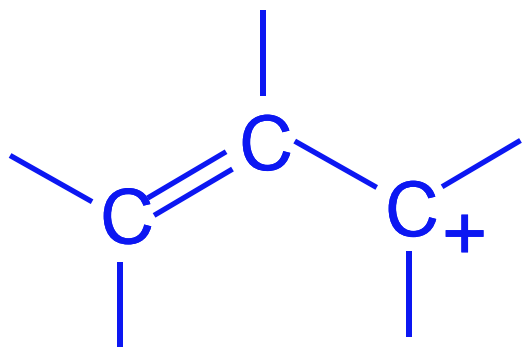


Chapter 10

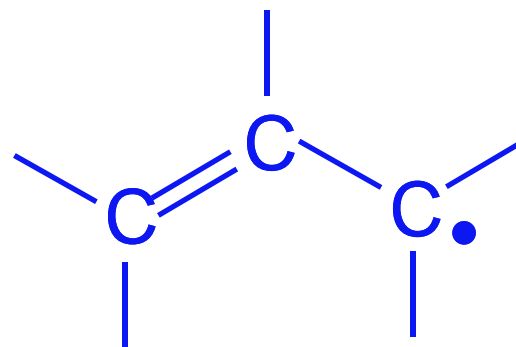
Conjugation in Alkadienes and Allylic Systems

Conjugare is a Latin verb meaning "to link or yoke together"

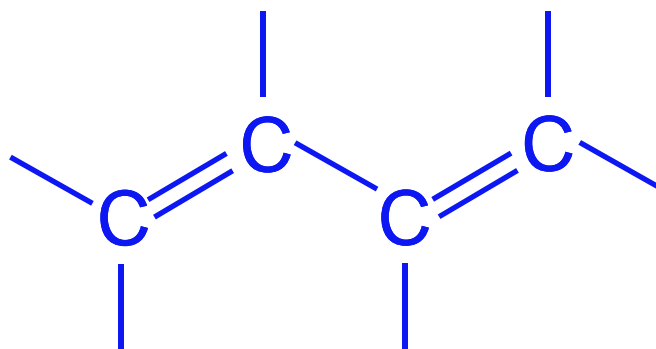
The Double Bond as a Substituent



Allylic carbocation

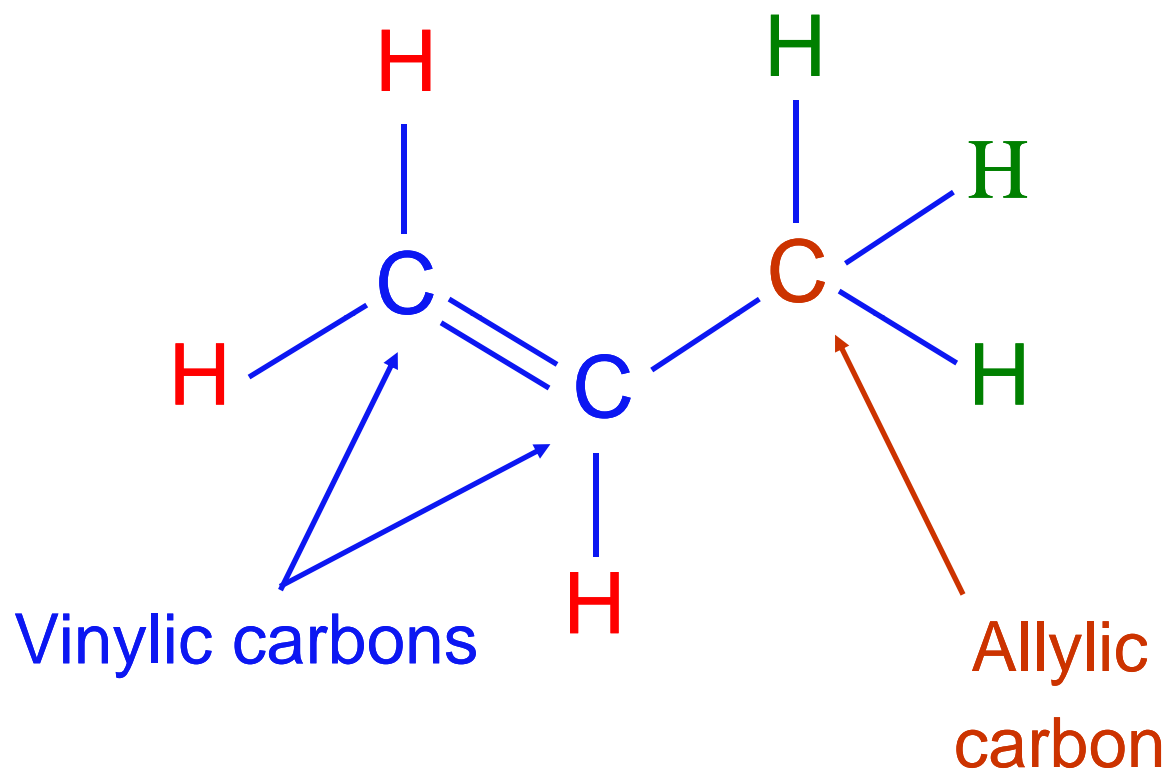


Allylic radical



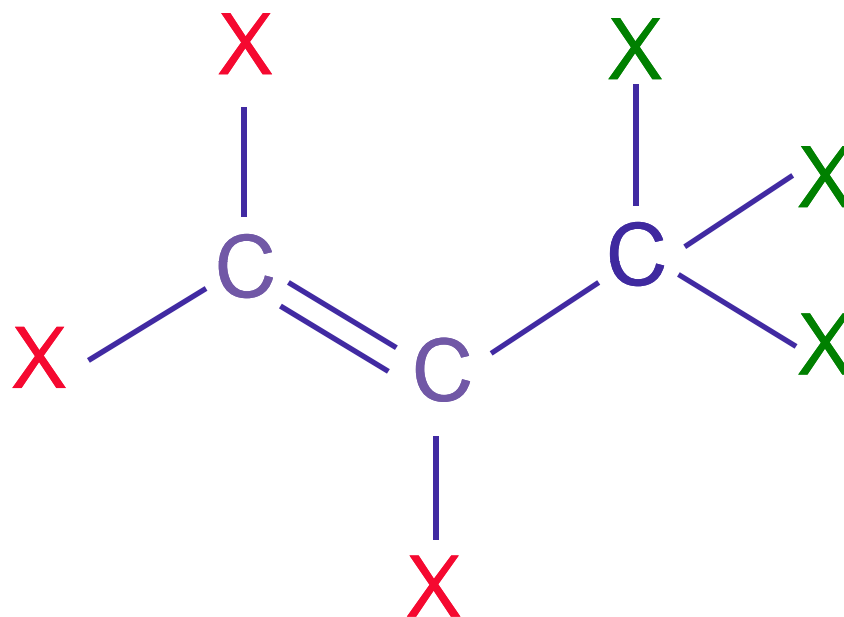
Conjugated diene

10.1. The Allyl Group



Vinylic hydrogens are attached to vinylic carbons.
Allylic hydrogens are attached to allylic carbons.

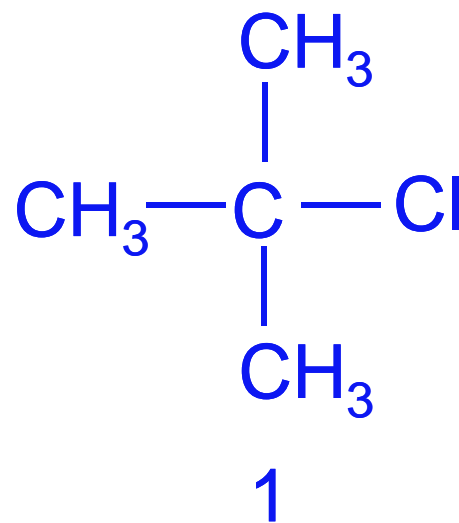
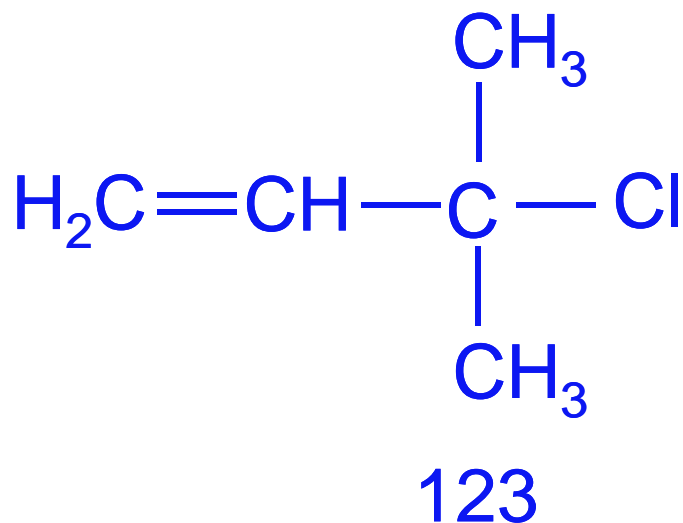
Vinylic versus Allylic



Vinylic substituents are attached to vinylic carbons
Allylic substituents are attached to allylic carbons

10.2. Allylic Carbocations

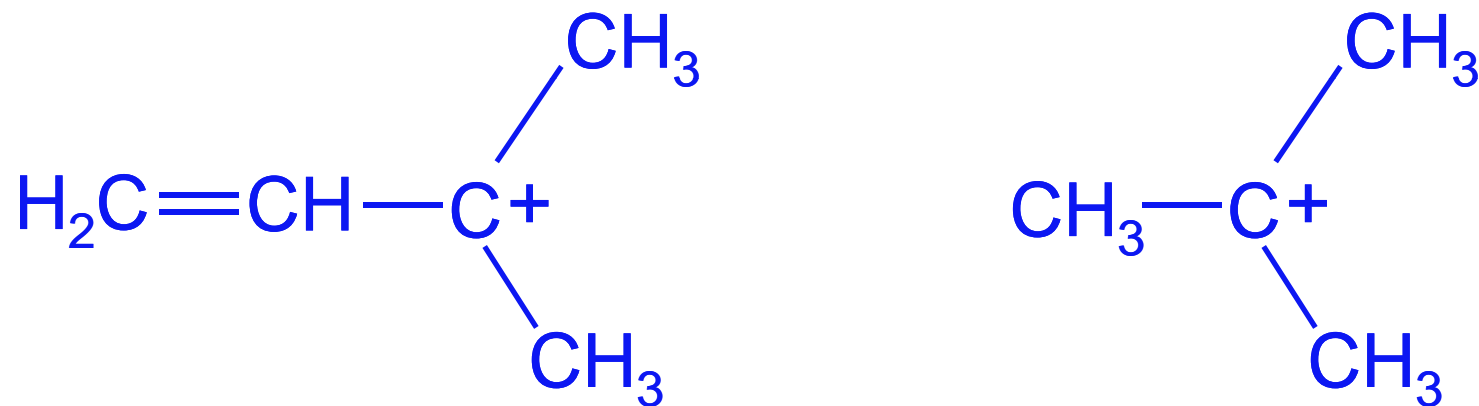
- A tertiary allylic halide undergoes solvolysis (S_N1) faster than a simple tertiary alkyl halide.



Relative rates: (ethanolysis, 45°C)

Allylic Carbocations

- Provides good evidence for the conclusion that allylic carbocations are more stable than other carbocations.

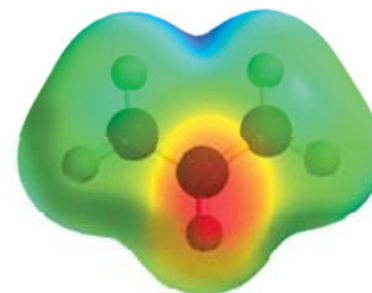
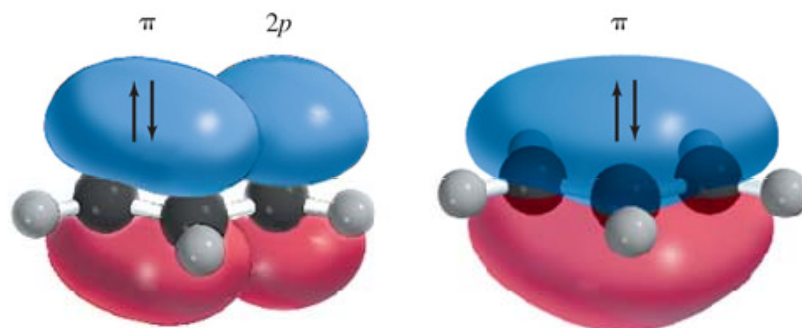
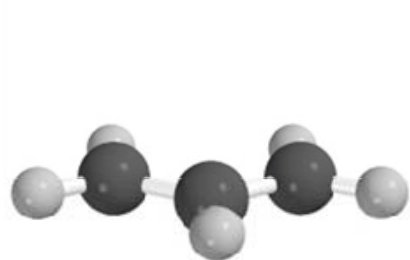
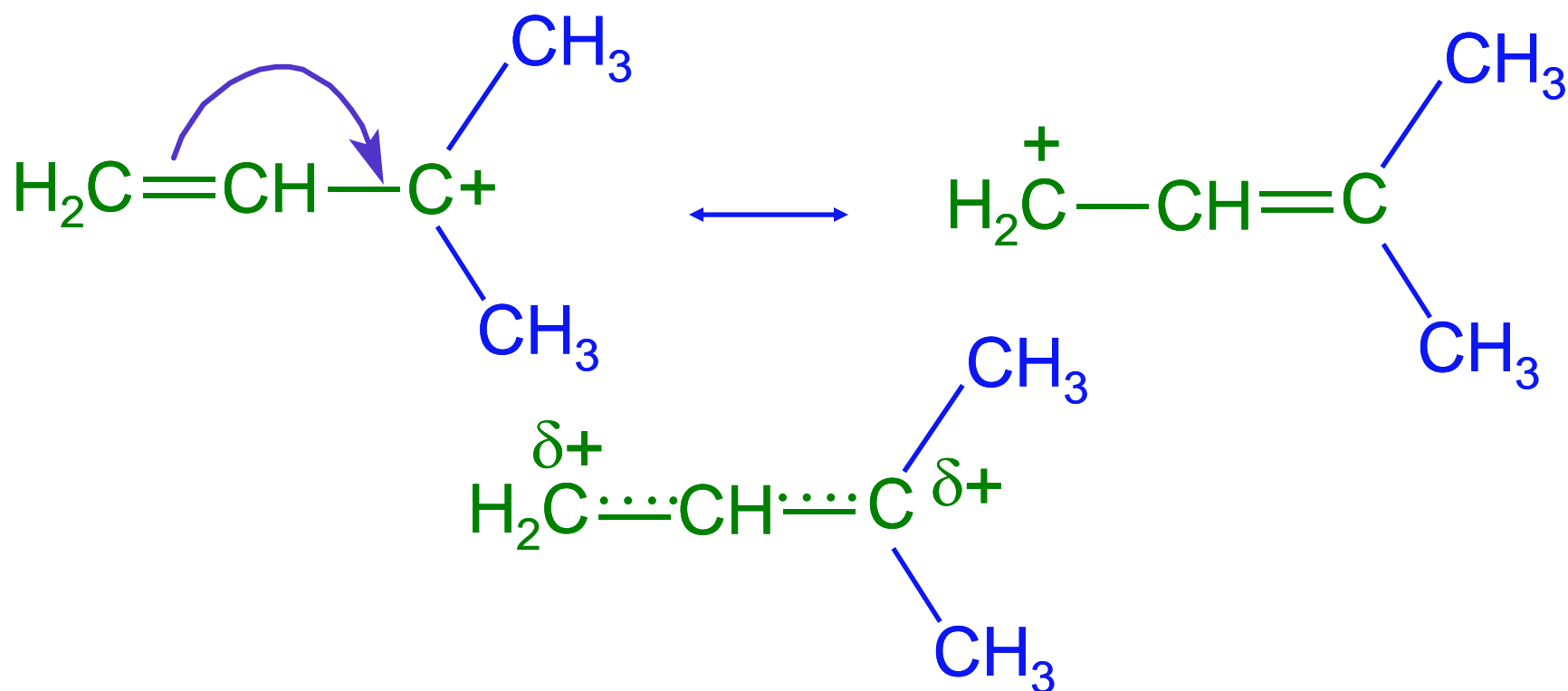


Formed faster!

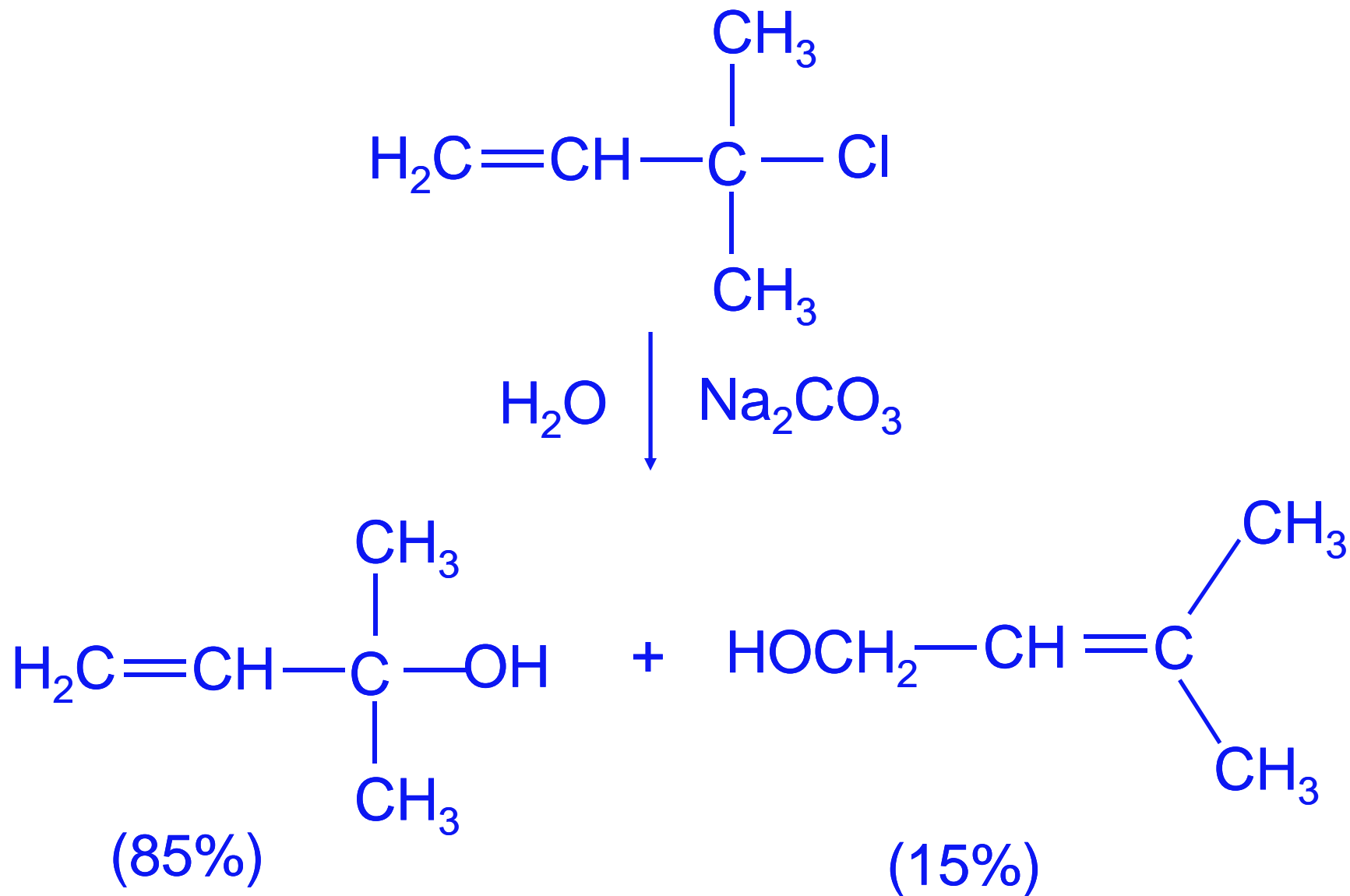
H₂C=CH— stabilizes C⁺ better than CH₃—

Stabilization of Allylic Carbocations

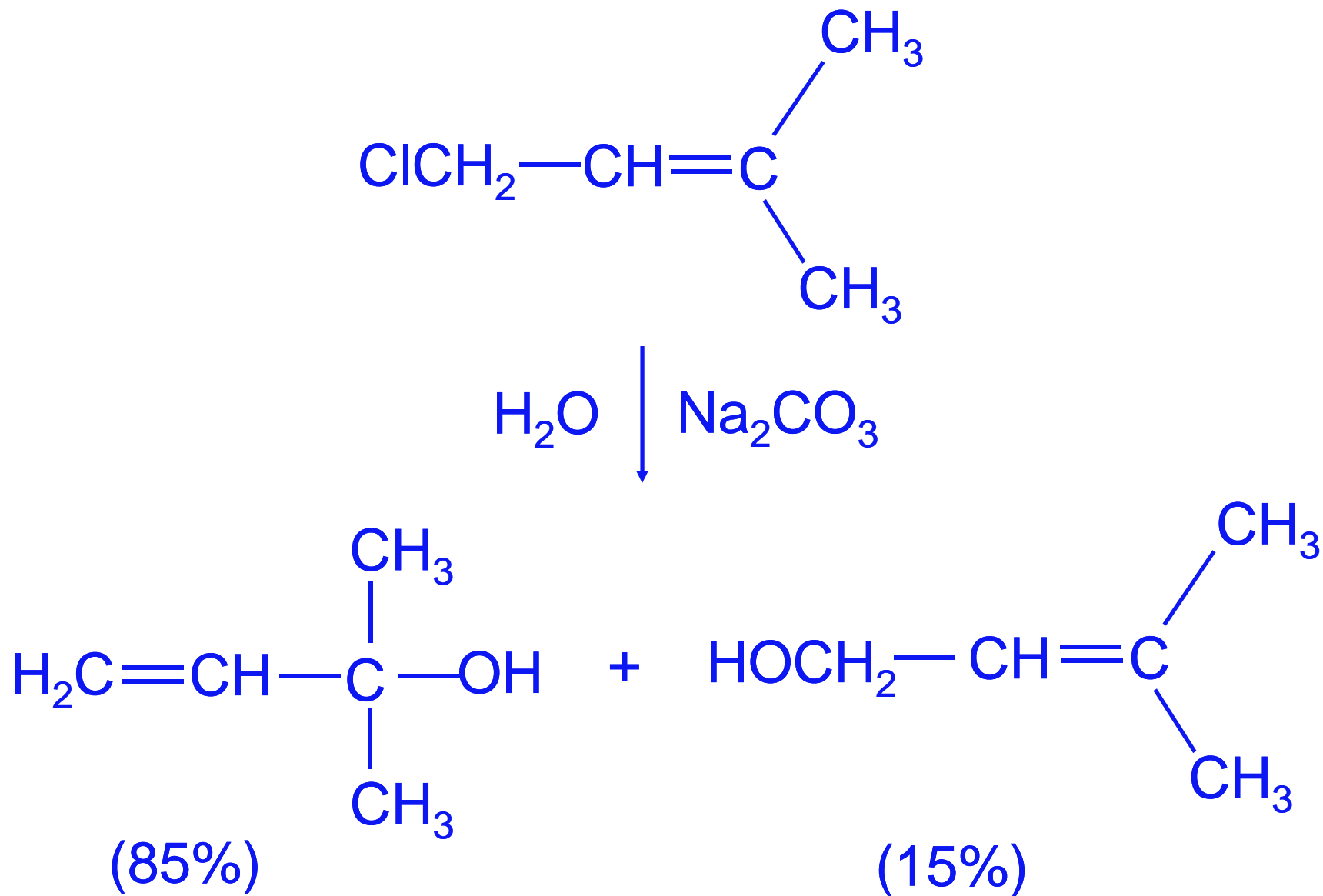
- Delocalization of electrons in the double bond stabilizes the carbocation.

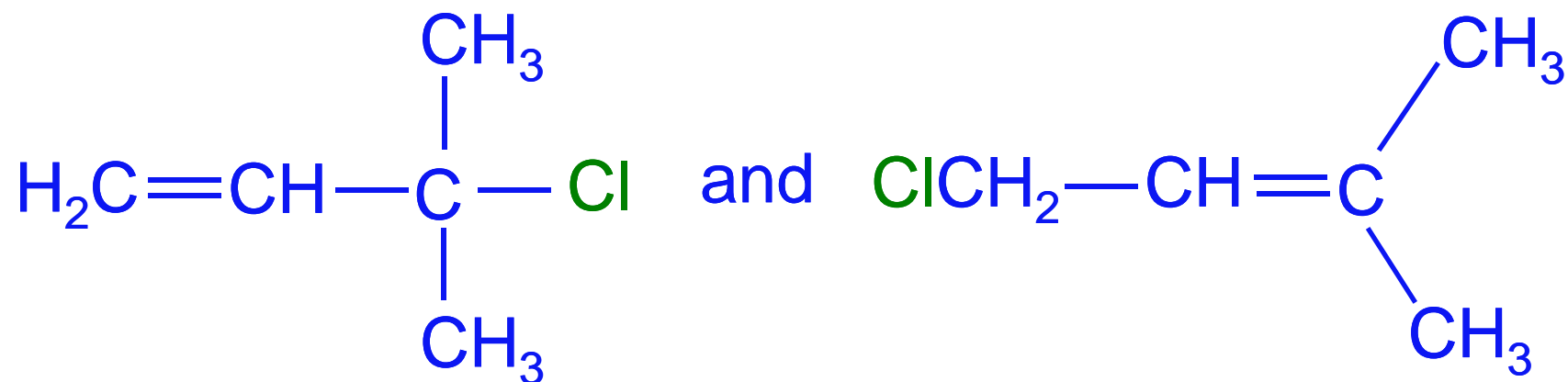


10.3. S_N1 Reactions of Allylic Halides (Hydrolysis)

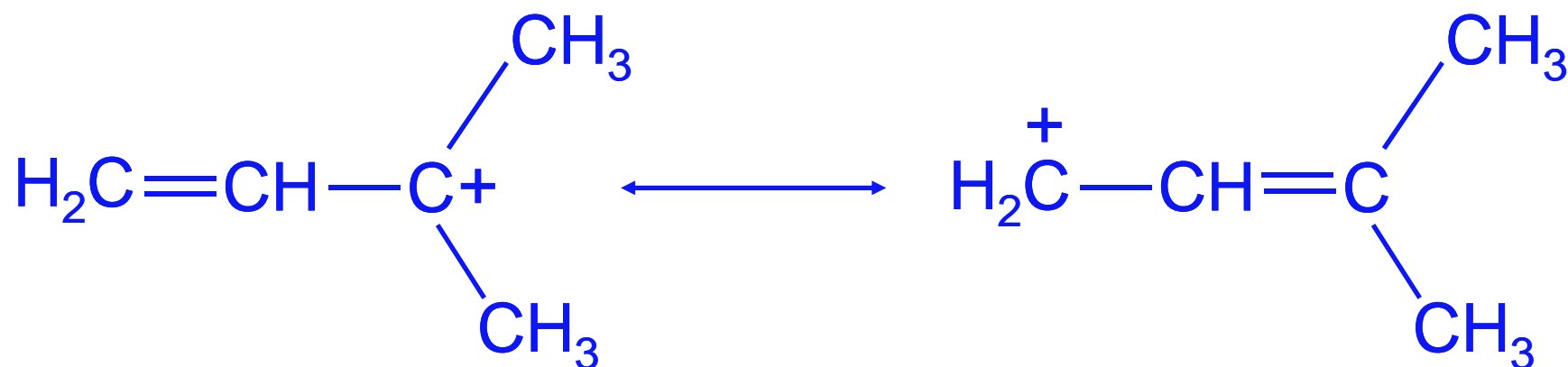


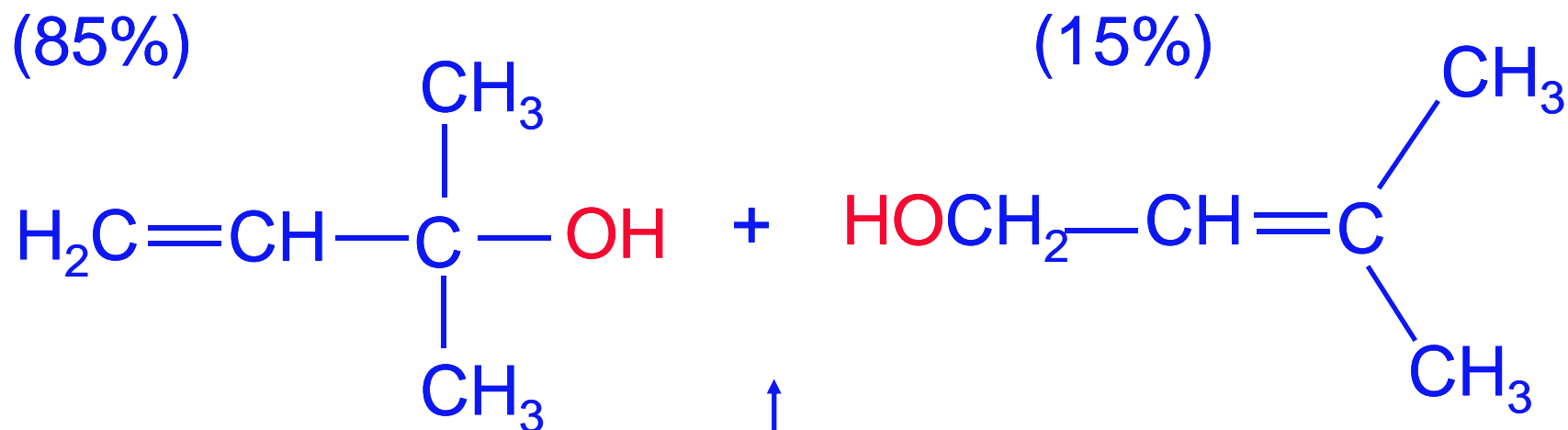
Corollary Experiment



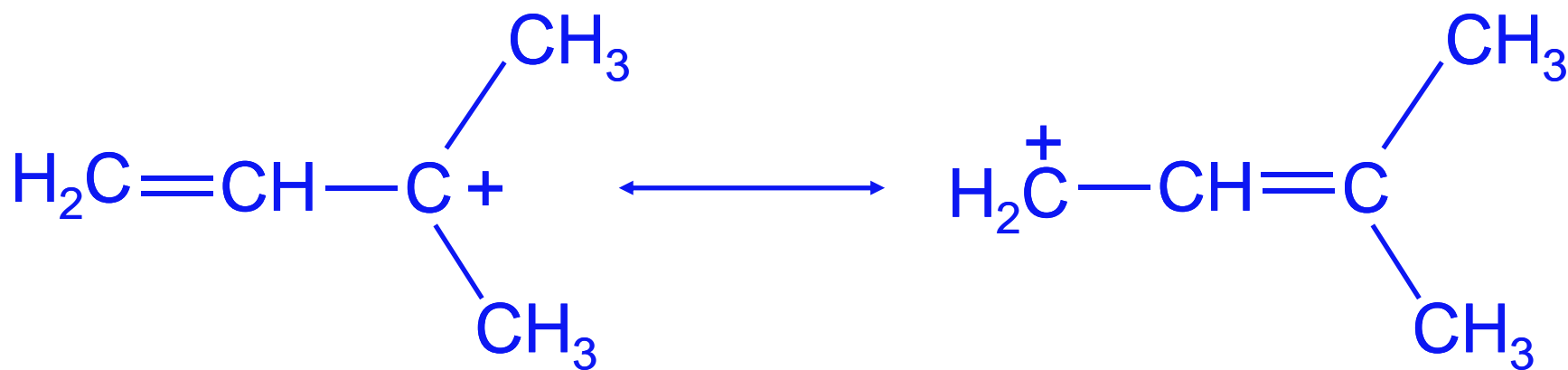


give the same products because they
form the same carbocation



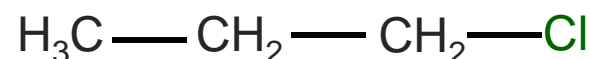


More positive charge on tertiary carbon;
therefore more tertiary alcohol in product



10.4. S_N2 Reactions of Allylic Halides

- Allylic halides also undergo S_N2 reactions.
- Faster than simple primary alkyl halides.



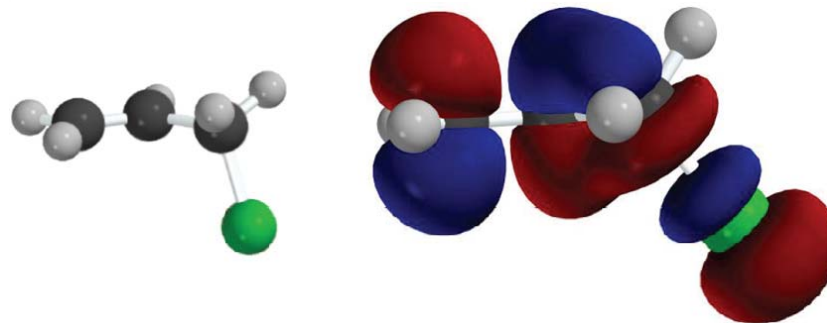
Relative rates:

80

1

(I⁻, acetone)

- Two factors:
 - Steric: trigonal carbon smaller than tetrahedral carbon.
 - Electronic: electron delocalization lowers LUMO energy which means lower activation energy.



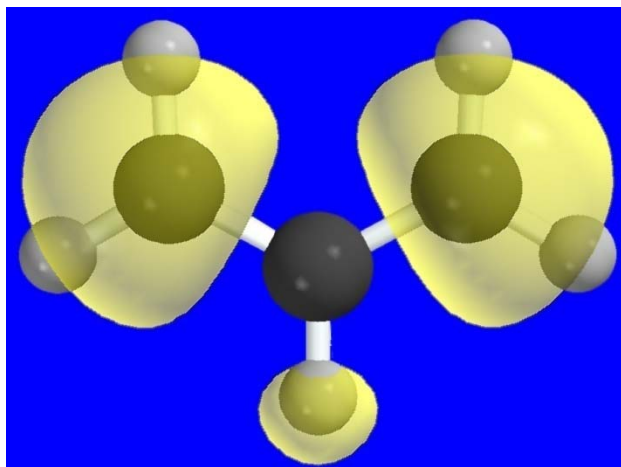
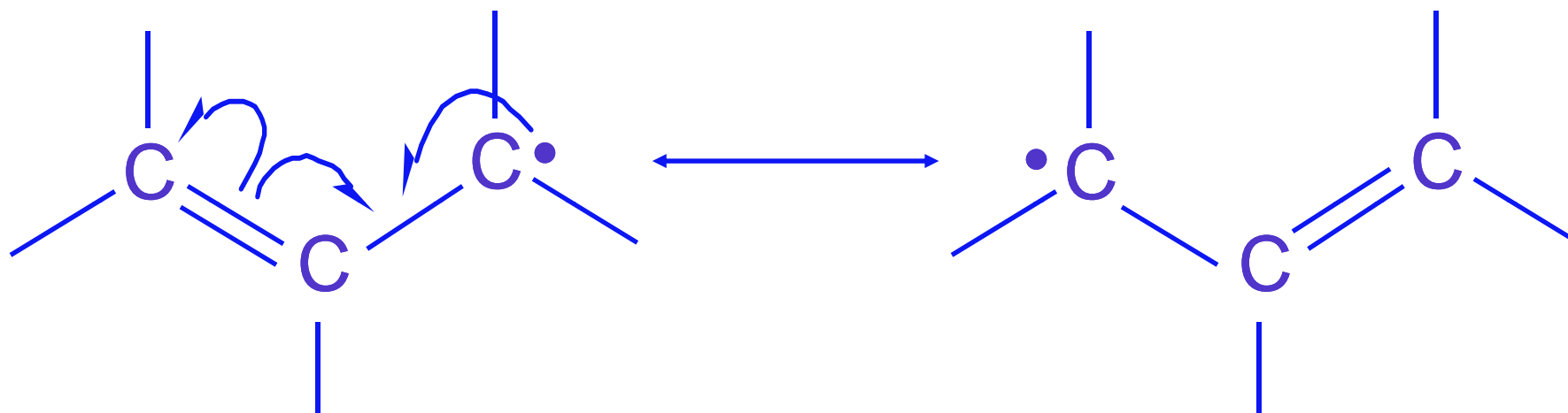
Allyl chloride

LUMO of allyl chloride

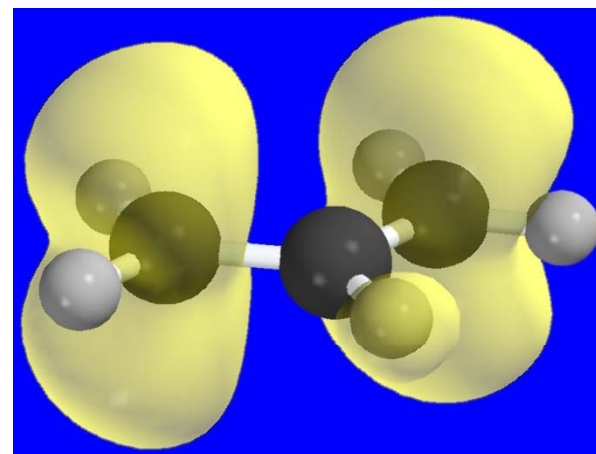
B. R. Kaafarani

10.5. Allylic Free Radicals

Allylic free radicals are stabilized by electron delocalization.



Spin
density in
allyl radical



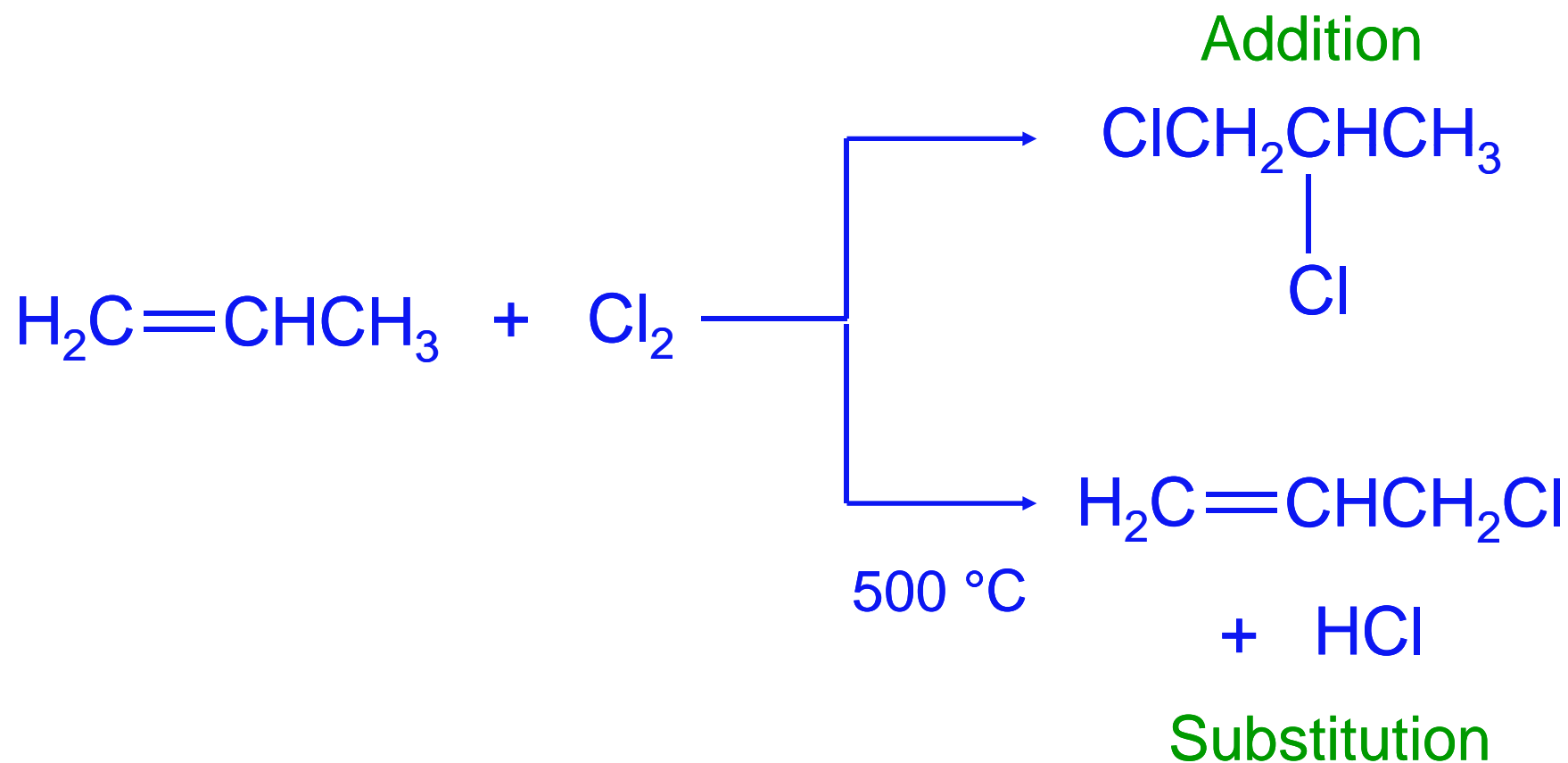
Free-radical stabilities are related to bond-dissociation energies



- C—H bond is weaker in propene because resulting radical (allyl) is more stable than radical (propyl) from propane.

10.6. Allylic Halogenation

Chlorination of Propene



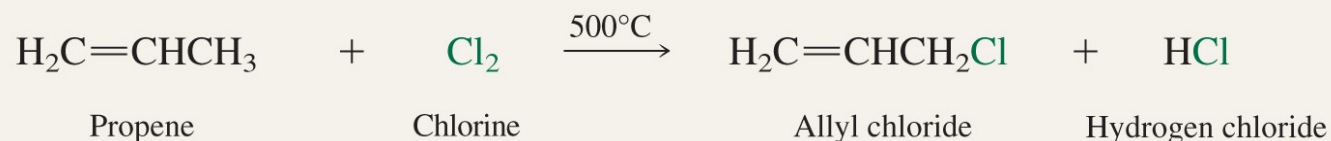
Allylic Halogenation

- Selective for replacement of allylic hydrogen.
- Free radical mechanism.
- Allylic radical is intermediate.

Mechanism 10.2

Allylic Chlorination of Propene

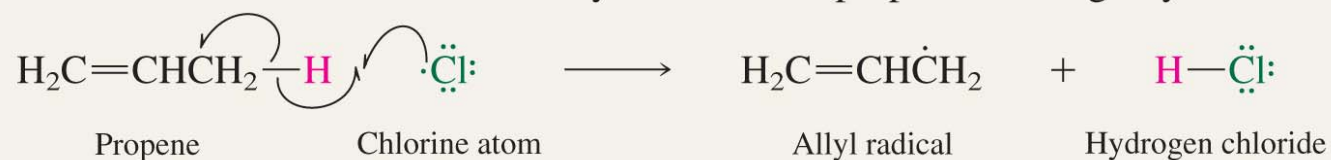
THE OVERALL REACTION:



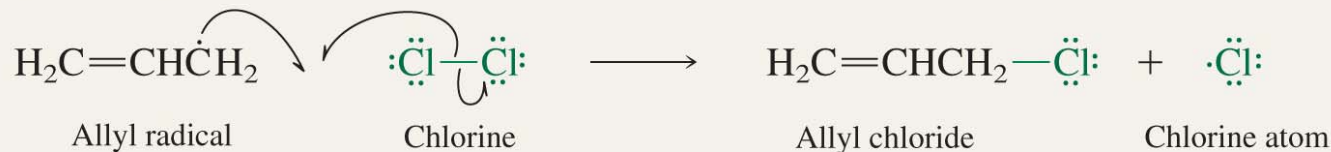
Initiation step: A chlorine molecule dissociates to two atoms.



Propagation steps: In the first propagation step a chlorine atom abstracts a hydrogen atom from the allylic carbon of propene forming allyl radical.



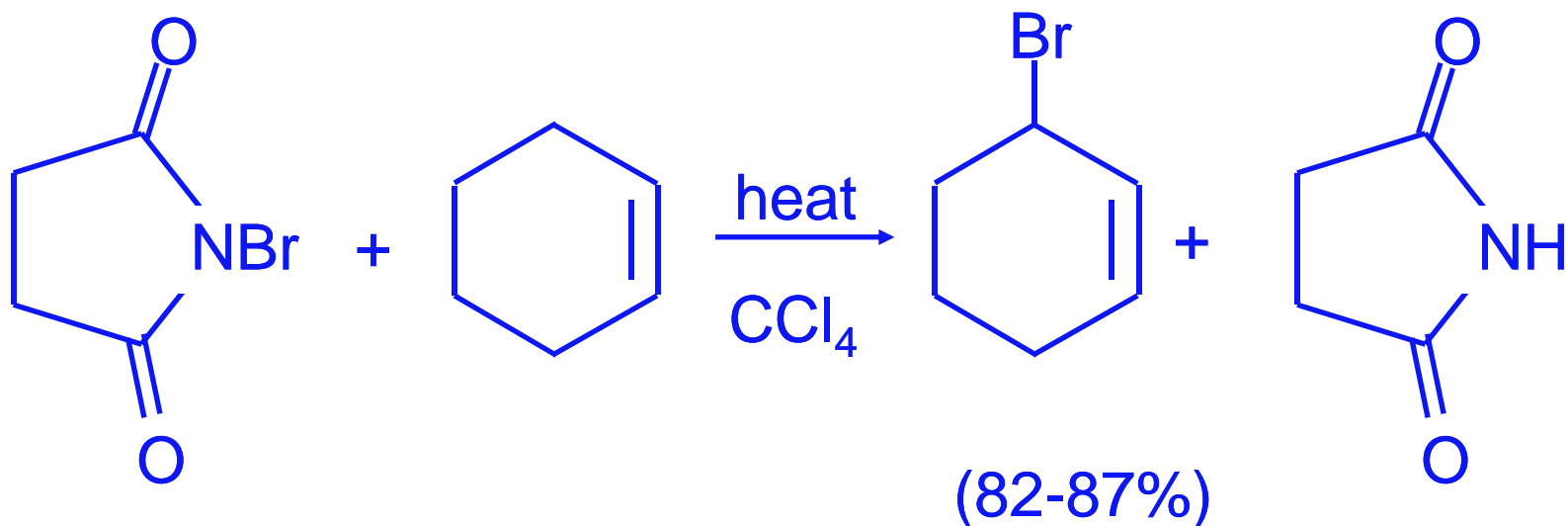
The allyl radical formed in the first propagation step reacts with Cl_2 to form allyl chloride.



The chlorine atom generated in this propagation step then abstracts a hydrogen atom from another molecule of propene and the two propagation steps repeat over and over again.

N-Bromosuccinimide

- Reagent used (instead of Br₂) for allylic bromination.

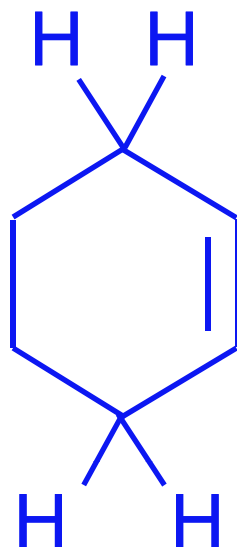


Limited Scope

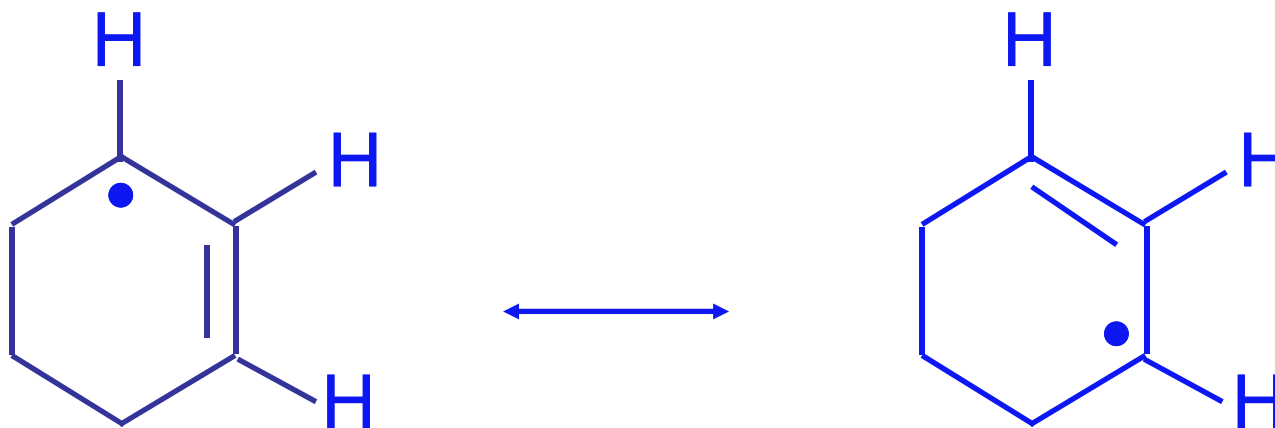
- Allylic halogenation is only used when: **All of the allylic hydrogens are equivalent and the resonance forms of allylic radical are equivalent.**

Example

Cyclohexene satisfies both requirements



All allylic hydrogens are equivalent



Both resonance forms are equivalent

Example

2-Butene



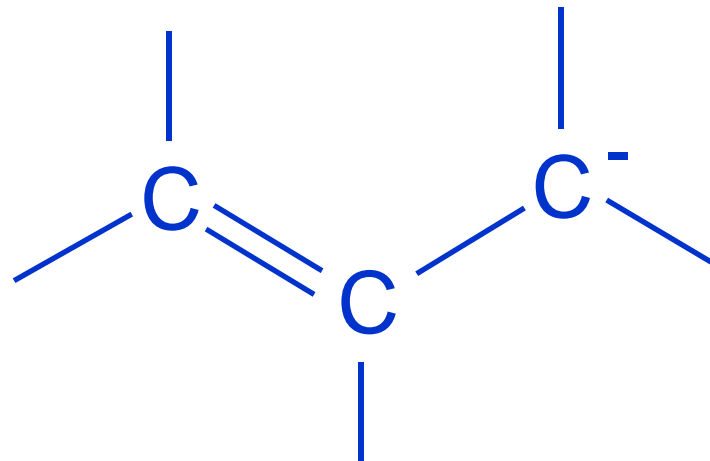
All allylic
hydrogens are
equivalent

But

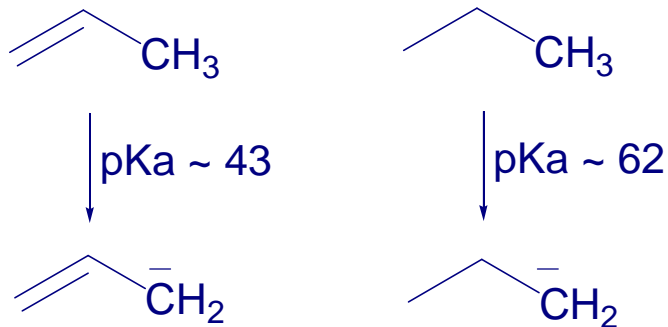


Two resonance forms are not equivalent;
gives mixture of isomeric allylic bromides.

10.7. Allylic Anions

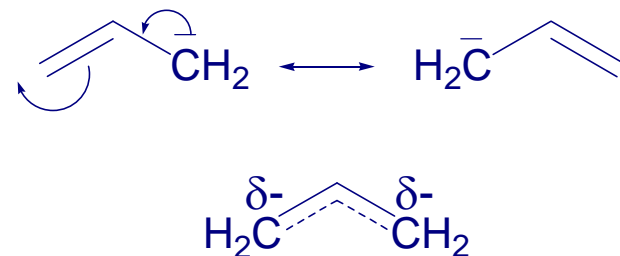


Acidity of Propene



➤ Propene is significantly more acidic than propane.

Resonance Model



➤ Charge is delocalized to both terminal carbons, stabilizing the conjugate base.

10.8. Classes of Dienes: Nomenclature



Isolated diene: $(2E,5E)$ -2,5-heptadiene

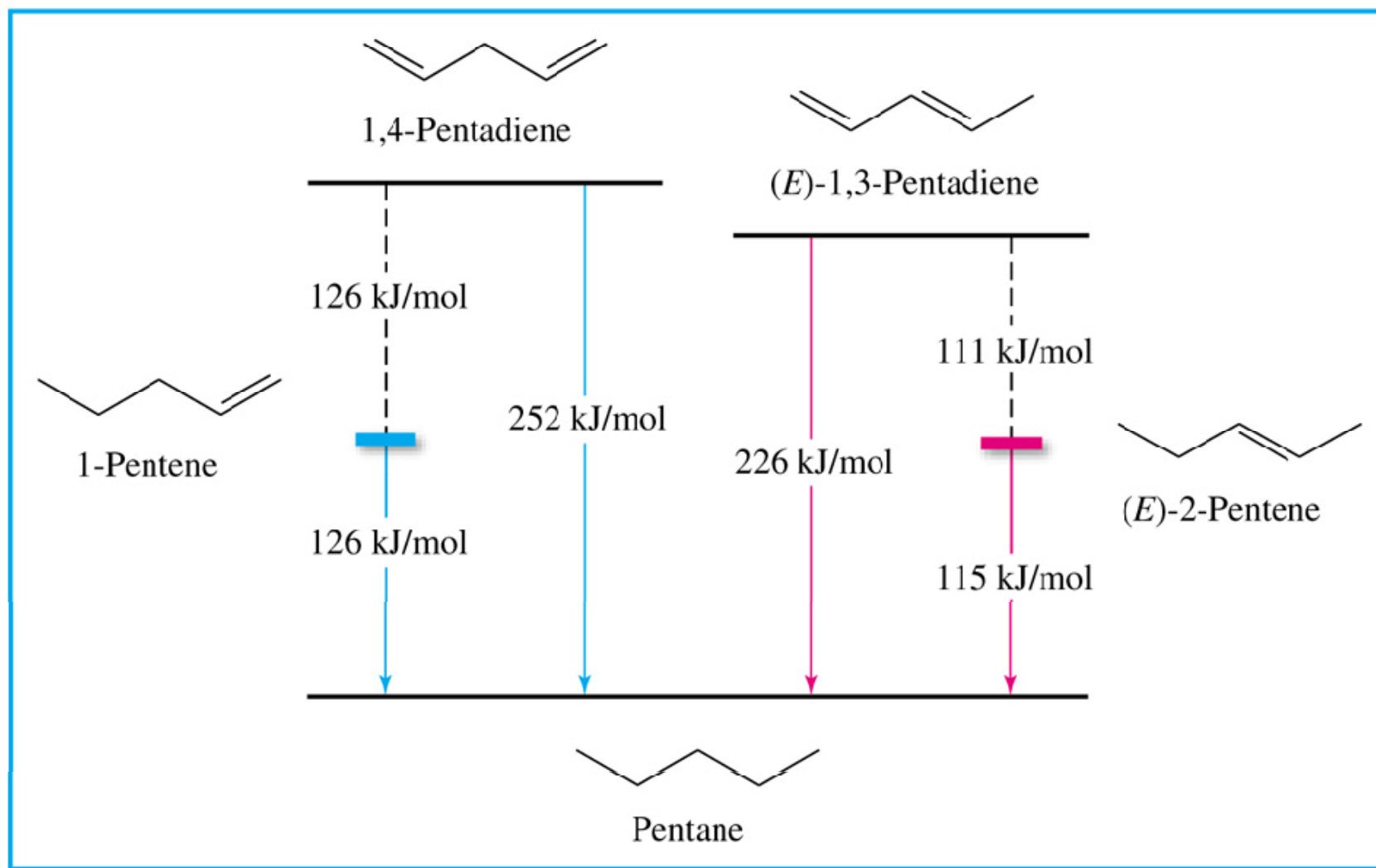


Conjugated diene $(2E,4E)$ -2,4-heptadiene

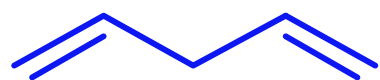


Cumulated diene: 3,4-heptadiene

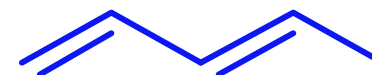
10.9. Relative Stabilities of Dienes *Heats of Hydrogenation*



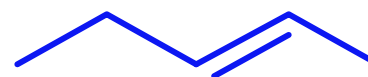
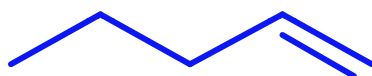
Heats of Hydrogenation



126 kJ/mol



111 kJ/mol

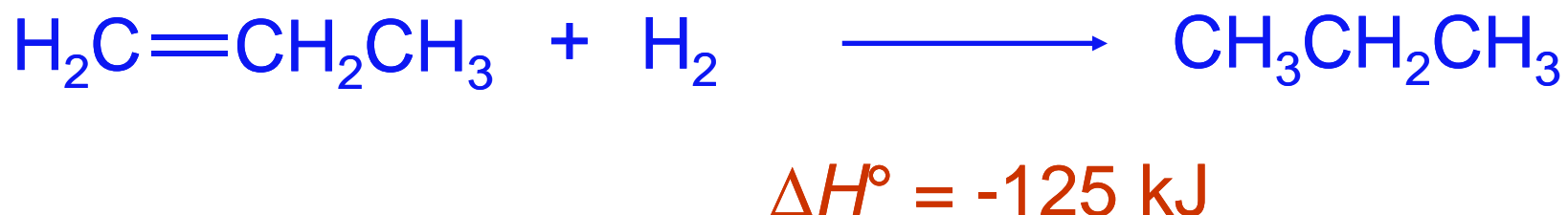
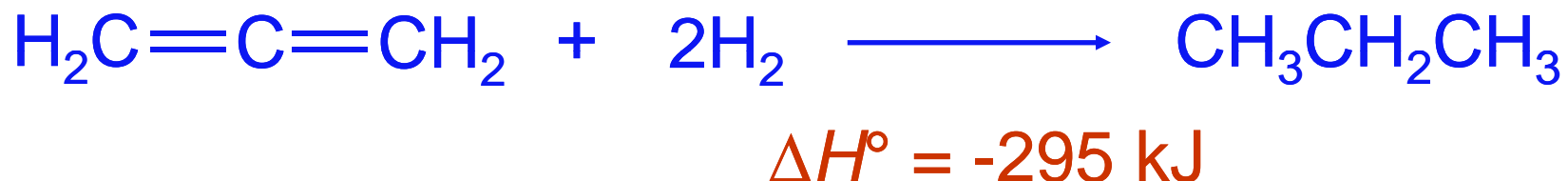


➤ When terminal double bond is conjugated with other double bond, its heat of hydrogenation is 15 kJ/mol less than when isolated.

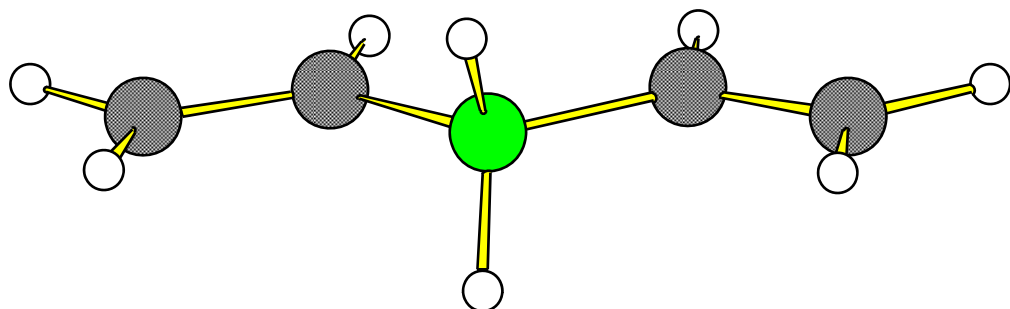
➤ This extra 15 kJ/mol is known by several terms: stabilization energy; delocalization energy; resonance energy.

Heats of Hydrogenation

➤ Cumulated double bonds have relatively high heats of hydrogenation.

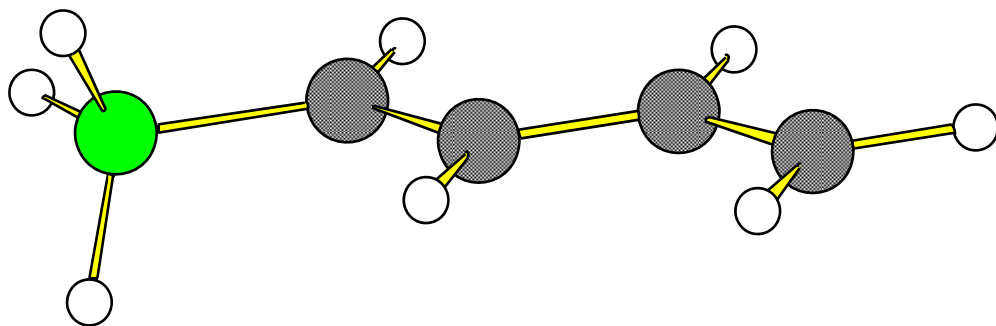


10.10. Bonding in Conjugated Dienes



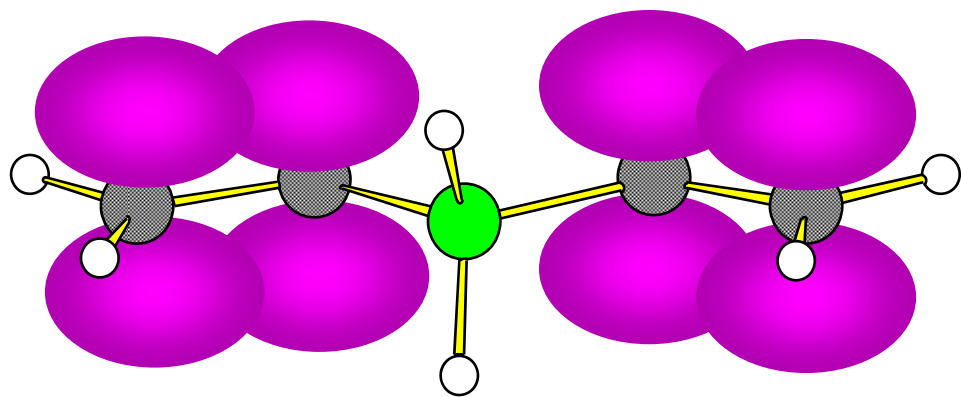
1,4-pentadiene

Isolated diene



1,3-pentadiene

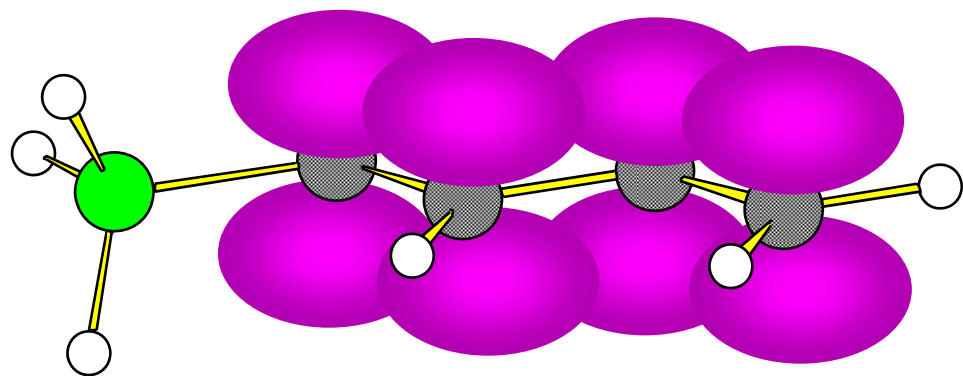
Conjugated diene



Isolated diene

π -bonds are independent of each other.

Less electron delocalization; less stable.

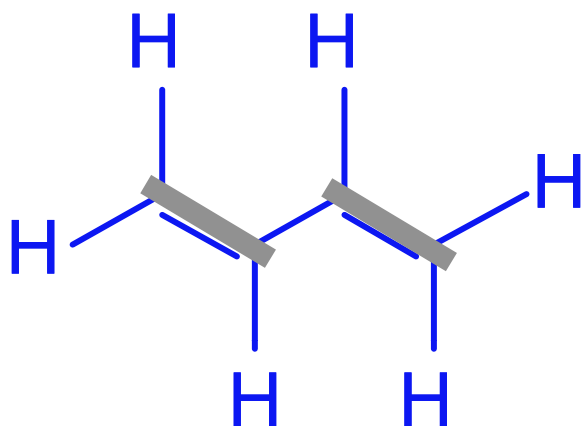


Conjugated diene

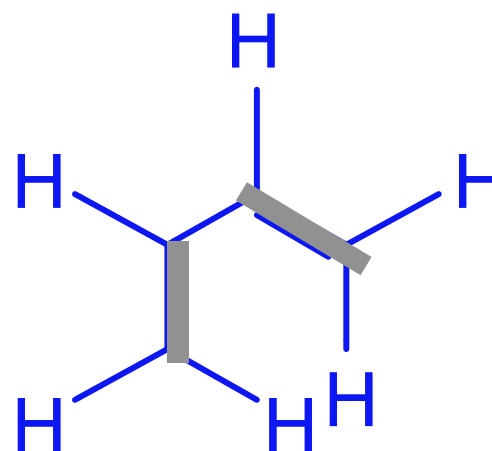
P orbitals overlap to give extended π -bond encompassing four carbons.

More electron delocalization; more stable.

Conformations of Dienes



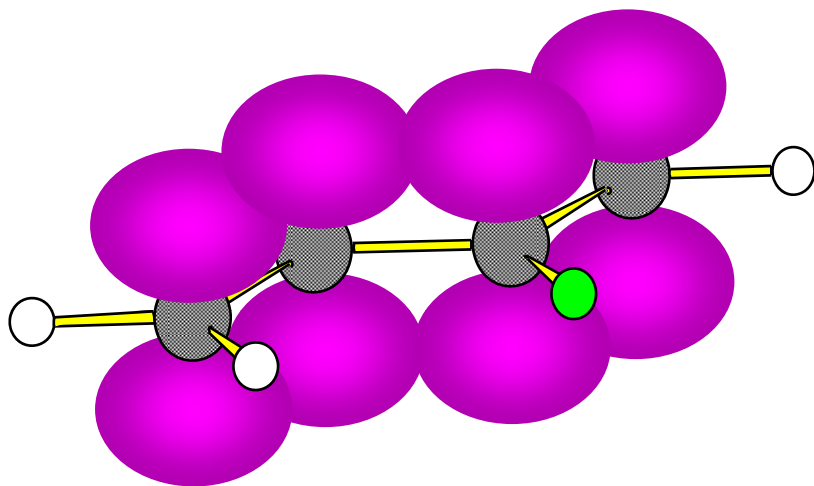
s-trans



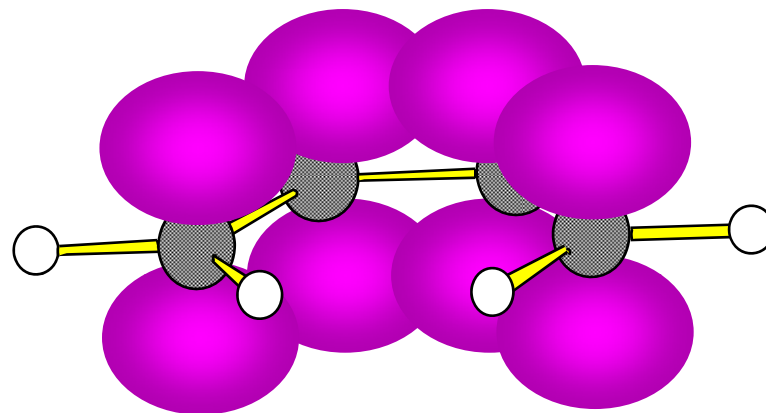
s-cis

- *s* prefix designates conformation around single bond.
- *s* prefix is lower case (different from Cahn-Ingold-Prelog *S* which designates configuration and is upper case).

Conformations of Dienes



s-trans

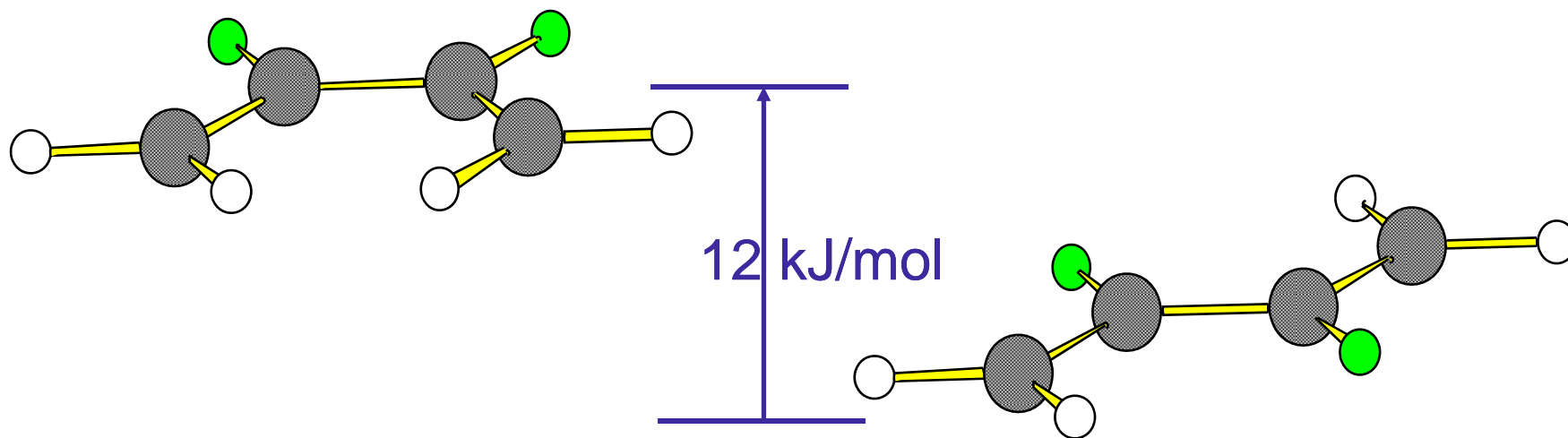


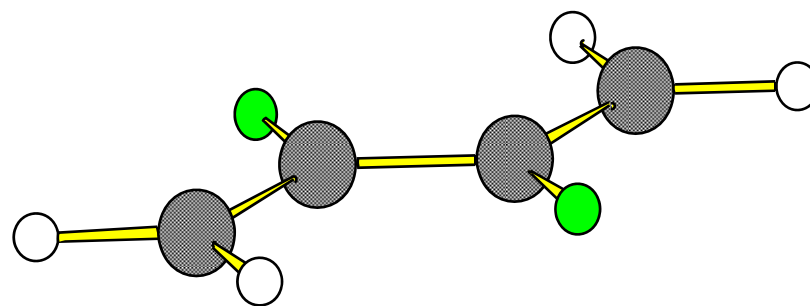
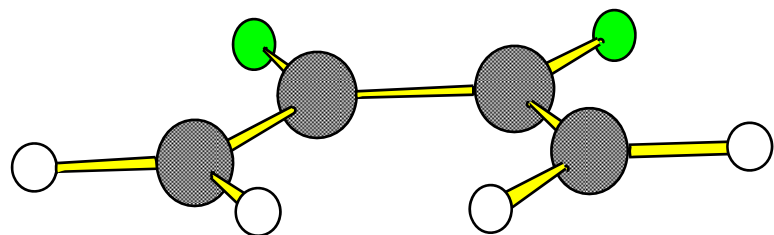
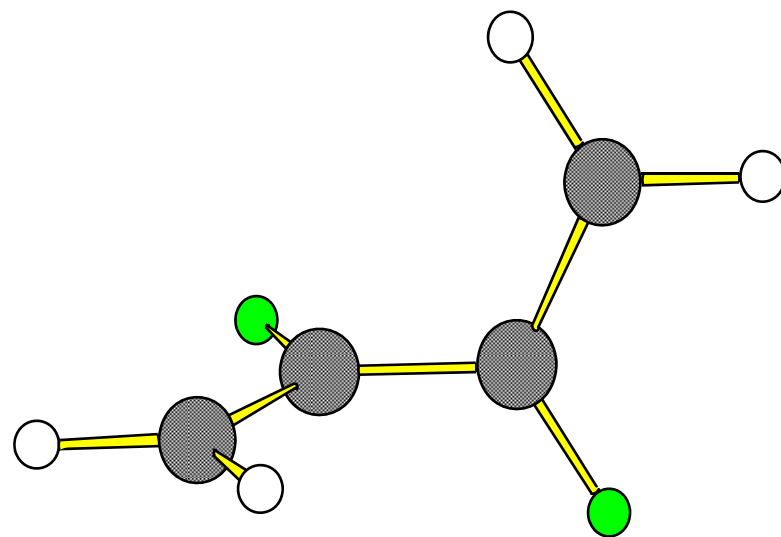
s-cis

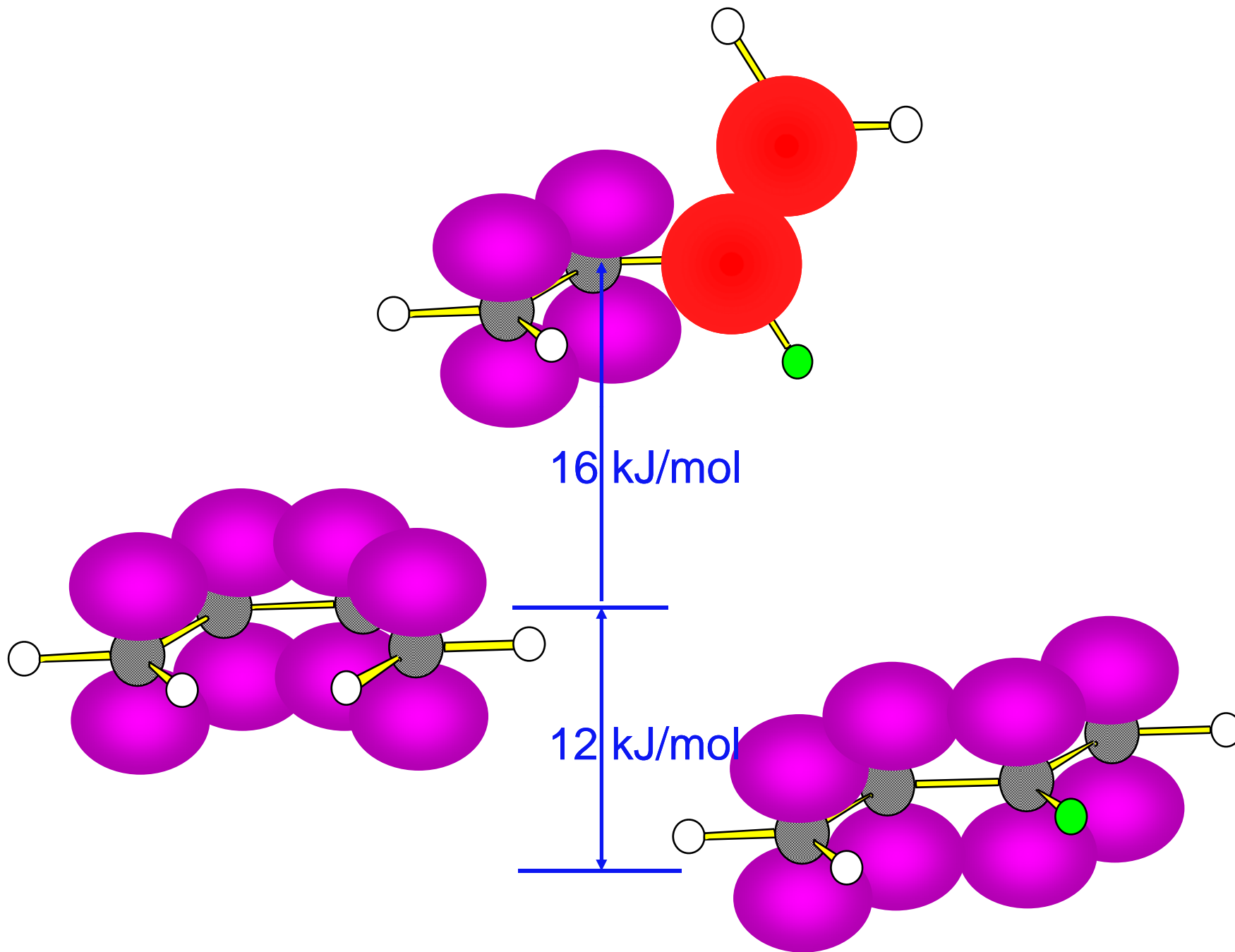
➤ Both conformations allow electron delocalization via overlap of p orbitals to give extended π system.

s-trans is more stable than s-cis

- Interconversion of conformations requires two π -bonds to be at right angles to each other and prevents conjugation.

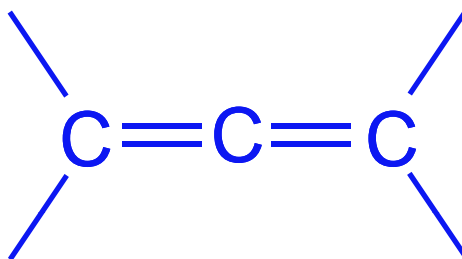






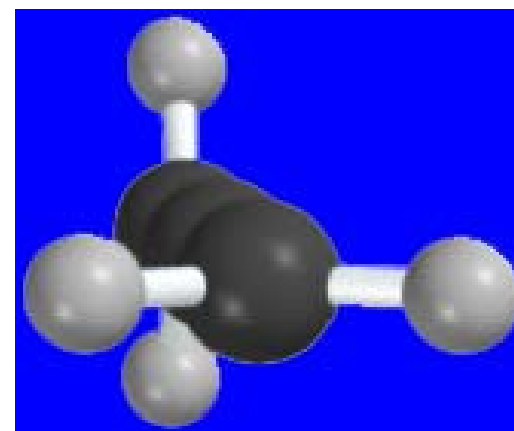
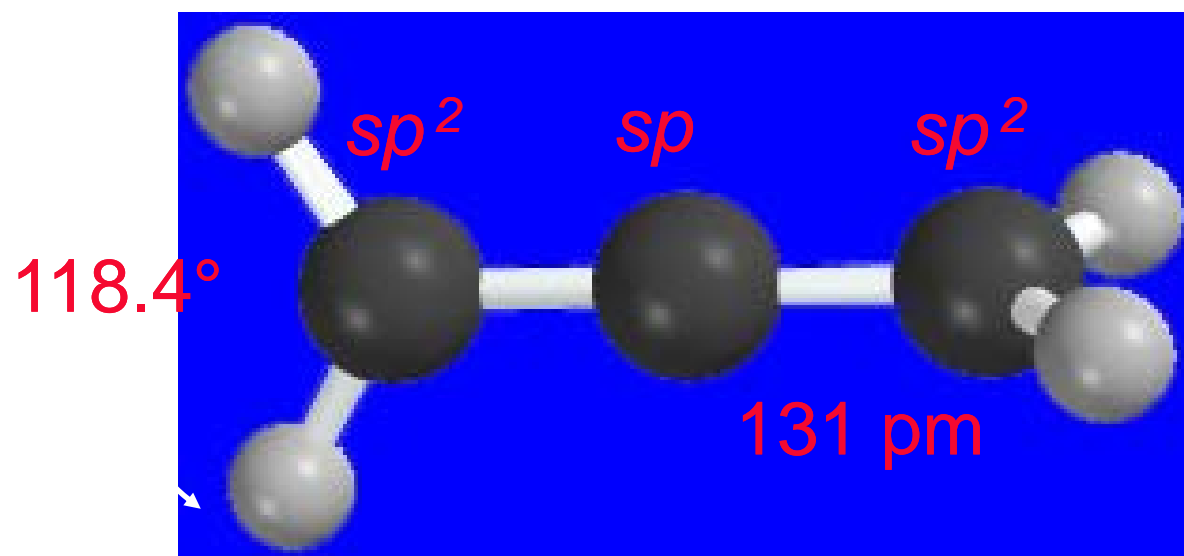
10.11. Bonding in Allenes

Cumulated Dienes



Cumulated dienes are less stable than isolated and conjugated dienes.

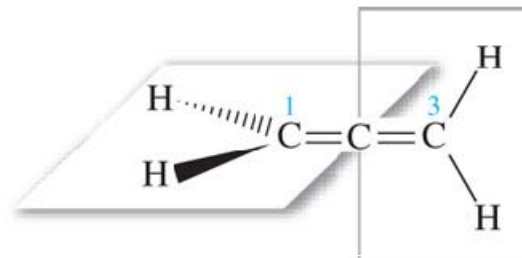
Structure & Bonding of Allene



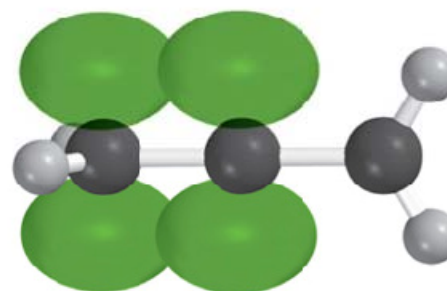
Linear arrangement of carbons
nonplanar geometry.

Bonding in Allene

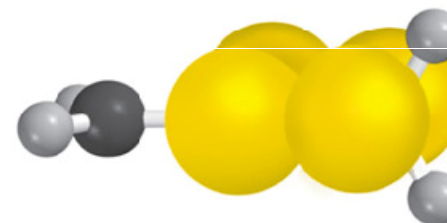
(a) Planes defined by H(C-1)H and H(C-3)H are mutually perpendicular.



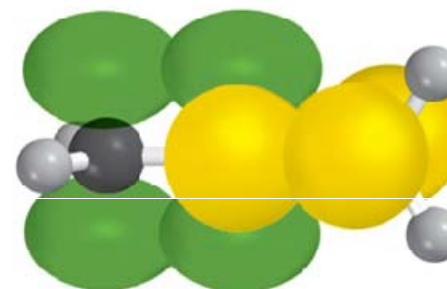
(b) The *p* orbital of C-1 and one of the *p* orbitals of C-2 can overlap so as to participate in π bonding.



(c) The *p* orbital of C-3 and one of the *p* orbitals of C-2 can overlap so as to participate in a second π orbital perpendicular to the one in (b).

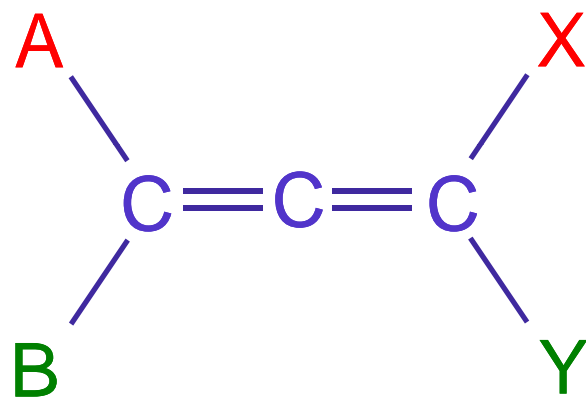


(d) Allene is a nonplanar molecule characterized by a linear carbon chain and two mutually perpendicular π bonds.



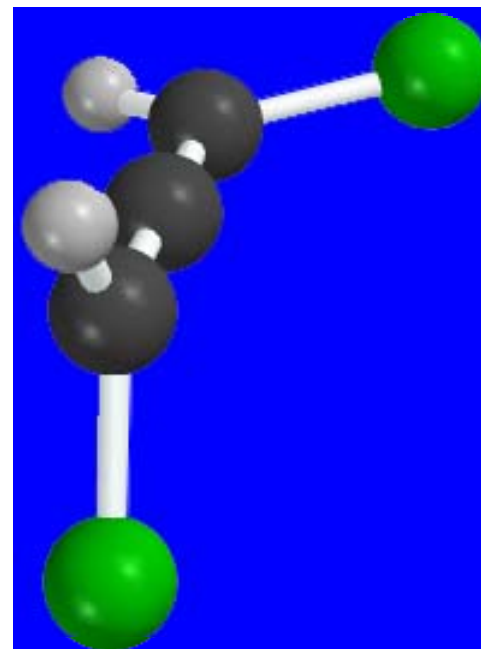
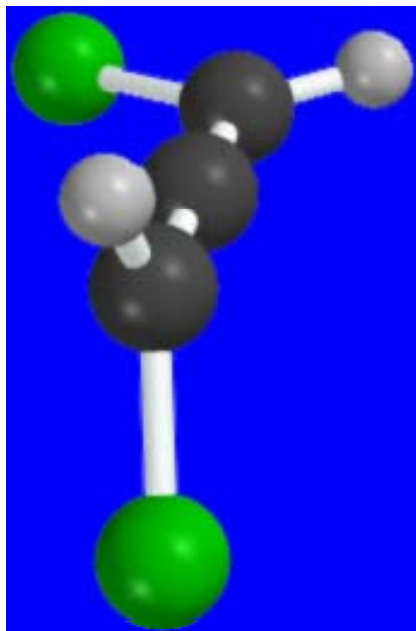
Chiral Allenes

Allenes of the type shown are chiral



Have a stereogenic axis

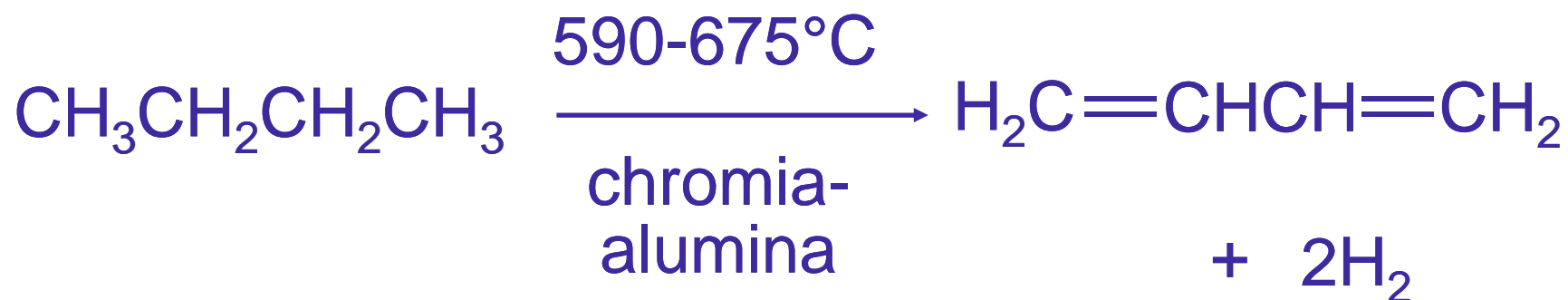
Stereogenic (Chiral) Axis



- Analogous to difference between:
 - A screw with a right-hand thread and one with a left-hand thread.
 - A right-handed helix and a left-handed helix.
- Allenes have chiral axis BUT no chiral center; they are chiral.

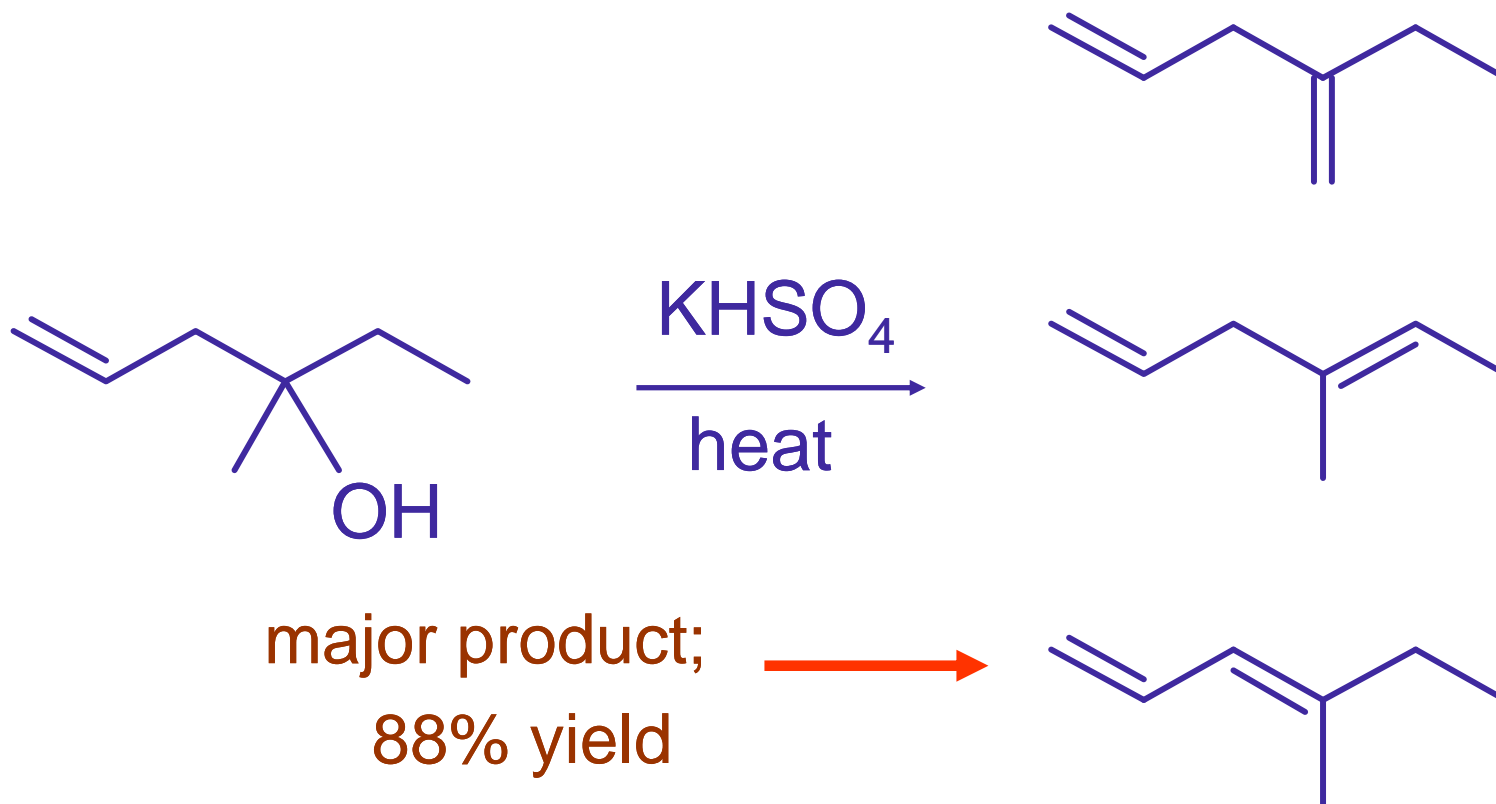
10.12. Preparation of Dienes

1,3-Butadiene

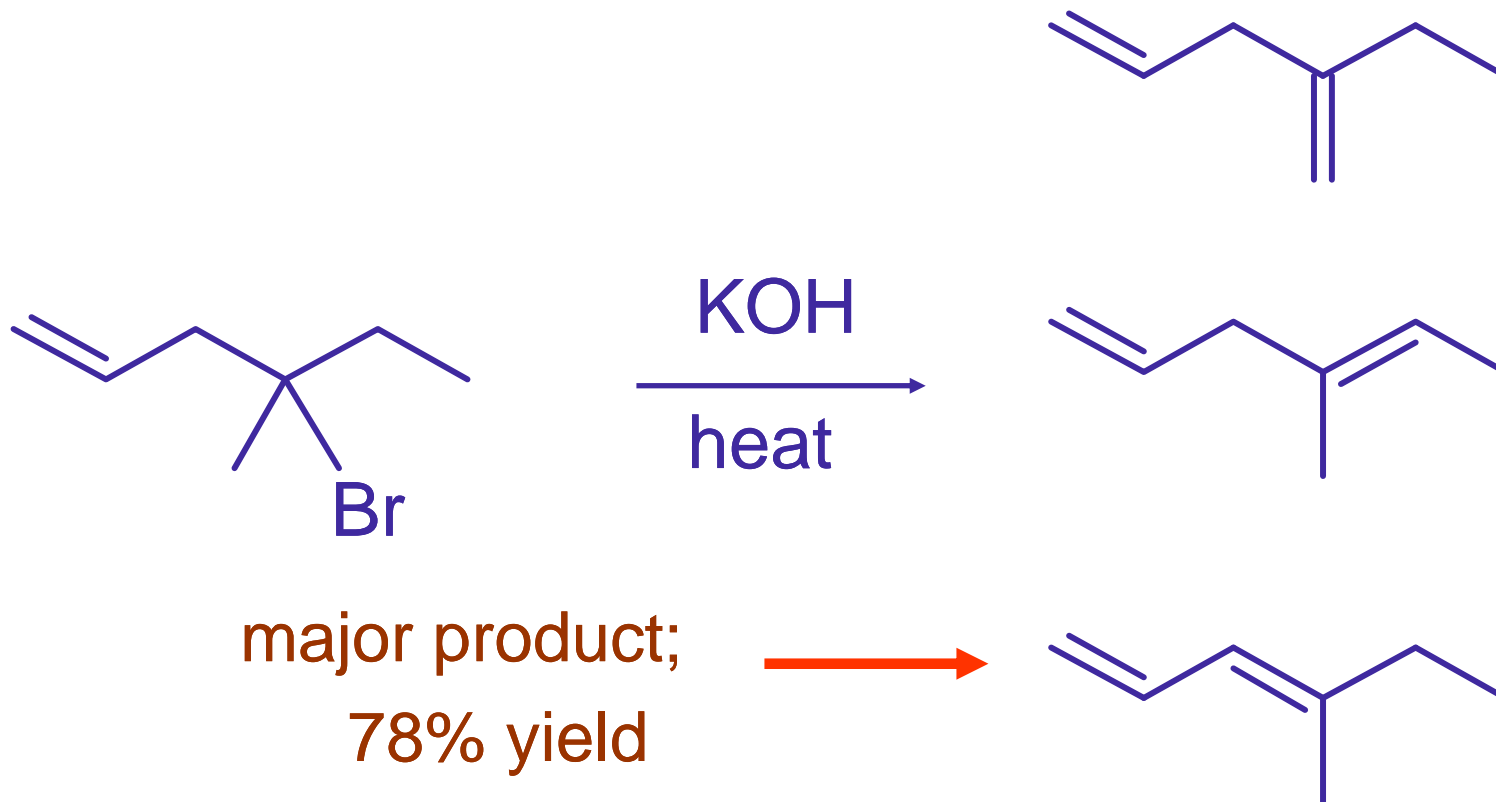


- More than 4 billion pounds of 1,3-butadiene prepared by this method in U.S. each year.
- Used to prepare synthetic rubber (See "Diene Polymers" box).

Dehydration of Alcohols



Dehydrohalogenation of Alkyl Halides



Reactions of Dienes

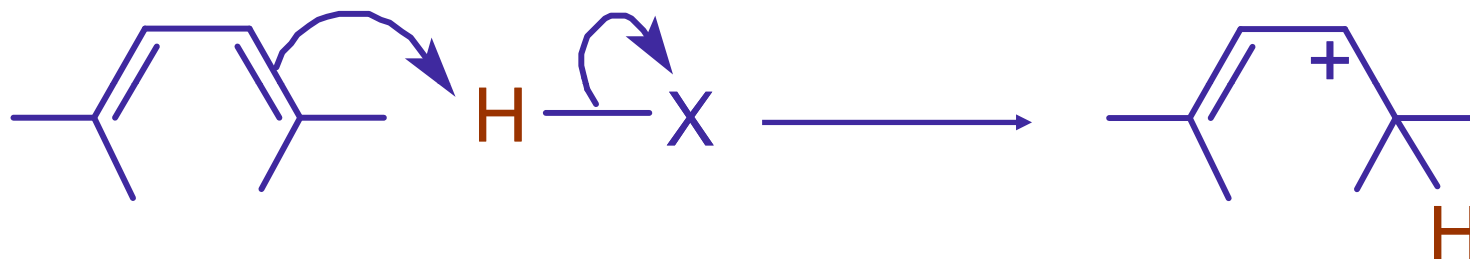
Isolated dienes: double bonds react independently of one another.

Cumulated dienes: specialized topic.

Conjugated dienes: reactivity pattern requires us to think of conjugated diene system as a functional group of its own.

10.13
Addition of Hydrogen Halides
to
Conjugated Dienes

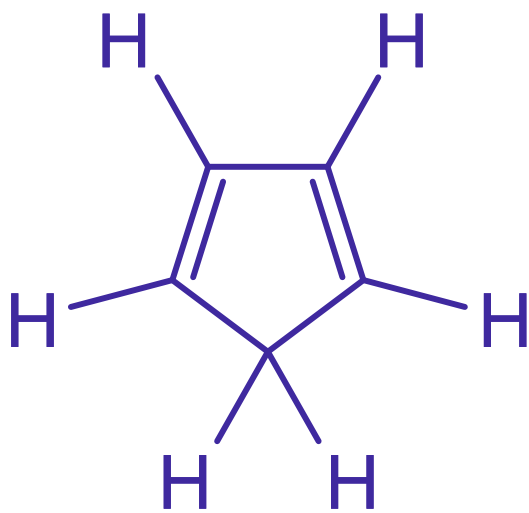
Electrophilic Addition to Conjugated Dienes



Proton adds to end of diene system.

Carbocation formed is allylic.

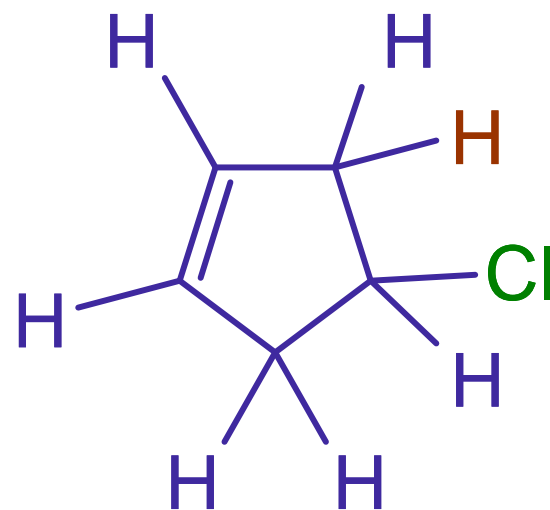
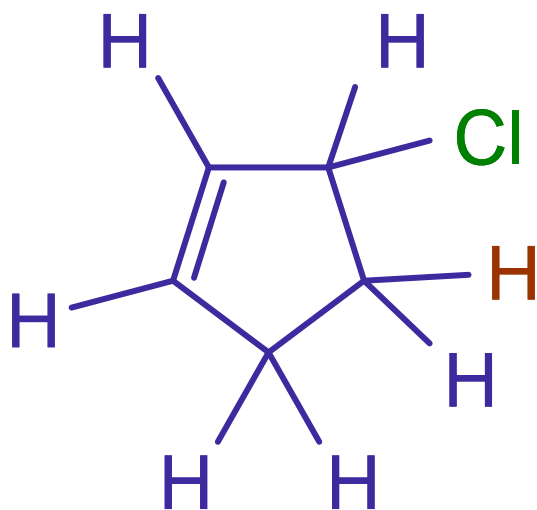
Example



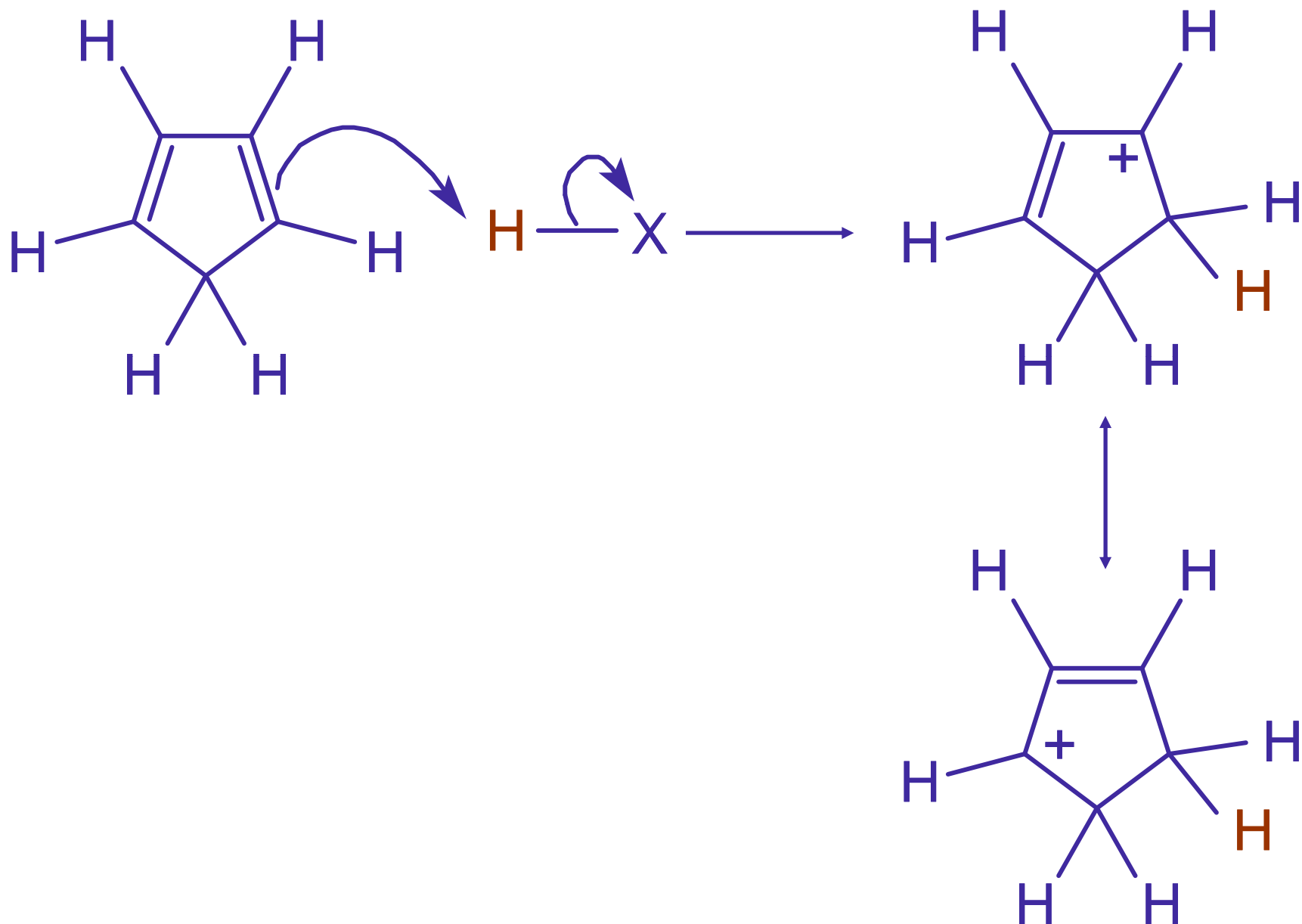
HCl

?

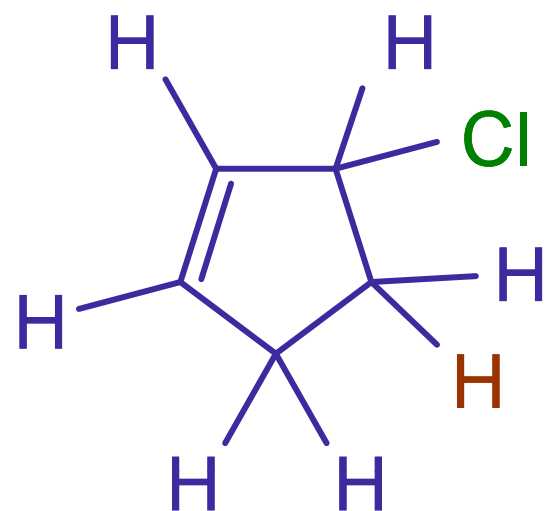
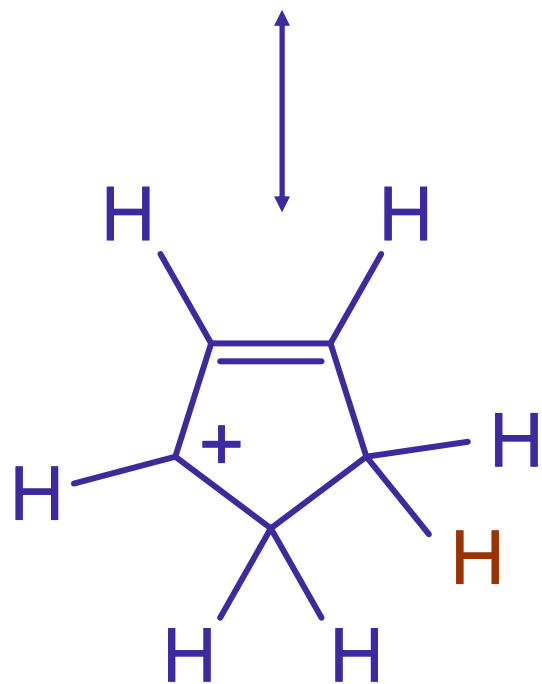
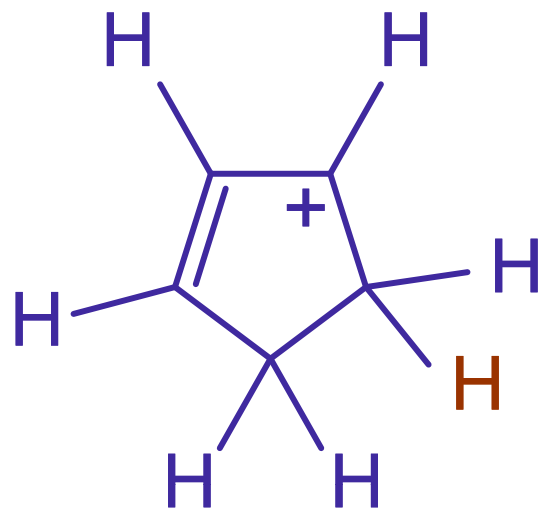
?



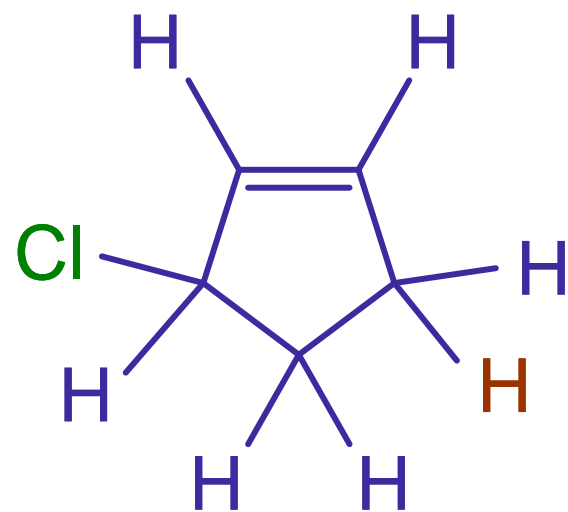
via:



and:



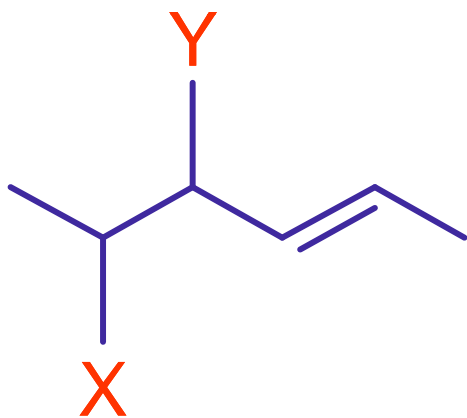
3-Chlorocyclopentene



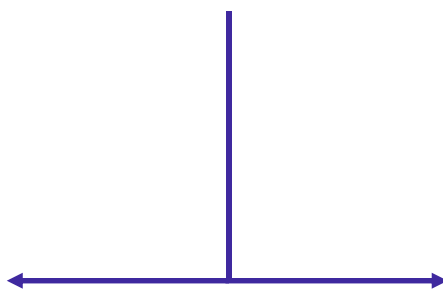
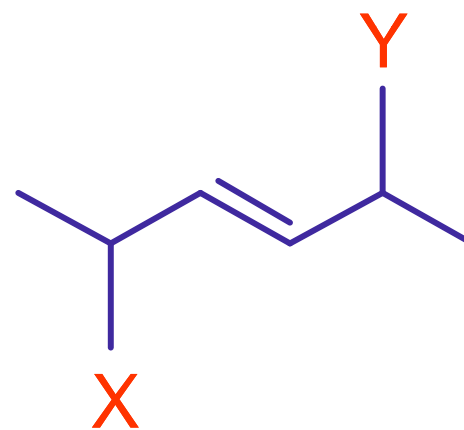
1,2-Addition versus 1,4-Addition



1,2-addition of XY



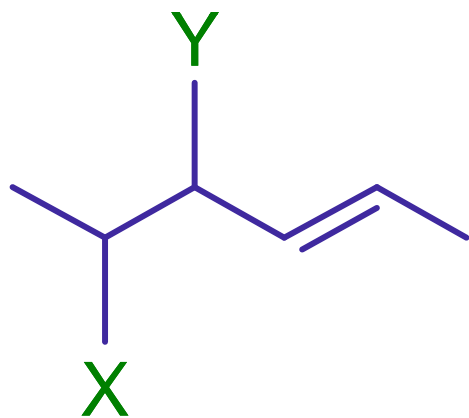
1,4-addition of XY



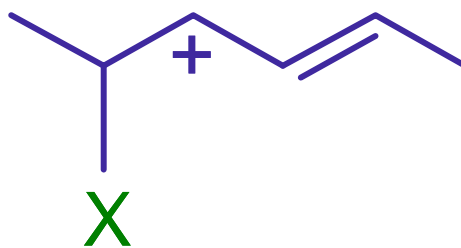
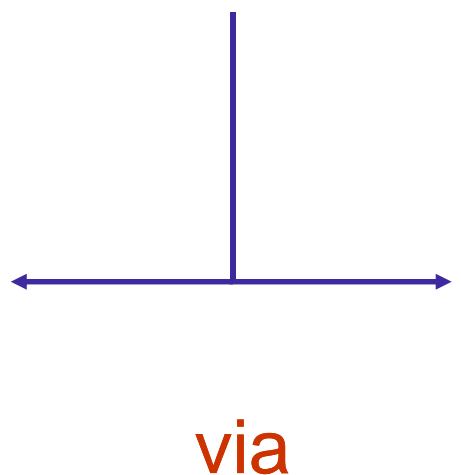
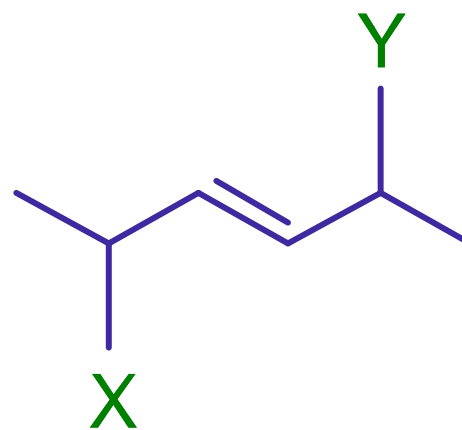
1,2-Addition versus 1,4-Addition



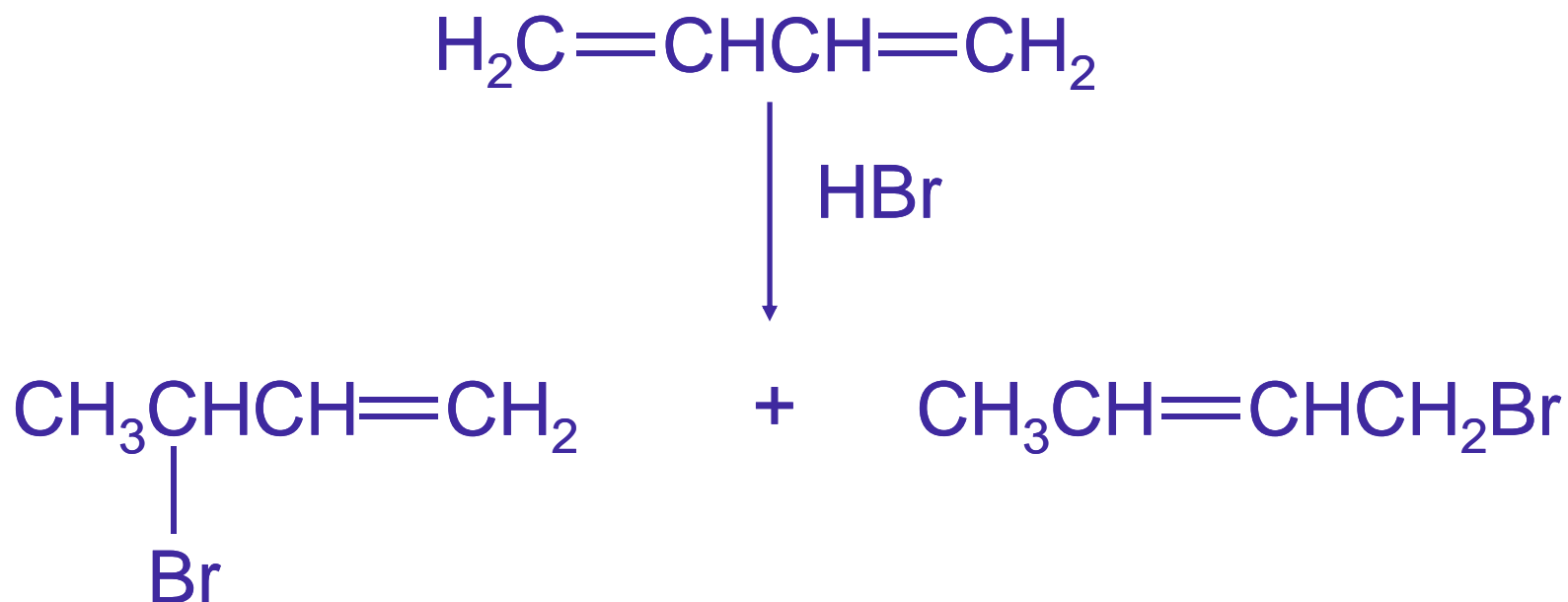
1,2-addition of XY



1,4-addition of XY



HBr Addition to 1,3-Butadiene



Electrophilic addition:

- 1,2 and 1,4-addition both observed.
- Product ratio depends on temperature.

Rationale

➤ 3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.

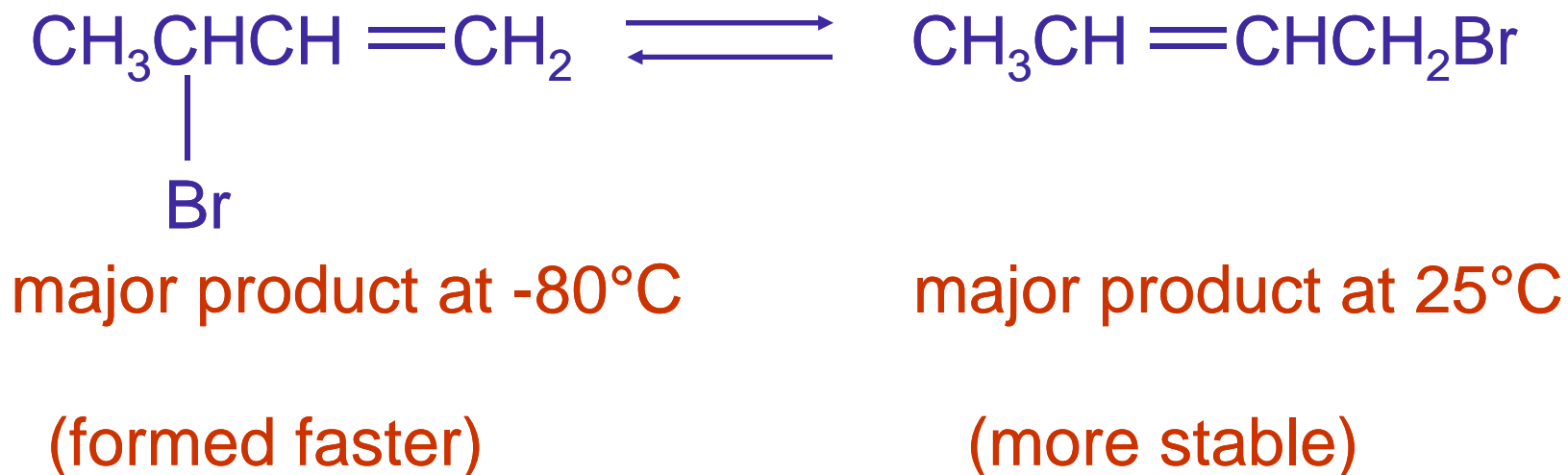


via:



Rationale

- The two products equilibrate at 25°C. Once equilibrium is established, the more stable isomer predominates.

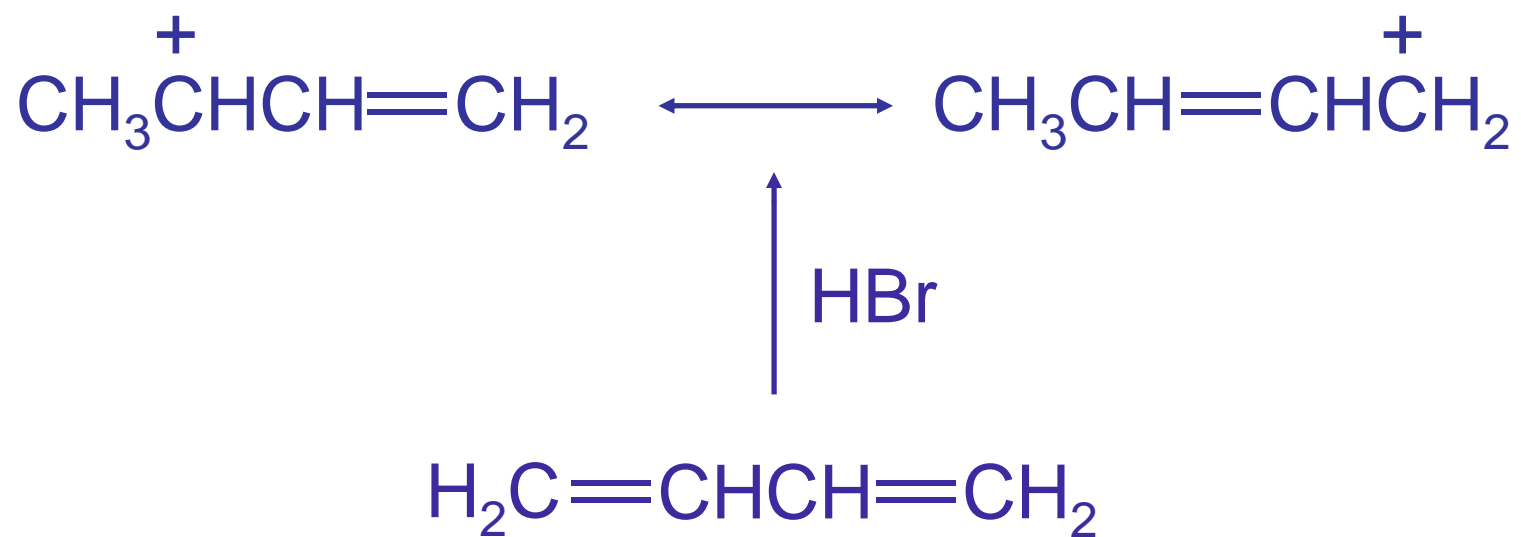


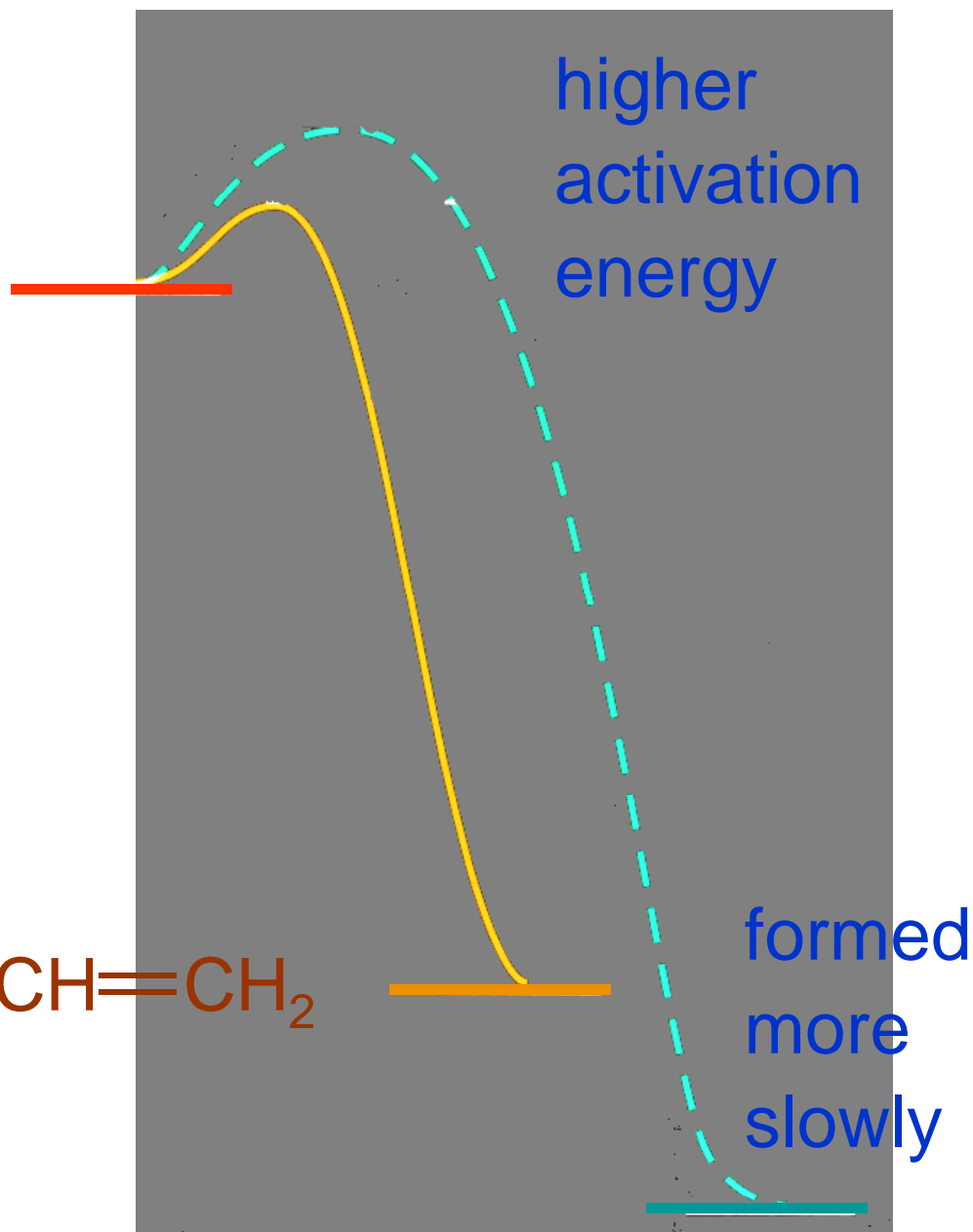
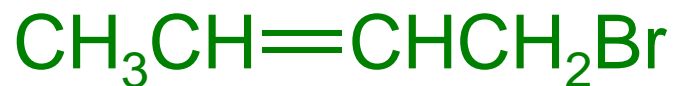
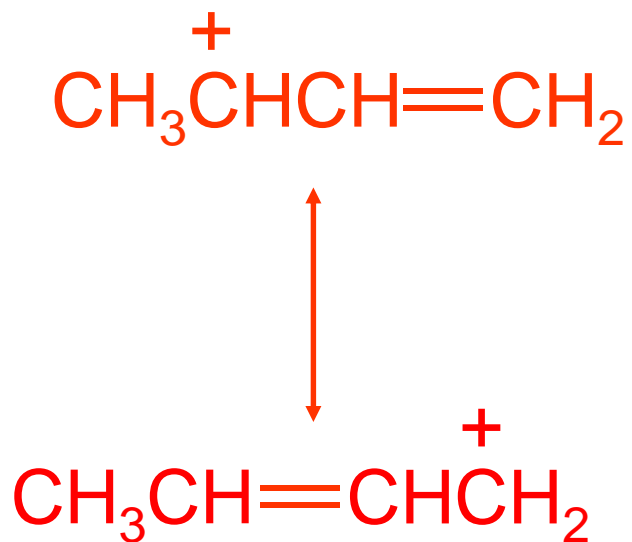
Kinetic Control

versus

Thermodynamic Control

- Kinetic control: major product is the one formed at the fastest rate.
- Thermodynamic control: major product is the one that is the most stable.

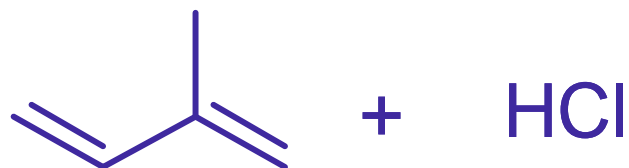




Question:

➤ Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?

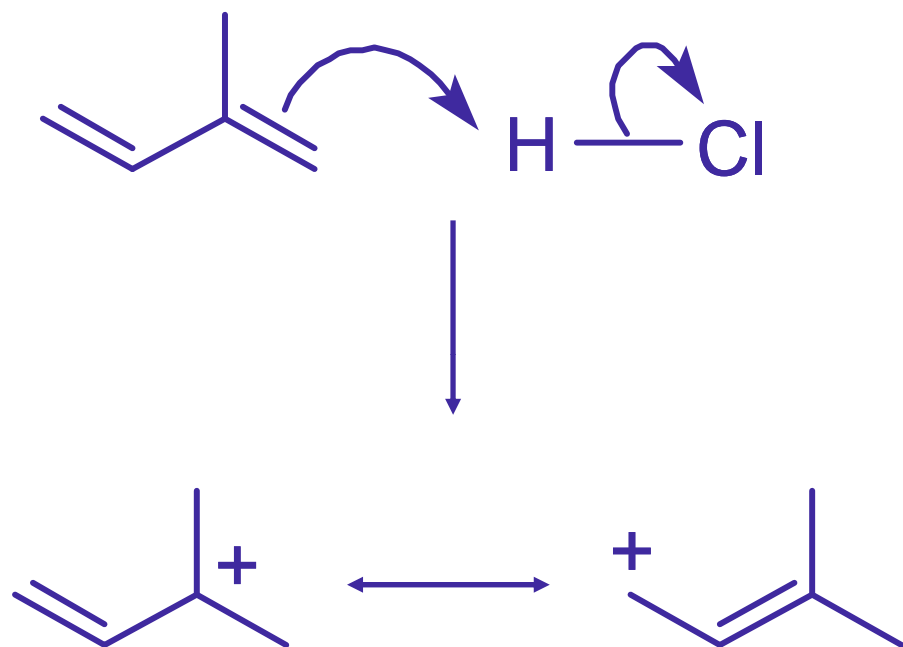




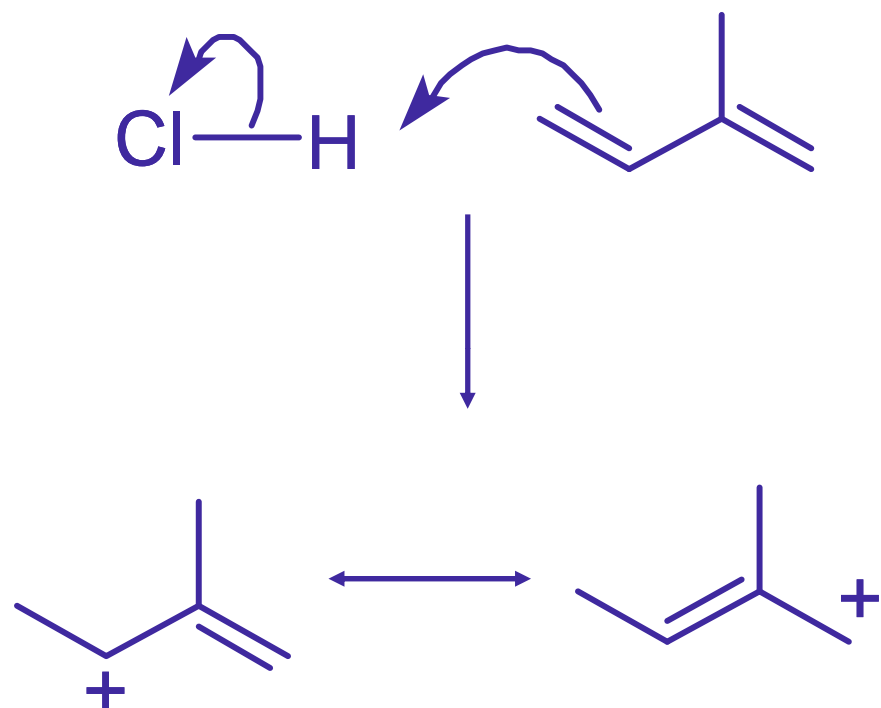
Think mechanistically!

- Protonation occurs: at end of diene system in direction that gives most stable carbocation.
- Kinetically controlled product corresponds to attack by chloride ion at carbon that has the greatest share of positive charge in the carbocation.

Think mechanistically

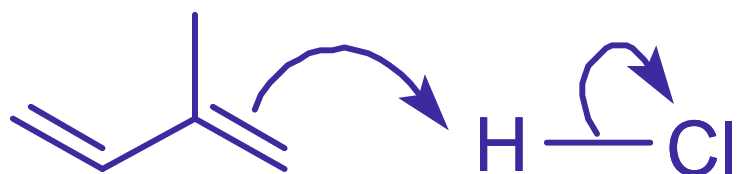


one resonance form is
tertiary carbocation;
other is primary

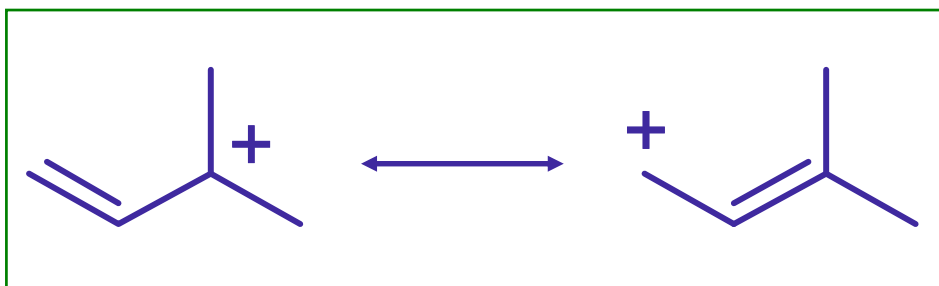


one resonance form is
secondary carbocation;
other is primary

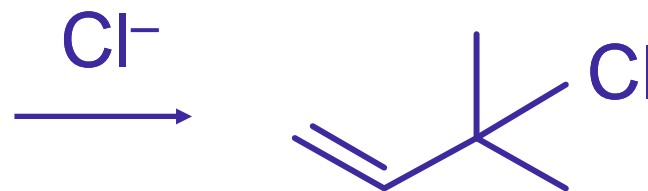
Think mechanistically



More stable carbocation is attacked by chloride ion at carbon that bears greater share of positive charge.



one resonance form is tertiary carbocation;
other is primary



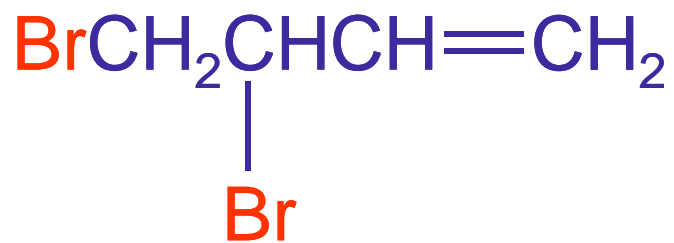
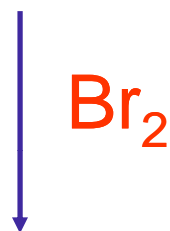
major product

10.14

Halogen Addition to Dienes

gives mixtures of 1,2 and
1,4-addition products

Example



(37%)



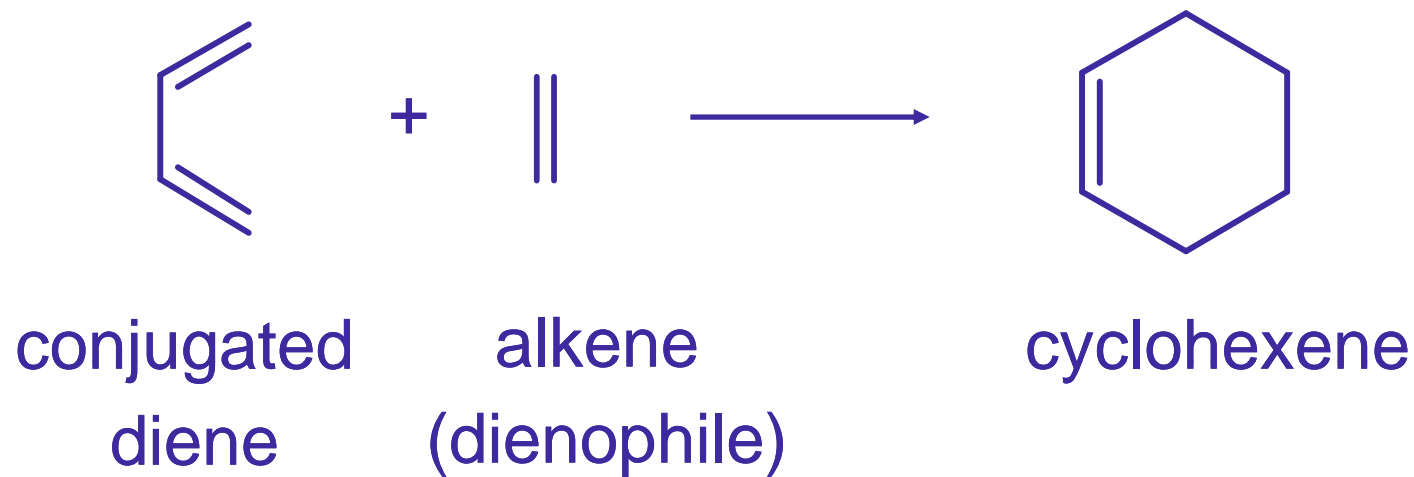
(63%)

10.15

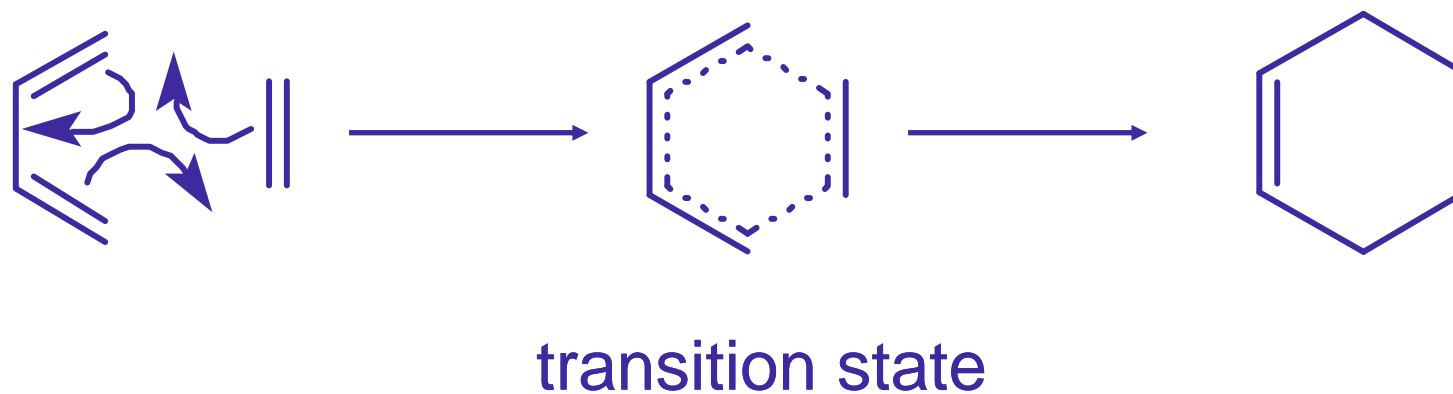
The Diels-Alder Reaction

*Synthetic method for preparing
compounds containing a cyclohexene ring.*

In general...



Via



Mechanistic features

- Concerted mechanism.
- Cycloaddition.
- Pericyclic reaction: a concerted reaction that proceeds through a cyclic transition state.

Recall the general reaction...



conjugated
diene

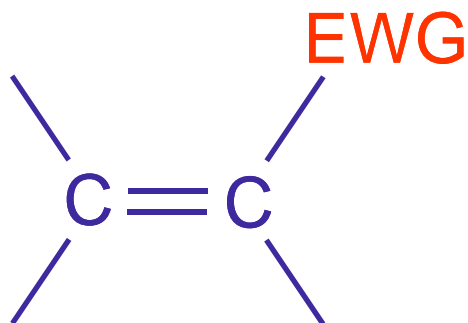
alkene
(dienophile)

cyclohexene

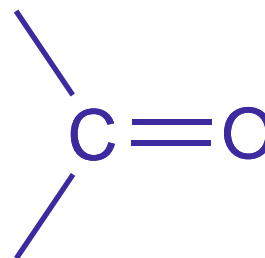
➤ The equation as written is somewhat misleading because ethylene is a relatively unreactive dienophile.

What makes a reactive dienophile?

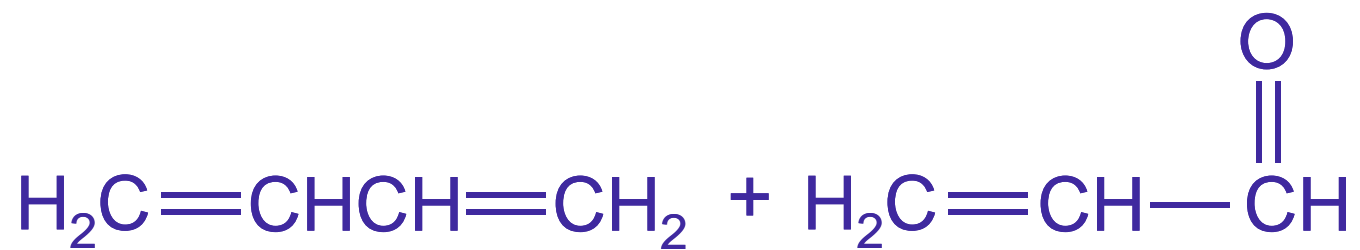
- The most reactive dienophiles have an electron-withdrawing group (EWG) directly attached to the double bond.



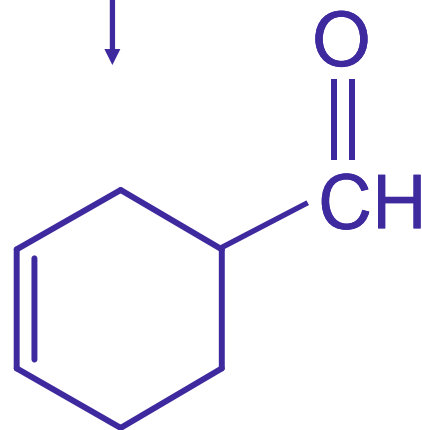
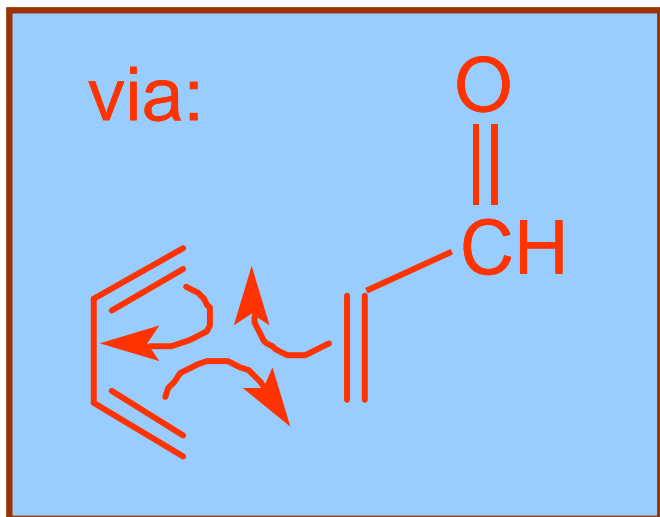
Typical EWGs



Example

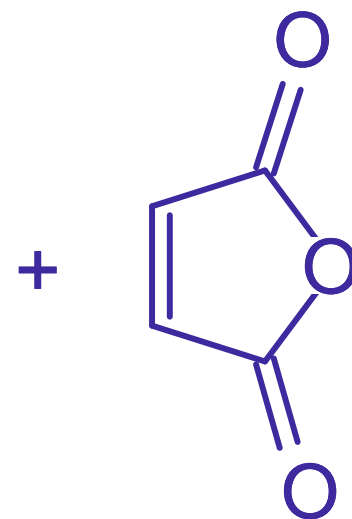
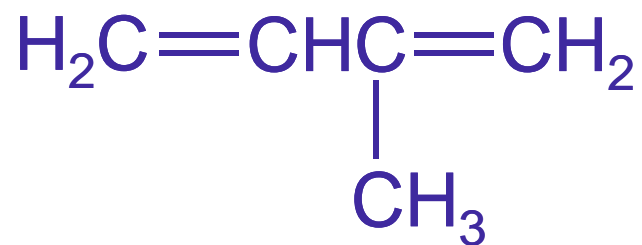


benzene 100°C



(100%)

Example

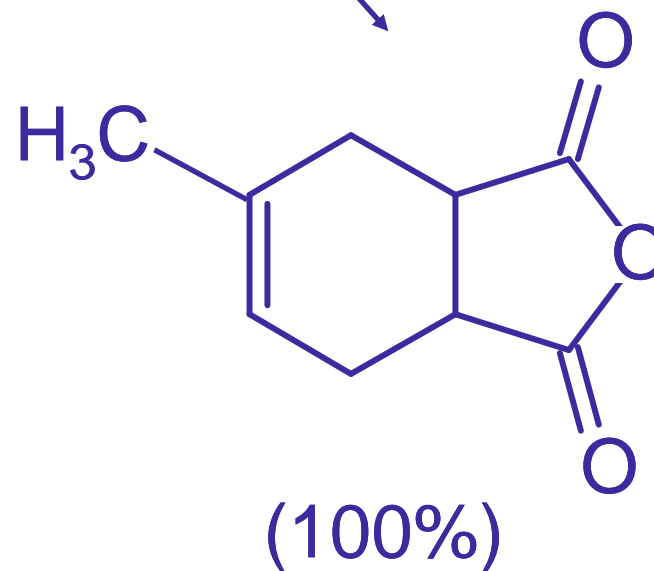
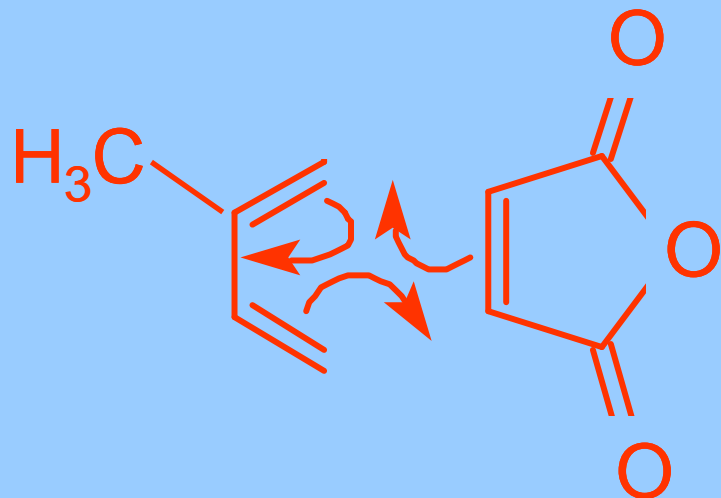


benzene

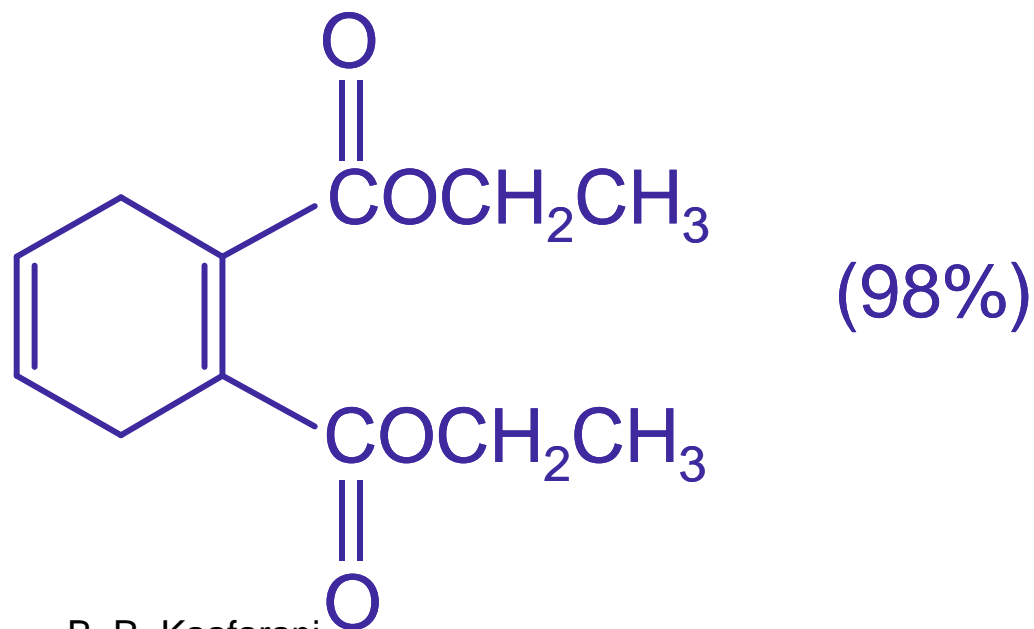
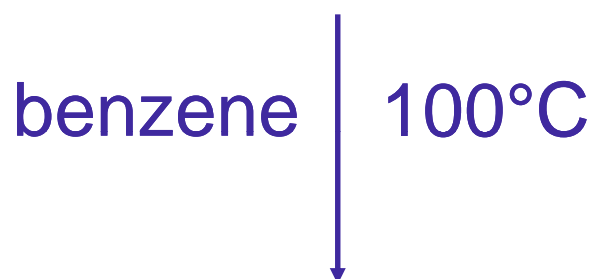
100°C

Maleic anhydride

via:



Acetylenic Dienophile

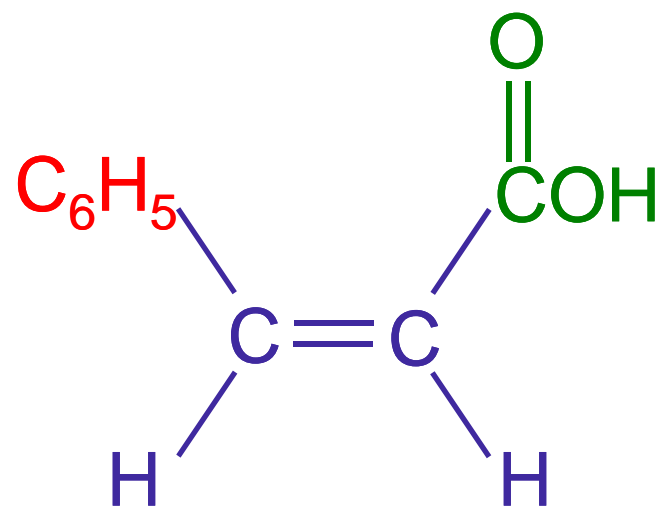


*Diels-Alder Reaction is Stereospecific**

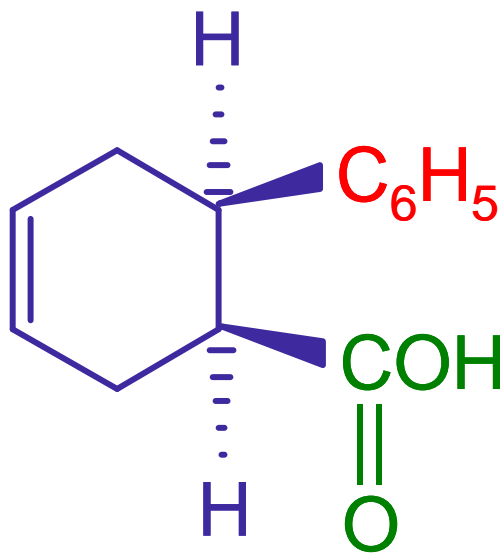
- *syn* addition to alkene.
- *cis-trans* relationship of substituents on alkene retained in cyclohexene product.

*A stereospecific reaction is one in which stereoisomeric starting materials give stereoisomeric products; characterized by terms like *syn* addition, *anti* elimination, *inversion* of configuration, etc.

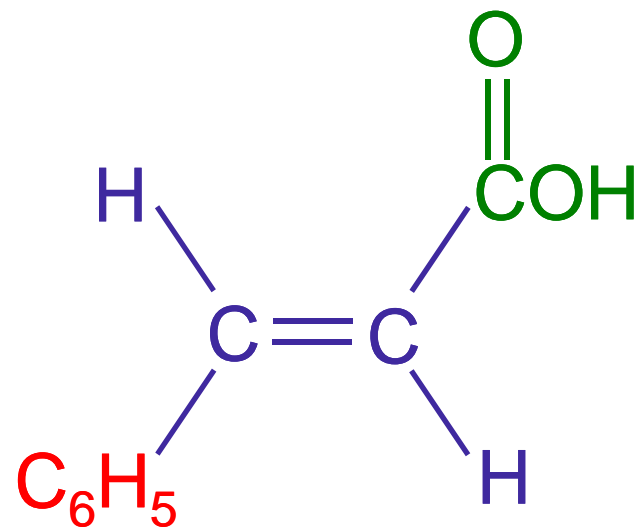
Example



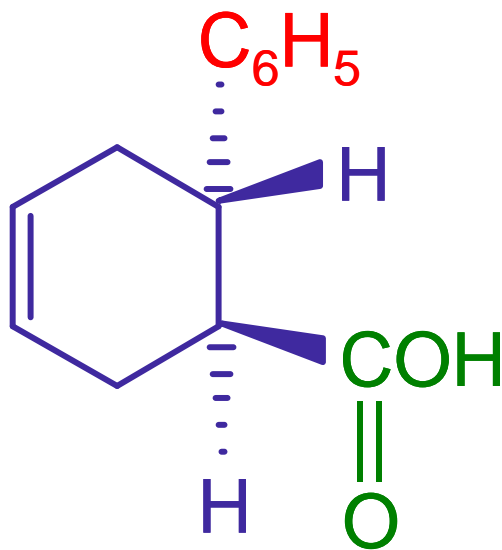
only product



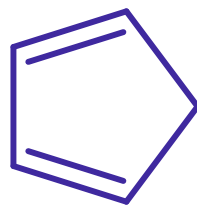
Example

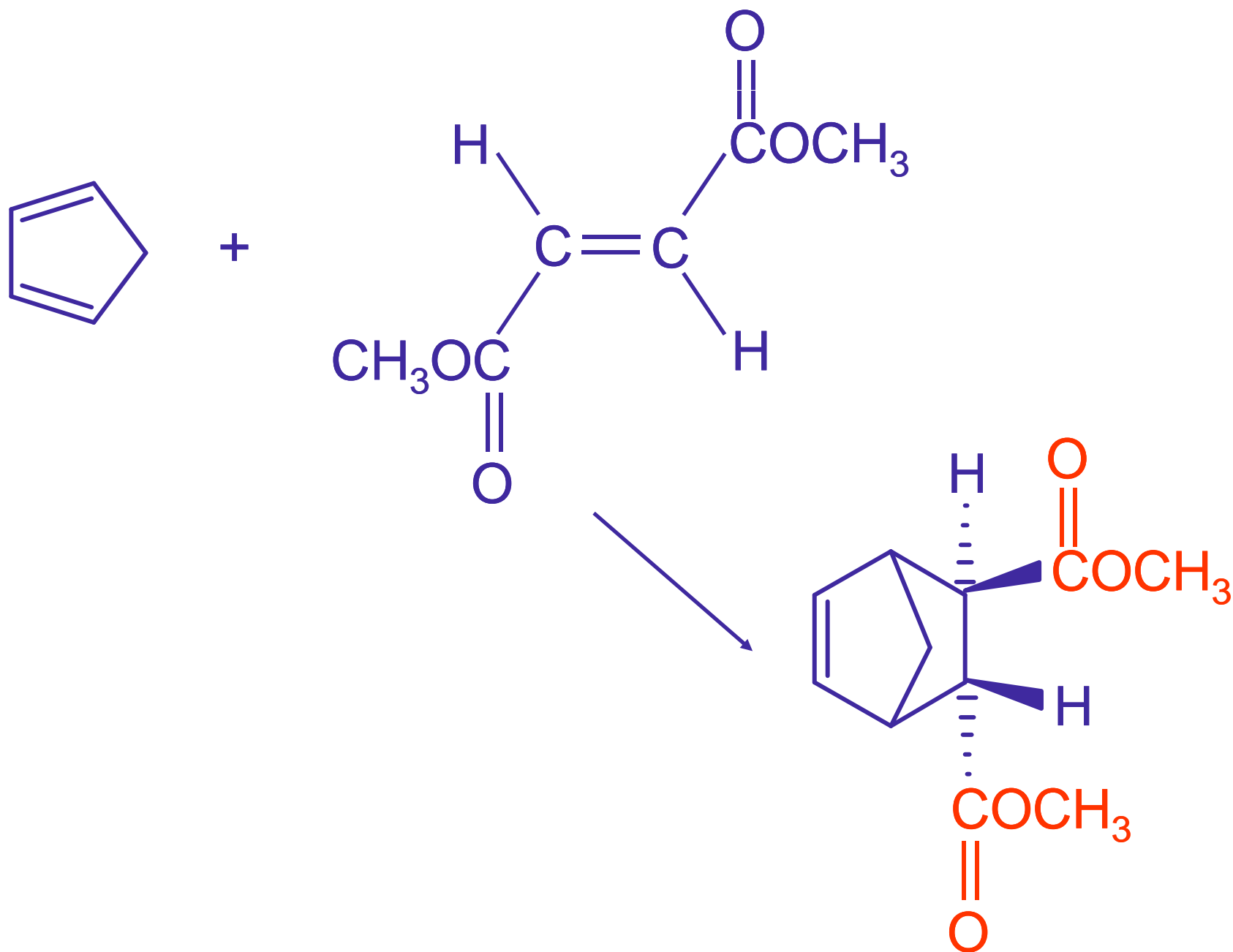


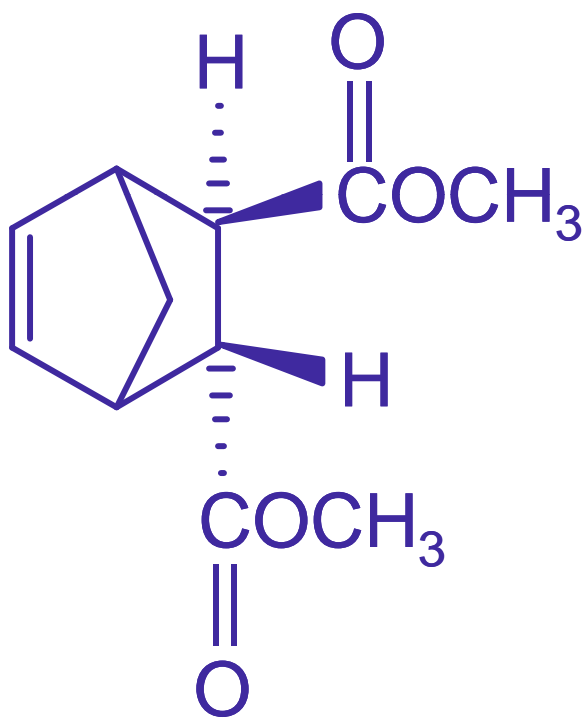
only product



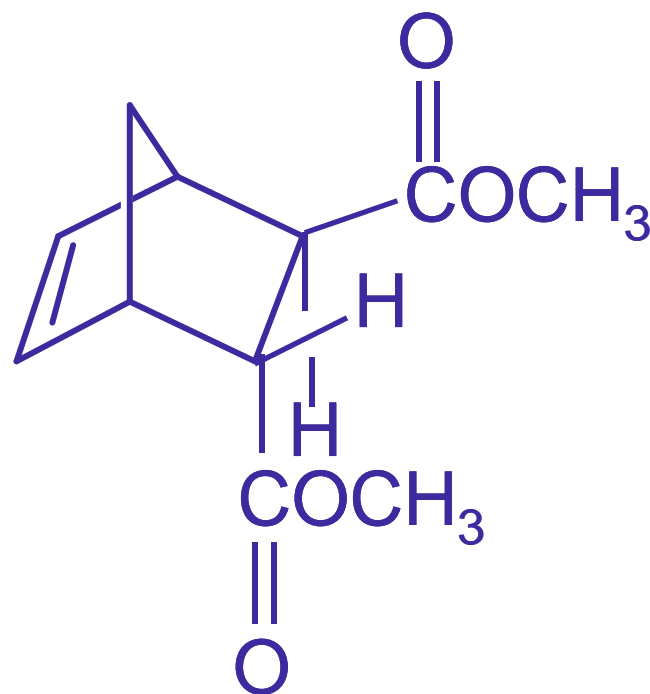
Cyclic dienes yield bridged bicyclic
Diels-Alder adducts.

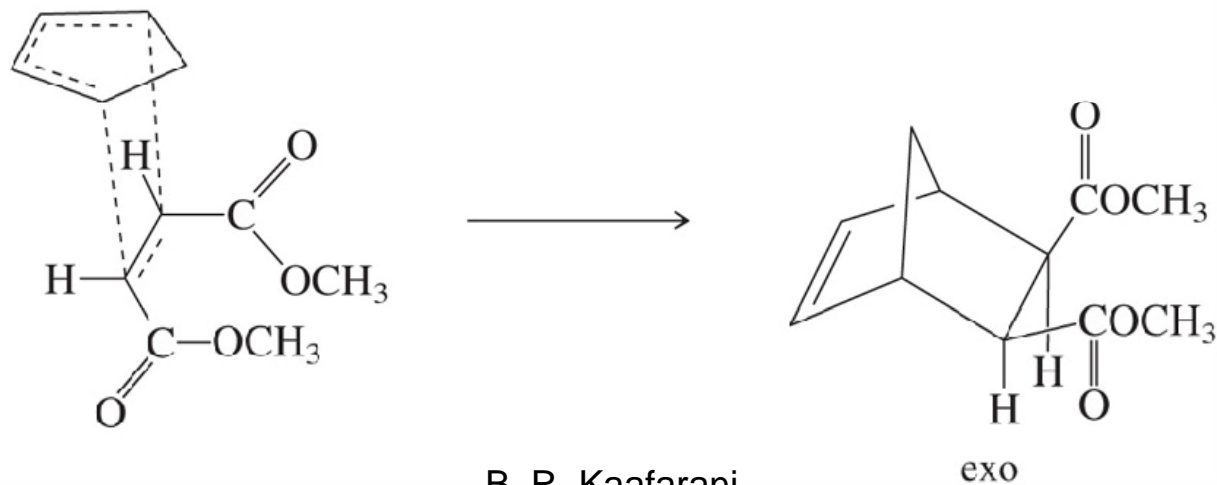
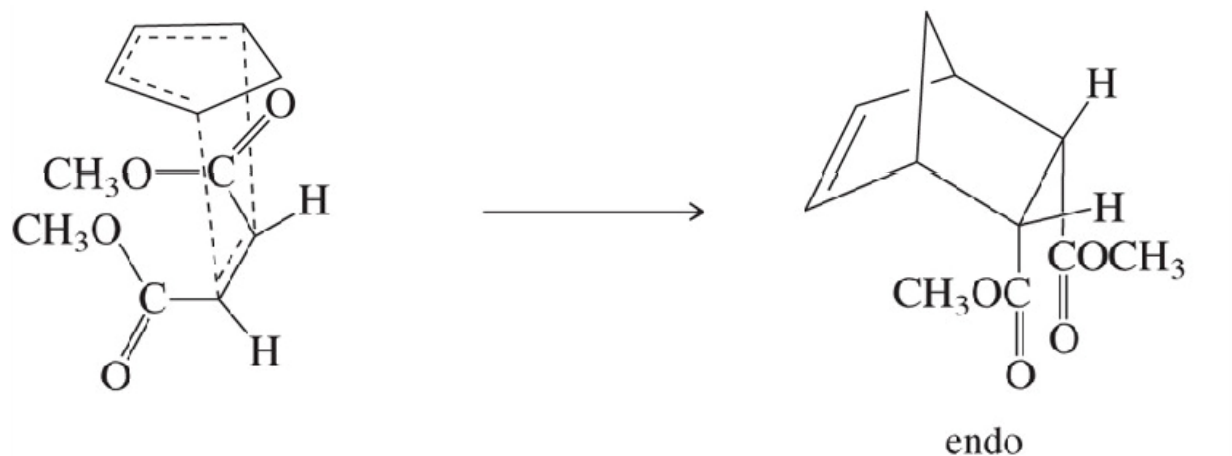
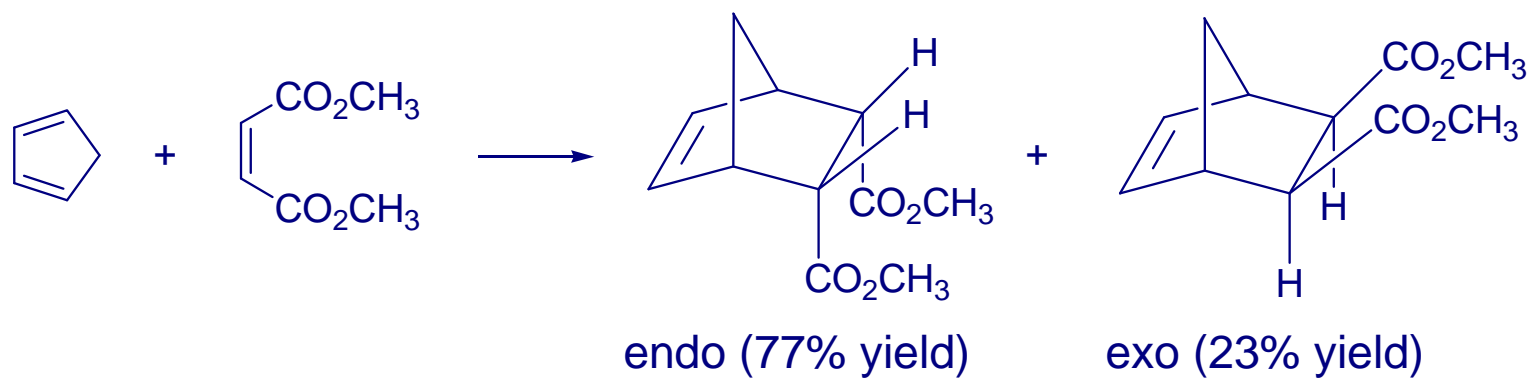






is the
same as



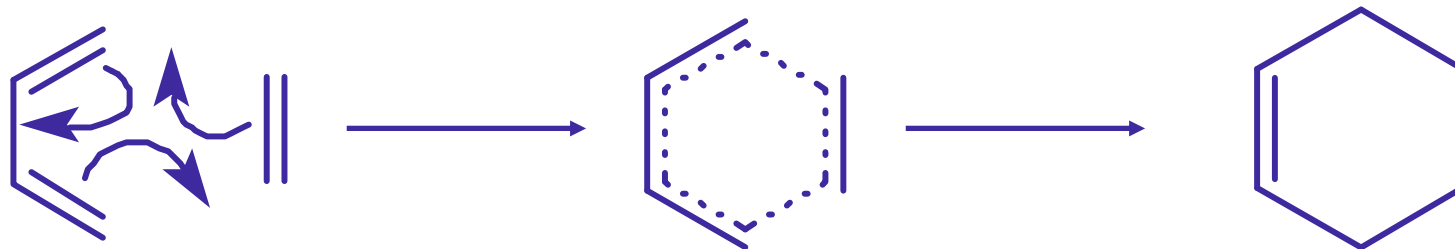


10.14
The π Molecular Orbitals
of
Ethylene and 1,3-Butadiene

Orbitals and Chemical Reactions

- A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.
- Electrons flow from the highest occupied molecular orbital (HOMO) of one reactant to the lowest unoccupied molecular orbital (LUMO) of the other.

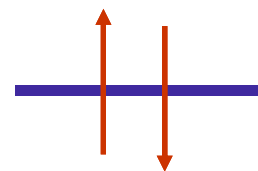
Orbitals and Chemical Reactions



- We can illustrate HOMO-LUMO interactions by way of the Diels-Alder reaction between ethylene and 1,3-butadiene.
- We need only consider only the π -electrons of ethylene and 1,3-butadiene. We can ignore the framework of σ bonds in each molecule.

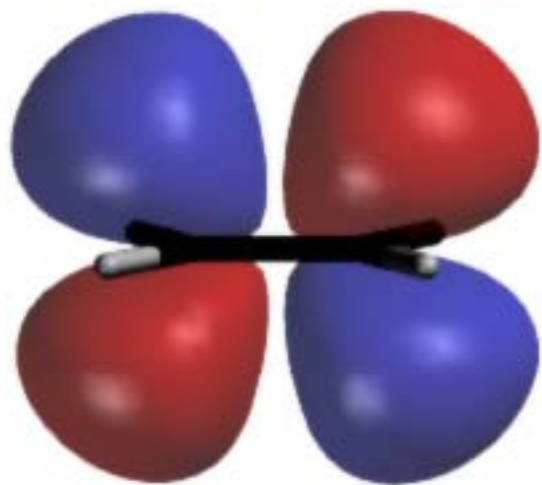
The π MO's of Ethylene

- Red and blue colors distinguish sign of wave function.
- Bonding π MO is antisymmetric with respect to plane of molecule.



Bonding π orbital of ethylene;
two electrons in this orbital.

The π MO's of Ethylene



Antibonding π orbital of ethylene;
no electrons in this orbital.

LUMO —————



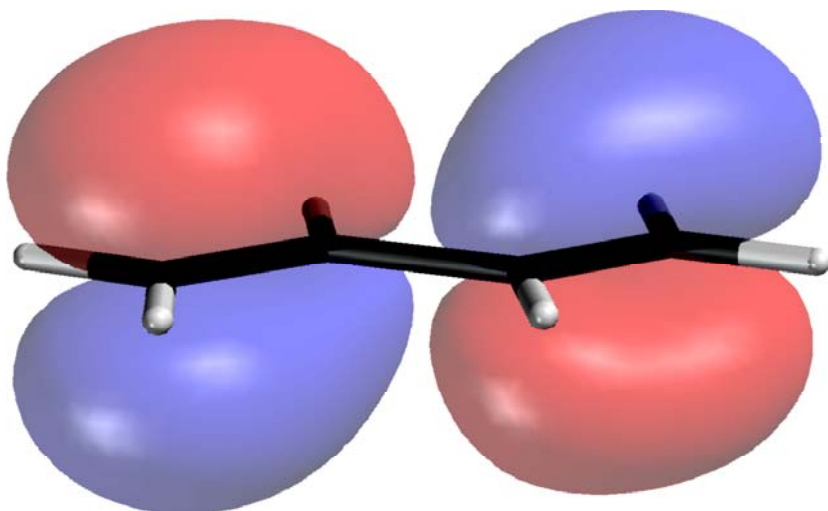
HOMO ————
↑ ↓

Bonding π orbital of ethylene;
two electrons in this orbital.

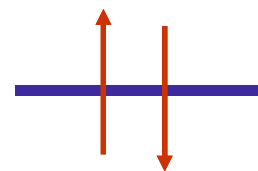
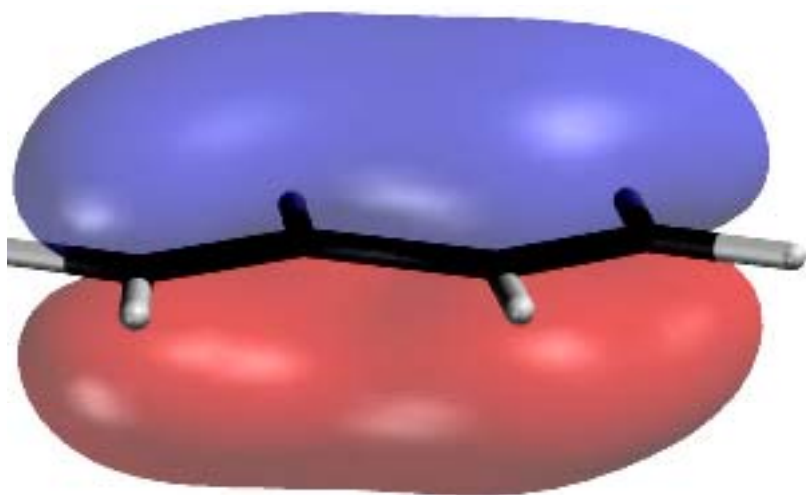
The π MO's of 1,3-Butadiene

- Four p orbitals contribute to the π system of 1,3-butadiene; therefore, there are four π molecular orbitals.
- Two of these orbitals are bonding; two are antibonding.

The Two Bonding π MOs of 1,3-Butadiene

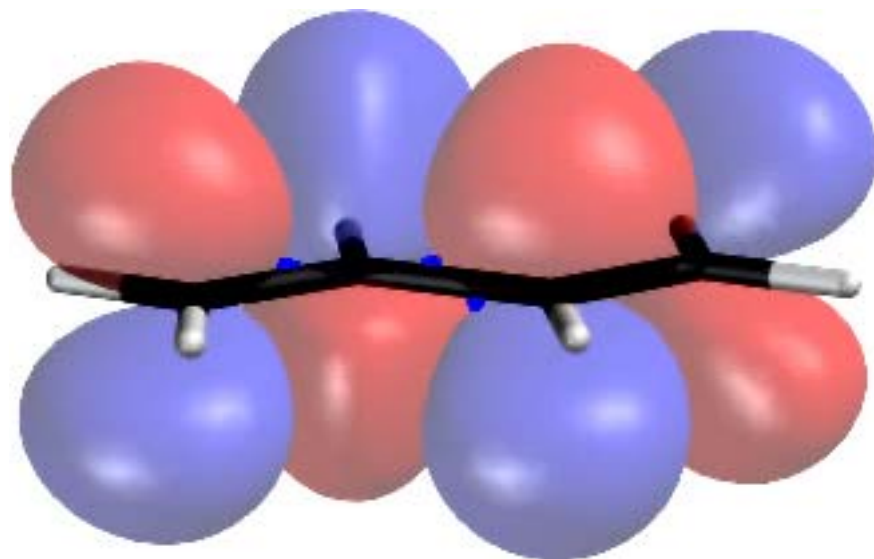


4 π electrons; 2 in each orbital

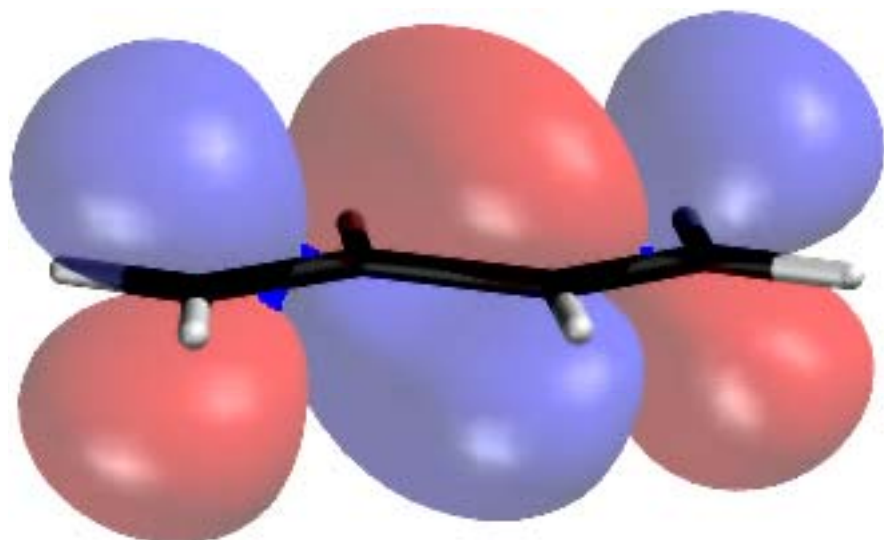


Lowest energy orbital

The Two Antibonding π MOs of 1,3-Butadiene



Highest energy orbital

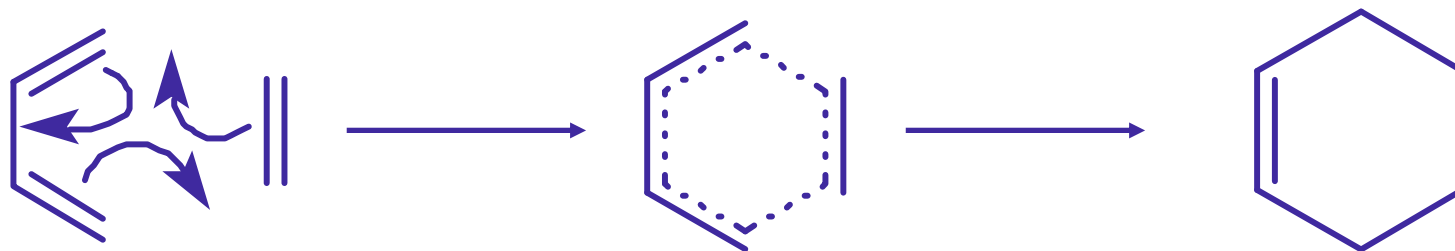


LUMO

Both antibonding
orbitals are vacant

10.17
A π Molecular Orbital Analysis
of the
Diels-Alder Reaction

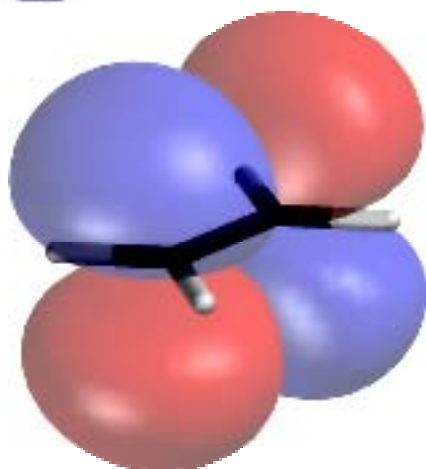
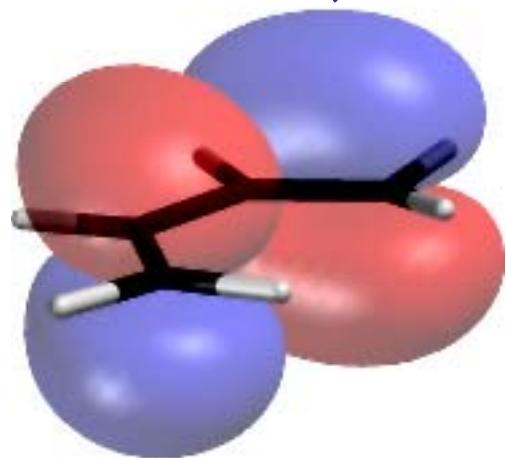
MO Analysis of Diels-Alder Reaction



- Inasmuch as electron-withdrawing groups increase the reactivity of a dienophile, we assume electrons flow from the HOMO of the diene to the LUMO of the dienophile.

MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene



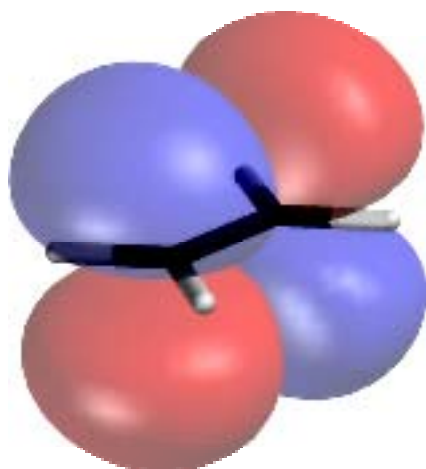
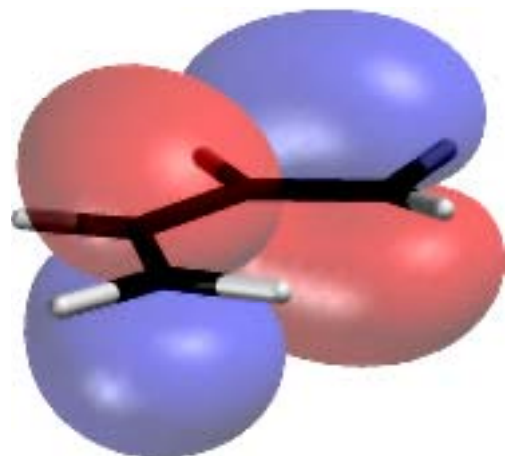
LUMO of ethylene (dienophile)

HOMO of 1,3-butadiene and LUMO of ethylene are in phase with one another.

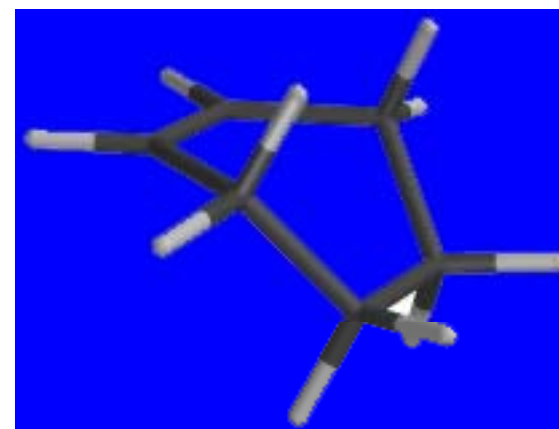
Allows σ bond formation between the alkene and the diene.

MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene

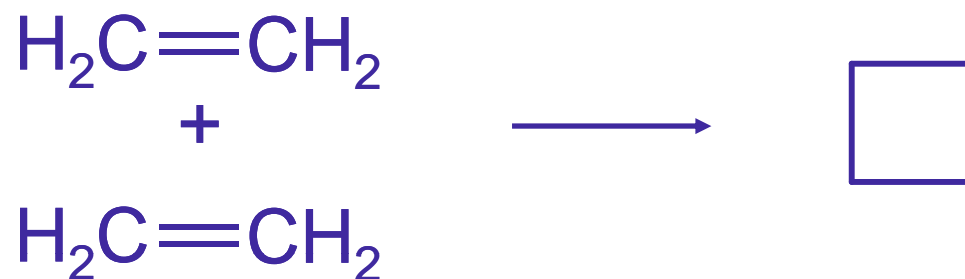


LUMO of ethylene (dienophile)



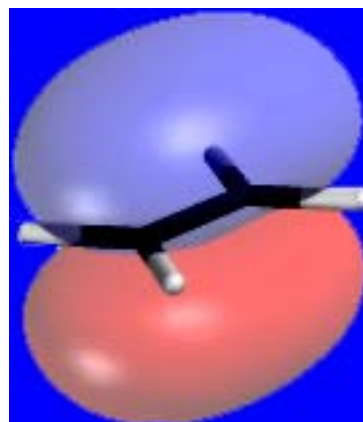
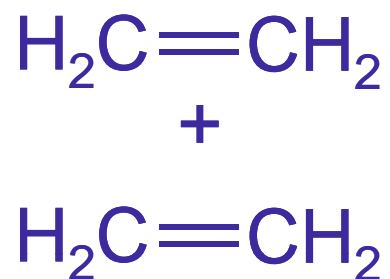
Woodward-Hoffmann rules

A "forbidden" reaction

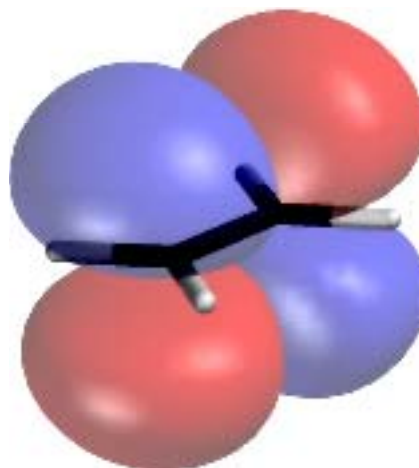


- The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions. Why not?

A "forbidden" reaction



HOMO of
one ethylene
molecule



LUMO of
other ethylene
molecule

➤ HOMO-LUMO mismatch of two ethylene molecules precludes single-step formation of two new σ bonds.