

Chapter 13

Conjugated Unsaturated Systems

13.1) Introduction:

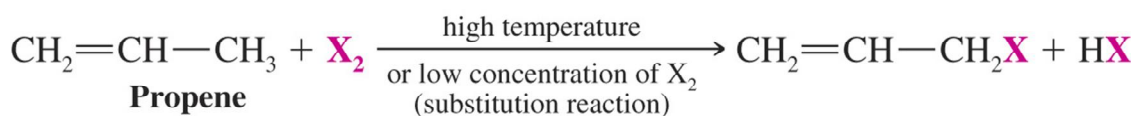
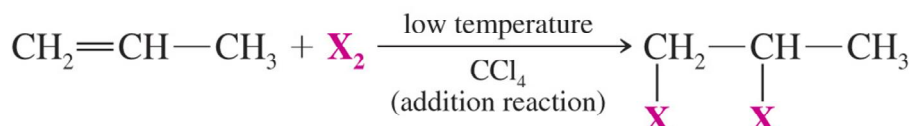
§ Conjugated unsaturated systems have a *p* orbital on a carbon adjacent to a double bond.

- The *p* orbital can come from another double or triple bond
- The *p* orbital may be the empty *p* orbital of a carbocation or a *p* orbital with a single electron in it (a radical)
- Conjugation affords special stability to the molecule
- Conjugated molecules can be detected using UV spectroscopy.

13.2) Allylic Substitution and the Allylic Radical:

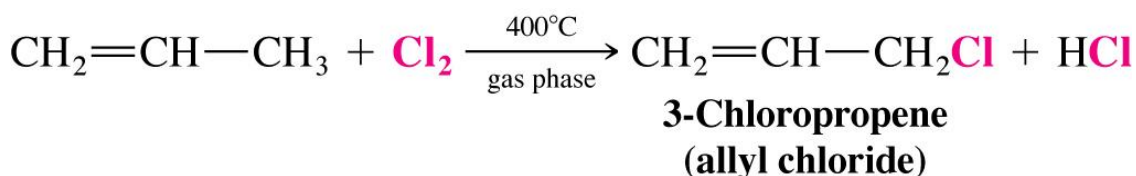
§ Reaction of propene with bromine varies depending on reaction conditions

- At low temperature the halogen adds across the double bond
- At high temperature or at very low concentration of halogen an allylic substitution occurs

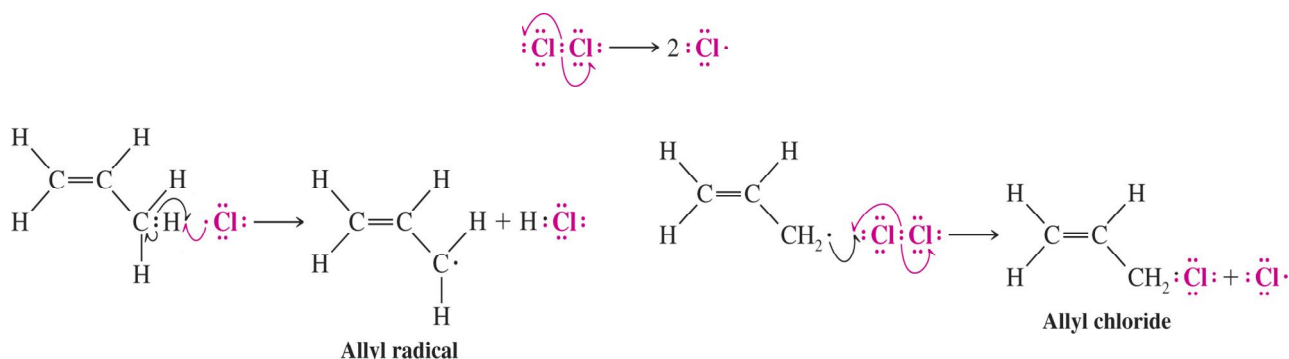


1 Allylic Chlorination (High Temperature):

§ Allylic chlorination can be performed at high temperature in the gas phase



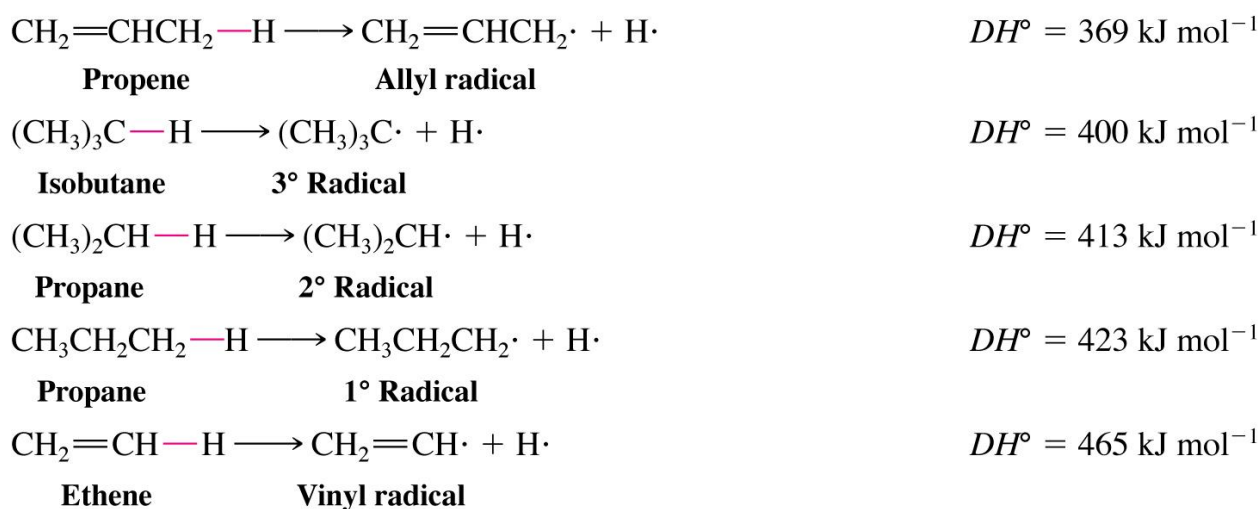
§ The reaction is a free radical chain reaction, including initiation step, first propagation and second propagation steps.



§ The relative stability of some carbon radicals is as follows:

Relative stability: allylic or allyl > 3° > 2° > 1° > vinyl or vinylic.

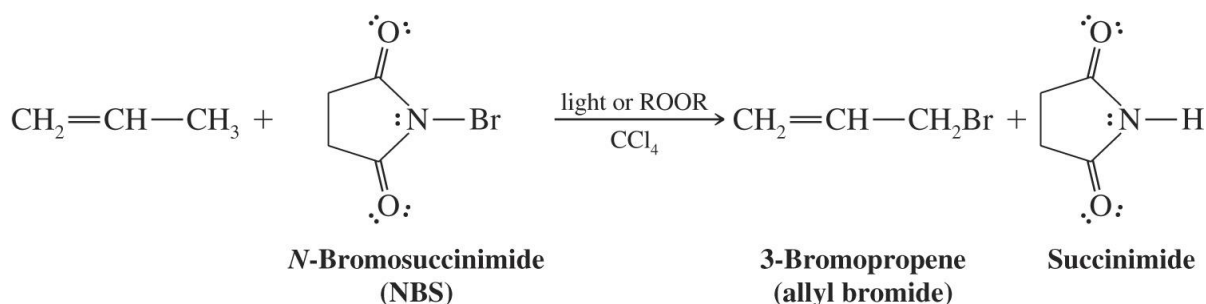
This trend is reflected in their respective C-H bond dissociation energies



1 Allylic Bromination with N-Bromosuccinimide:

§ Propene undergoes allylic bromination with N-bromosuccinimide (NBS) in the presence of light or peroxides.

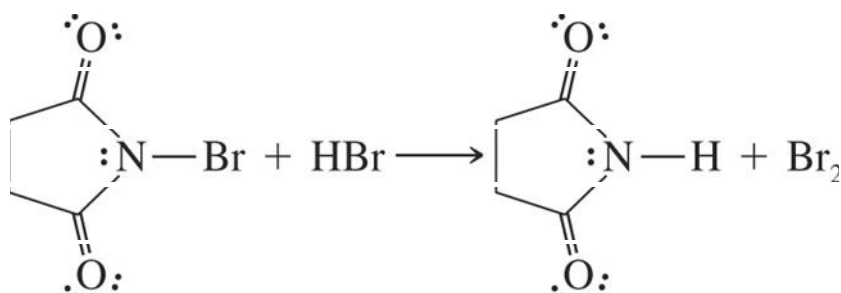
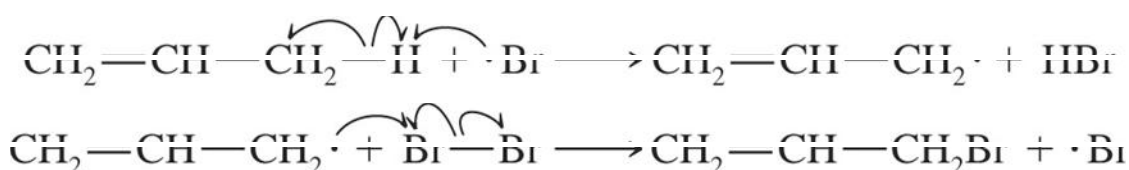
NBS provides a continuous low concentration of bromine for the radical reaction, which favors allylic substitution over alkene addition.



§ The radical reaction is initiated by a small amount of bromine radical formed by exposure of NBS to light or peroxides

§ The propagation steps for allylic bromination with NBS are:

- A bromine radical reacts with propene to produce an allylic radical and HBr
- HBr reacts with NBS to produce a bromine molecule
- A molecule of bromine reacts with a propene radical to regenerate a bromine radical



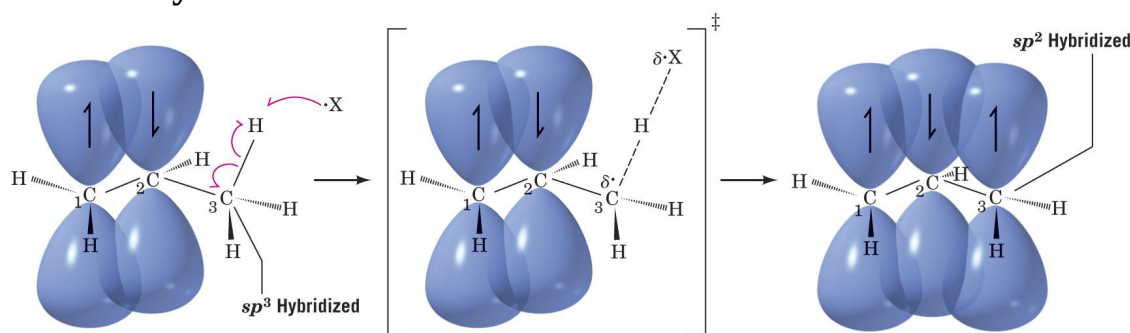
13.3) The Stability of the Allyl Radical:

Both molecular orbital theory and resonance theory can explain the stability of allyl radicals

1 Molecular Orbital Description of the Allyl Radical:

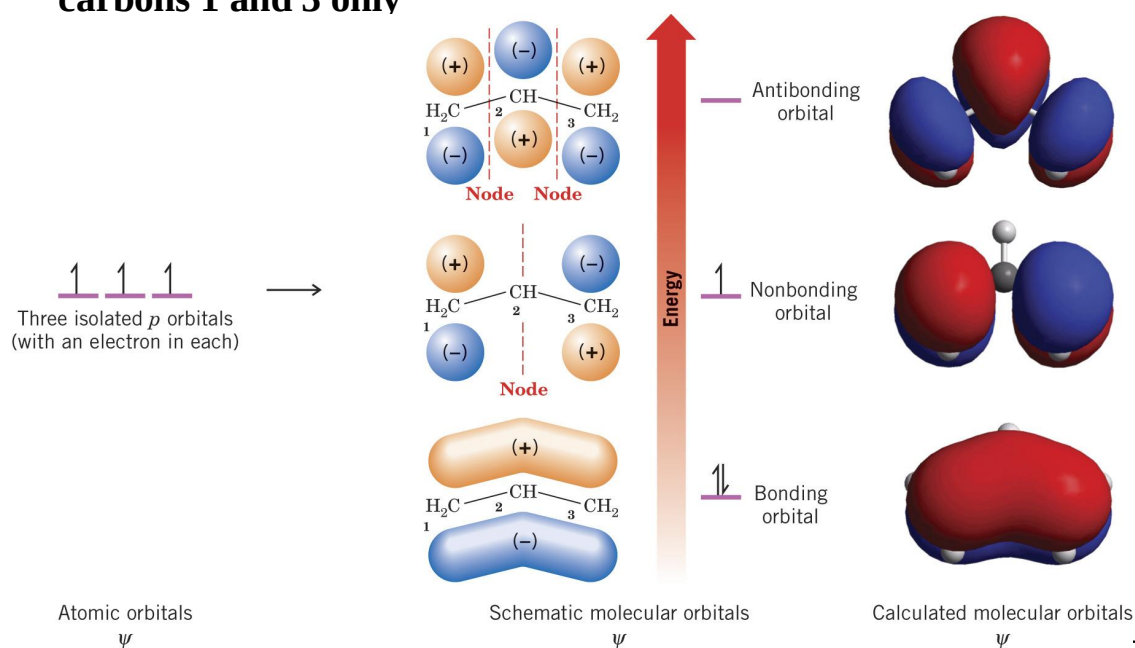
When an allylic hydrogen is abstracted to form an allyl radical, the developing p orbital on the sp^2 carbon overlaps with the p orbitals of the alkene.

- The new p orbital is conjugated with the double bond p orbitals
- The radical electron and the p electrons of the alkene are delocalized over the entire conjugated system
- Delocalization of charge and electron density leads to increased stability



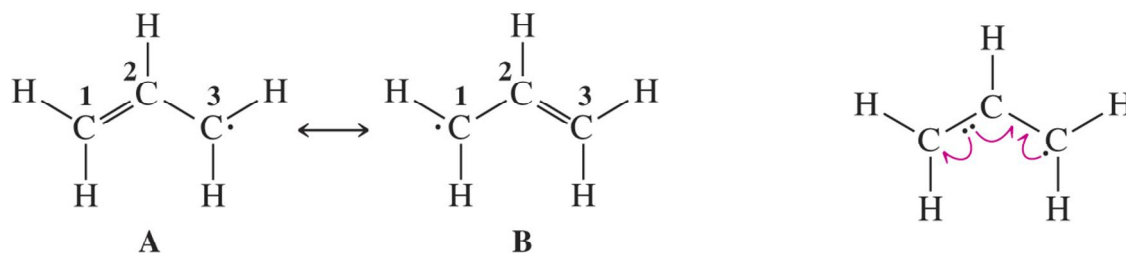
§ The three p orbitals of the allylic system combine to form three molecular orbitals

- The bonding molecular orbital contains two spin-paired electrons and this orbital increases bonding between the carbons
- The nonbonding orbital contains a lone electron which is located at carbons 1 and 3 only

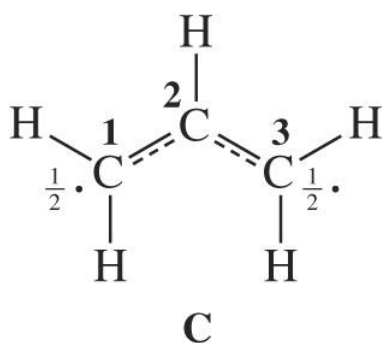


13.4) Resonance Description of the Allyl Radical:

§ The allyl radical has two contributing resonance forms. These resonance structures are equivalent, which lead to a much greater stability of the molecule.

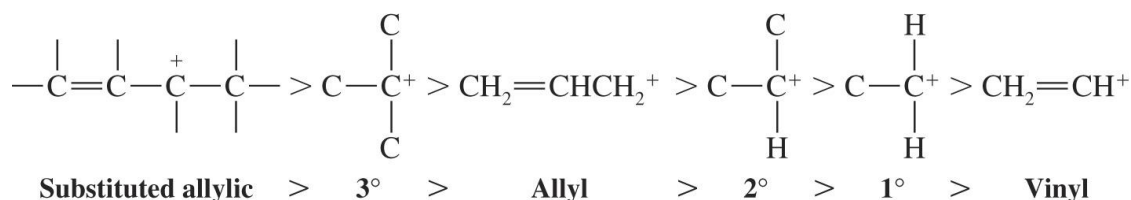


§ The true structure of the allyl radical, as suggested by the resonance theory, is a hybrid of the equivalent structures A & B.

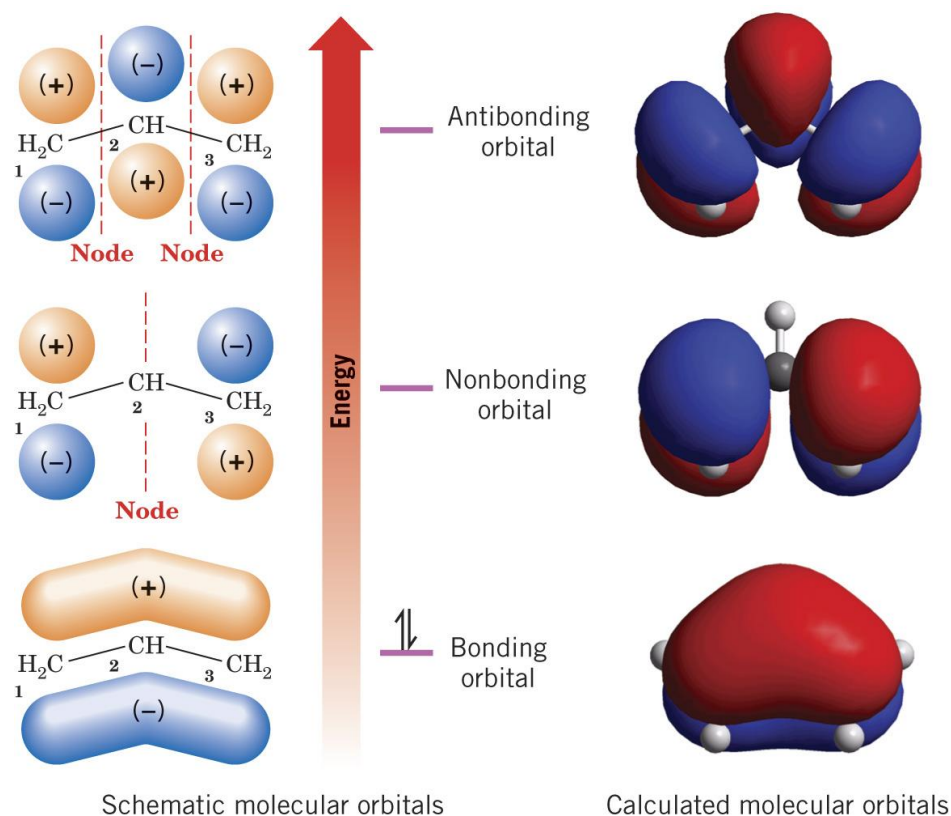


13.5) The Allyl Cation:

§ The allyl cation is intermediate in stability between a tertiary and secondary carbocation

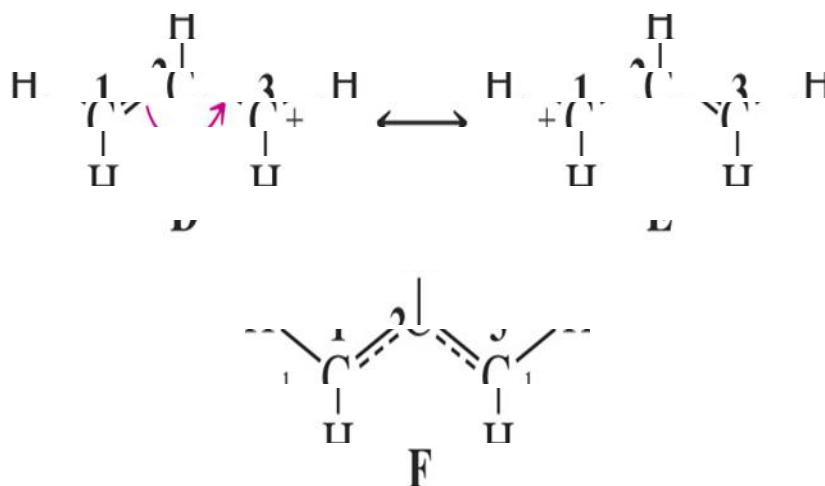


§ The molecular orbital description of the allyl cation is very similar to the allyl radical except it contains one fewer electrons. Stability arises from the delocalization of the positive charge over C1 and C3.



§ Resonance theory predicts that the allyl cation is a hybrid of equivalent structures D and E.

- Both molecular orbital theory and resonance theory suggest that structure F (below) is the best representation for the allyl cation



13.6) Summary of Rules for Resonance:

1 Rules for Writing Resonance Structures

§ Individual resonance structures are not a true representation of the real structure of a molecule

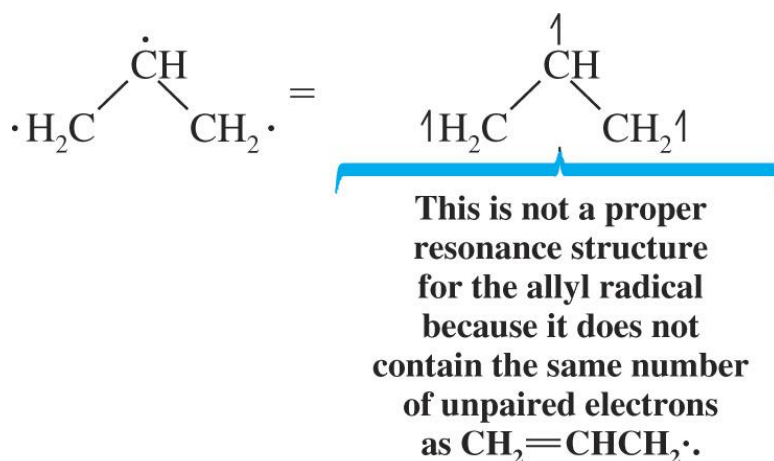
- A hybrid of all major resonance structures gives an indication of the true structure.

§ Only electrons may be moved in resonance structures, not atoms

- Only p and nonbonding electrons are moved.

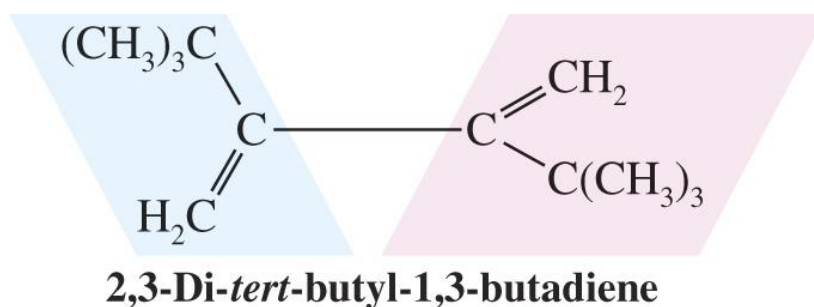
§ All resonance structures must be proper Lewis structures.

§ All resonance structures must have the same number of paired and unpaired electrons



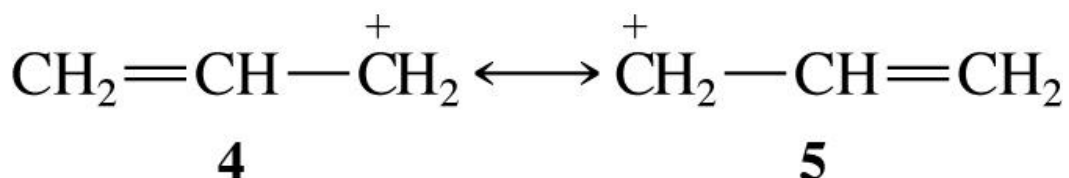
§ All atoms that are part of the delocalized p-electron system must lie in a plane or be nearly planar.

- The molecule below does not behave like a conjugated diene because the large tert-butyl groups twist the structure and prevent the diene from being planar.



§ The energy of the actual molecule is lower than the energy calculated for any one contributing resonance structure.

- Allyl cation has much lower energy than either contributing structures 4 or 5

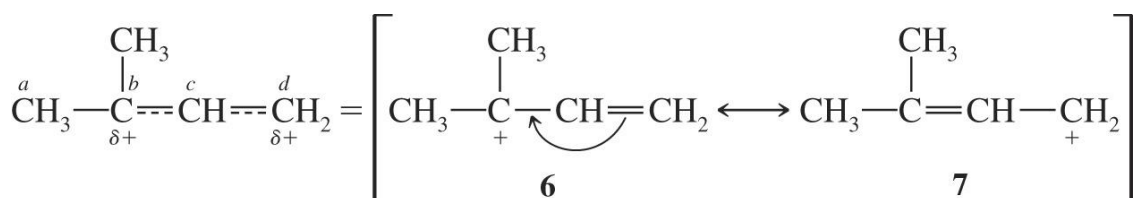


§ A system with equivalent resonance structures is particularly stable

- The allyl cation has two equivalent resonance structures and is therefore particularly stable

§ The more stable a resonance structure is, the more important it is and the more it contributes to the hybrid

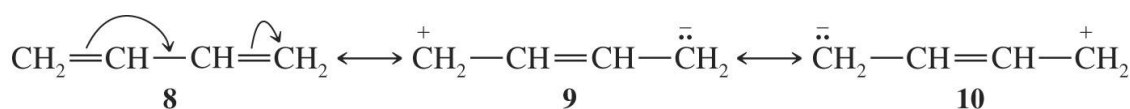
- Structure 6 is a more stable tertiary carbocation and contributes more than structure 7



1 Estimating the Relative Stability of Resonance Structures:

§ Structures with more covalent bonds are more important

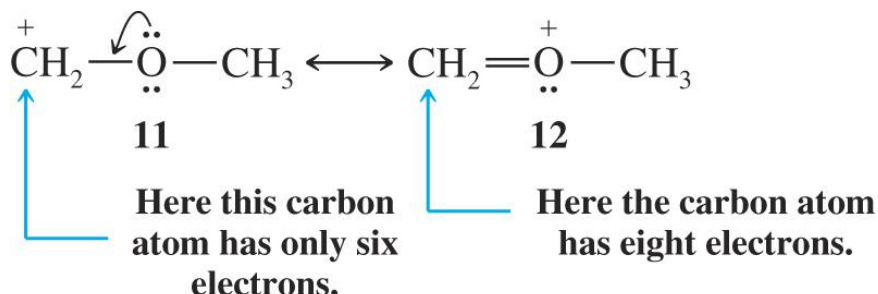
- Structure 8 is more important than 9 or 10



This structure is the most stable because it contains more covalent bonds.

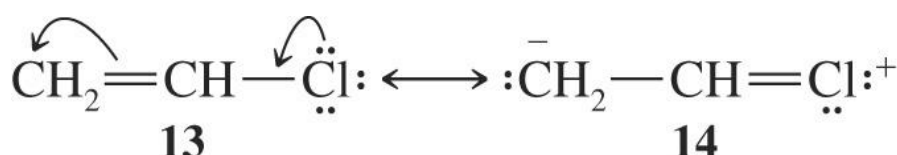
§ Structures in which all atoms have complete octets are more important

- Structure 12 is more important than structure 11



§ Separation of charge decreases stability

- Structure 13 is more important because it does not have a separation of charge



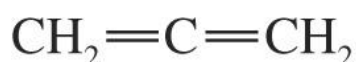
13.7) Alkadienes and Polyunsaturated Hydrocarbons:

§ Alkadienes contain two double bonds.

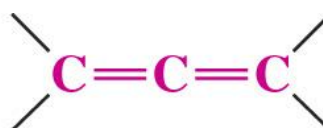
- These are often referred to simply as dienes
- Alkadiynes contain 2 triple bonds and alkenynes contain a double and a triple bond

§ Polyunsaturated compounds can be classified as being cumulated, conjugated or isolated

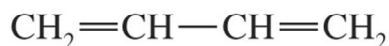
- Conjugated dienes affect each other when they react, isolated double bonds react separately and do not affect each other



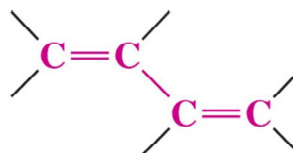
Allene



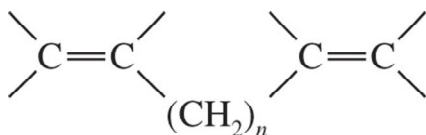
A cumulated diene



1,3-Butadiene



A conjugated diene



An isolated diene
($n \neq 0$)



1,4-Pentadiene

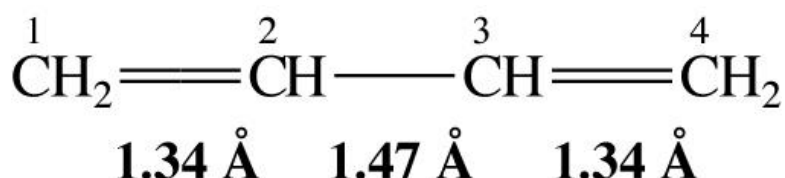
13.8) 1,3-Butadiene: Electron Delocalization:

1 Bond Lengths of 1,3-Butadiene:

§ The double bonds of 1,3-butadiene have the expected length of regular double bonds

§ The central bond is much shorter than a regular carbon-carbon single bond

- Ethane has a carbon-carbon bond length of 1.54 Å



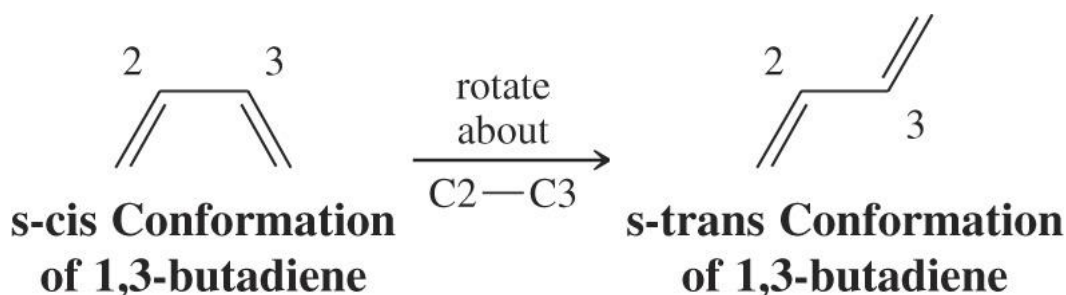
§ The central bond in 1,3-butadiene is shorter than that in ethene for two reasons

- The s bond between C2 and C3 is made from sp^2-sp^2 overlap
- There is significant overlap between the C2-C3 p orbitals

1 Conformations of 1,3-Butadiene:

§ There are two possible planar conformations of 1,3-butadiene called s-cis and s-trans

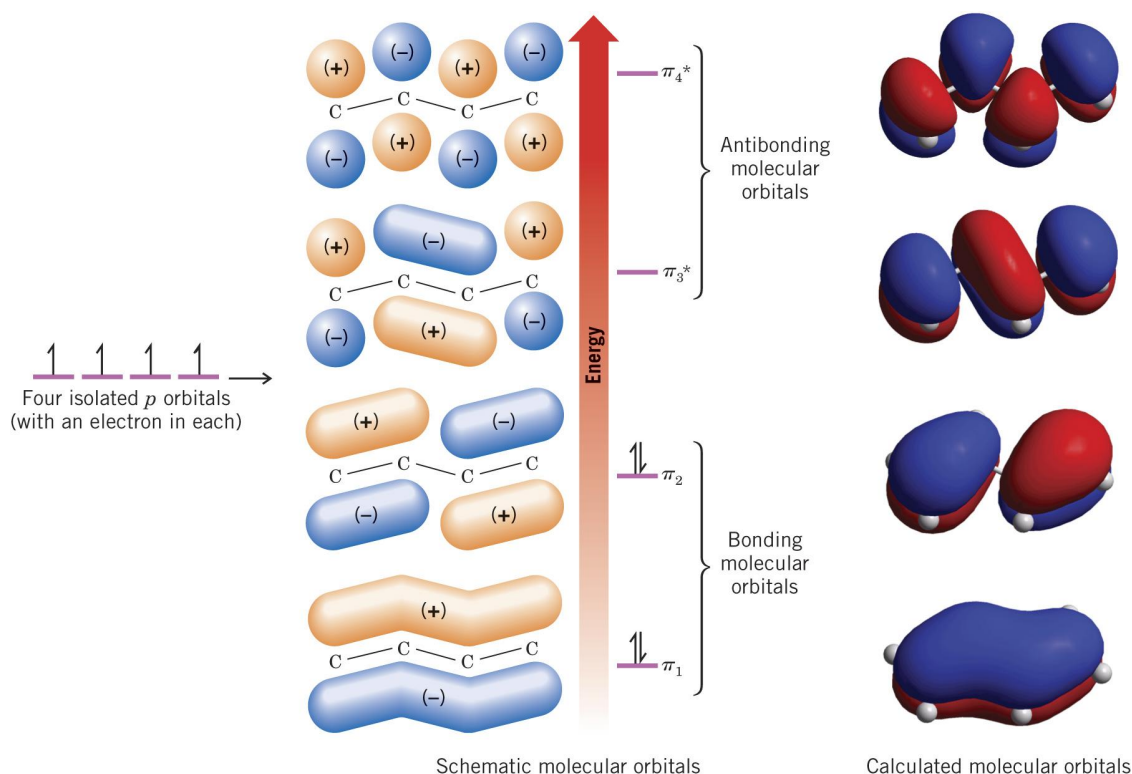
- s Indicates the conformations originate from rotation around a single bond
- s-Trans is more stable because it is less sterically hindered



1 Molecular Orbitals of 1,3-Butadiene:

§ The first (lowest energy) p bonding molecular orbital in 1,3-butadiene shows significant overlap of the p orbitals between C2 and C3.

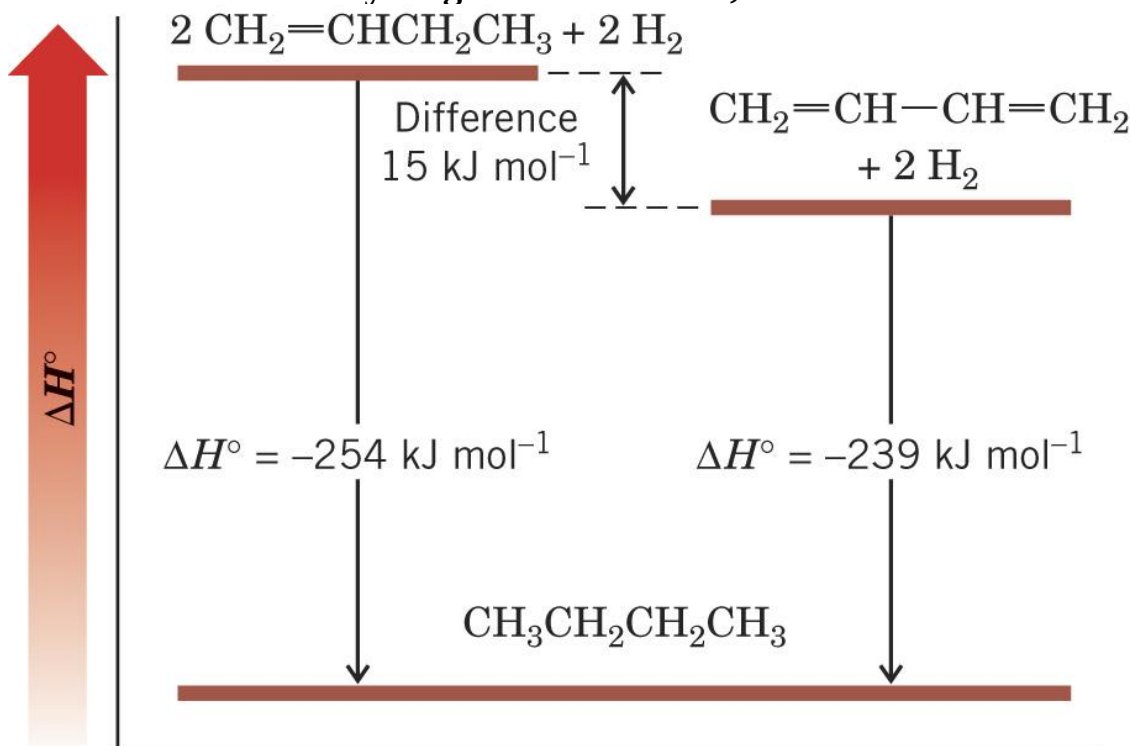
- The second p bonding molecular orbital in 1,3-butadiene is the highest occupied molecular orbital (HOMO) and shows no overlap between C2 and C3



13.9) The Stability of Conjugated Dienes:

§ 1,3-butadiene has a lower heat of hydrogenation by 15 kJ mol⁻¹ than two molecules of 1-butene

- A lower heat of hydrogenation means 1,3-butadiene is more stable



13.10) Ultraviolet-Visible Spectroscopy:

§ Conjugated compounds absorb energy in the ultraviolet (UV) and visible (Vis) regions on the electromagnetic spectrum.

- The wavelength of radiation absorbed and the intensity of the absorption depend on the structure of the molecule.

1 UV-Vis Spectrophotometers:

§ A UV-Vis spectrum is typically measured from 200-800 nm,

