Lecture 7

Dienes

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Classification of Dienes

- isolated diene

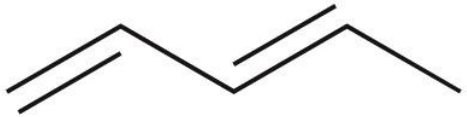
- conjugated diene

- cumulated diene

Classes of Dienes

- There are three categories for dienes

Cumulated



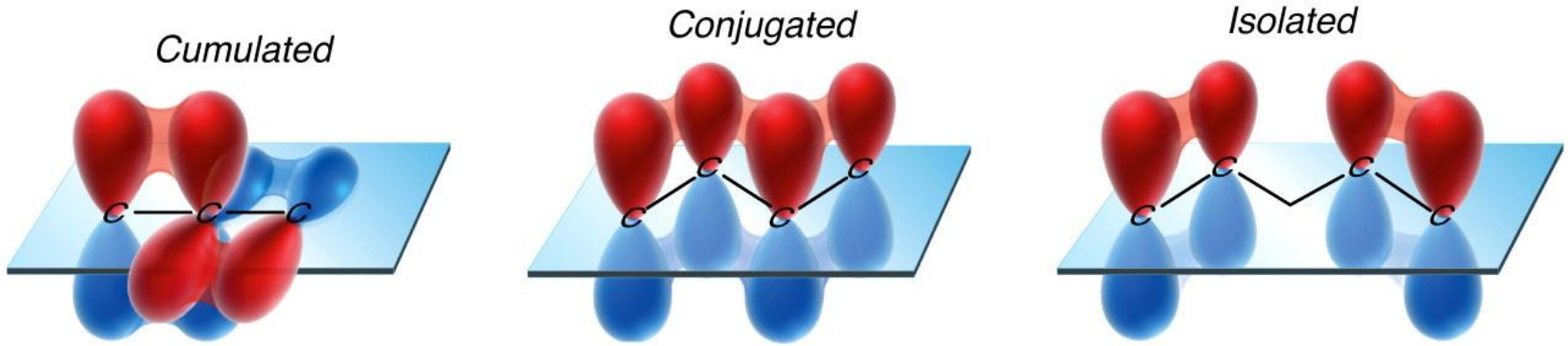
Conjugated

Isolated

- Cumulated – pi bonds are adjacent
- Conjugated – pi bonds are separated by exactly ONE single bond
- Isolated – pi bonds are separated by any distance greater than ONE single bond

Classes of Dienes

- There are three categories for dienes



- Conjugated – pi bond overlap extends over the entire system
- Isolated – pi bonds are separated by too great a distance to experience extra overlap

Nomenclature

▶(2*E*,5*E*)-2,5-heptadiene

▶(2*E*,4*E*)-2,4-heptadiene

▶3,4-heptadiene

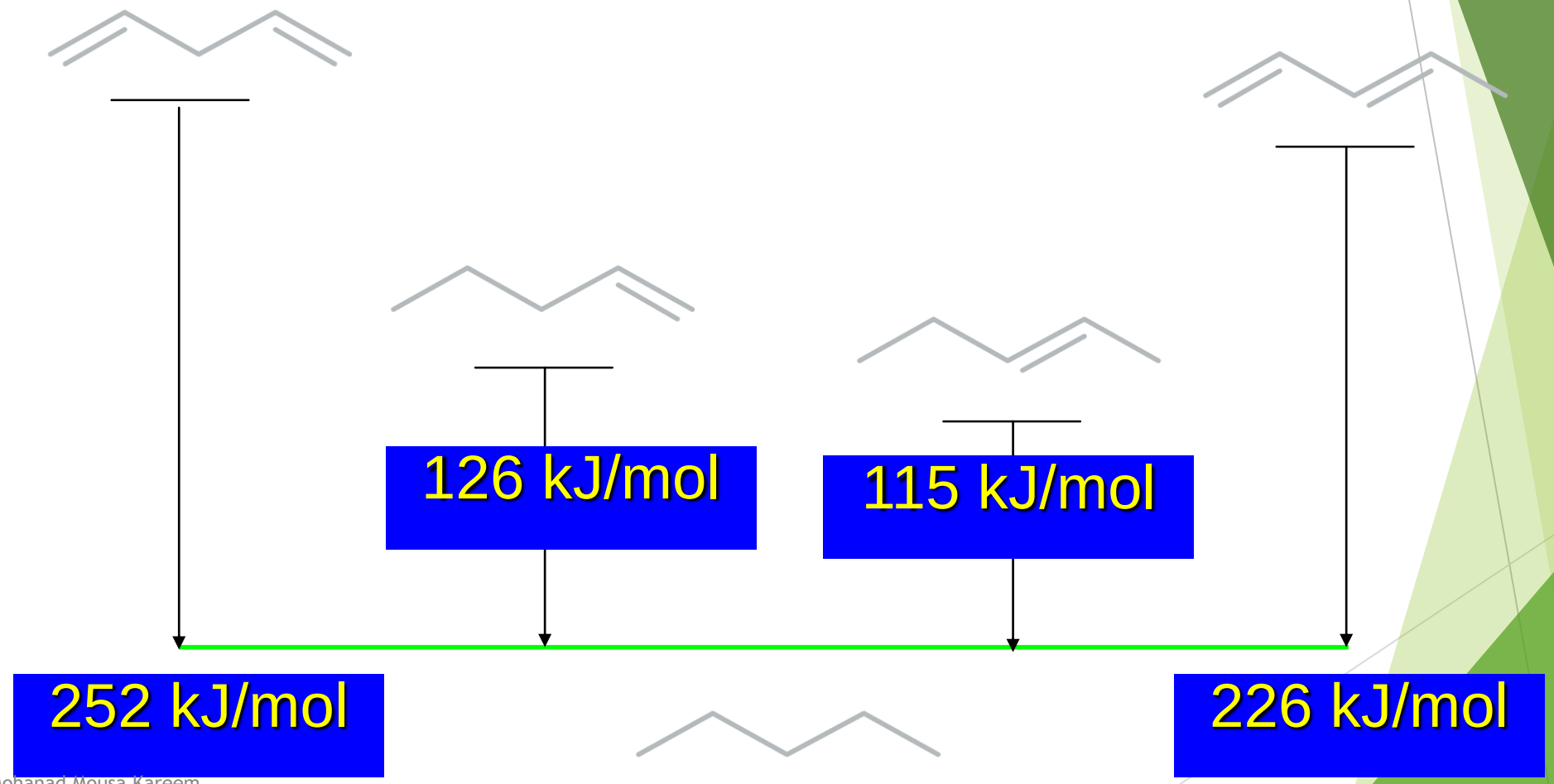
Heats of Hydrogenation

252 kJ/mol

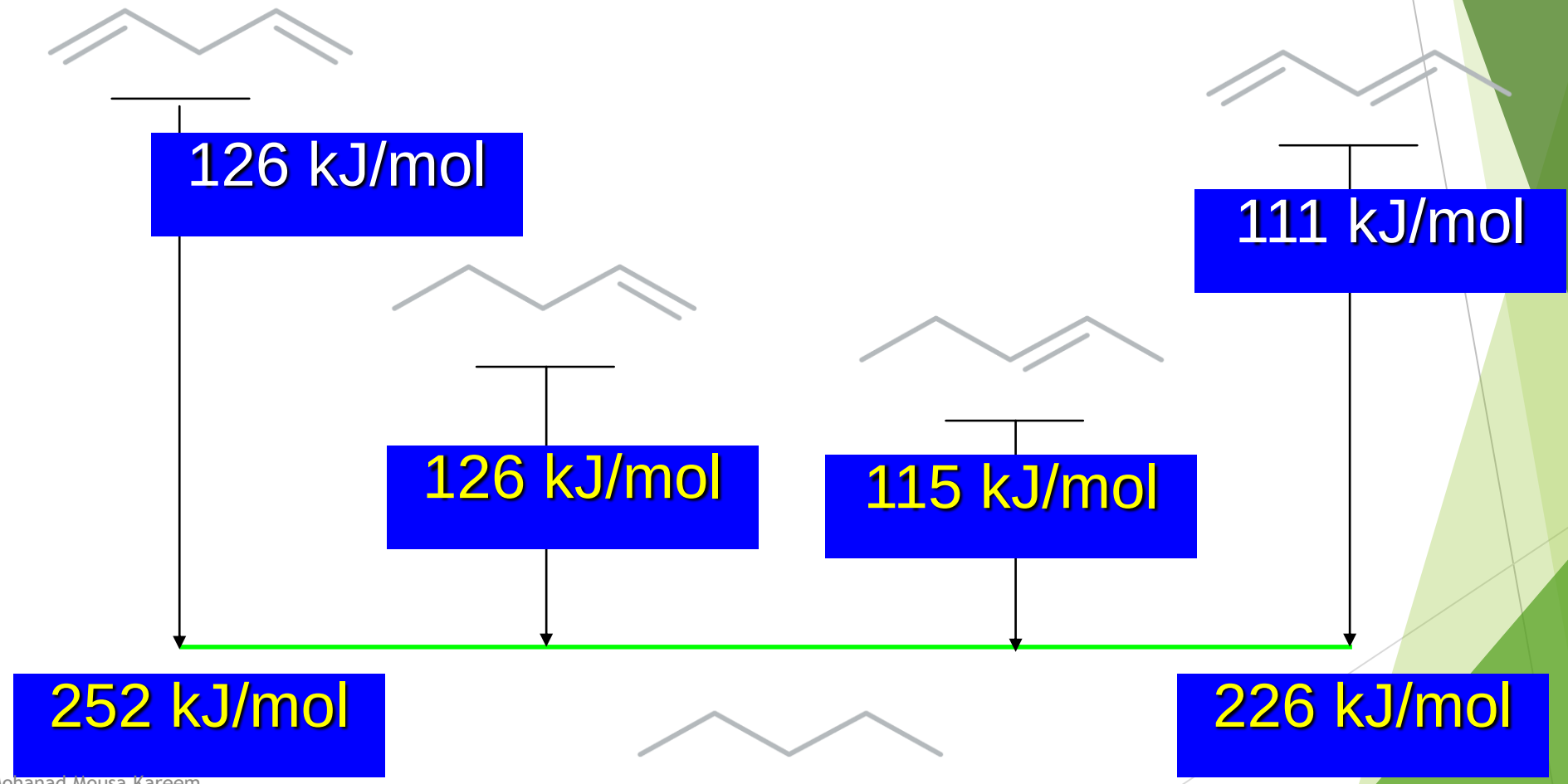
- 1,3-pentadiene is 26 kJ/mol more stable than 1,4-pentadiene, but some of this stabilization is because it also contains a more highly substituted double bond

226 kJ/mol

Heats of Hydrogenation



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

Heats of Hydrogenation

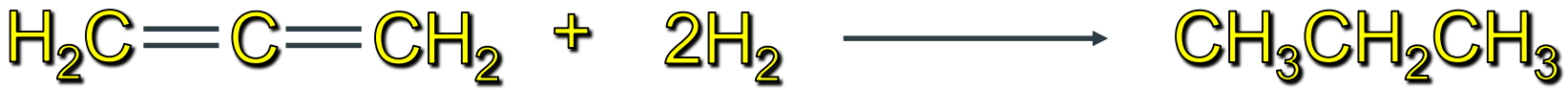
126 kJ/mol

111 kJ/mol

- 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

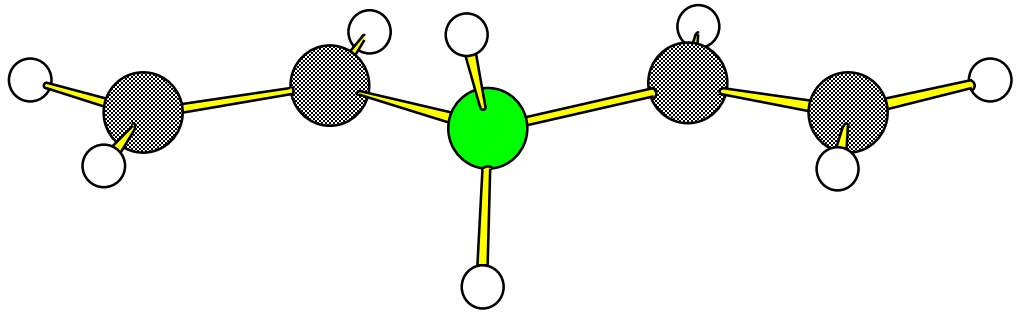


ΔH° = -295 kJ

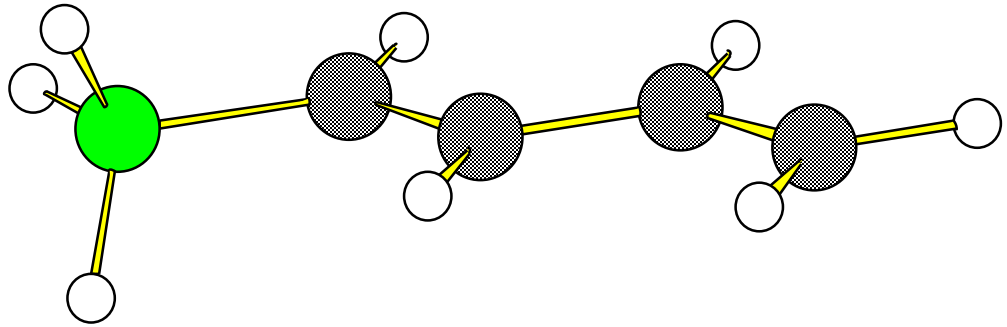
ΔH° = -125 kJ

Bonding in Conjugated Dienes

Isolated diene



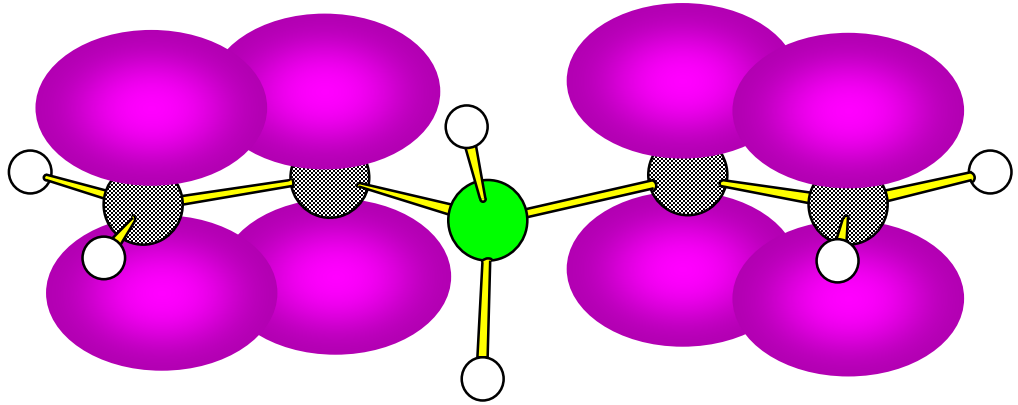
1,4-pentadiene



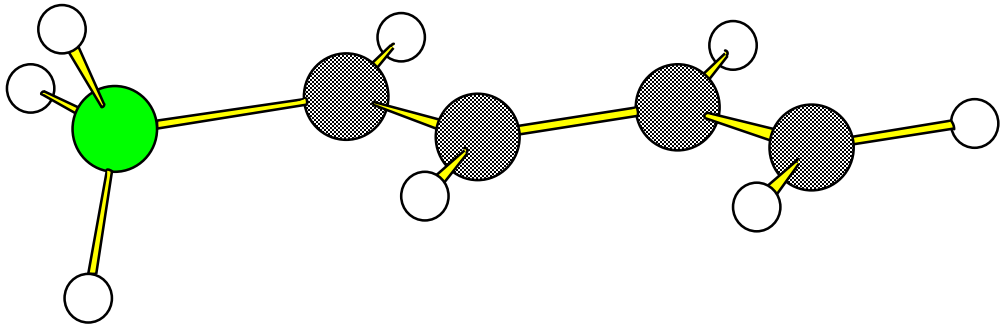
1,3-pentadiene

Conjugated diene

Isolated diene



π bonds are independent of each other



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Conjugated diene

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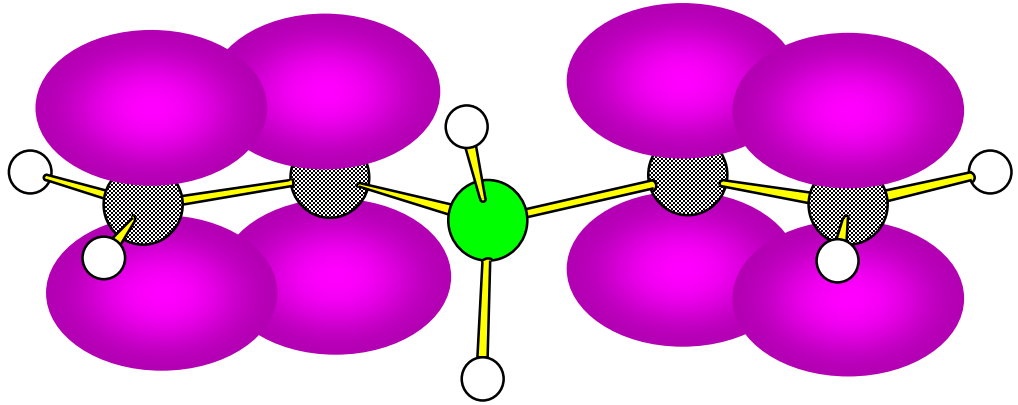

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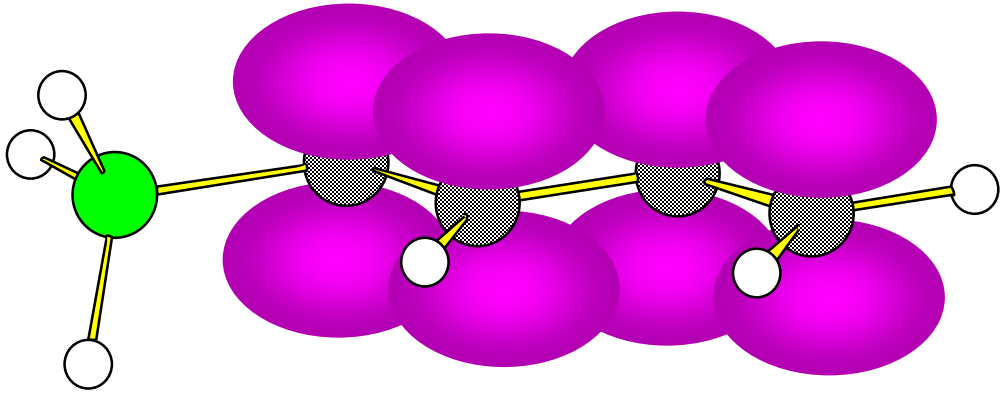
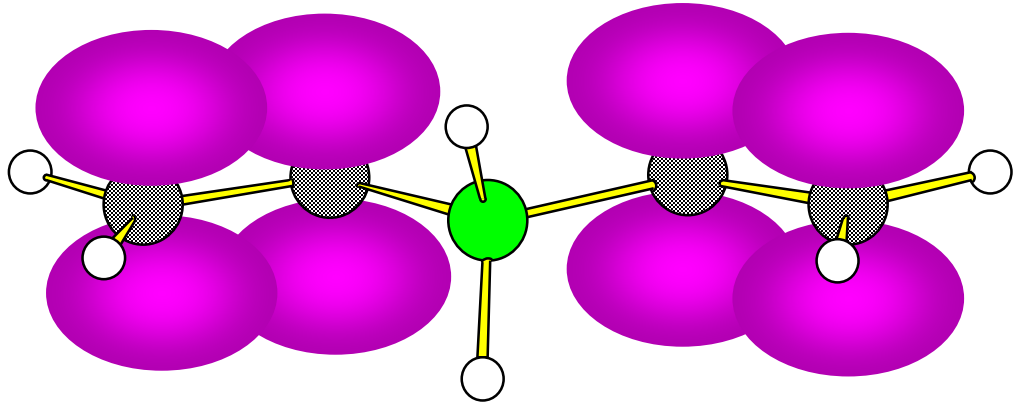


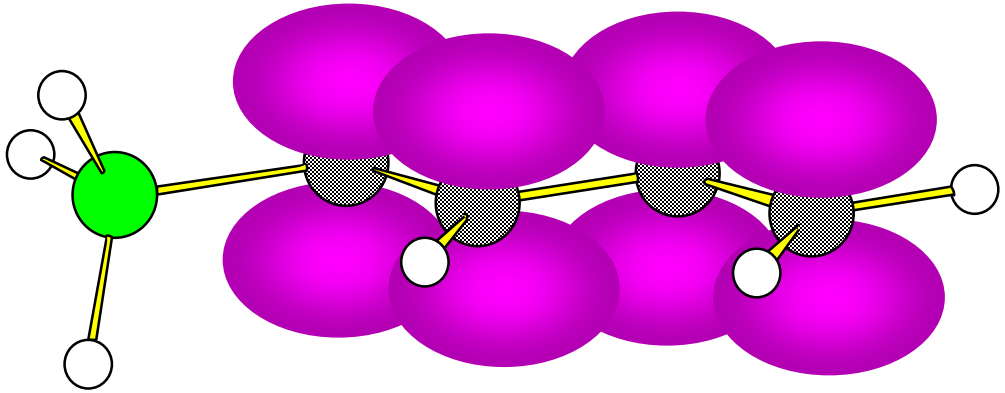
p orbitals overlap to give extended π bond encompassing four carbons

Conjugated diene

Isolated diene



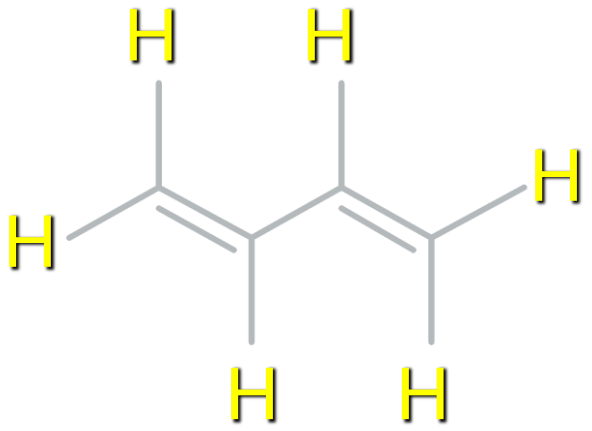
less electron delocalization; less stable



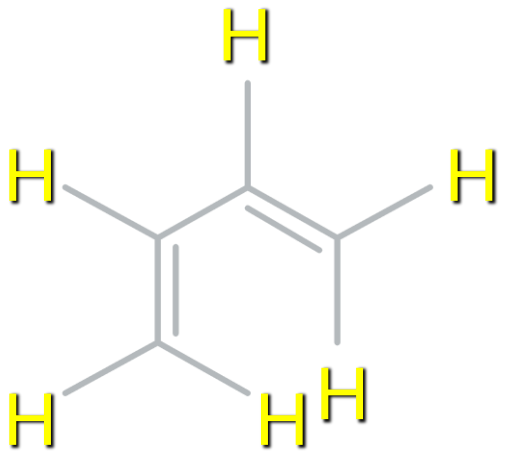
more electron delocalization; more stable

Conjugated diene

Conformations of Dienes



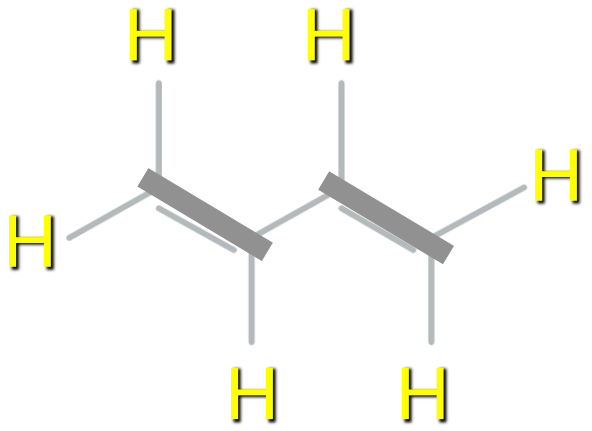
s-trans



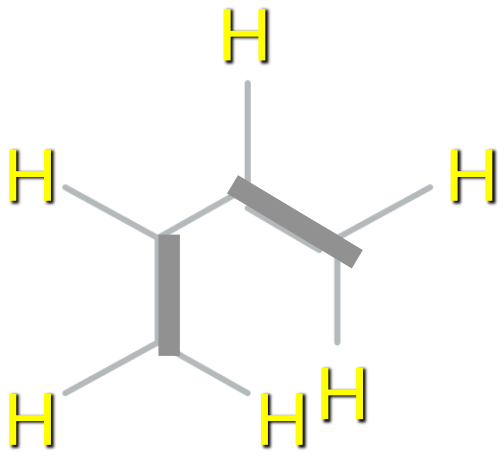
s-cis

- *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



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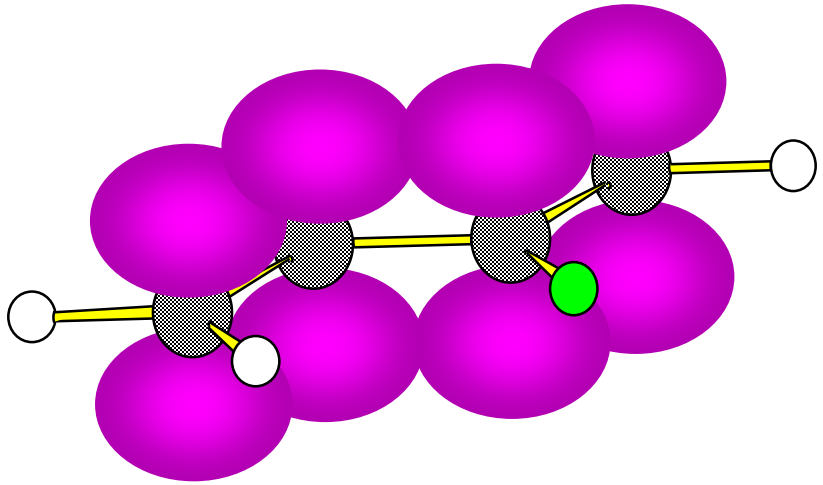
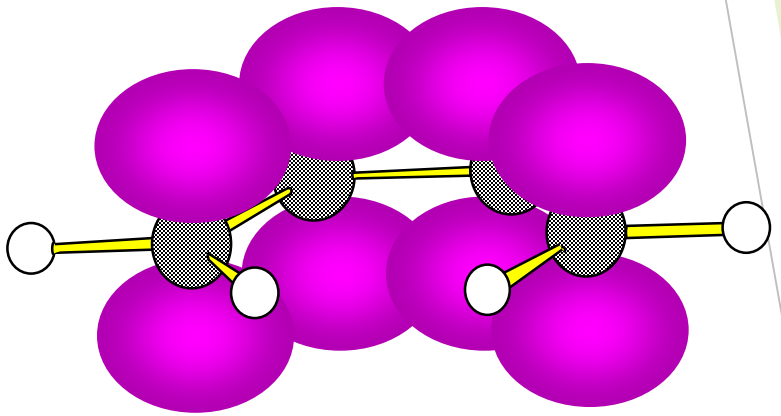
Conformations of Dienes



s-trans

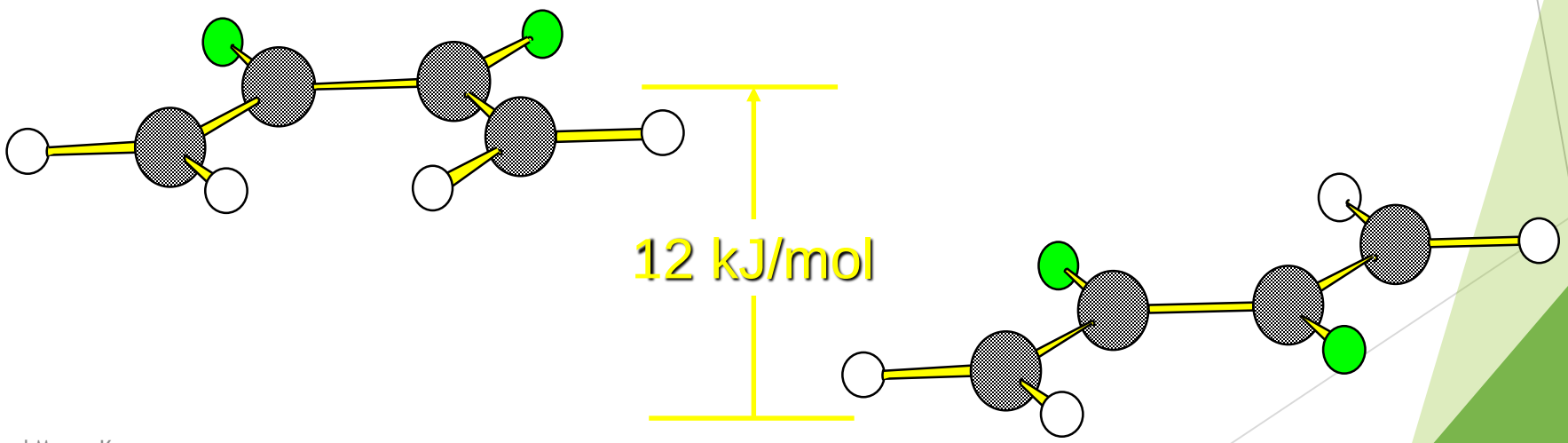


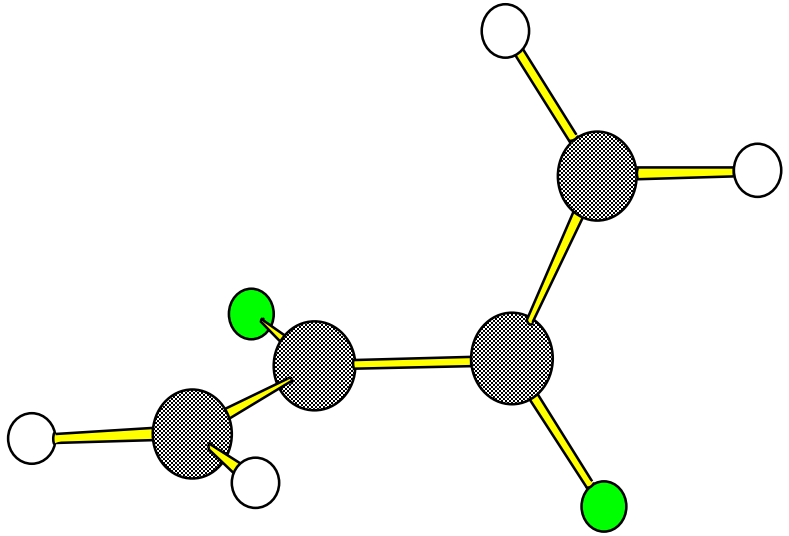
s-cis

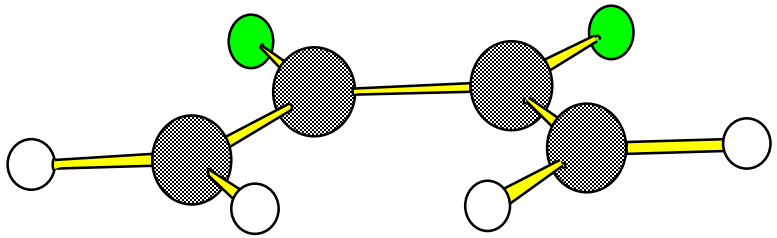
- Both conformations allow electron delocalization via overlap of *p* orbitals to give extended π system

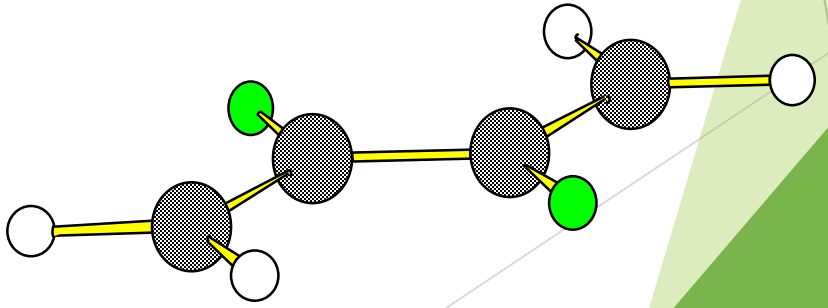
s-trans is more stable than s-cis

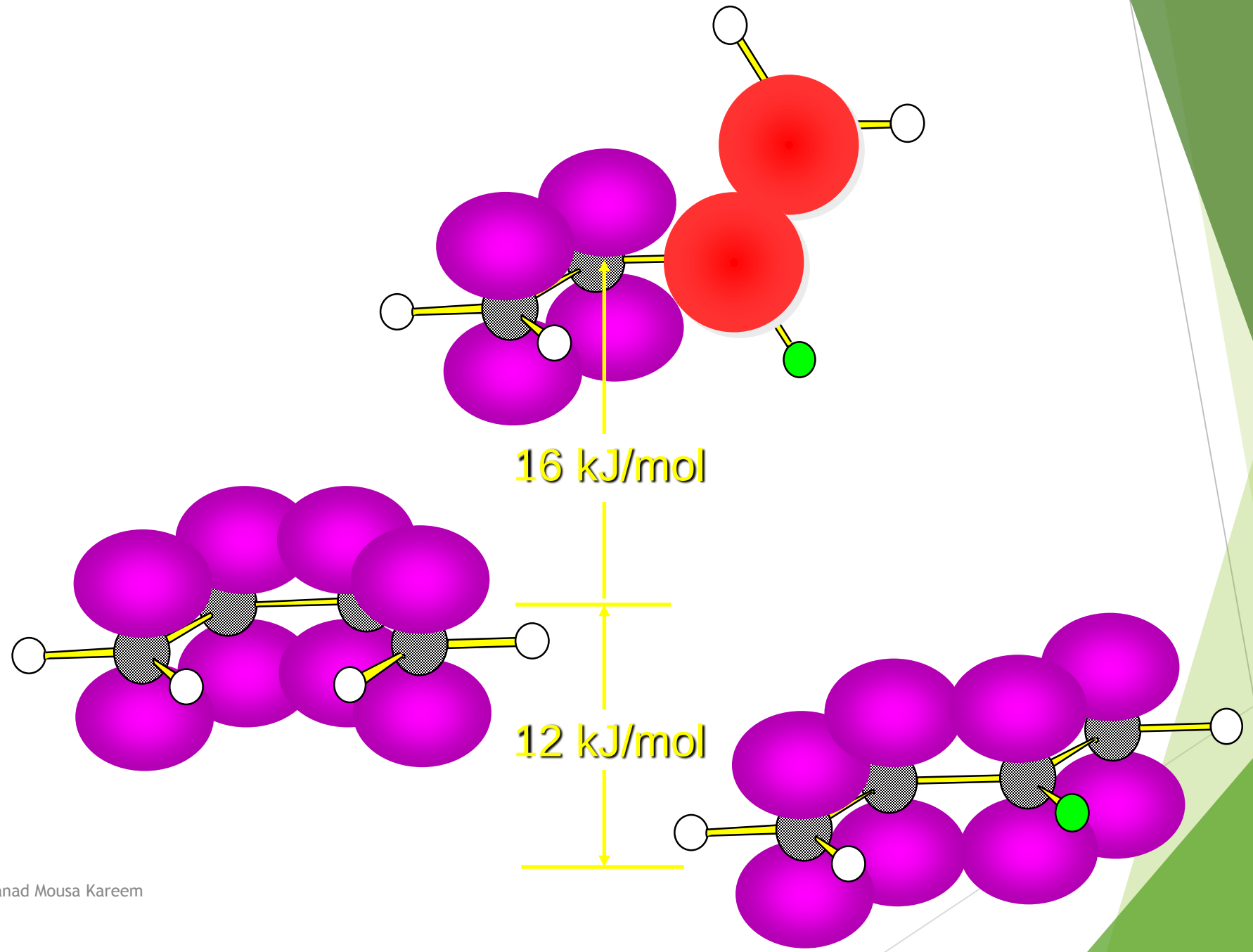
- Interconversion of conformations requires two π bonds to be at right angles to each other and prevents conjugation





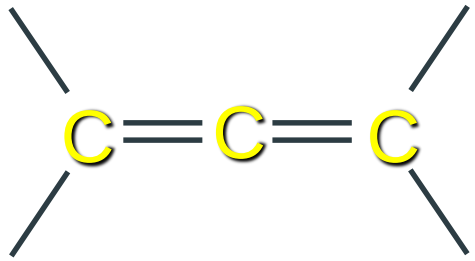





16 kJ/mol
12 kJ/mol

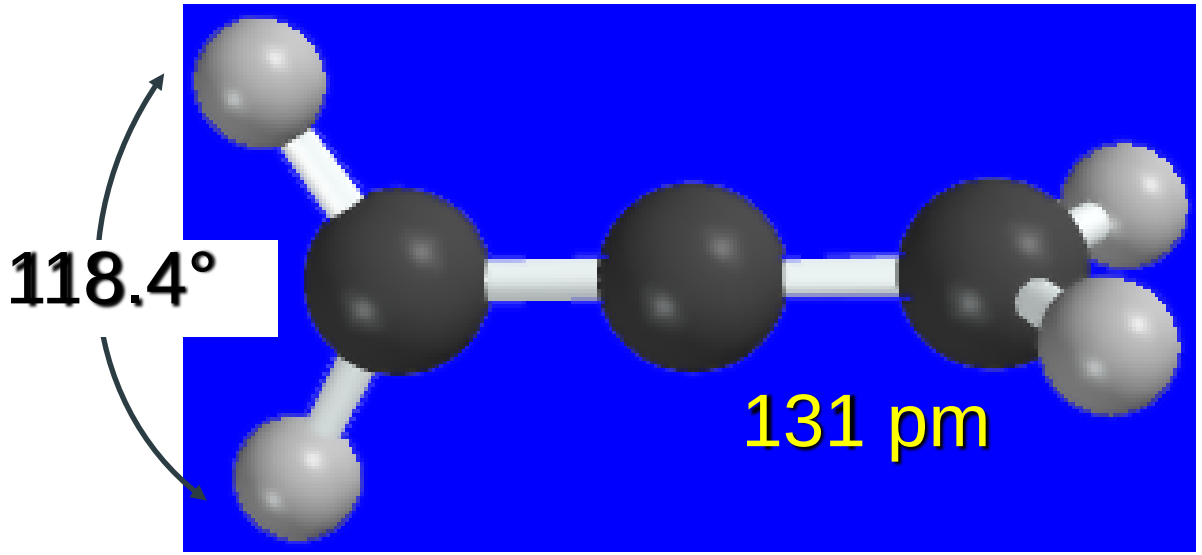
Bonding in Allenes

Cumulated Dienes



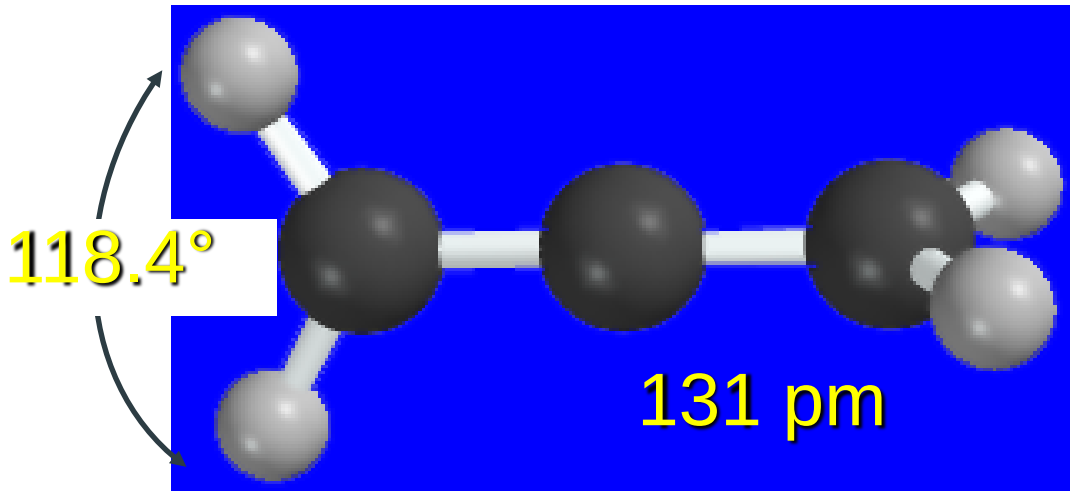
- cumulated dienes are less stable than isolated and conjugated dienes

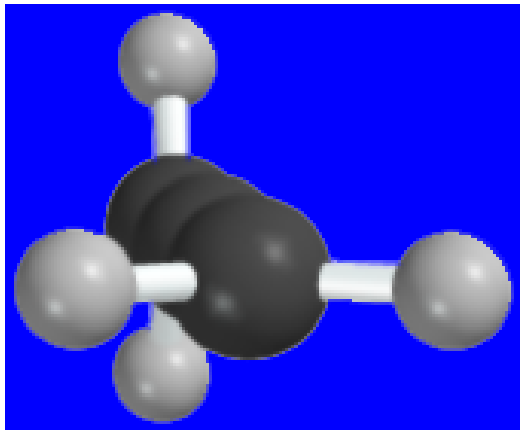
Structure of Allene



- linear arrangement of carbons
- nonplanar geometry

Structure of Allene





- linear arrangement of carbons
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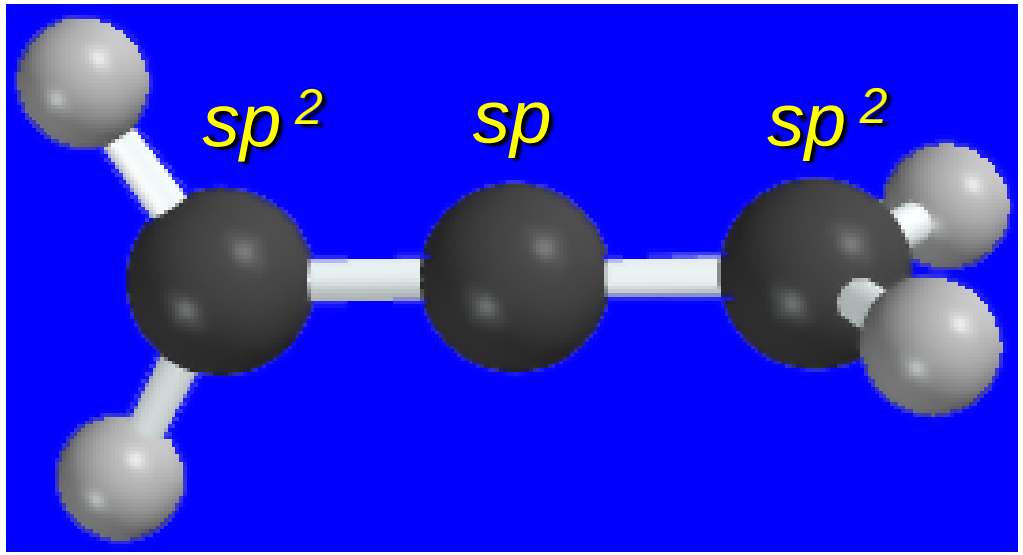
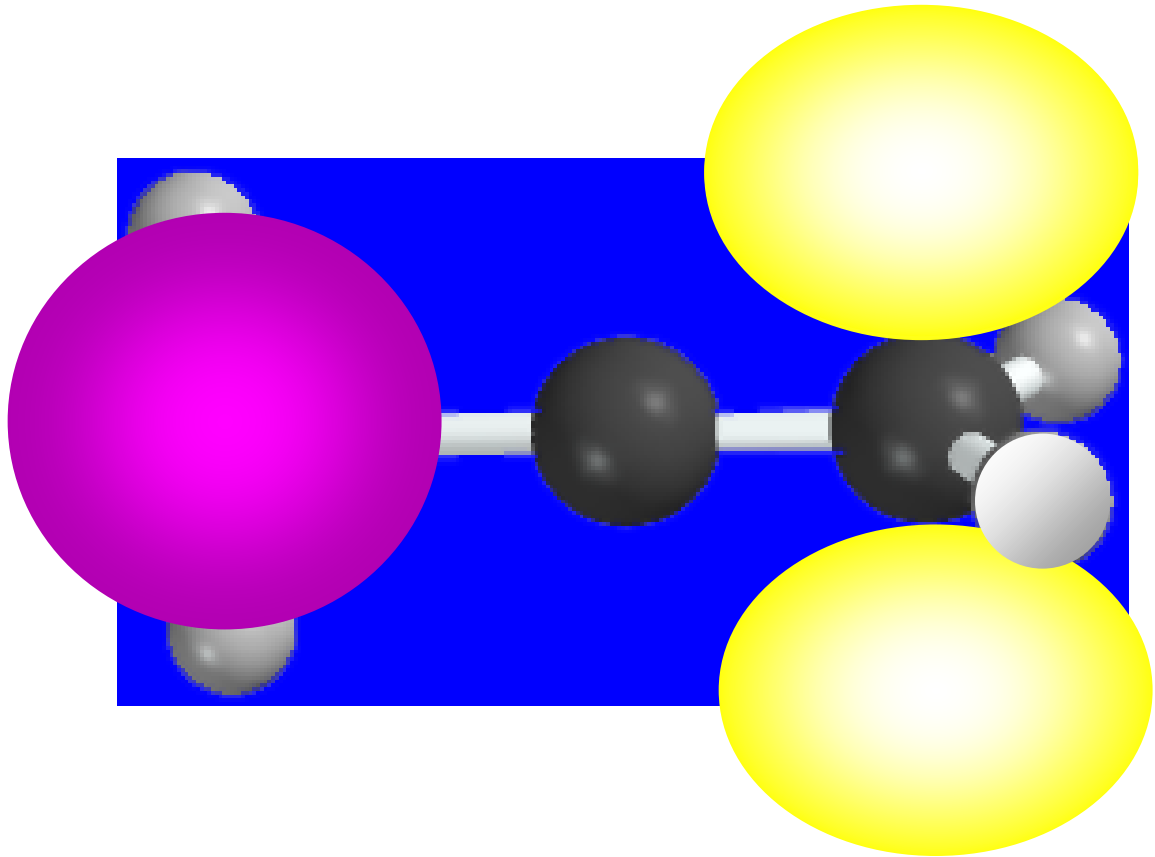
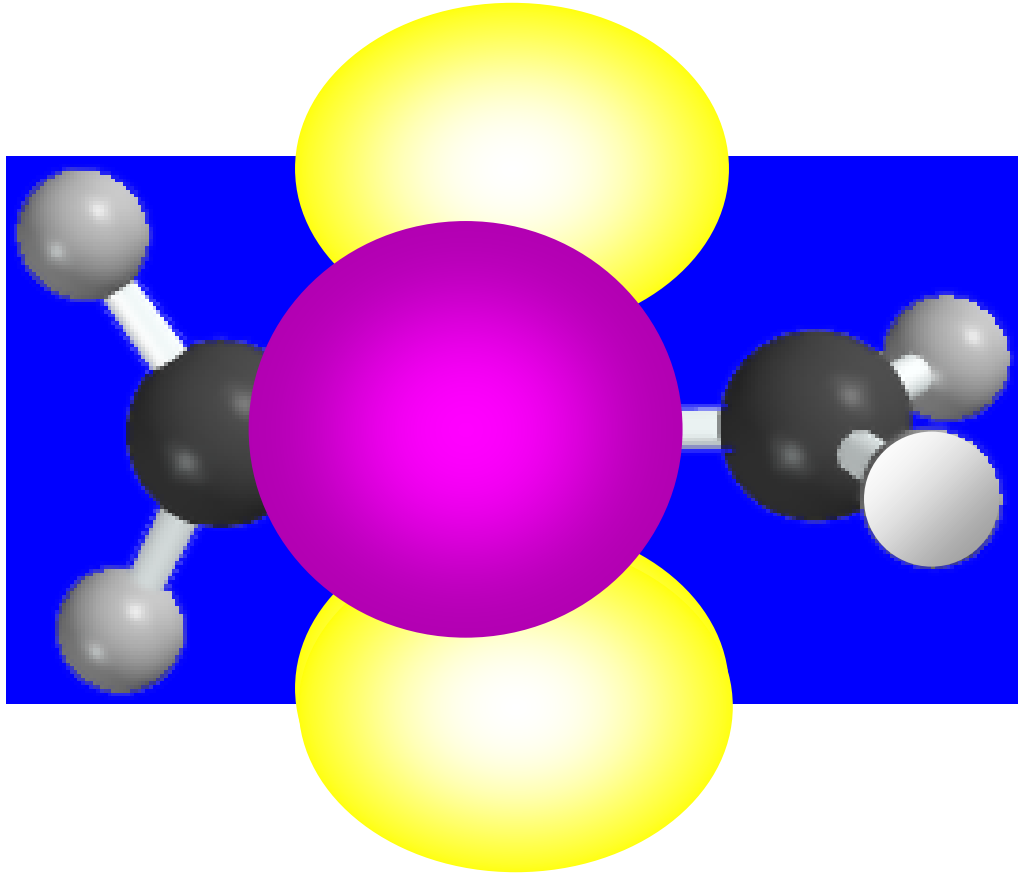
Bonding in Allene



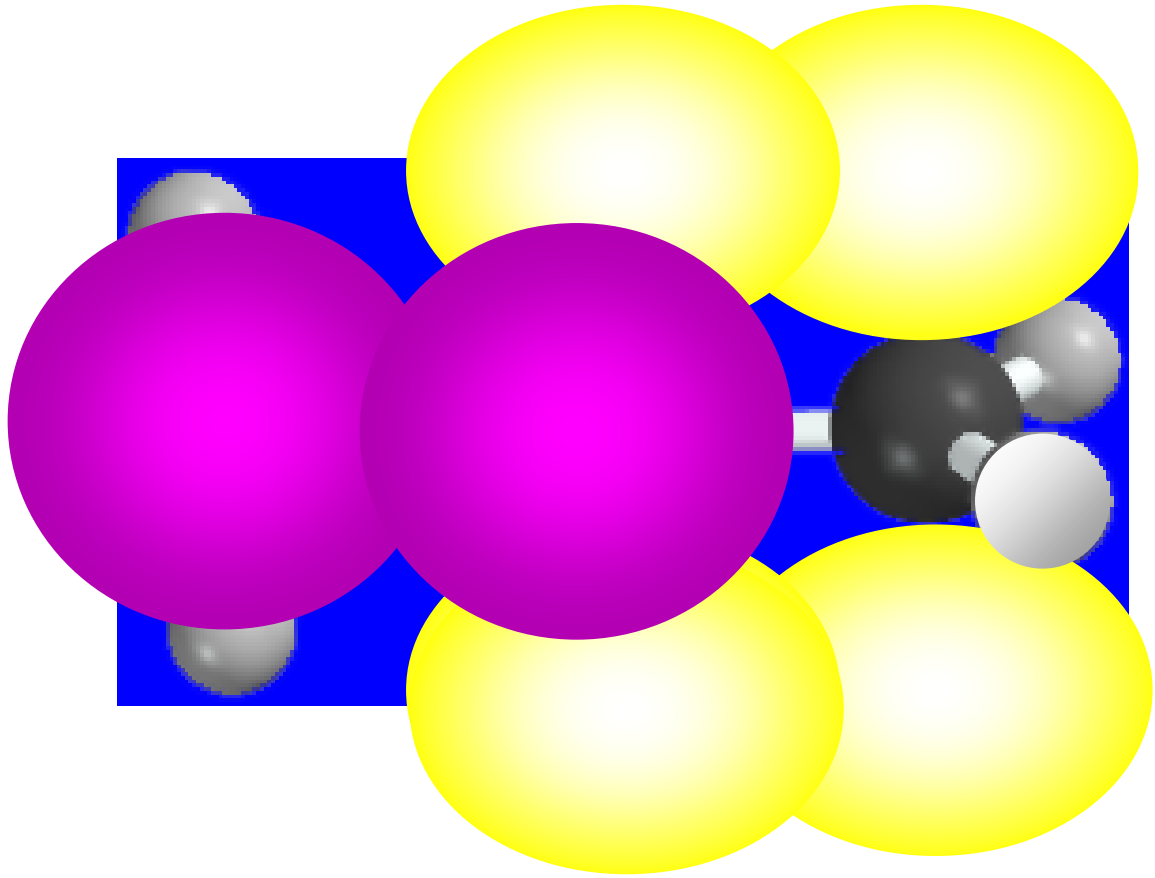
Bonding in Allene



Bonding in Allene

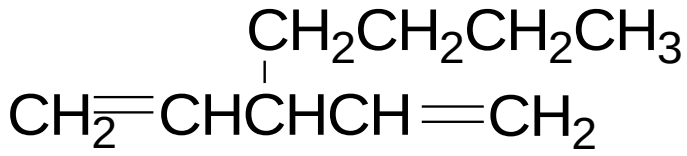


Bonding in Allene



IUPAC Nomenclature of Dienes

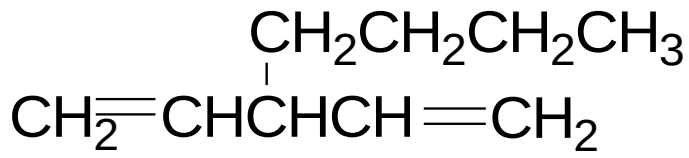
1. Find the longest chain containing both double bonds



3-butyl-1,4-pentadiene

IUPAC Nomenclature of Dienes

2. Use corresponding alkane name but replace the "*ne*" ending with "*diene*"

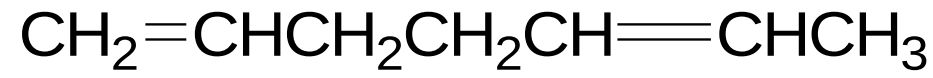


3-butyl-1,4-pentadiene

"pentane" changed to "pentadiene"

IUPAC Nomenclature of Dienes

3. Number in the direction that gives the lowest number to a double bond

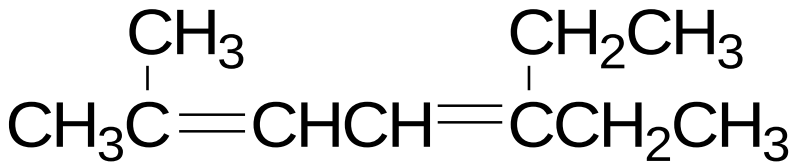


1,5-heptadiene

not 2,6-heptadiene

IUPAC Nomenclature of Dienes

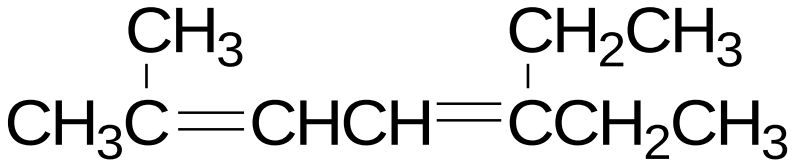
4. List substituents in alphabetical order



5-ethyl-2-methyl-2,4-heptadiene

IUPAC Nomenclature of Dienes

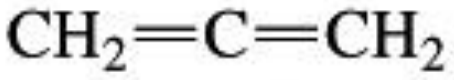
5. Place numbers indicating the double bond positions either in front of the parent compound or in the middle of the name immediately before the *diene* suffix



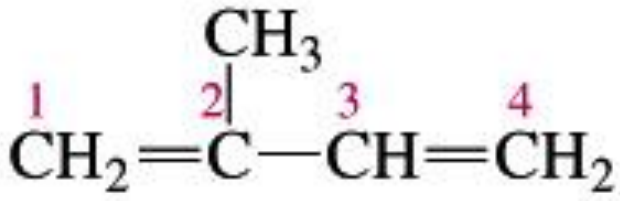
5-ethyl-2-methyl-2,4-heptadiene

or 5-ethyl-2-methyl-hepta-2,4,-diene

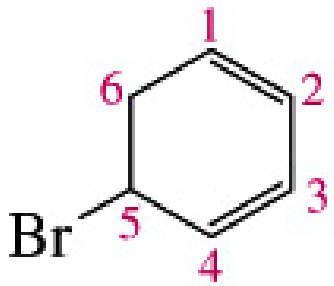
IUPAC Nomenclature of Dienes



systematic: propadiene
common: allene

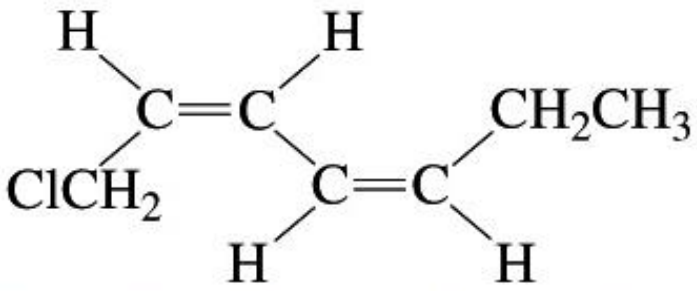


2-methyl-1,3-butadiene
isoprene

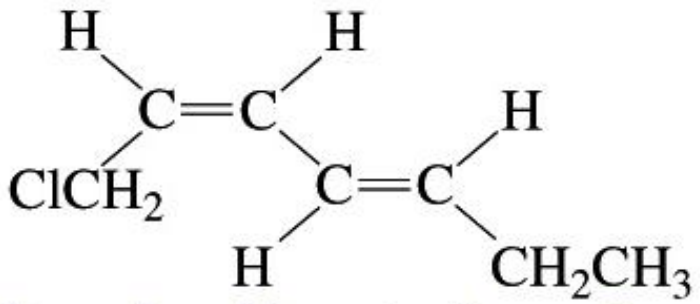


5-bromo-1,3-cyclohexadiene

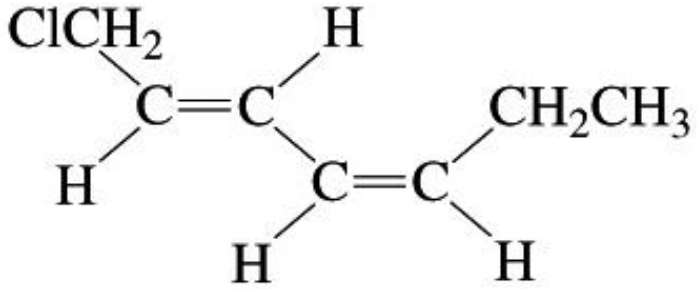
Configurational Isomers of Dienes



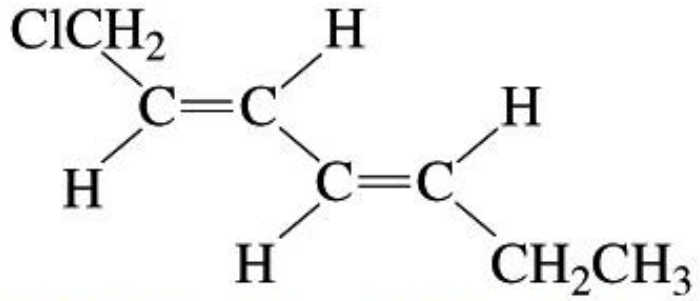
(2*Z*,4*Z*)-1-chloro-2,4-heptadiene



(2*Z*,4*E*)-1-chloro-2,4-heptadiene



(2*E*,4*Z*)-1-chloro-2,4-heptadiene



(2*E*,4*E*)-1-chloro-2,4-heptadiene

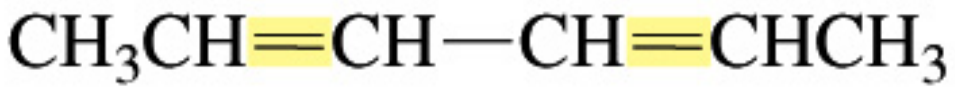
Types of Dienes

- When double bonds are separated by at least one sp^3 carbon, **isolated diene**

an isolated diene

Types of Dienes

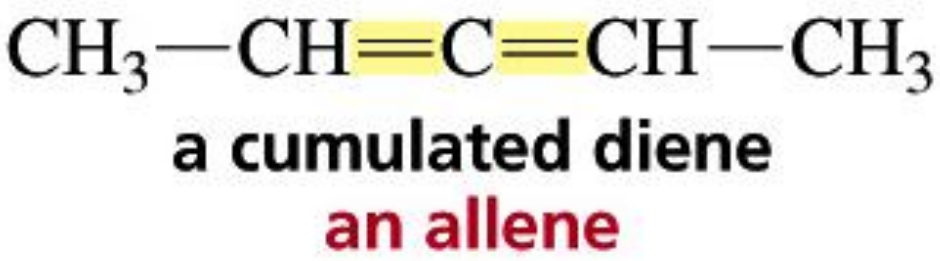
- When double bonds are separated by only one single bond (i.e. four sp^2 carbons in a row), **conjugated diene**



a conjugated diene

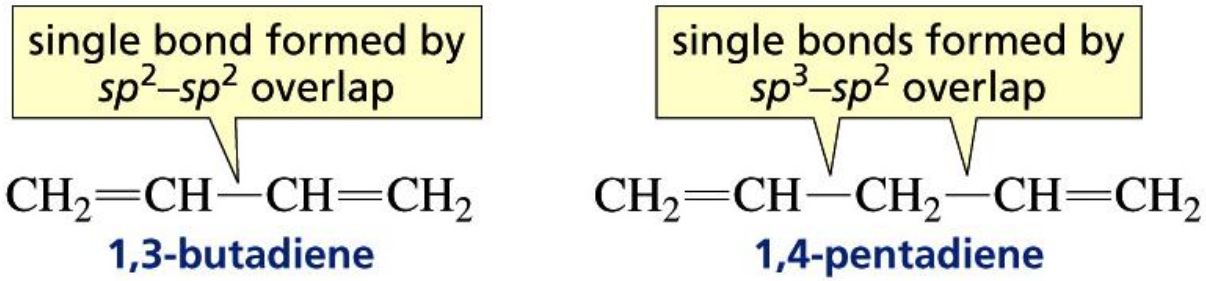
Types of Dienes

- When both sets of double bonds emanate from the same carbon, **cumulated diene**

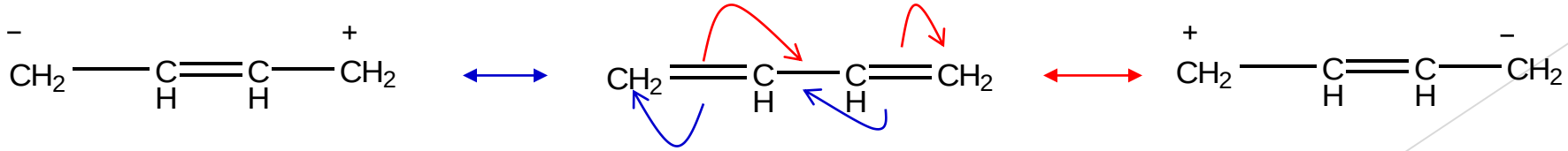


Relative Stabilities of Dienes

- Conjugated dienes are more stable than isolated dienes because
  - An sp^2-sp^2 single bond is shorter and stronger than a sp^3-sp^2 single bond

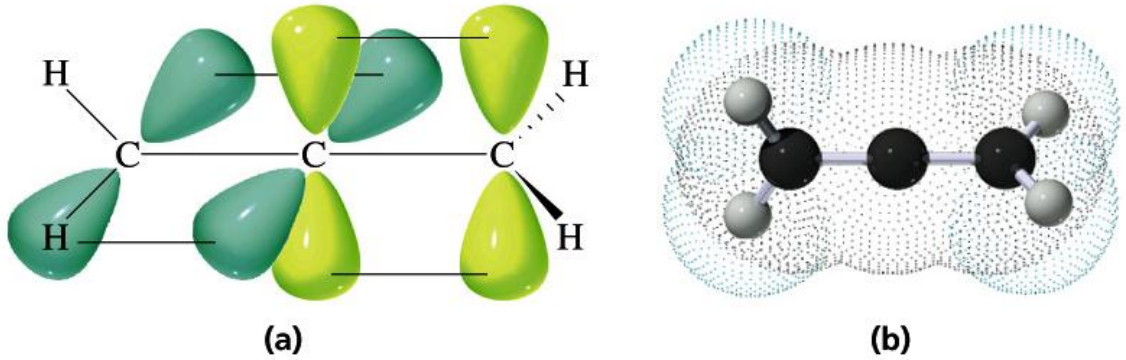


- Resonance also stabilizes the conjugated diene

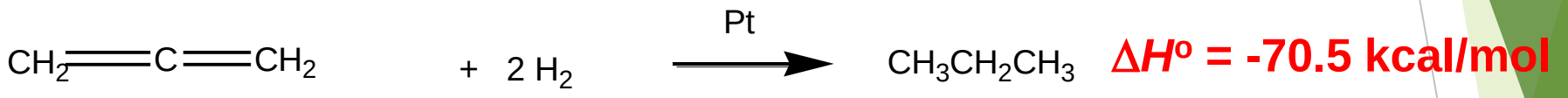


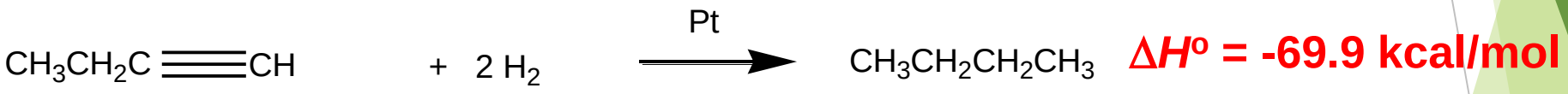
Relative Stabilities of Dienes

- Doubly-bonded carbons in isolated and conjugated dienes all are sp^2 hybridized
- The central carbon in a cumulated diene is *sp* hybridized



Relative Stabilities of Dienes





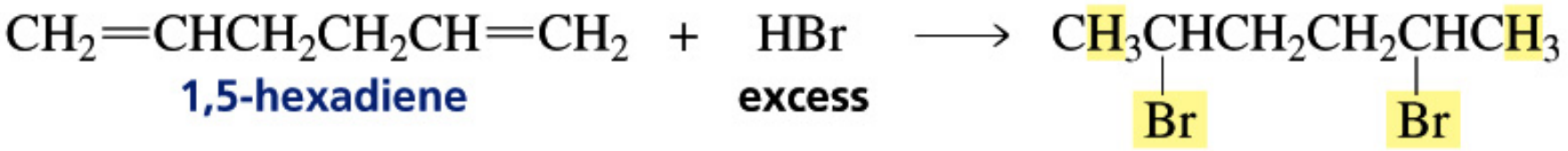
- The heat of hydrogenation of allene is similar to that of 1-butyne; both have at least one *sp* carbon
- Additional reactivity of cumulated dienes will not be considered in this course

Reactivity Considerations

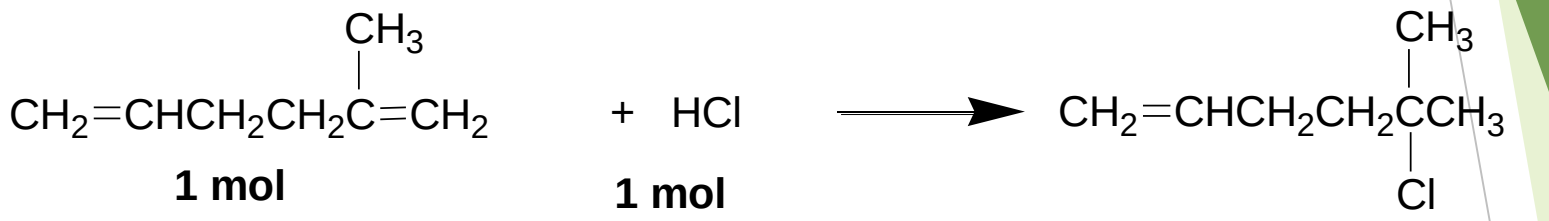
- Dienes, like alkenes and alkynes, are nucleophilic - they have π electrons to contribute to bonding

Electrophilic Addition Reactions of Isolated Dienes

- Reaction of 1,5-hexadiene with excess HBr adds HBr independently to each double bond
- Markovnikov's Rule is followed



Electrophilic Addition Reactions of Isolated Dienes



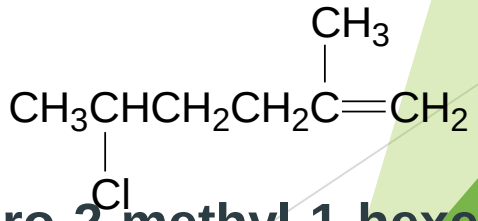
2-methyl-1,5-hexadiene

5-chloro-5-methyl-1-hexene

major product

If there is only enough electrophile to add to one double bond, a mixture of products will be obtained

+

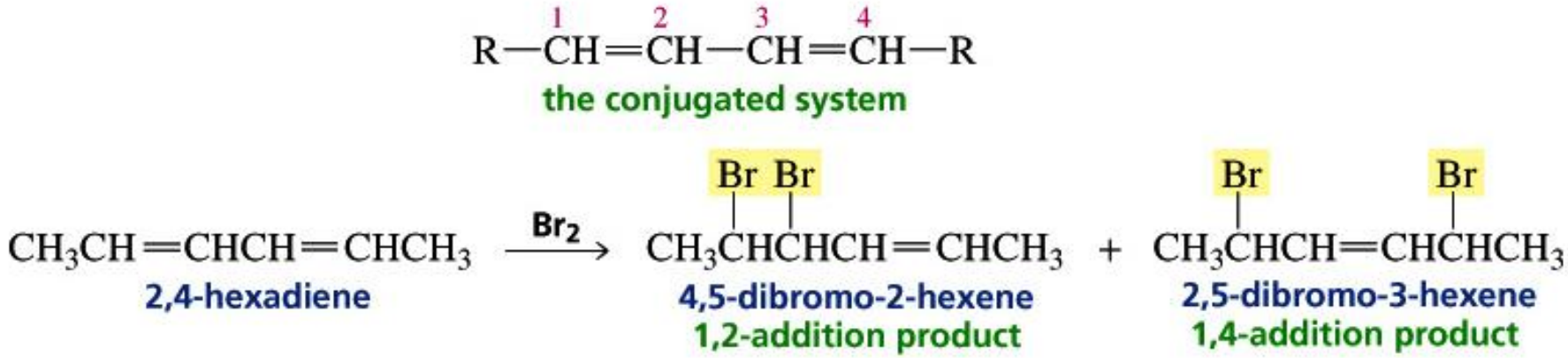


5-chloro-2-methyl-1-hexene

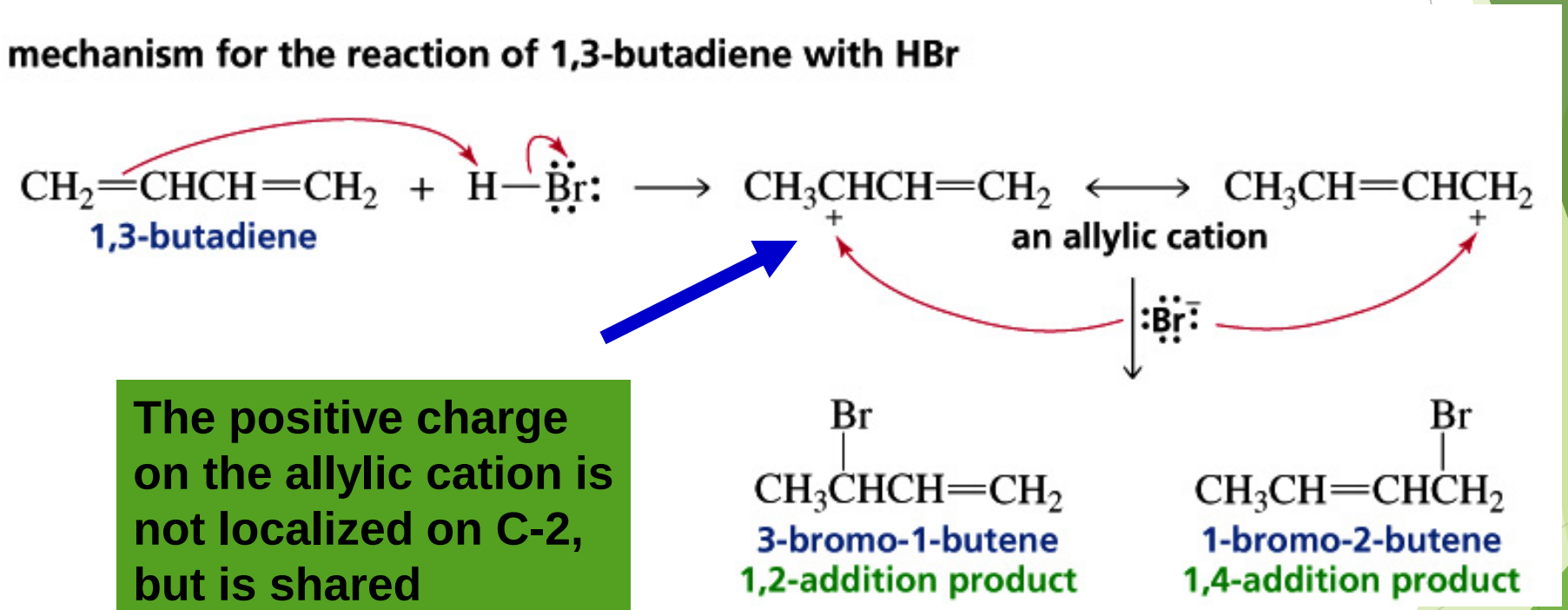
minor product

Electrophilic Addition Reactions of Conjugated Dienes

- Conjugated dienes can give both 1,2- and 1,4- addition products



Mechanism of Addition of HBr to Conjugated Dienes



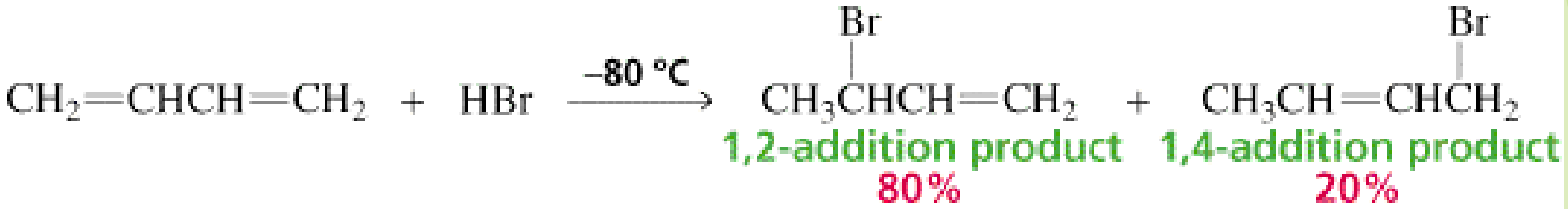
The positive charge on the allylic cation is not localized on C-2, but is shared between C-2 and C-4

Thermodynamic vs. Kinetic Control

- The product that is formed most rapidly is the **kinetic product**
- The most stable product is the **thermodynamic product**

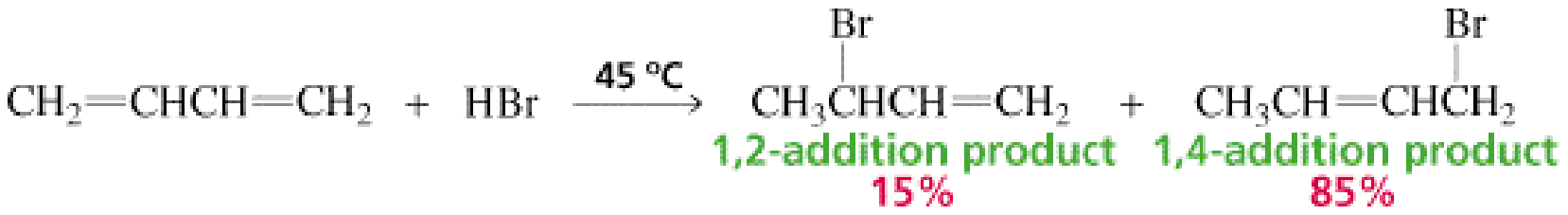
Thermodynamic vs. Kinetic Control

- Reactions that produce the kinetic product are said to be **kinetically controlled**

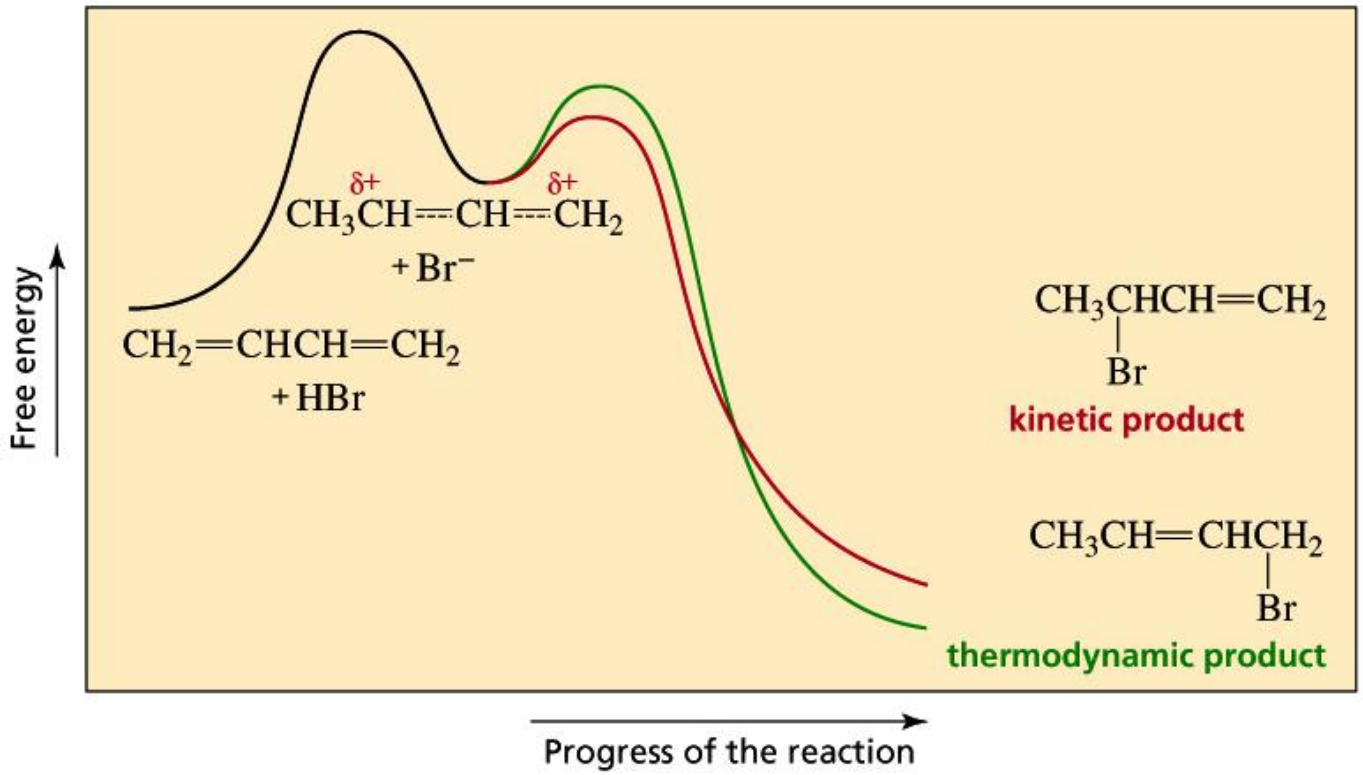


Thermodynamic vs. Kinetic Control

- Reactions that produce the thermodynamic product are said to be **thermodynamically controlled**

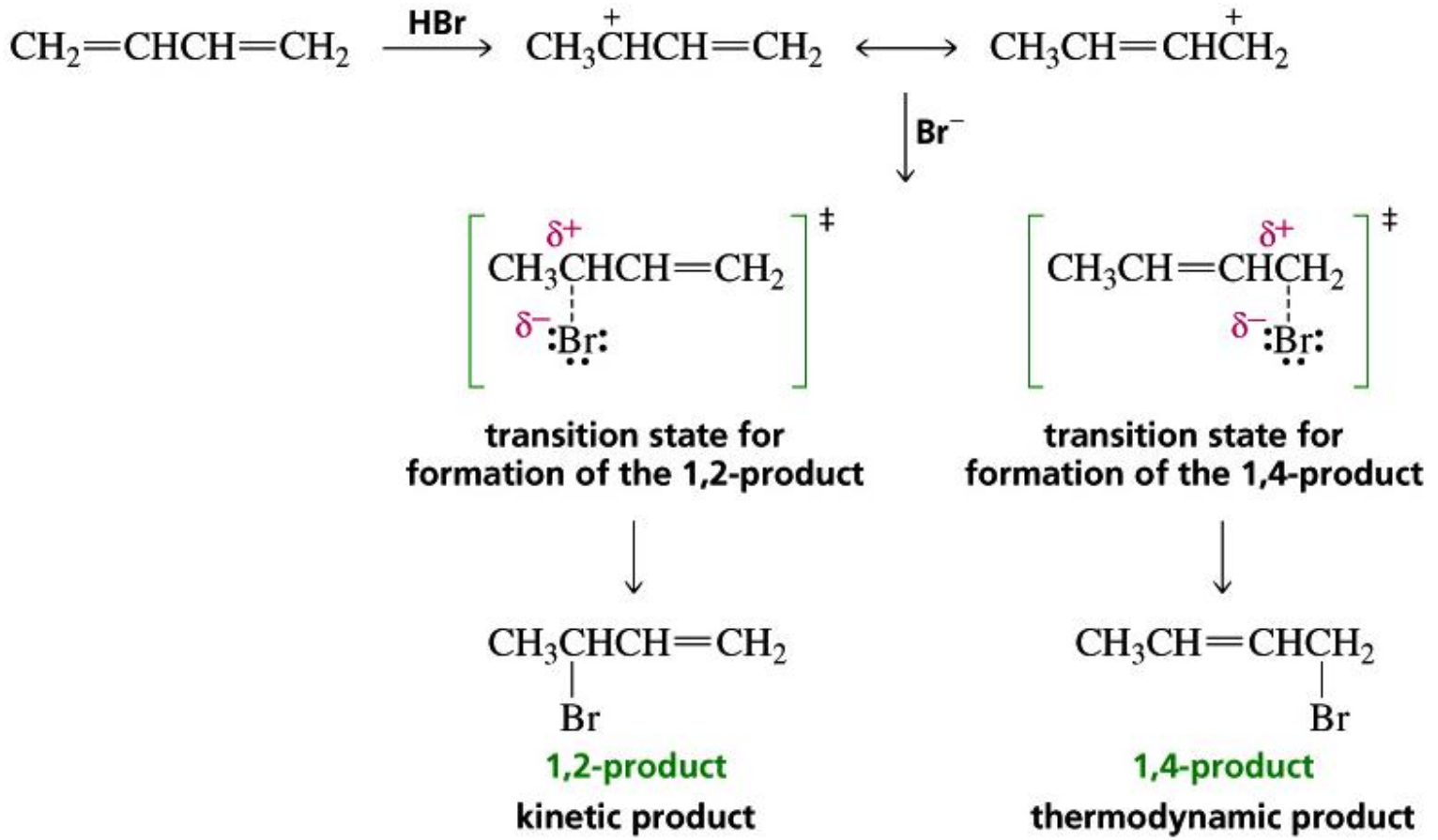


Thermodynamic vs. Kinetic Control



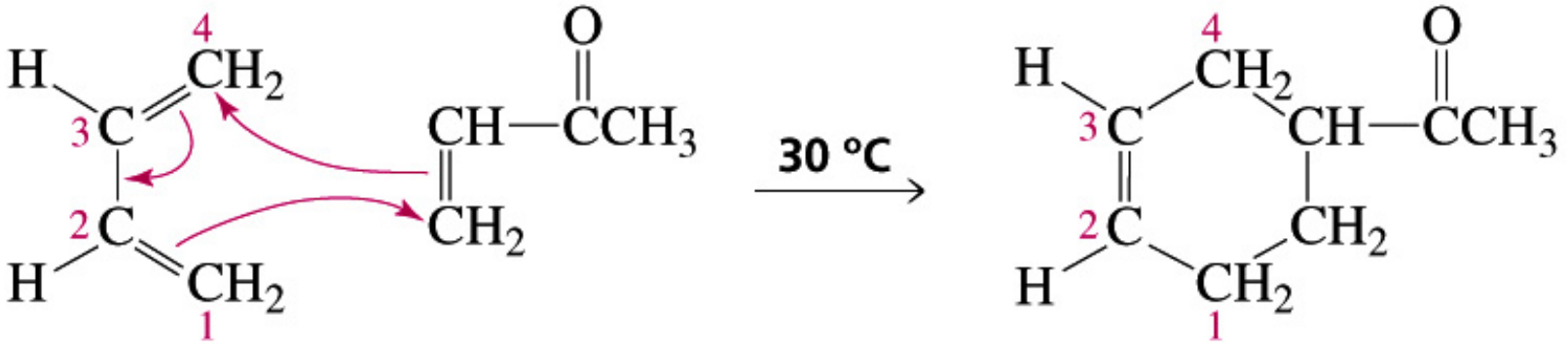
more stable product ⇌ common intermediate ⇌ less stable product

Thermodynamic vs. Kinetic Control



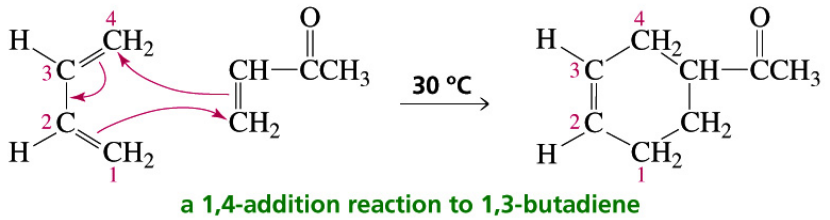
Diels–Alder Reaction

- A conjugated diene reacts with a compound that contains a carbon–carbon double bond

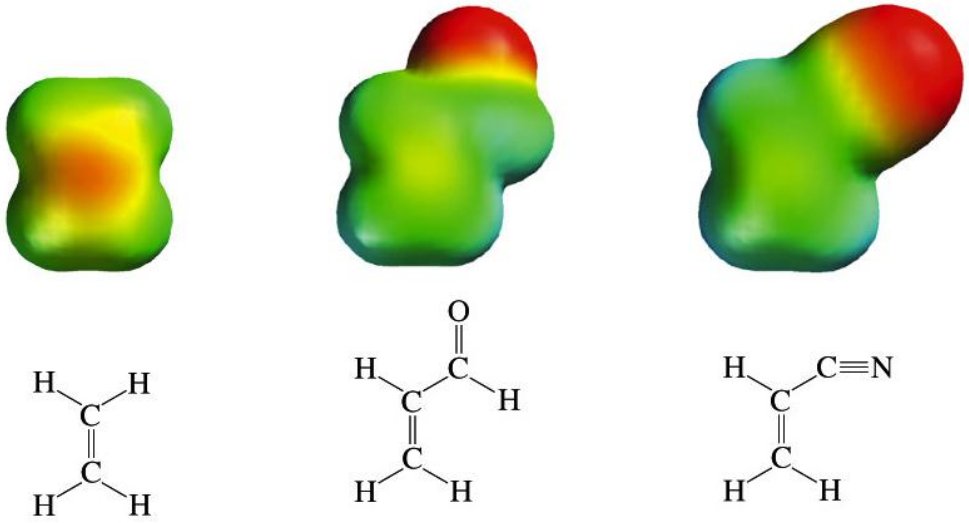


a 1,4-addition reaction to 1,3-butadiene

Diels–Alder Reaction



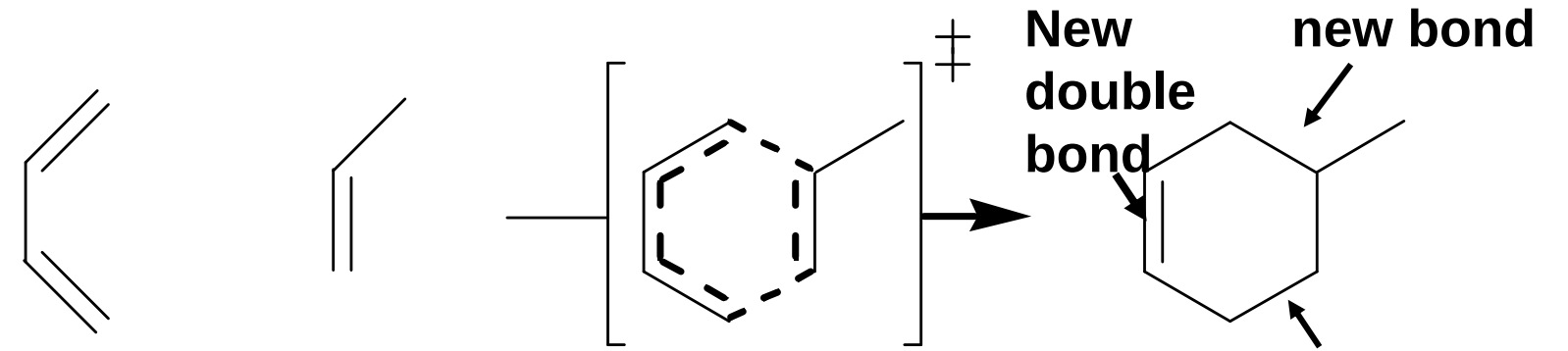
a 1,4-addition reaction to 1,3-butadiene



Typically the compound containing the lone double bond (also known as the **dienophile**) must have an electron withdrawing group bonded to one of the sp^2 carbons in order to polarize the double bond

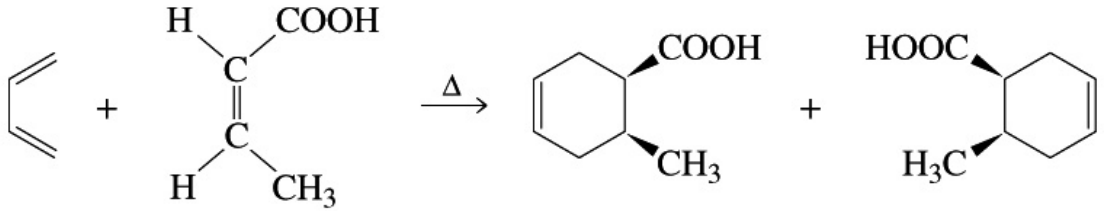
Diels–Alder Reaction

- Addition of a double bond to a conjugated diene is similar to other 1,4- additions but in this case the reaction takes place in a single step
- It is a concerted reaction



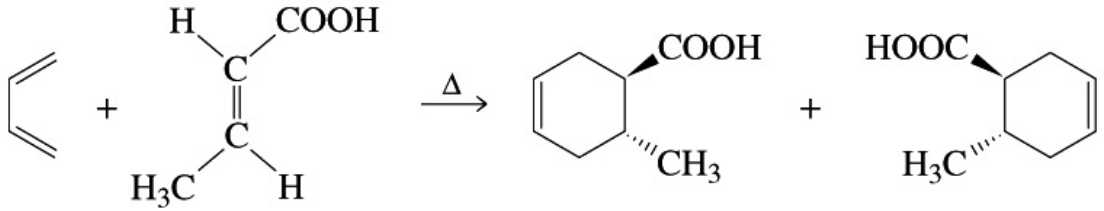
Diels–Alder Reaction Stereoselectivity

- The Diels–Alder reaction is stereoselective because different stereoisomeric reactants give different stereoisomeric products



cis dienophile

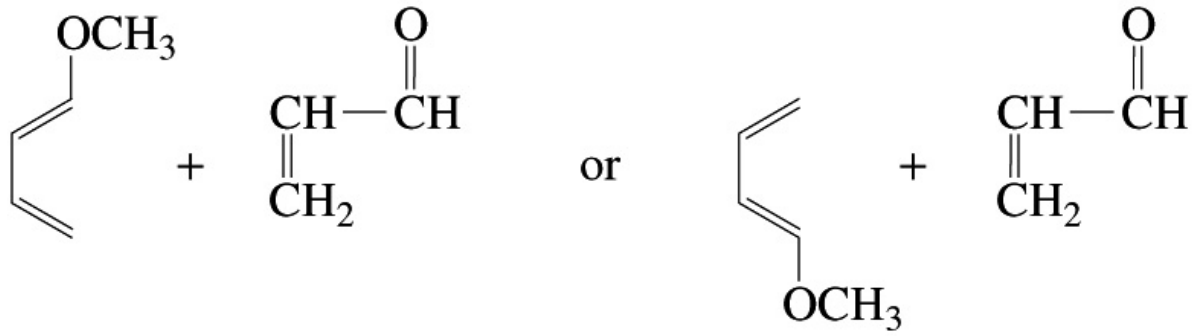
cis products

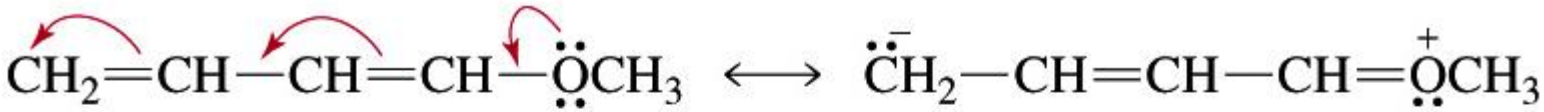


trans dienophile

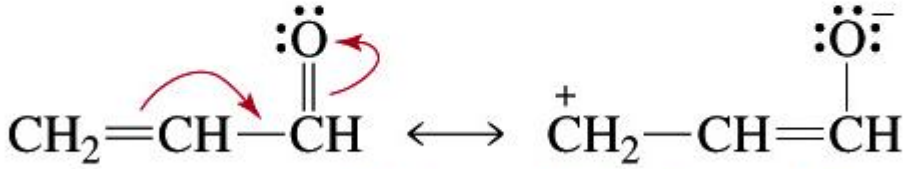
trans products

Diels–Alder Reaction Regioselectivity



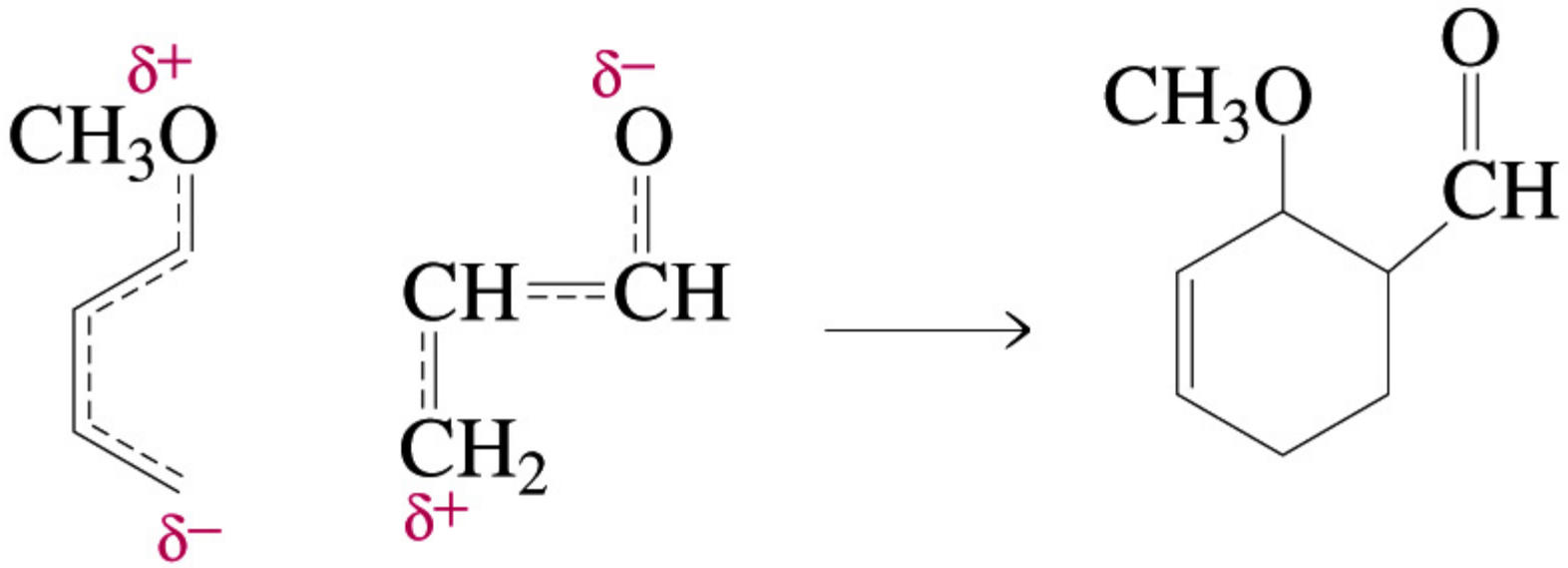


resonance contributors of the diene



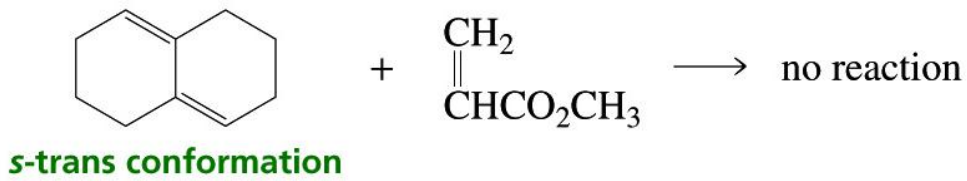
resonance contributors of the dienophile

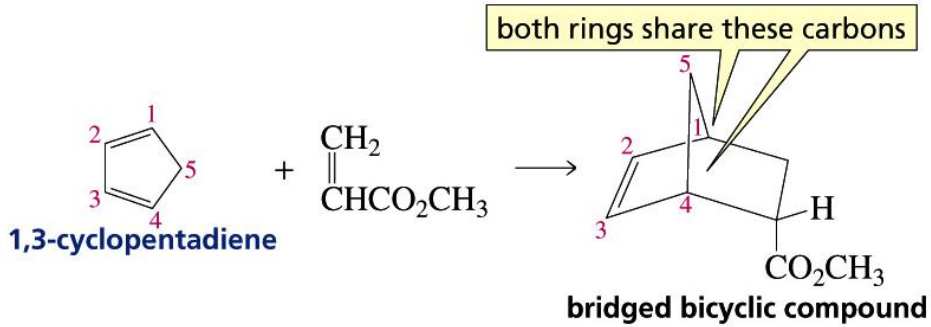
Diels–Alder Reaction Regioselectivity

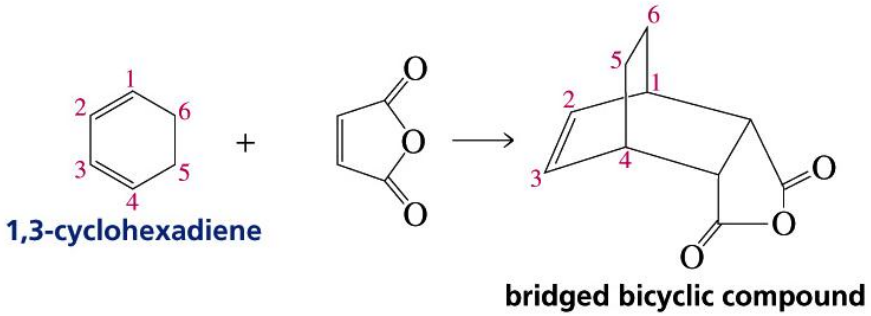


Diels–Alder Reaction

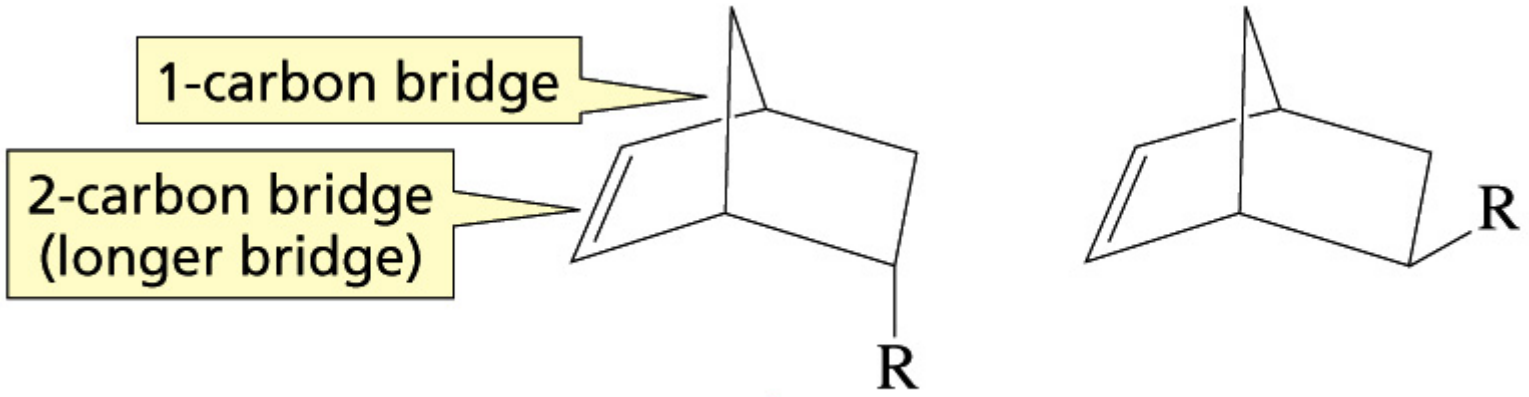
The Diels–Alder reaction requires an s-cis conformation







Diels–Alder Reaction Stereoselectivity



endo **exo**

Diels–Alder Reaction Stereoselectivity

- When the diene is cyclic, the **endo** product is preferred