

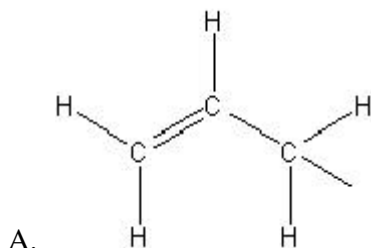
Chapter 10

Conjugation in Alkadienes and Allylic Systems

Chapter 10 suggested problems:

Class Notes

I. The allyl group



B. The allyl group is both a common name and an accepted IUPAC name

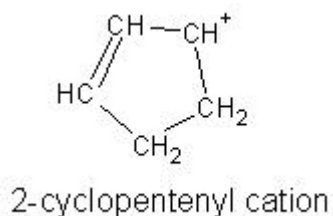
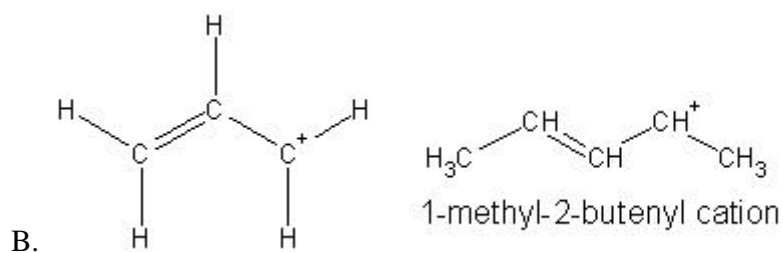
1. Allyl alcohol
2. Allyl chloride
3. Allyl bromide

C. "Allylic" refers to the C=C-C unit

1. The sp^3 hybridized carbon is the allylic carbon; substituents bonded to it are referred to as allylic substituents
2. The sp^2 hybridized carbons are the vinylic carbons; substituents bonded to them are referred to as vinylic substituents

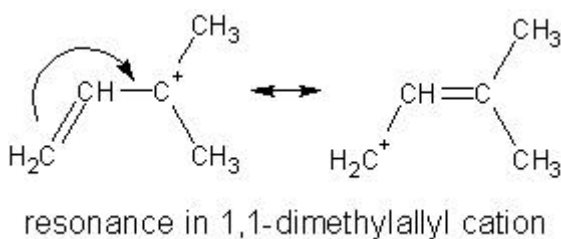
II. Allylic carbocations

A. Allylic carbocations have the positive charge on the allylic carbon

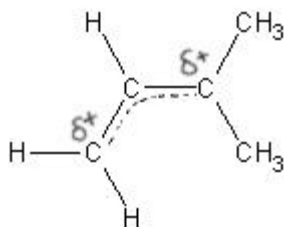


C. Vinyl groups are effective electron-releasing groups

D. The electron delocalization represented by the resonance structures results in stabilization of the carbocation



1.

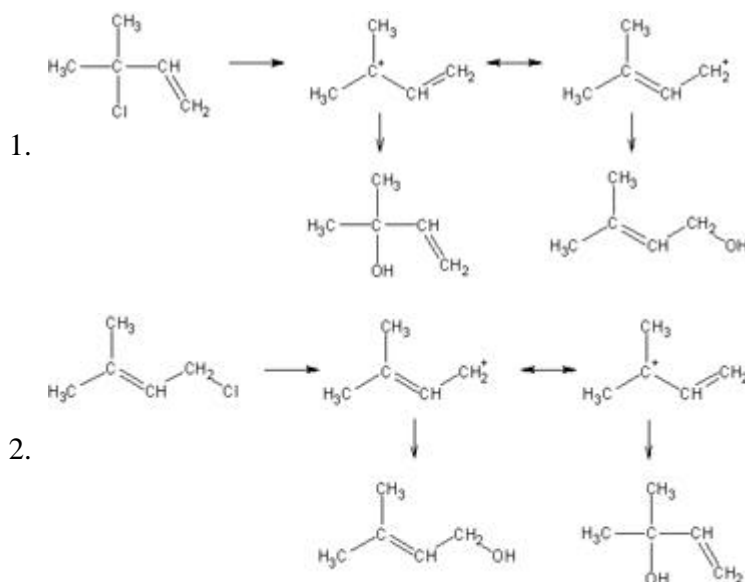


2. Each of the two carbons has a partial charge of 1/2

3. Carey: 369: "it must be emphasized that we are not dealing with an equilibrium between two isomeric carbocations. *There is only one carbocation.* Its structure is not adequately represented by either of the individual resonance forms but is a hybrid having qualities of both of them."

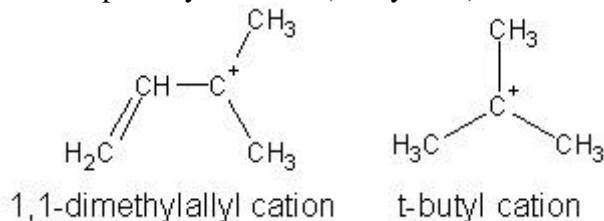
E. Note: both of the alkene carbons and the carbocation carbon are sp^2 hybridized. The empty p orbital on the carbocation can overlap with the occupied p orbitals that make up the pi bond, resulting in an extended pi bond system

F. Examples: reactions of 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene



G. Those reactions which generate two products as a consequence of double-bond migration are said to have resulted from *allylic rearrangement* or *allylic shift*

H. "A substantial body of evidence indicates that allylic carbocations are more stable than simple alkyl cations" (Carey: 366)



- This statement and the depictions of 1,1-dimethylallyl cation and t-butyl cation seem to suggest that the order of carbocation stability is: allyl > 3° > 2° > 1° > methyl
- In Morrison and Boyd (p. 269) it states specifically that the order of carbocation stability is: 3° > allyl, 2° > 1° > methyl
- This is supported by hydride affinity data compiled by Aue et. al. and Houle et. al. as reported in Carey and Sundberg (*Advanced Organic Chemistry, Part A*: p. 253)
 - Hydride affinity - gas-phase studies of the amount of energy required to remove a hydrogen anion from an alkene, resulting in the formation of a carbocation

b.

hydride affinity (kcal/mol)			
CH_3^+	314	$\text{CH}_2=\text{CHCH}_2^+$	256
CH_3CH_2^+	274	$\text{CH}_2=\text{CHCH}^+\text{CH}_3$	237
$(\text{CH}_3)_2\text{CH}^+$	247	$\text{CH}_2=\text{CHC}^+(\text{CH}_3)_2$	225
$(\text{CH}_3)_3\text{C}^+$	230	$\text{CH}_3\text{CH}=\text{CHCH}^+\text{CH}_3$	225

4. Carey sidebar (p. 367): "A rule of thumb is that a C=C substituent stabilizes a carbocation about as well as two alkyl groups. Although allyl cation is a primary carbocation, it is about as stable as a typical secondary carbocation such as isopropyl cation."

III. Allylic free radicals

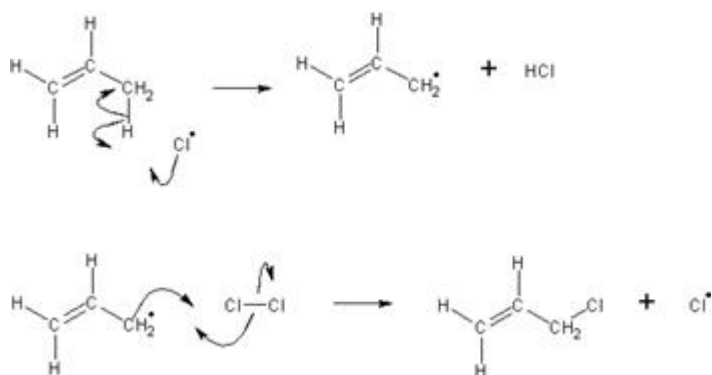
- A. The allyl radical is also stabilized by electron delocalization: the odd electron is delocalized over the three carbons resulting in a 3 electron - three atom system
- B. This enhanced stability means that it is easier to form radicals from allylic systems than from the corresponding alkane

IV. Allylic hydrogenation

A. General

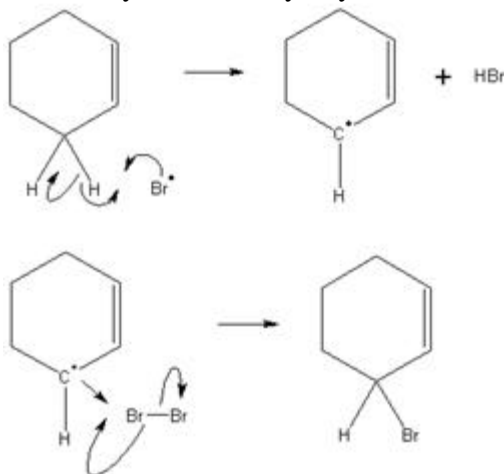
1. Halogens usually add to double bonds at room temperature and lower
2. Substitution becomes competitive at high temperature, especially when [halogen] is low
3. The substitution is a free-radical mechanism
4. Substitution is highly selective for the allylic position
5. Limitations of free radical allylic halogenation
 - a. All the hydrogens in the starting alkene must be equivalent
 - b. both resonance forms of the allylic radical must be equivalent
 - c. If these criteria are not met two or more constitutional isomers (allylic halides) will result

B. Chlorination

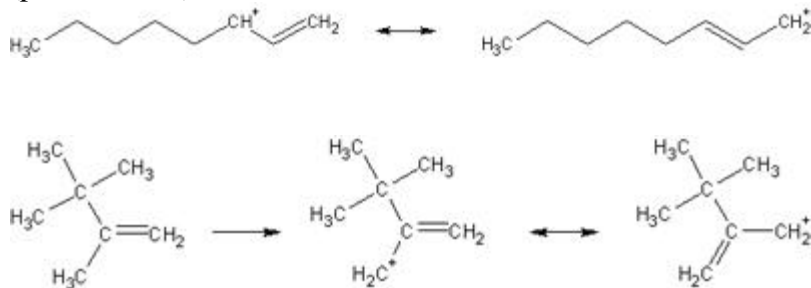


C. Bromination

1. Allylic brominations are generally carried out with special brominating agents: N-bromosuccinimide is commonly used in the presence of heat &/or light
2. Example (problem 10.4): Assume that NBS serves as a source of bromine: write equations for the propagation steps in the formation of 3-bromocyclohexene by allylic bromination of cyclohexene



D. Halogenation of nonequivalent compounds: 2,3,3-trimethyl-1-butene and 1-octene (problem 10.5)



V. Classes of dienes

- A. Isolated dienes: carbon-carbon double bonds separated by two or more sp^3 hybridized carbon atoms

- B. Conjugated dienes: carbon-carbon double bonds separated by a single sp^3 hybridized carbon atom
- C. Cumulated dienes: carbon-carbon double bonds not separated by any sp^3 hybridized carbon atoms, i.e. adjacent to each other, one carbon atom is common to two carbon-carbon double bonds

D. Examples



1. beta-springene

VI. Relative stabilities of dienes

A. Stabilities established by measuring heats of hydration

1. Monosubstituted alkenes: about 30 kcal/mol
2. Disubstituted alkenes: about 28 kcal/mol
3. Trisubstituted alkenes: about 27 kcal/mol
4. The heats of hydration of isolated alkenes are roughly twice the value of monosubstituted alkenes

diene	dH (kcal/mol)
1,4-pentadiene	60.8
1,5-hexadiene	60.5
1,3-butadiene	57.1
1,3-pentadiene	54.1
2-methyl-1,3-butadiene	53.4
2,3-dimethyl-1,3-butadiene	53.9
1,2-propadiene	71.3

- B. Order of stability: conjugated > isolated > cumulated
- C. Conjugated dienes differ from simple alkenes in three ways
1. They are more stable
 2. They undergo 1,4 addition
 3. They are more reactive when involved in free radical reactions

VII. Bonding in conjugated dienes

A. Two factors account for the enhanced stability of conjugated dienes

1. Strengthening of sigma bonds
2. Extended delocalization

B. Compare 1,3-pentadiene and 1,4-pentadiene

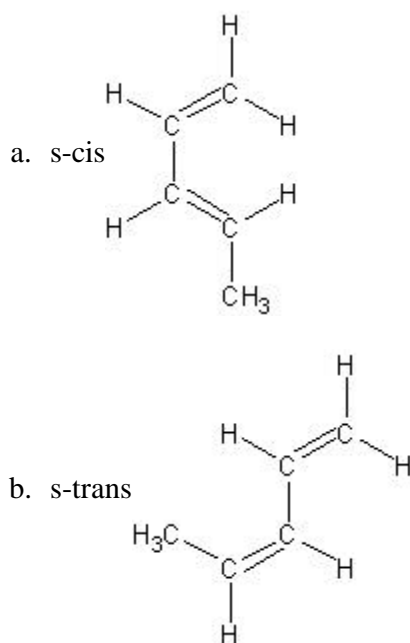
1. The single bond between C2 and C3 in the 1,3-diene is shorter than in the 1,4-diene
2. Overlap between the pi systems in the 1,3-diene result in extended electron delocalization that cannot occur in the 1,4-diene
3. Resonance in the 1,3-diene: the dotted line represents a formal bond, which means that an electron on C1 and an electron on C4 have opposite spins and are paired



- a. This adds a certain amount of double bond character to the C2-C3 sigma bond and a certain amount of single bond character to both double bonds (intermediate bond strengths and bond lengths)
 - b. The formation of bonds releases energy and stabilizes a system
 - c. All other things being equal, the more bonds, the more stable a structure
 - d. Counting the number of bonds in resonance structures can provide insight into the relative stabilities of resonance structures and, as a consequence, the relative importance of contributing structures
 - e. Structure II contributes less than structure I
4. The net effect: the 1,3-diene is about 28 kJ/mol (6.7 kcal/mol) more stable than the 1,4 diene

C. Conformations of conjugated dienes

1. Pi overlap is optimal when the four atoms are coplanar
2. Remember that rotation around the C2-C3 sigma bond can and does occur
3. Two conformations permit planar orientation of the atoms



VIII. Bonding in allenes

- A. The middle carbon is sp hybridized while the two outer carbons are sp^2 hybridized
- B. This results in slightly shortened $C=C$ bond lengths (131 pm vs. 134 pm in ethene)
- C. The central carbon forms two pi bonds that are perpendicular to each other w.r.t. the outer carbons

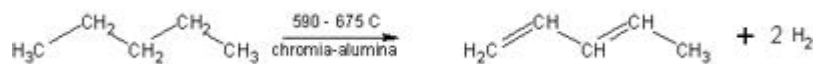
IX. Preparation of dienes

A. Industrial significance of 1,3-butadiene

1. Annual production varied from 1100 - 1800 thousand tons (3.6 billion pounds) in the U.S. between 1970 - 1995
2. Production increased by about 3.3% between 1990 - 1995
3. Ranked #34 on the 1995 U.S. production list (1995)
 - a. 1. Sulfuric acid: 47,681 thousand tons
 - b. 2. Nitrogen: 34,018 thousand tons
 - c. 3. Oxygen: 27,111 thousand tons
 - d. 4. Ethylene: 21,462 thousand tons
 - e. 5. Lime: 20,617 thousand tons
 - f. 7. Propylene: 13,563 thousand tons

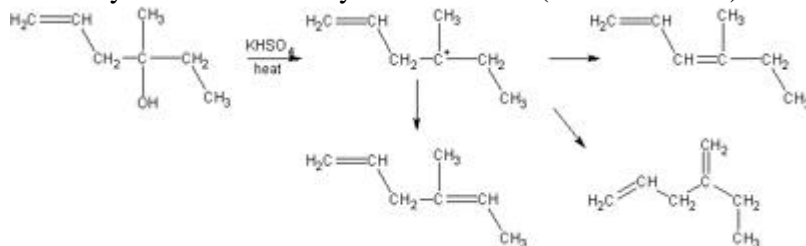
B. Industrial preparation

1. Thermal dehydrogenation of butane in the presence of either (alumina-chromia)

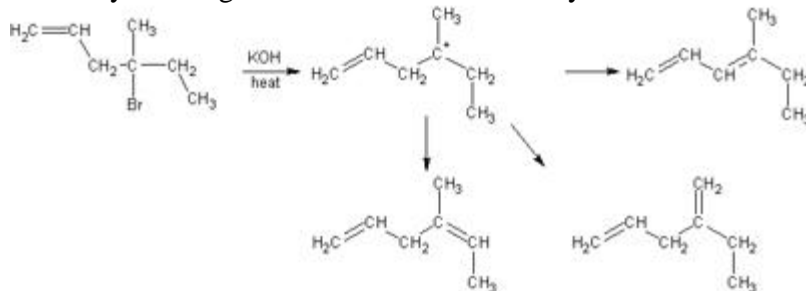


- C. Laboratory preparations - achieved by elimination reactions of unsaturated alcohols or alkyl halides

1. The dehydration of 3-methyl-5-hexen-3-ol (E1 elimination)



2. The dehydrohalogenation of 4-bromo-4-methyl-1-hexene

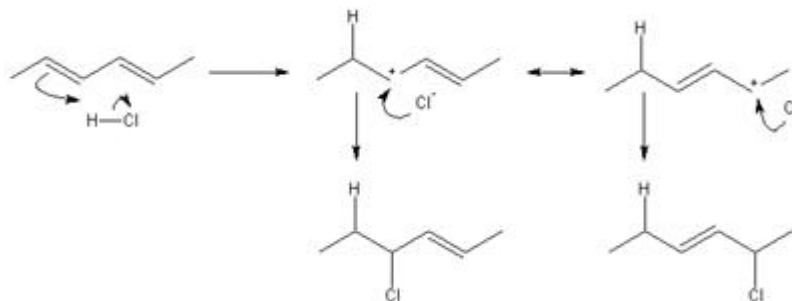


3. Dienes with isolated double bonds can be formed when the structure of the starting material will not permit conjugated diene formation

X. Addition of hydrogen halides to conjugated dienes

- A. In addition reactions with conjugated dienes, both 1,2- addition and 1,4-addition may be observed

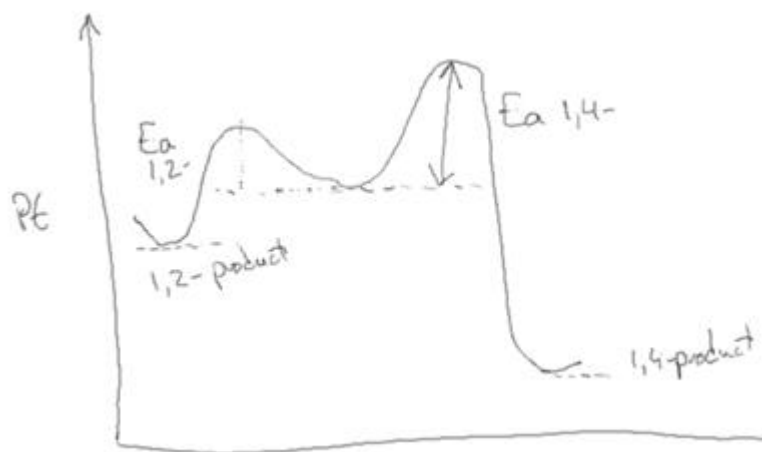
1. Example: the reaction of HCl with 2,4-hexadiene forms 4-chloro-2-hexene and 2-chloro-3-hexene



2. The hydrogen adds initially to C-2 rather than C-3 because the C-3 carbocation is an allylic carbocation and hence more stable than the secondary carbocation that would form upon addition of hydrogen to C-3

B. Rate vs. equilibrium

1. "There are many cases in which a compound under a given set of reaction conditions may undergo competing reactions to give different products" (March: 187)
2. An example is the hydrobromination of 1,3-butadiene
3. Addition of HBr to 1,3-butadiene yields both the 1,2- and 1,4- addition products, but the relative amounts of the products depend on temperature
 - a. At -80°C : 80% 3-bromo-1-butene, 20% 1-bromo-2-butene
 - b. At $+40^{\circ}\text{C}$: 20% 3-bromo-1-butene, 80% 1-bromo-2-butene
 - c. Each isomer is stable at low temperatures but prolonged heating of either the 1,2- or the 1,4- compound will result in the same mixture
 - d. An equilibrium exists between the two compounds
 - e. Interconversion between the two isomers takes place, and any change in temperature will disturb the equilibrium until it is restored through interconversion
4. The amounts of 1,2- and 1,4-products formed at low temperature is directly linked to the rates of their formation (more 1,2- product is formed at low temperature because it is formed faster)
 - a. When the major product in a reaction is the one that is formed the fastest, the reaction is governed by kinetic control
5. The E_a for formation of the 1,2- product is lower than that for the 1,4- product, but the 1,4 product is more stable than the 1,2- product (i.e., lower in energy)



6. The 1,2- product is formed rapidly, but at elevated temperatures it also ionizes rapidly
7. The 1,4- product is formed slowly, and at any temperature it ionizes even

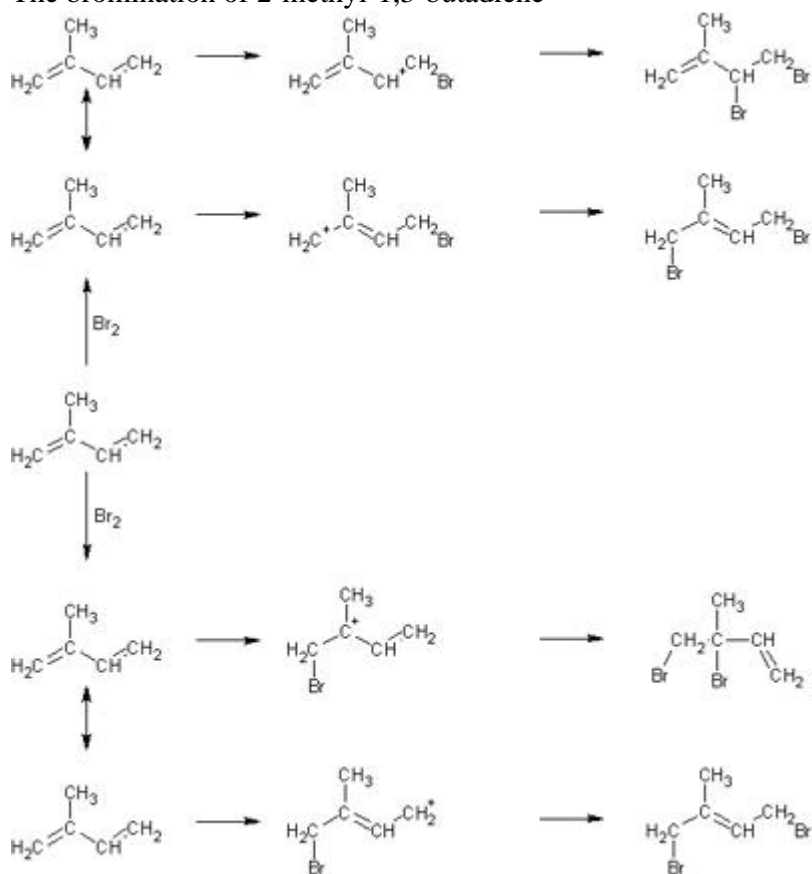
more slowly (because it is low in energy relative to the E_a that must be overcome to reform the resonance form of the carbocation)

- a. When the major product in a reaction is the one that is the most stable and does not reflect the relative rates of reaction, the reaction is governed by thermodynamic control

XI. Halogen addition to dienes

- A. The reaction of 1,3-butadiene with either chlorine or bromine (molecular) results in formation of the 1,2- and 1,4- addition products

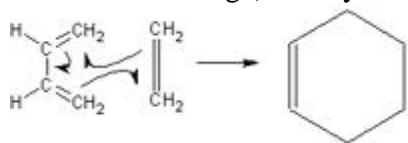
- B. The bromination of 2-methyl-1,3-butadiene



- C. Those products resulting from conjugate (1,4-) addition are almost exclusively in the E configuration

XII. The Diels-Alder reaction (Carey: 382ff, March: 745ff)

- A. A double bond adds 1,4 to a conjugated diene resulting in the formation of a six-membered ring (4 + 2 cycloaddition)



- B. The Diels-Alder transition state is cyclic with six carbon atoms, six pi electrons, and

the diene must be in the s-cis configuration during the transition state

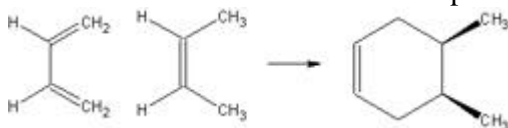
C. An outcome of the reaction is that the product always has one more ring than was present in the reactants

1. Two new carbon-carbon bonds are formed in a single reaction
2. Reagents such as acids or bases which might affect the outcome of the reaction are not required

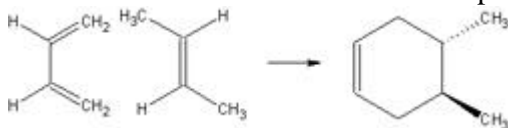
D. The double bond compound is called the dienophile

E. The reaction is stereospecific (Carey: 284ff)

1. Substituents that are cis in the dienophile remain cis in the product



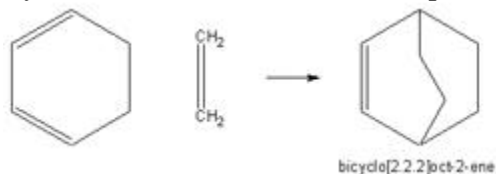
2. Substituents that are trans in the dienophile remain trans in the product



F. Any alkene can serve as a dienophile

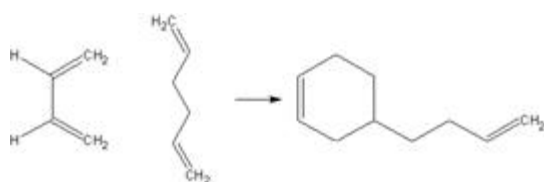
1. Simple alkenes are more reactive when electron-withdrawing groups are directly attached to one (or both) of the bonding carbons
2. Electron-withdrawing groups tend to weaken (destabilize) the double bond, which makes it more reactive in Diels-Alder reactions
 - a. Carey: 464 - Table 12.2, listed as deactivating substituents
 - b. Halogens, halogen-substituted alkyl groups, carbonyl compounds, nitriles (cyanide ion), nitro groups
 - c. Due to electronegativity effects or to resonance structures with a formal charge on an electronegative atom

G. Cycloalkenes can be used as dienophiles

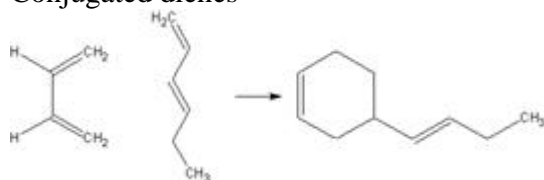


H. Dienes can themselves serve as dienophiles

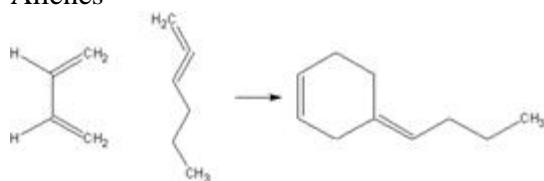
1. Isolated dienes



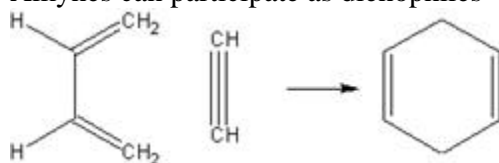
2. Conjugated dienes



3. Allenes



I. Alkynes can participate as dienophiles



XIII. The pi molecular orbitals of ethylene and 1,3-butadiene: [omit Sec. 10.13](#)

XIV. A pi molecular orbital analysis of the Diels-Alder reaction: [omit Sec. 10.14](#)

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