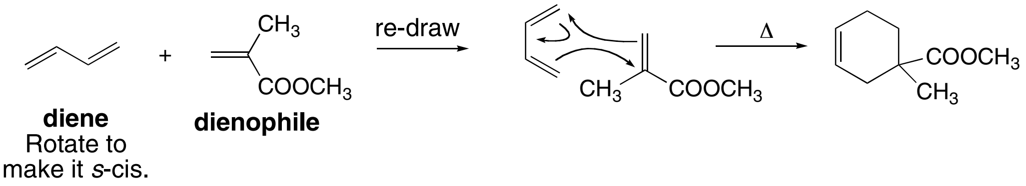
[2] Arrange them so the diene is on the left and the dienophile is on the right.

[3] Cleave three bonds and use arrows to show where the new bonds will be formed.

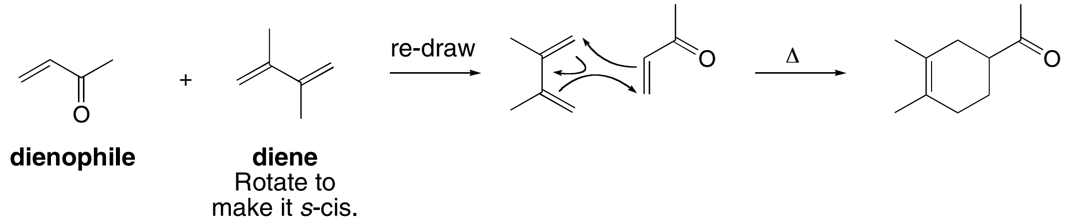
a.



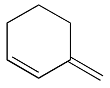
b.



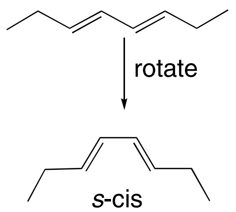
c.



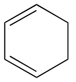
16.22 For a diene to be reactive in a Diels–Alder reaction, **a diene must be able to adopt an *s*-cis conformation.**



s-trans
cannot rotate
unreactive



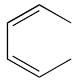
s-cis
reactive



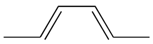
s-cis
most reactive

The diene is always in the
s-cis conformation.

16.23



(2*Z*,4*Z*)-2,4-hexadiene
sterically hindered



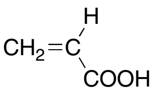
(2*E*,4*E*)-2,4-hexadiene
sterically unhindered
more reactive

Steric interactions between the two CH_3 groups make it difficult for the diene to adopt the needed *s*-cis conformation.

16.24 Electron-withdrawing substituents in the dienophile increase the reaction rate.

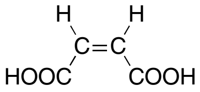
$CH_2{=}CH_2$

no electron-withdrawing groups
least reactive



$CH_2{=}CH(COOH)$

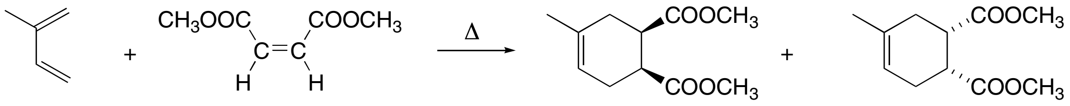
one electron-withdrawing group
intermediate reactivity



$HOOC(H)C{=}C(H)COOH$

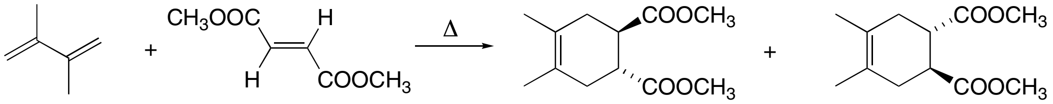
two electron-withdrawing groups
most reactive

16.25 A cis dienophile forms a cis-substituted cyclohexene.
A trans dienophile forms a trans-substituted cyclohexene.

a.


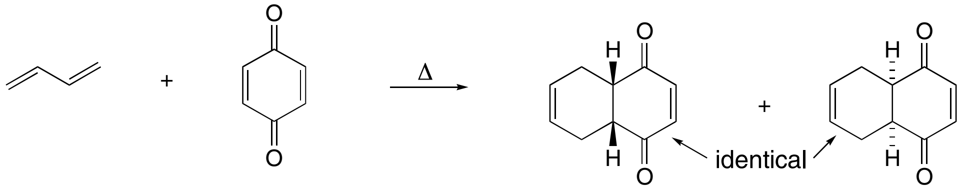
cis dienophile

cis-substituted products

b.


trans dienophile

trans-substituted products

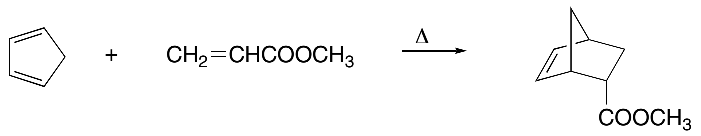
c.


cis dienophile

cis-substituted product

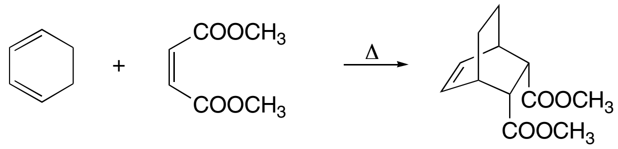
16.26 The **endo product** (with the substituents under the plane of the new six-membered ring) is the preferred product.

a.



endo substituent

b.

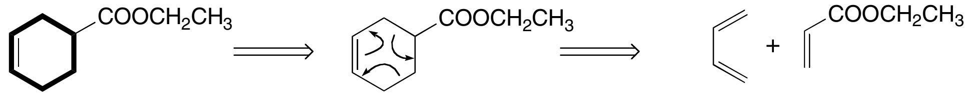


both groups **endo**

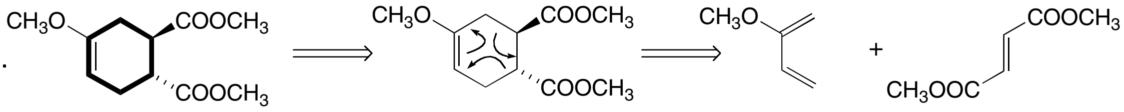
16.27 To find the diene and dienophile needed to make each of the products:

[1] Find the six-membered ring with a C–C double bond.
[2] Draw three arrows to work backwards.
[3] Follow the arrows to show the diene and dienophile.

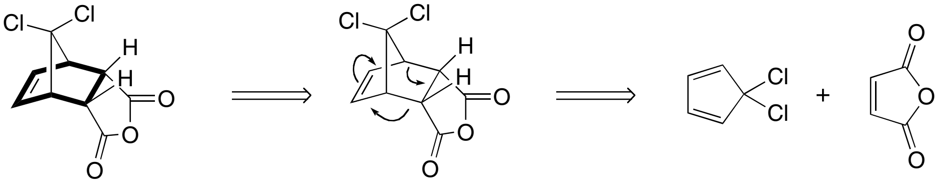
a.



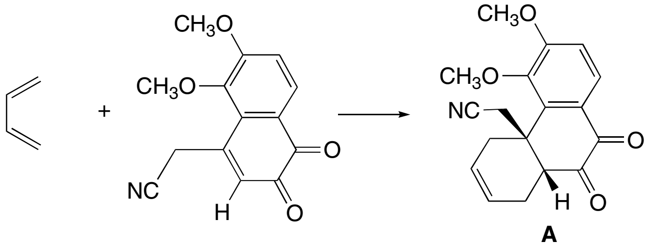
b.



c.



16.28

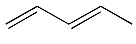


A

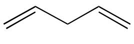
(+ enantiomer)

16.29 Conjugated molecules absorb light at a longer wavelength than molecules that are not conjugated.

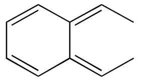
a.



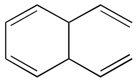
or



b.



or



conjugated
longer wavelength

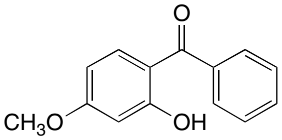
not conjugated

all double bonds conjugated
longer wavelength

one set of
conjugated dienes

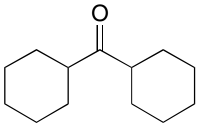
16.30 Sunscreens contain conjugated systems to absorb UV radiation from sunlight. Look for conjugated systems in the compounds below.

a.



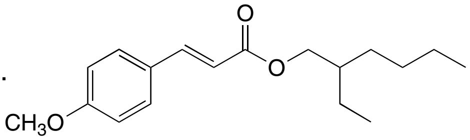
conjugated system
could be a sunscreen

b.



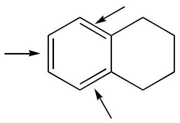
not a conjugated system

c.

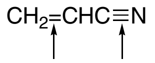


conjugated system
could be a sunscreen

16.31 Use the definition from Answer 16.1.

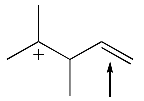


3 π bonds with only
1 σ bond between
conjugated

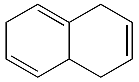


$CH_2=CHC\equiv N$

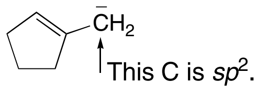
2 multiple bonds with only
1 σ bond between
conjugated



1 π bond with
no adjacent sp^2 hybridized atoms
NOT conjugated



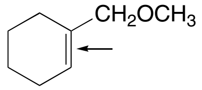
3 π bonds with 2 or
more σ bonds between
NOT conjugated



1 π bond with
an adjacent sp^2 hybridized atom

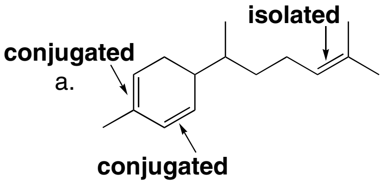
The lone pair occupies a *p* orbital,
so there are *p* orbitals on
three adjacent atoms.

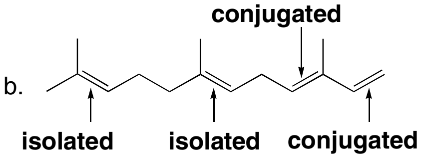
conjugated

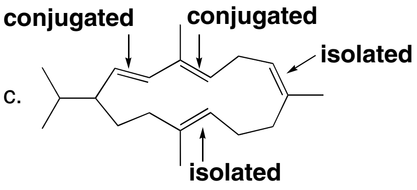


1 π bond with
no adjacent sp^2 hybridized atoms
NOT conjugated

16.32 Use the definition from Answer 16.1.

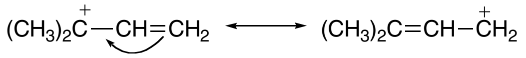




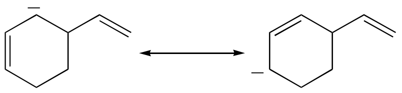


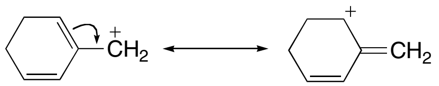
16.33 Although 2,3-di-*tert*-butyl-1,3-butadiene has four adjacent *p* orbitals, the bulky *tert*-butyl groups prevent the diene from adopting the *s*-cis conformation needed for the Diels–Alder reaction. Thus, this diene does not undergo a characteristic reaction of conjugated dienes.

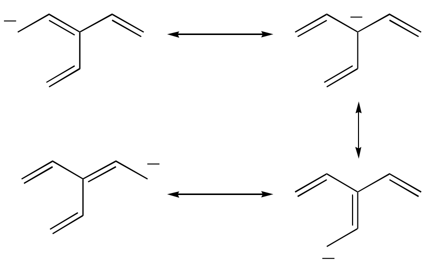
16.34

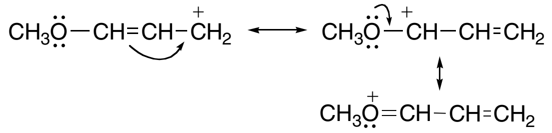
a. 

$(CH_3)_2\overset{+}{C}-CH=CH_2 \longleftrightarrow (CH_3)_2C=CH-\overset{+}{C}H_2$

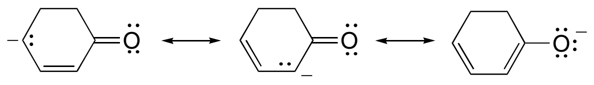
b. 

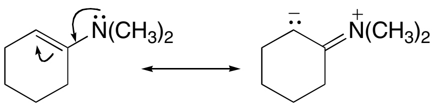
c. 

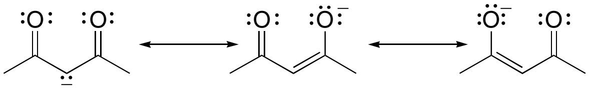
d. 

e. 

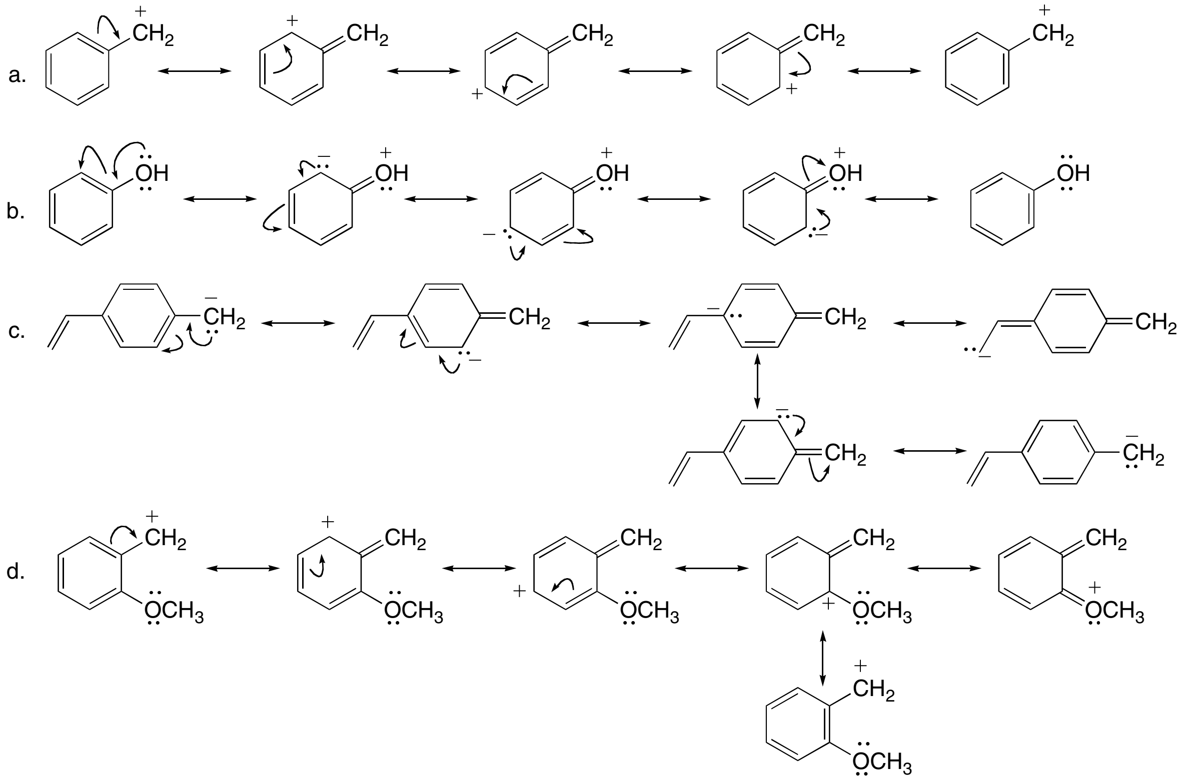
$CH_3\ddot{O}-CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_3\ddot{O}-\overset{+}{C}H-CH=CH_2 \longleftrightarrow CH_3\overset{+}{O}=CH-CH=CH_2$

f. 

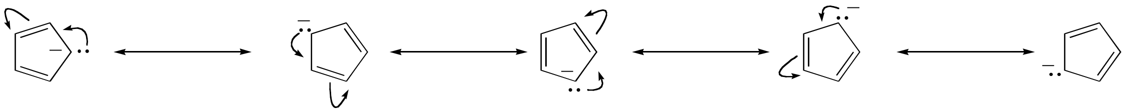
g. 

h. 

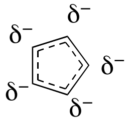
16.35



16.36



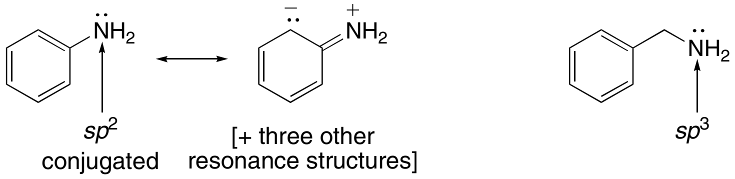
resonance hybrid:



Five resonance structures delocalize the negative charge on five C's making them all equivalent.

All of the carbons are identical in the anion.

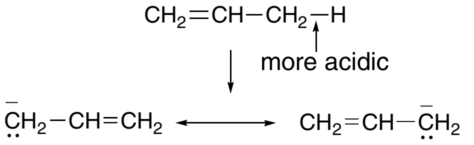
16.37 The N atom of $C_6H_5CH_2NH_2$ is surrounded by four groups and is *sp*^{3} hybridized. Although the N atom of $C_6H_5NH_2$ is surrounded by four groups, it is also bonded to a benzene ring. To be conjugated with the benzene ring, the N atom must be *sp*^{2} hybridized and its lone pairs must occupy a *p* orbital. In this way the lone pair can be delocalized, as shown in one resonance structure.



The N atom is *not* conjugated with the benzene ring.

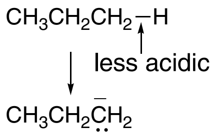
16.38

a.



$$CH_2{=}CH{-}CH_2{-}H \rightarrow \overset{-}{\underset{\cdot\cdot}{C}}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\overset{-}{\underset{\cdot\cdot}{C}}H_2$$

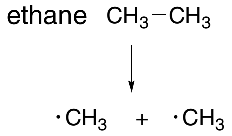
Resonance stabilization delocalizes the negative charge on 2 C's after loss of a proton. This makes propene more acidic than propane.



$$CH_3CH_2CH_2{-}H \rightarrow CH_3CH_2\overset{-}{\underset{\cdot\cdot}{C}}H_2$$

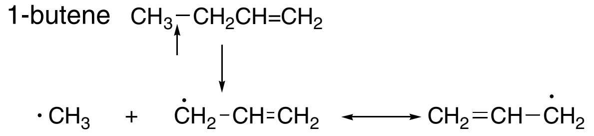
only one Lewis structure

b. Draw the products of cleavage of the bond.



$$CH_3{-}CH_3 \rightarrow \cdot CH_3 + \cdot CH_3$$

Two unstable radicals form.

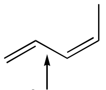


$$CH_3{-}CH_2CH{=}CH_2 \rightarrow \cdot CH_3 + \dot{C}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\dot{C}H_2$$

One resonance-stabilized radical forms.
This makes the bond dissociation
energy lower because a more stable radical is formed.

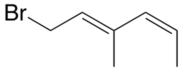
16.39 Use the directions from Answer 16.12.

a. (3*Z*)-1,3-pentadiene in the *s*-trans conformation

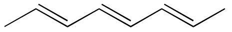


double bonds on opposite sides
***s*-trans**

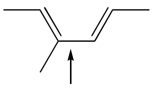
b. (2*E*,4*Z*)-1-bromo-3-methyl-2,4-hexadiene



c. (2*E*,4*E*,6*E*)-2,4,6-octatriene

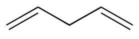


d. (2*E*,4*E*)-3-methyl-2,4-hexadiene in the *s*-cis conformation

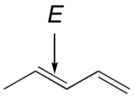


***s*-cis**

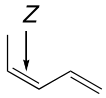
16.40



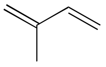
1,4-pentadiene



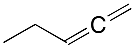
(3*E*)-1,3-pentadiene



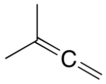
(3*Z*)-1,3-pentadiene



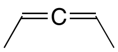
2-methyl-1,3-butadiene



1,2-pentadiene

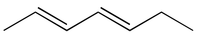


3-methyl-1,2-butadiene

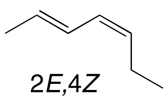


2,3-pentadiene

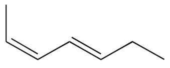
16.41



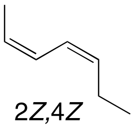
2*E*,4*E*



2*E*,4*Z*



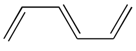
2*Z*,4*E*



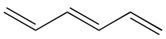
2*Z*,4*Z*

16.42

a.



and

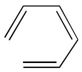


(3*E*)-1,3,5-hexatriene
both *s*-cis

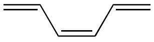
(3*E*)-1,3,5-hexatriene
both *s*-trans

different conformations

b.



and

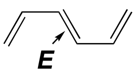


(3*Z*)-1,3,5-hexatriene
both *s*-cis

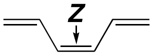
(3*Z*)-1,3,5-hexatriene
both *s*-trans

different conformations

c.



and



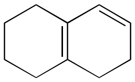
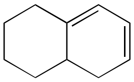
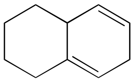
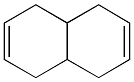
(3*E*)-1,3,5-hexatriene

(3*Z*)-1,3,5-hexatriene

different stereoisomers

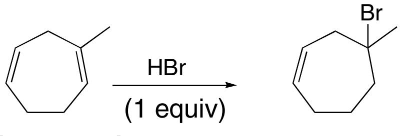
16.43 Use the directions from Answer 16.16 and recall that more substituted double bonds are more stable.

Increasing heat of hydrogenation →

			
conjugated diene one tetra-, one disubstituted double bond **smallest** heat of hydrogenation	conjugated diene one di-, one trisubstituted double bond **smaller intermediate** heat of hydrogenation	isolated diene one di-, one trisubstituted double bond **larger intermediate** heat of hydrogenation	isolated diene both disubstituted double bonds **largest** heat of hydrogenation

16.44 Conjugated dienes react with HX to form 1,2- and 1,4-products.

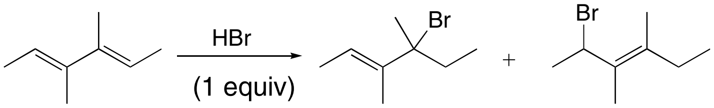
a.



isolated diene

major product, formed by addition of HBr to the more substituted C=C

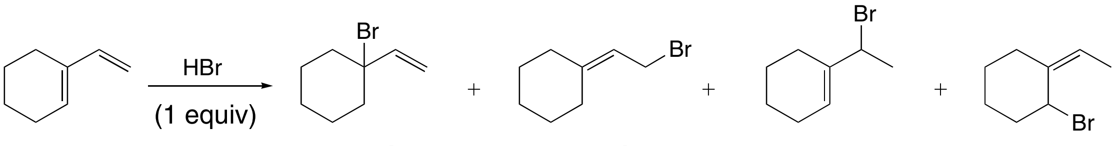
b.



1,2-product **1,4-product**

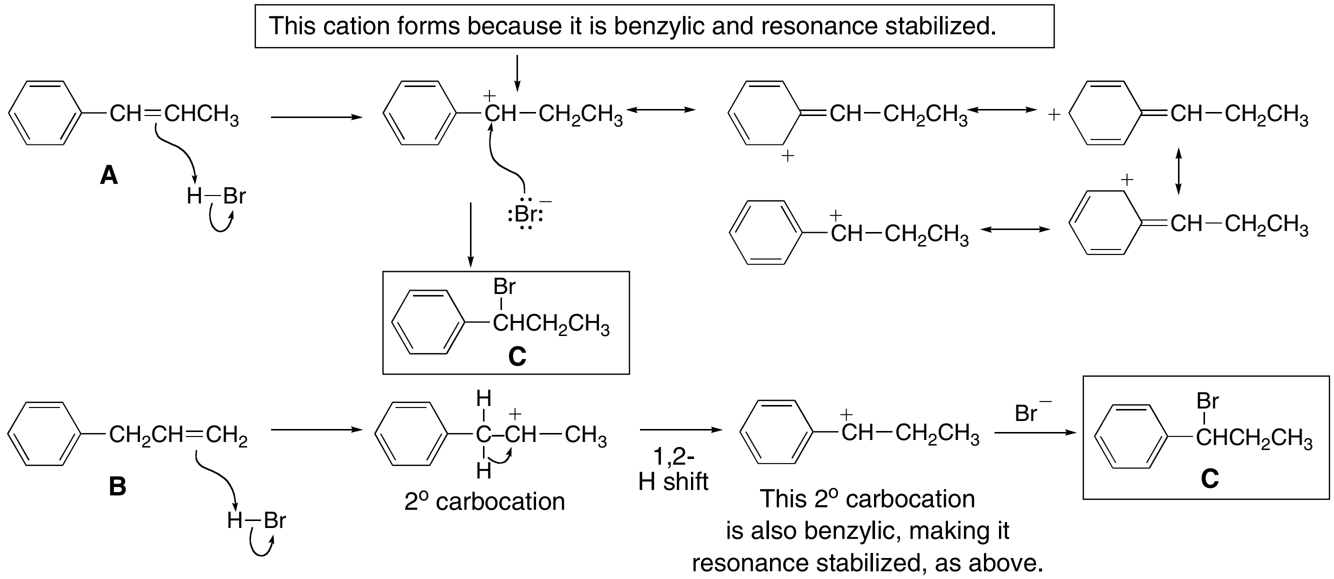
(*E* and *Z* isomers can form.)

c.



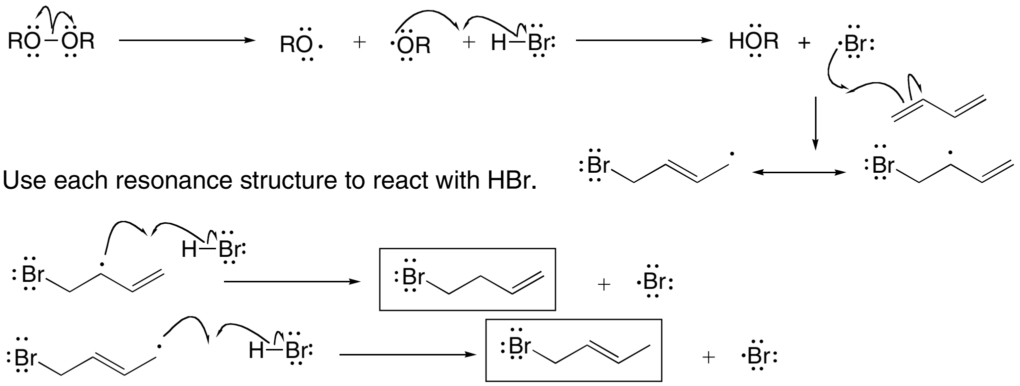
1,2-product **1,4-product** **1,2-product** (*E* and *Z* isomers)
1,4-product

16.45

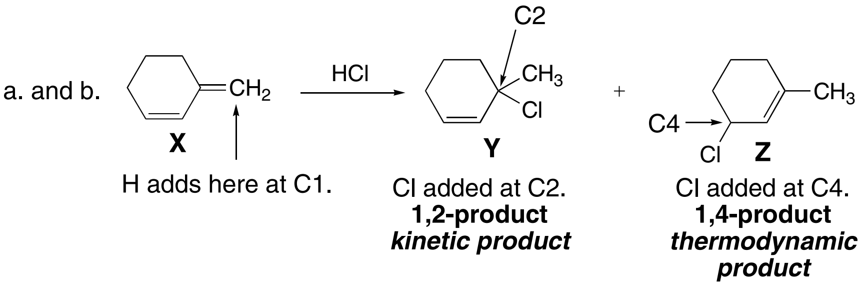

This cation forms because it is benzylic and resonance stabilized.

This 2° carbocation is also benzylic, making it resonance stabilized, as above.

16.46 To draw the mechanism for reaction of a diene with HBr and ROOR, recall from Chapter 15 that when an alkene is treated with HBr under these radical conditions, the Br ends up on the carbon with more H's to begin with.


Use each resonance structure to react with HBr.

16.47

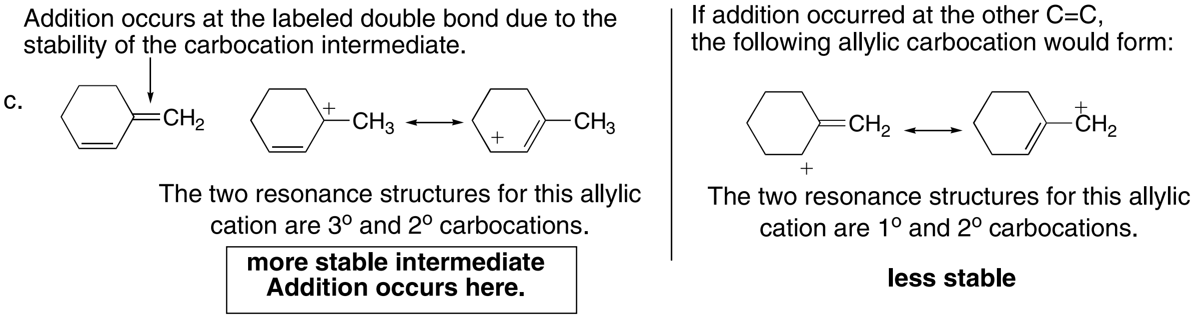


H adds here at C1.

Cl added at C2.
1,2-product
kinetic product

Cl added at C4.
1,4-product
thermodynamic product

Y is the kinetic product because of the proximity effect. H and Cl add across two adjacent atoms.
Z is the thermodynamic product because it has a more stable trisubstituted double bond.


c.

Addition occurs at the labeled double bond due to the stability of the carbocation intermediate.

The two resonance structures for this allylic cation are 3° and 2° carbocations.

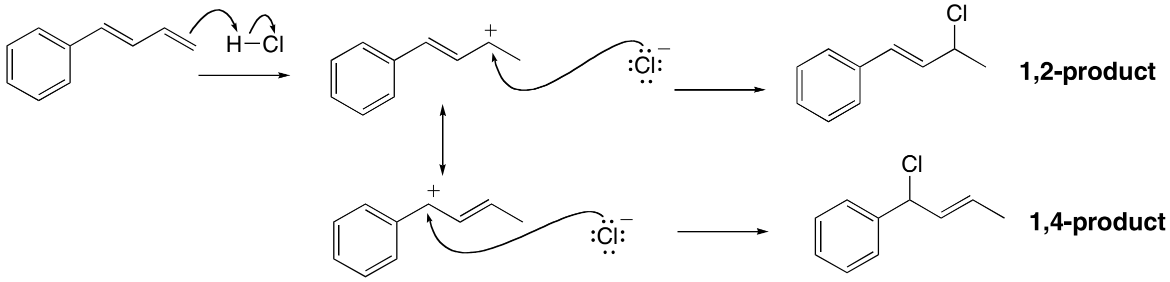
more stable intermediate
Addition occurs here.

If addition occurred at the other C=C, the following allylic carbocation would form:

The two resonance structures for this allylic cation are 1° and 2° carbocations.

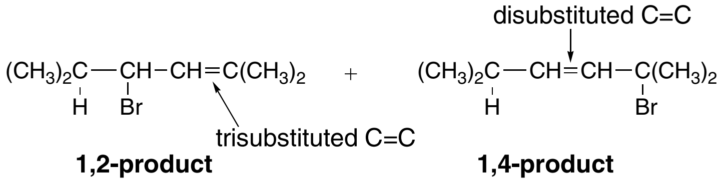
less stable

16.48 Addition of HCl at the terminal double bond forms a carbocation that is highly resonance stabilized since it is both allylic and benzylic. Such stabilization does not occur when HCl is added to the other double bond. This gives rise to two products of electrophilic addition.



(+ three more resonance structures that delocalize the positive charge onto the benzene ring)

16.49 There are two possible products:



$$\underset{\mathrm{H}}{(CH_3)_2C}-\underset{\mathrm{Br}}{CH}-CH=C(CH_3)_2 \quad + \quad \underset{\mathrm{H}}{(CH_3)_2C}-CH=CH-\underset{\mathrm{Br}}{C(CH_3)_2}$$

disubstituted C=C

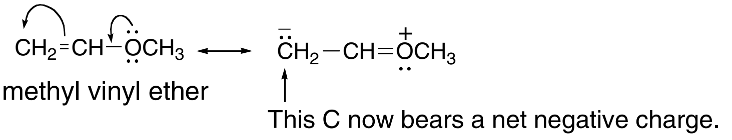
trisubstituted C=C

1,2-product

1,4-product

The 1,2-product is always the kinetic product because of the proximity effect. In this case, it is also the thermodynamic (more stable) product because it contains a more highly substituted C=C (trisubstituted) than the 1,4-product (disubstituted). Thus, the 1,2-product is the major product at high and low temperature.

16.50 The electron pairs on O can be donated to the double bond through resonance. This increases the electron density of the double bond, making it less electrophilic and therefore less reactive in a Diels–Alder reaction.

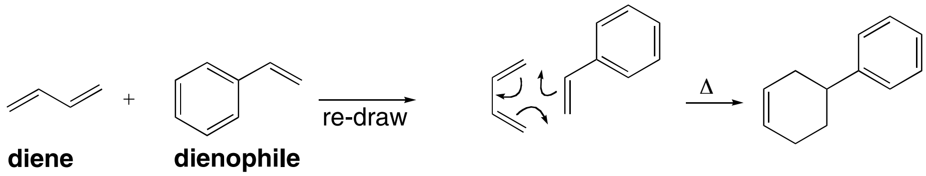


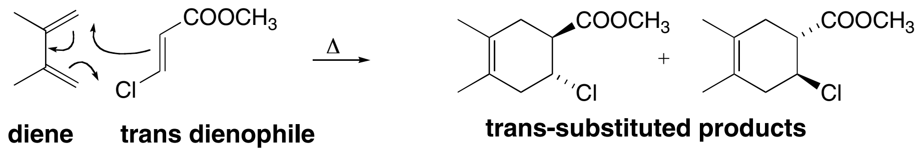
$$CH_2=CH-\ddot{\underset{..}{O}}CH_3 \longleftrightarrow \overset{-}{\ddot{C}}H_2-CH=\overset{+}{\underset{..}{O}}CH_3$$

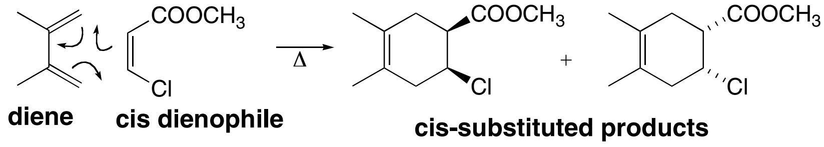
methyl vinyl ether

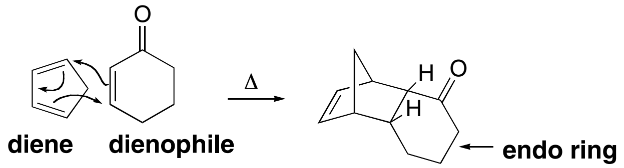
This C now bears a net negative charge.

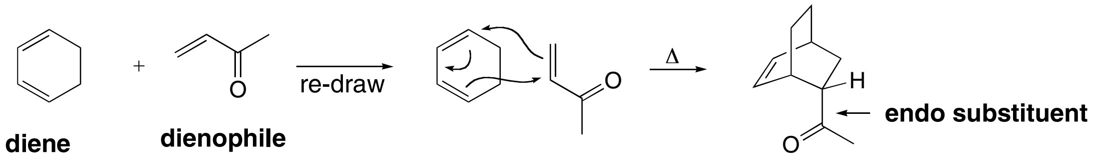
16.51 Use the directions from Answer 16.21.

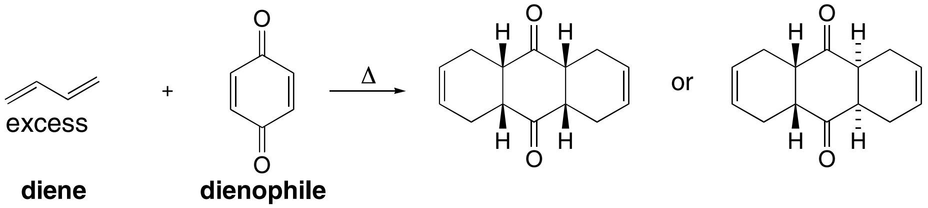
a.


b.


c.


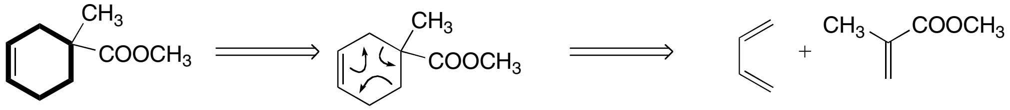
d.


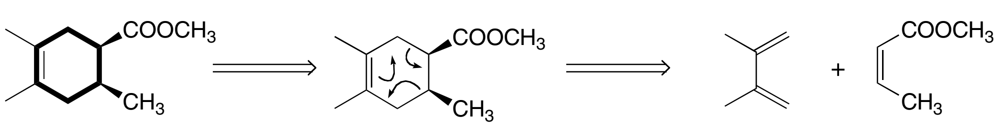
e.


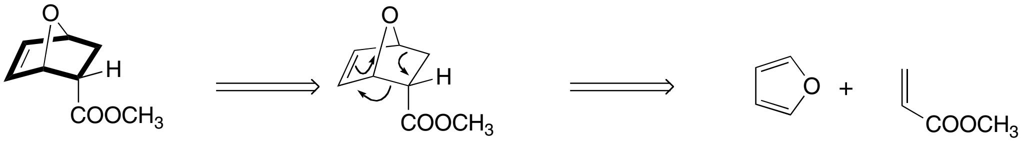
f.


Both C=C's of the dienophile react so two Diels–Alder reactions take place.

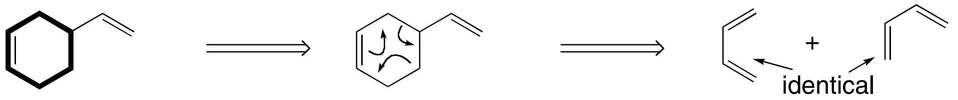
16.52 Use the directions from Answer 16.27.

a.


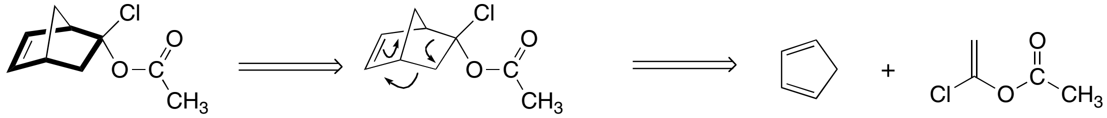
b.


c.


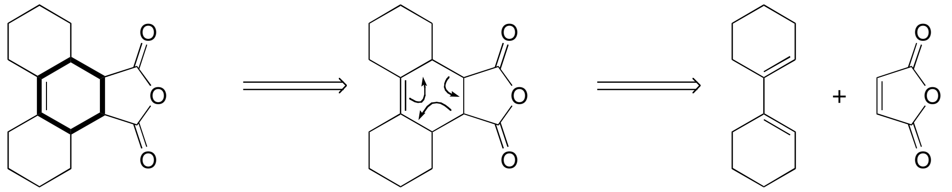
d.



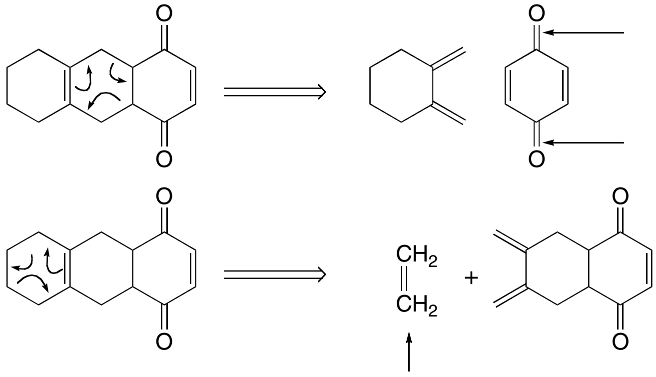
e.



f.



16.53

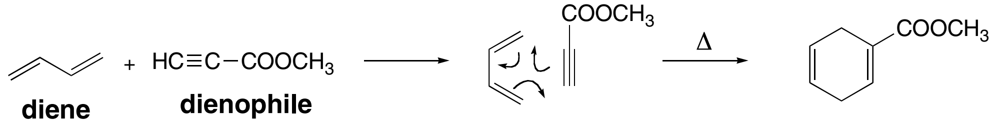


This pathway is **preferred** because the dienophile has electron-withdrawing C=O groups that make it more reactive.

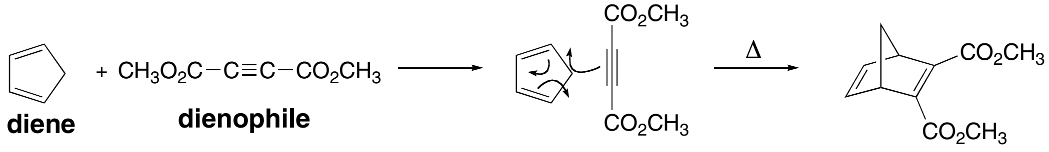
no electron-withdrawing groups
less reactive

16.54

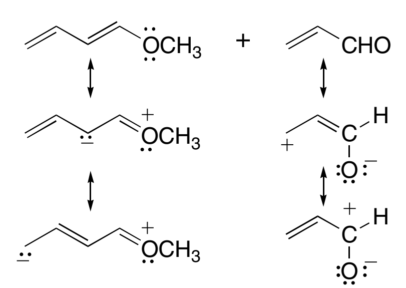
a.

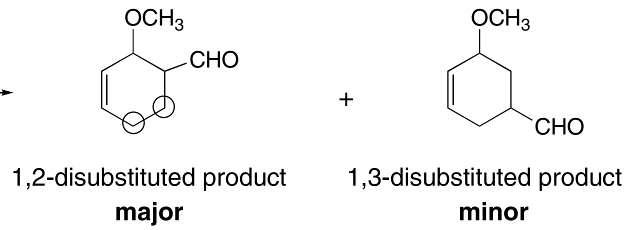


b.



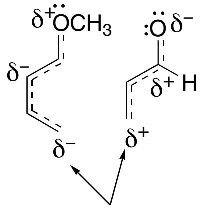
16.55



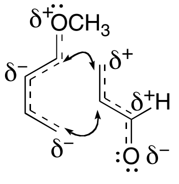


The major product is formed when the circled carbons with a δ+ and δ− react.

resonance hybrids:

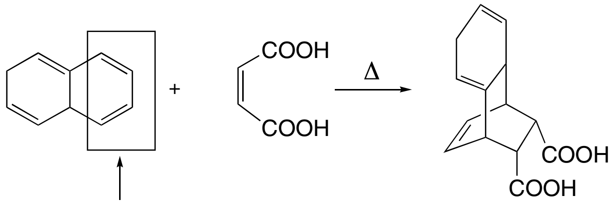


For the 1,2-product, carbons with unlike charges would react. This is favored because the electron-rich and the electron-poor C's can bond.



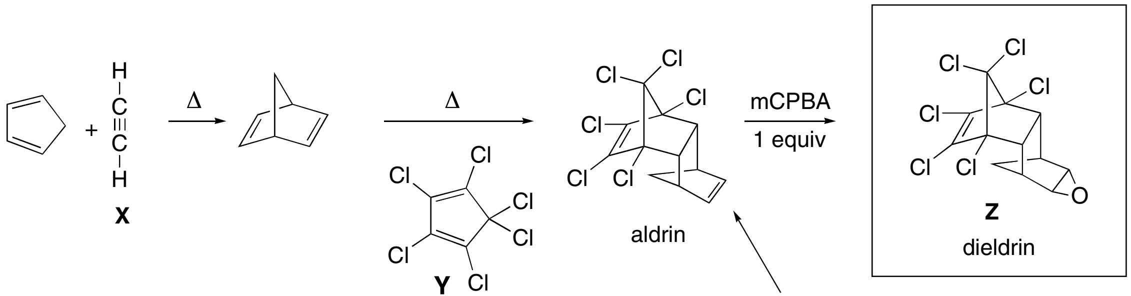
For the 1,3-product, there are no partial charges of opposite sign on reacting carbons. This arrangement is less attractive.

16.56



These are the only two double bonds that are conjugated and have the *s*-cis conformation needed for a Diels–Alder reaction.

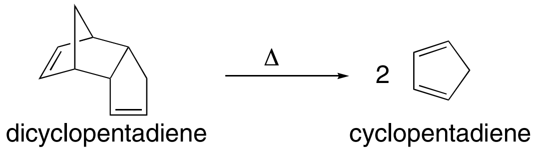
16.57



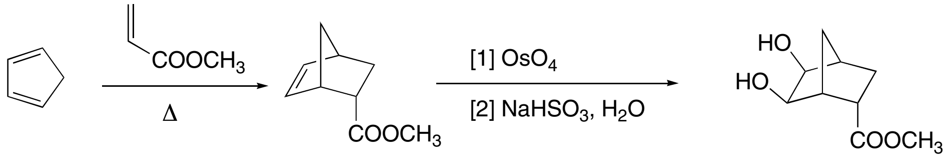
This double bond is more electron rich, so it is epoxidized more readily.

16.58

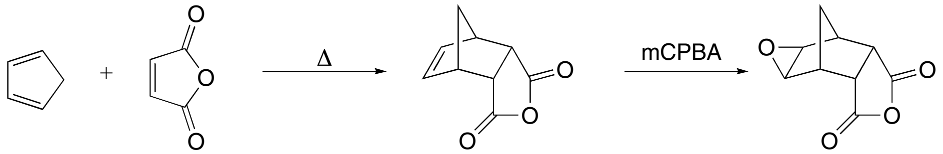
In each problem, the synthesis must begin with the preparation of cyclopentadiene from dicyclopentadiene.



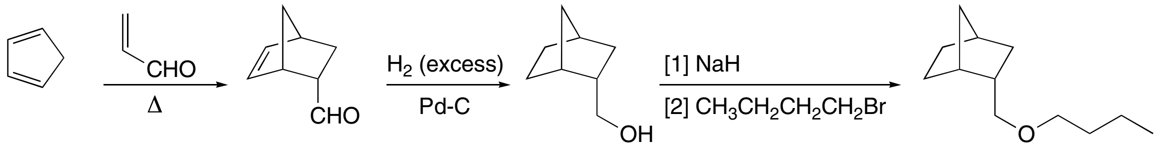
a.



b.

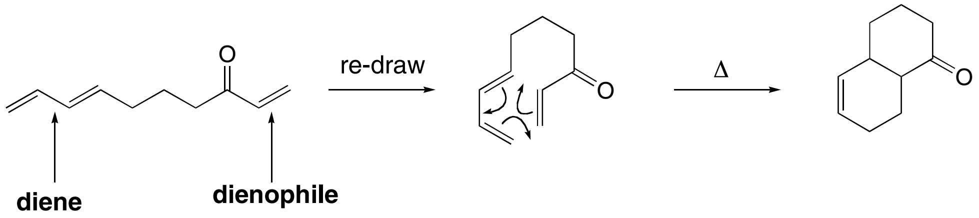


c.

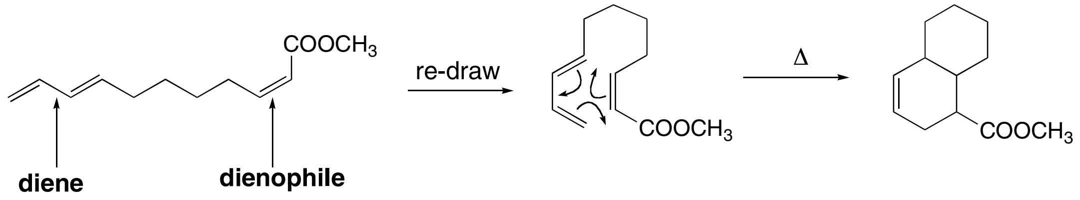


16.59

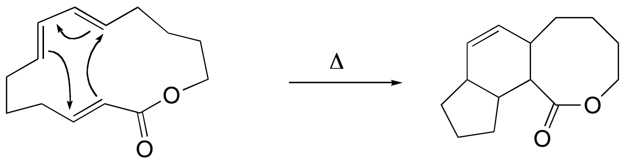
a.



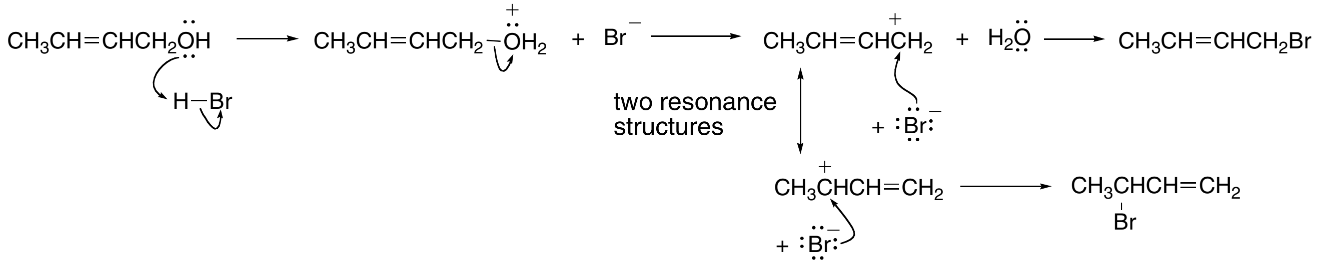
b.



16.60 A transannular Diels–Alder reaction forms a tricyclic product from a monocyclic starting material.



16.61

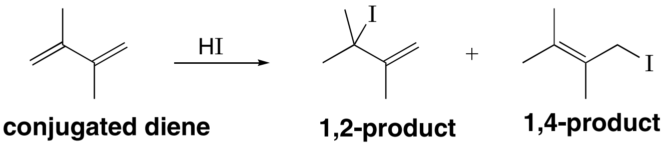


16.62

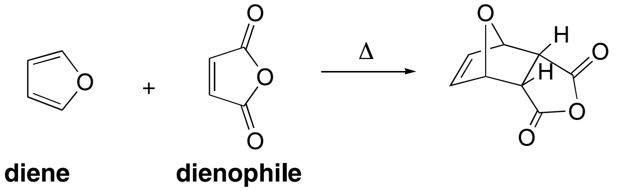
a. $(CH_3)_2C{=}CHCH_2CH_2CH{=}CH_2 \xrightarrow{HCl} (CH_3)_2C(Cl)CH_2CH_2CH_2CH{=}CH_2 + (CH_3)_2C{=}CHCH_2CH_2CHClCH_3$

isolated diene **major product** **minor product**

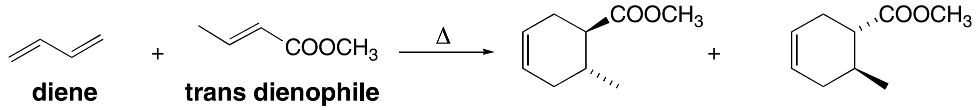
b.



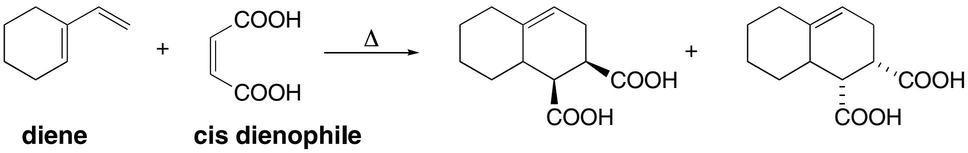
c.



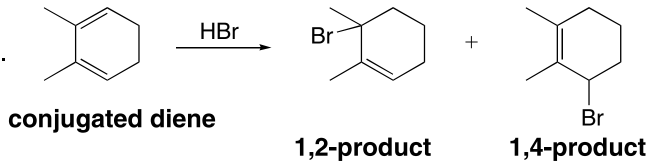
d.



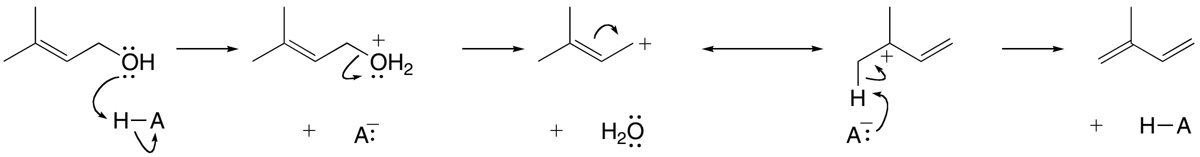
e.



f.

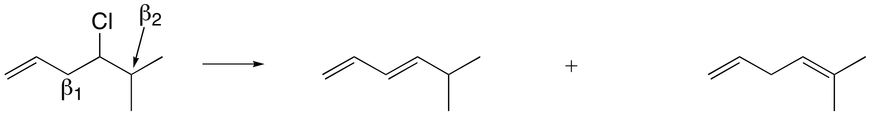


16.63 The mechanism is E1, with formation of a resonance-stabilized carbocation.



16.64

a.

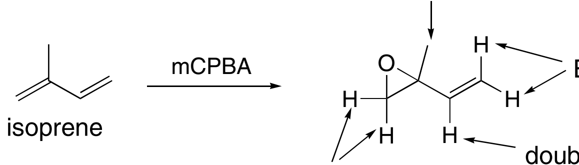


loss of H (from β_1 C) + Cl
conjugated
more stable
major product

loss of H (from β_2 C) + Cl
more substituted

b. Dehydrohalogentaion generally forms the more stable product. In this reaction, loss of H from the β_1 carbon forms a more stable conjugated diene, so this product is preferred even though it does not contain the more substituted C=C.

16.65



isoprene

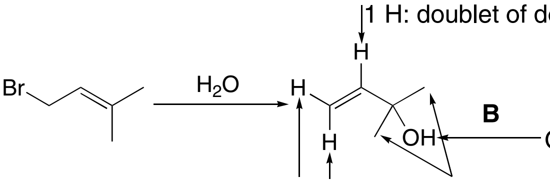
singlet at 1.42 ppm

Each H is a doublet of doublets in the 5.2–5.4 ppm region.

doublet of doublets at 5.5–5.7 ppm

two doublets at 2.7–2.9 ppm

16.66



1 H: doublet of doublets at 6.0 ppm

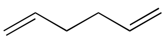
OH peak at 1.5 ppm

6 H: singlet at 1.3 ppm

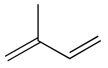
Each H is a doublet
of doublets in the
4.9–5.2 ppm region.

The IR shows an OH absorption at 3200–3600 cm^{-1}.

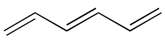
16.67



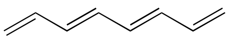
isolated diene
shortest wavelength
1



2 conjugated bonds
intermediate
wavelength
2



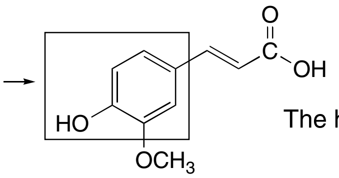
3 conjugated bonds
intermediate
wavelength
3



4 conjugated bonds
longest wavelength
4

16.68

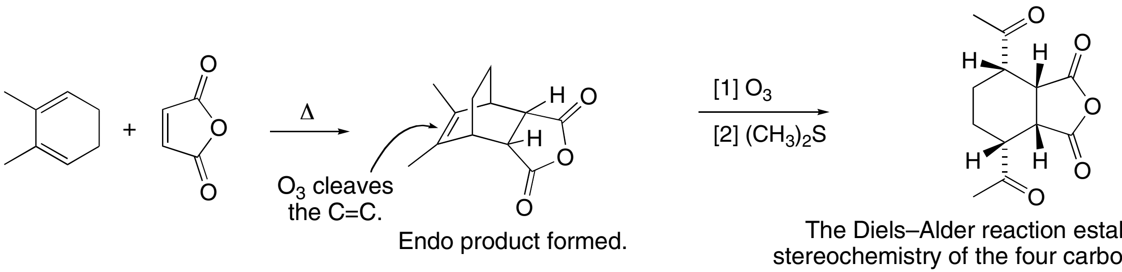
The phenol makes ferulic acid an antioxidant. Loss of H forms a highly stabilized phenoxy radical that inhibits radical formation during oxidation.



ferulic acid

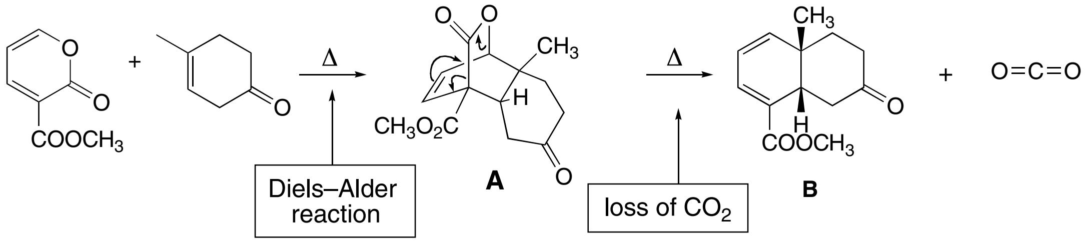
The highly conjugated π system makes it a sunscreen.

16.69

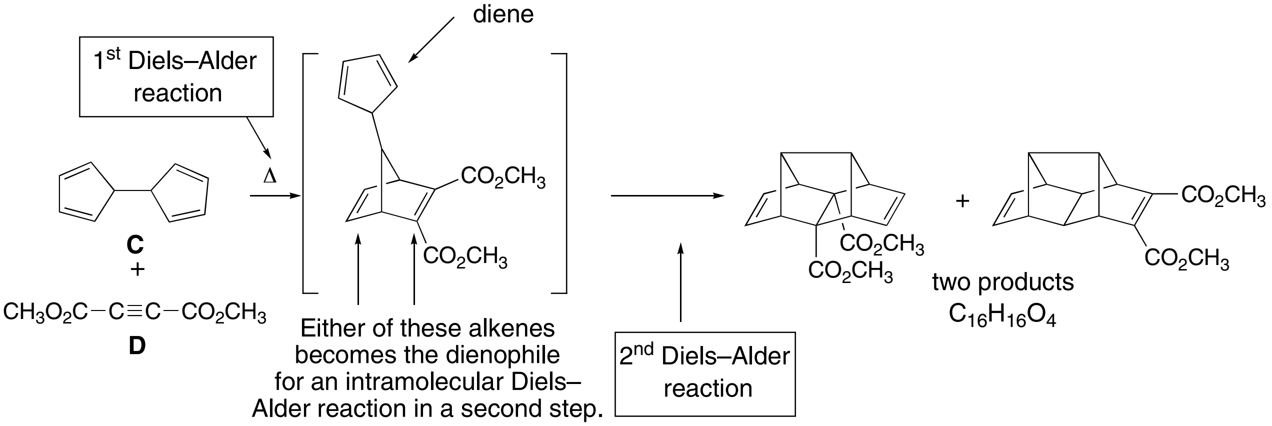


The Diels–Alder reaction establishes the stereochemistry of the four carbons on the six-membered ring. All four carbon atoms bonded to the six-membered ring are on the same side.

16.70



16.71



16.72 Retro Diels–Alder reaction forms a conjugated diene. Intramolecular Diels–Alder reaction then forms **N**.