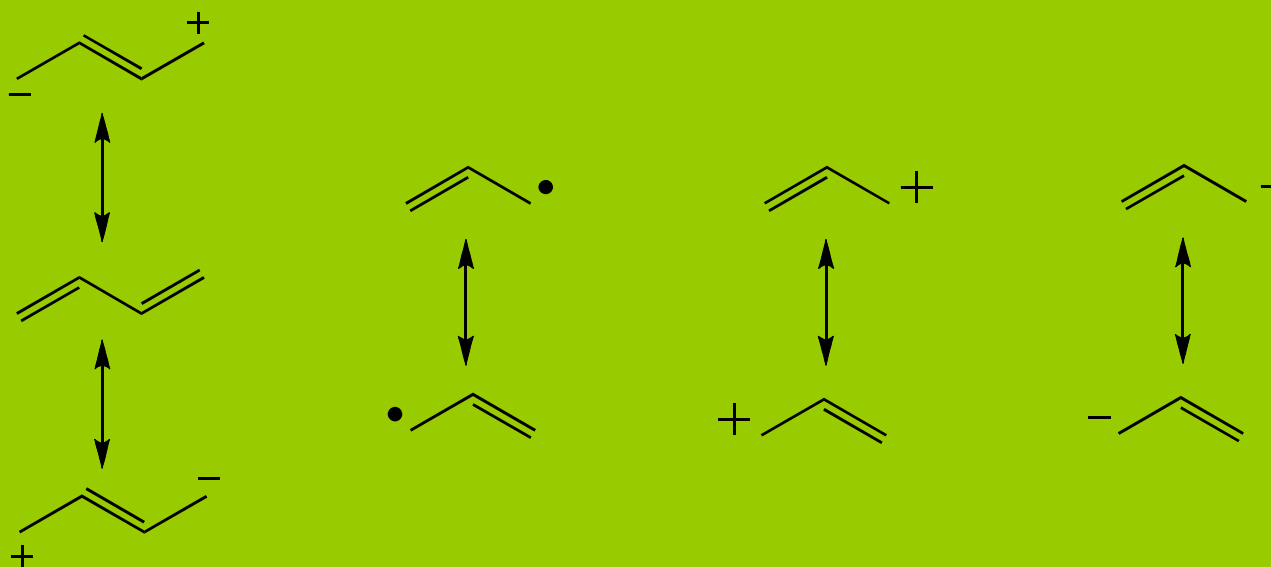


Chapter 13

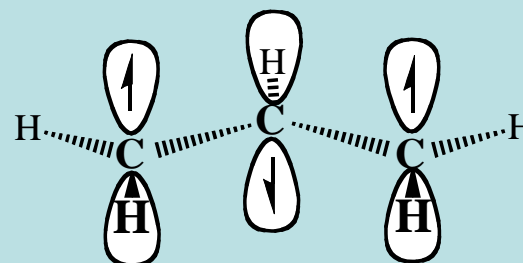
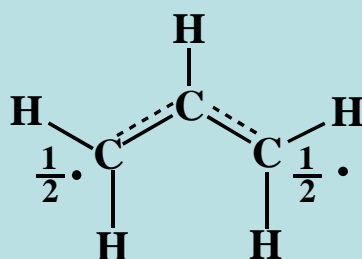
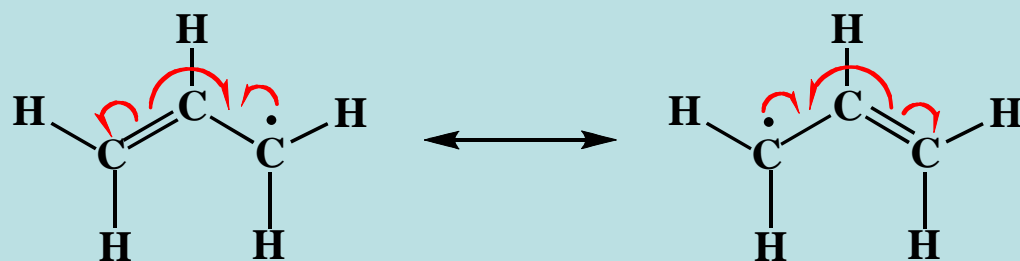
CONJUGATED UNSATURATED SYSTEMS

Examples:



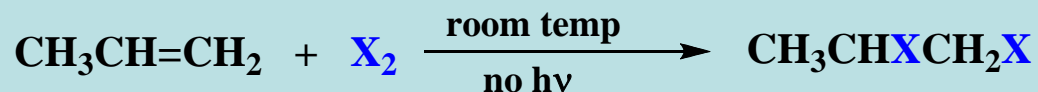
All have enhanced stability because of resonance.

All of these examples have a p orbital on an atom adjacent to a double bond. This allows the formation of an extended π bond, one that encompasses more than two nuclei. Consider the allyl radical, which may be depicted in these ways:

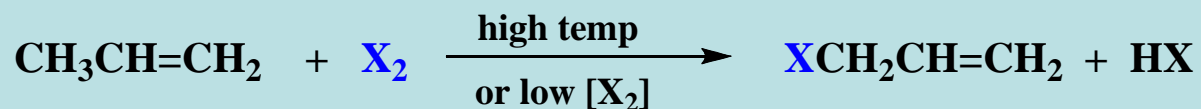


Allylic Substitution and the Allylic Radical

Propene reacts with Br₂ and Cl₂ by the usual **electrophilic addition reaction** at room temperature in the absence of ultraviolet radiation.



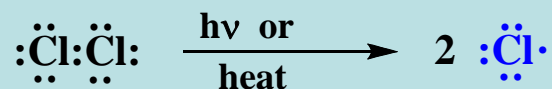
But at high temperatures, and under conditions where [X₂] is low, **allylic substitution** occurs:



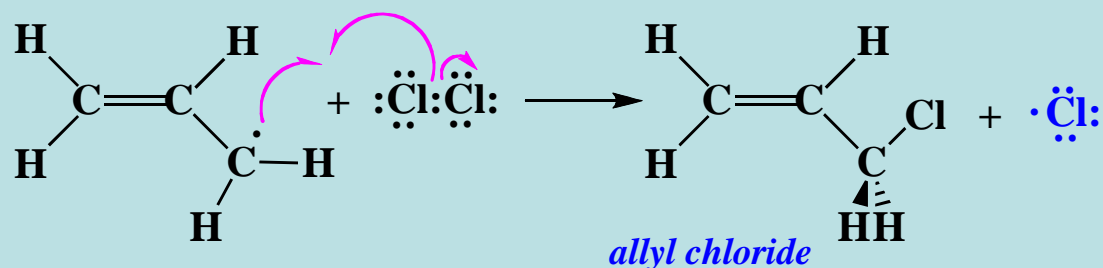
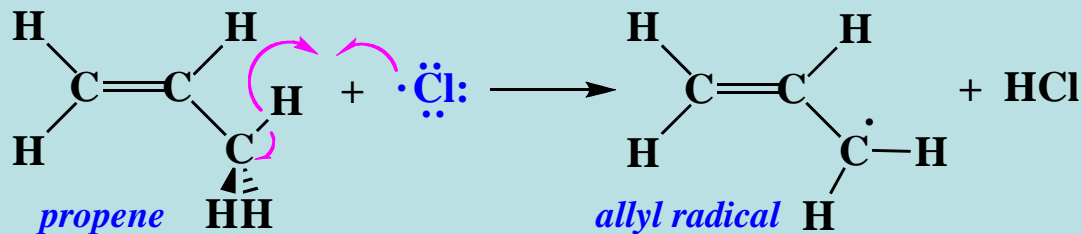
Allylic substitution is a general reaction that proceeds by a **free radical chain mechanism** that involves **allylic radicals**.

A Free Radical Chain Mechanism

Initiation



Propagation steps

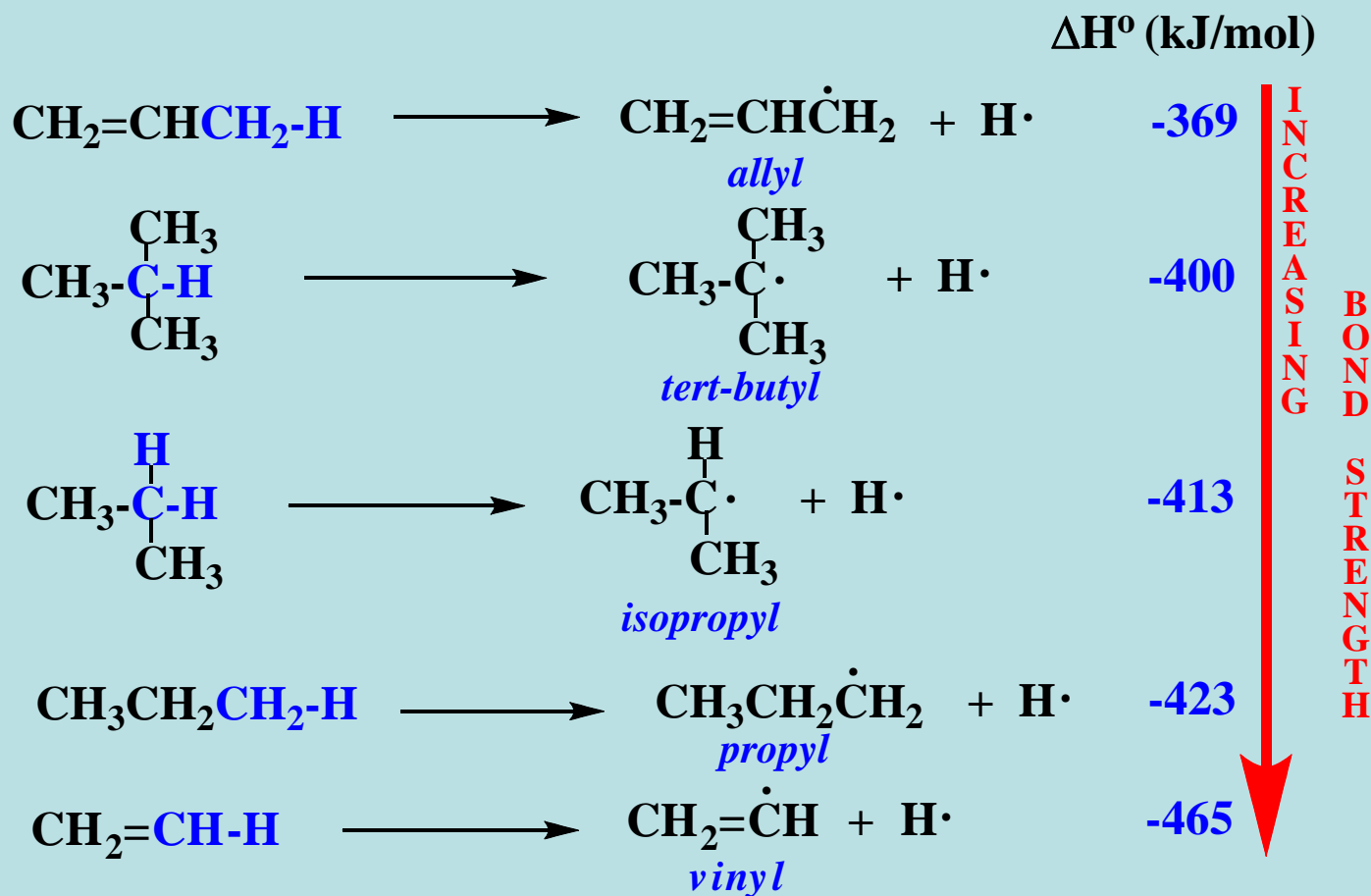


In this free radical chain reaction, the **chain carriers** are the **allyl radical** and the **chlorine radical**. The two propagating steps recycle thousands of times before termination reactions scavenge the chain carriers.

Role of Bond Dissociation Energy (ΔH°)

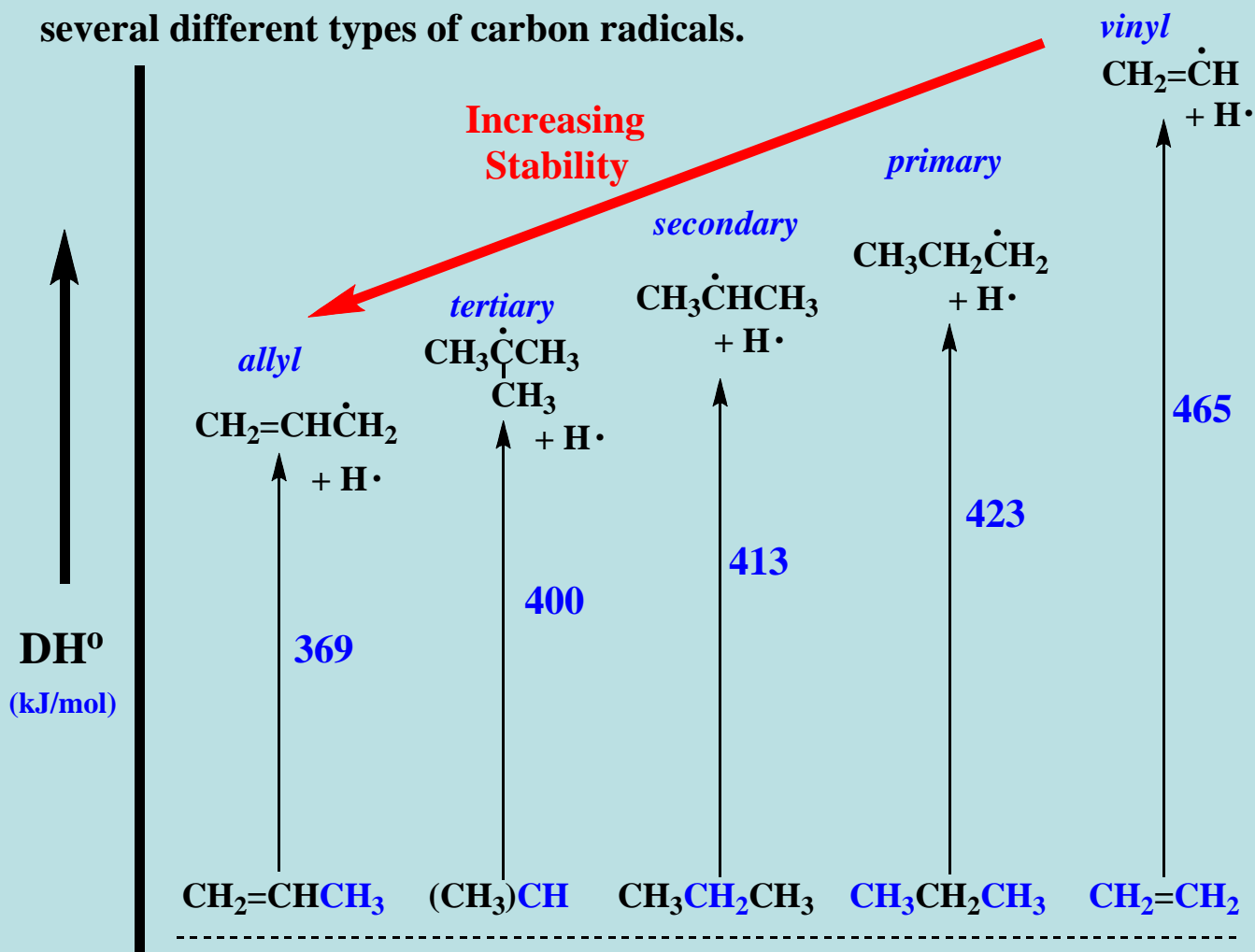
The stability of the allyl radical intermediate, as revealed below by the lower bond dissociation energy for an allylic C-H bond, is a key feature of this reaction.

A Comparison of ΔH° Values for C-H Bonds



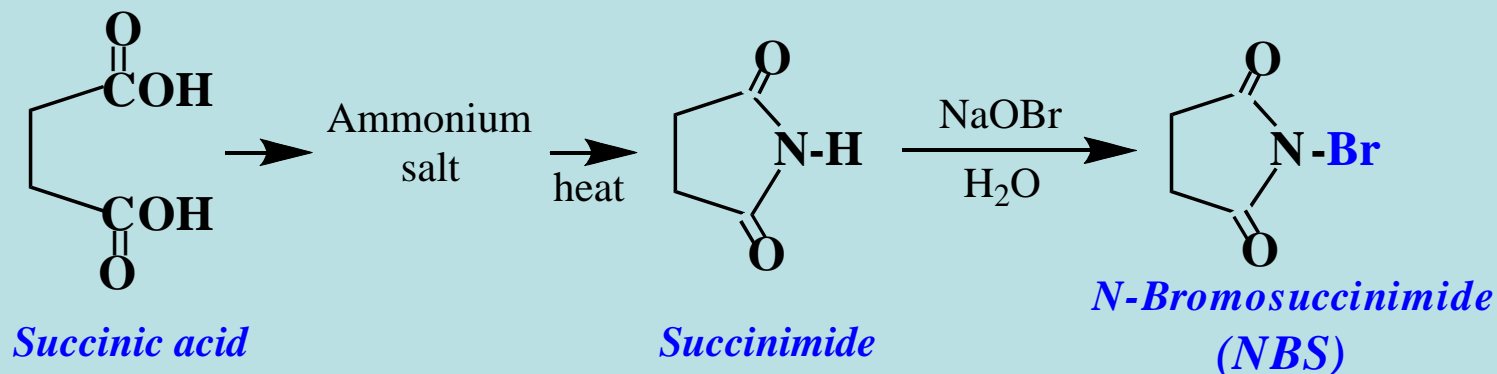
Relative Stabilities of the Carbon Radicals

Since the DH° values are the **standard heats evolved in forming the C-H bonds**, they provide a measure of the **relative stabilities** of the several different types of carbon radicals.

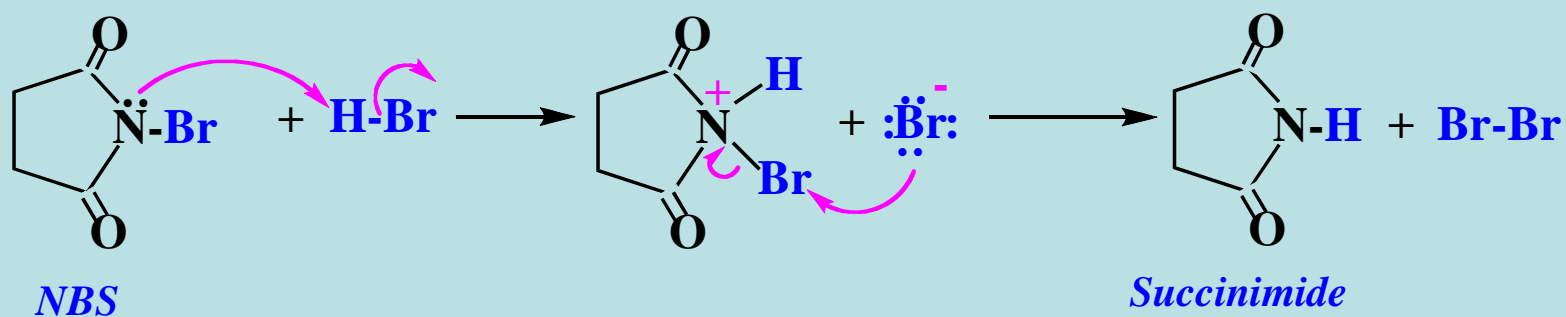


N-Bromosuccinimide (NBS), Used for Allylic Bromination

N-Bromosuccinimide is a derivative of succinimide:



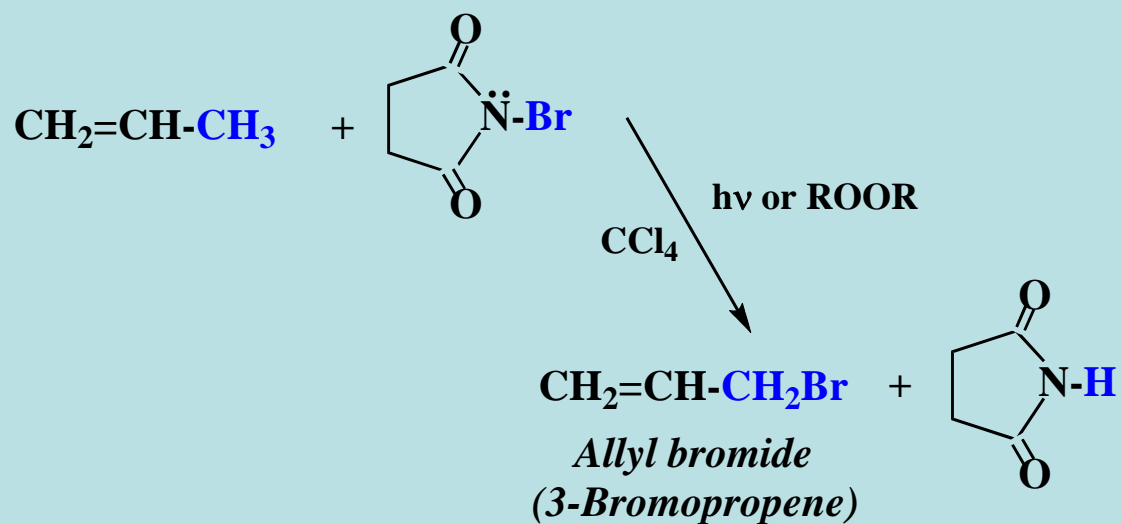
NBS reacts with HBr to produce Br₂:



This is the reaction that constantly provides the low concentration of bromine needed yet never affords so much bromine that addition of bromine to the double bond occurs. It also helps limit addition by scavenging bromide ion needed to complete the addition process.

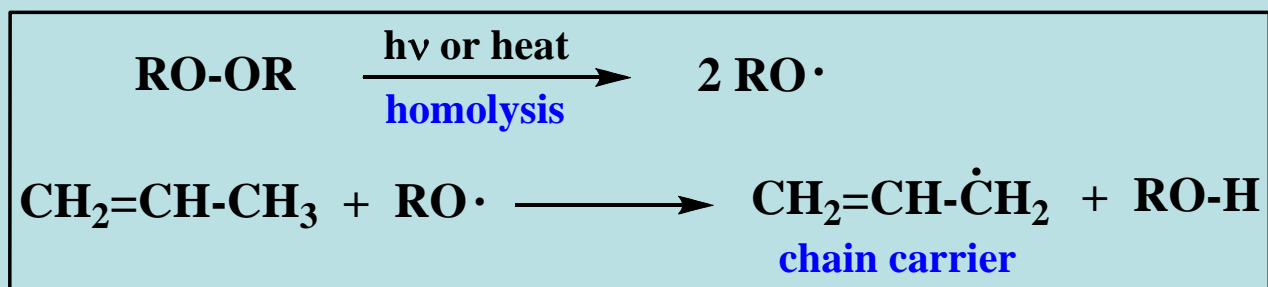
Allylic Bromination

Bromination of the allylic position is carried out in the presence of a catalytic amount of peroxide (ROOR), or under irradiation, to initiate radical production.

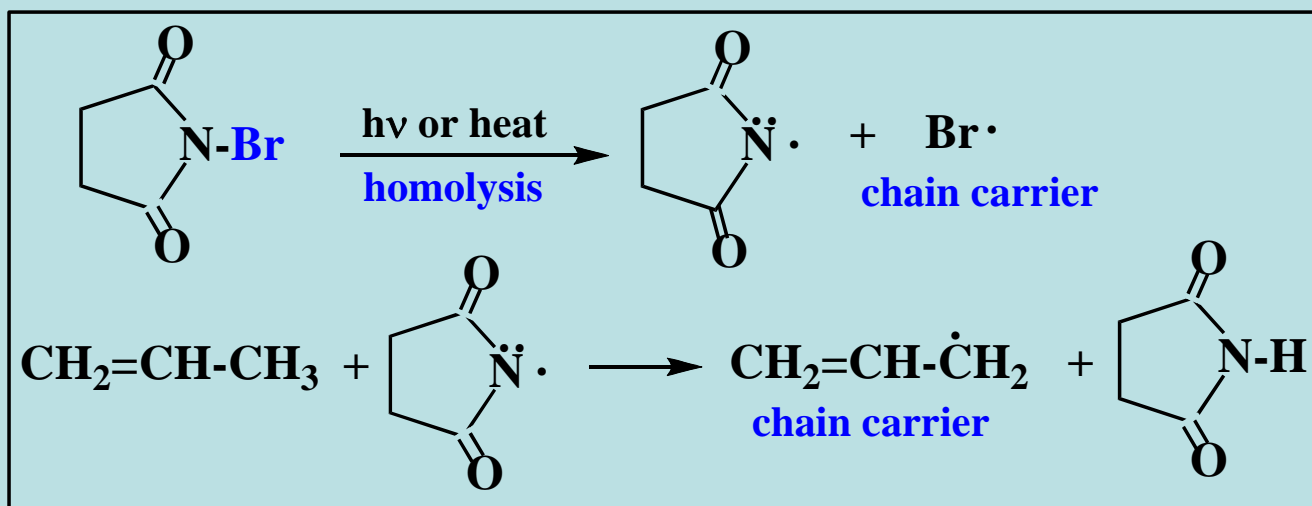


A Mechanism for Allylic Bromination with NBS

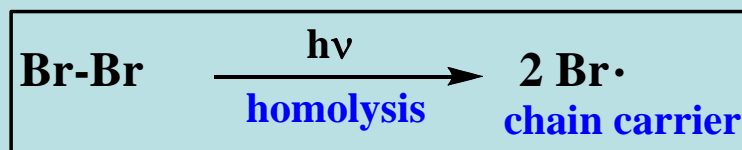
Initiation of the free radical chain reaction may be by any or all of the reaction sequences below:



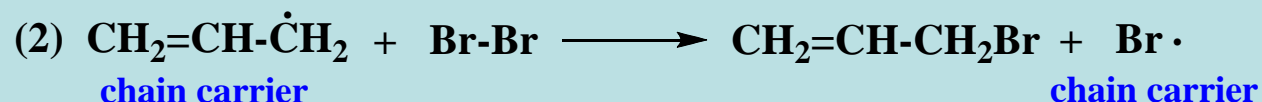
or



or

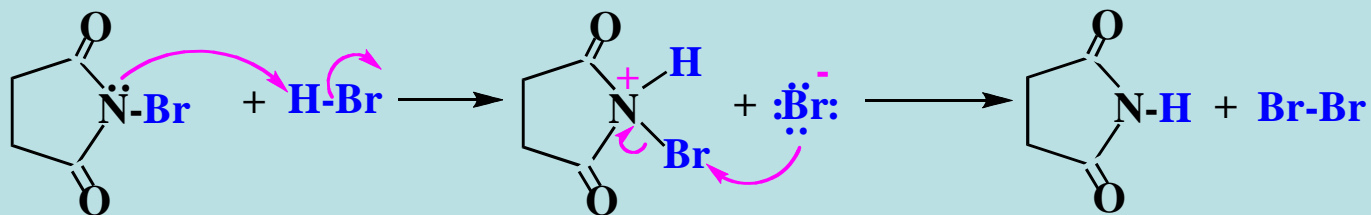


Propagating Steps in Allylic Bromination



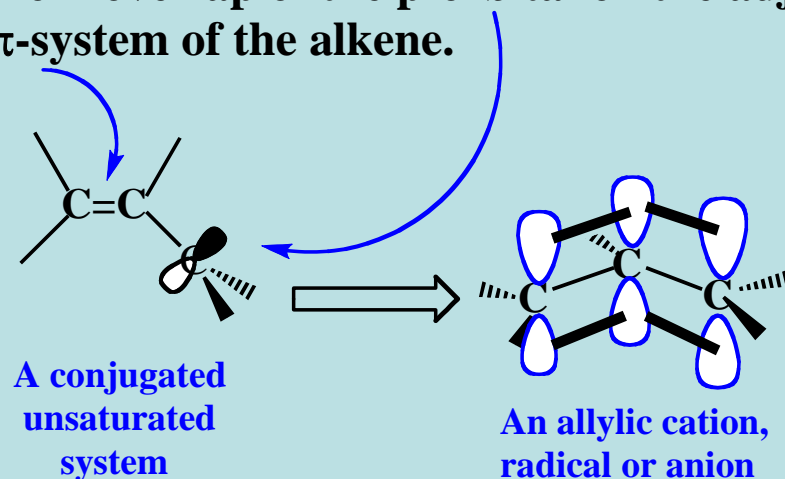
As in all free radical chain reactions, the concentrations of the **chain carriers (radical intermediates)** are extremely low, so radical-radical recombination reactions (terminations) only occur infrequently. The propagating steps cycle thousands of times before terminations occur.

The H-Br produced reacts rapidly with NBS to give succinimide and Br₂. Thus, while Br₂ is not an explicit reagent, it is constantly being produced by the reaction below. In the nonpolar solvent (CCl₄), and at the low concentrations of Br₂ and HBr, little electrophilic bromination of the alkene function occurs.



Extended π -Systems; Conjugated Systems

The special properties of **conjugated unsaturated systems** arise from overlap of the p-orbital on the adjacent carbon with the π -system of the alkene.

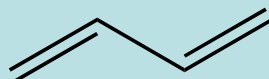


Conjugation means a π -system has been extended by overlap with p-orbitals on adjacent carbons.

A π -system of three overlapping p-orbitals is called **allylic**.

Other important conjugated systems include **those that contain directly attached multiple bonds**, e. g.

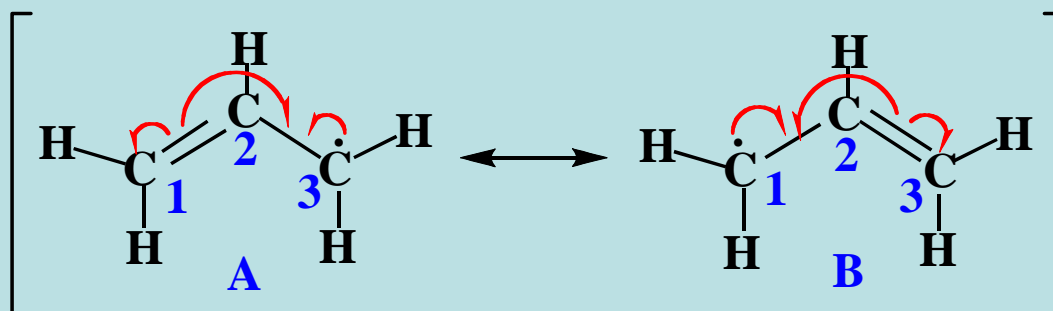
1,3-butadiene.



Resonance Theory Description of the Allyl Radical

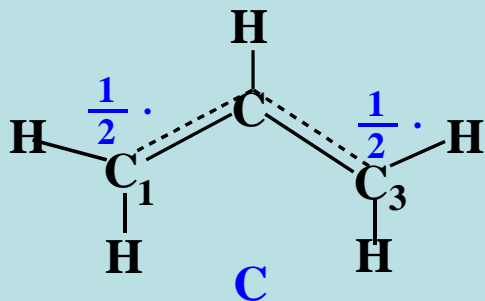
Two equivalent resonance structures can be drawn for the allyl radical:

THEY DO NOT HAVE SEPARATE EXISTENCE. The radical is a hybrid of the two.



Structures **A** and **B** are interchanged by moving single electrons, as shown by the use of single barbed arrows. **The positions of nuclei do not change.**

A single structure depiction of the allyl radical is **C** below. It has the great advantage that it avoids giving the erroneous impression that this radical is a mixture of **A** and **B**, a common misconception.

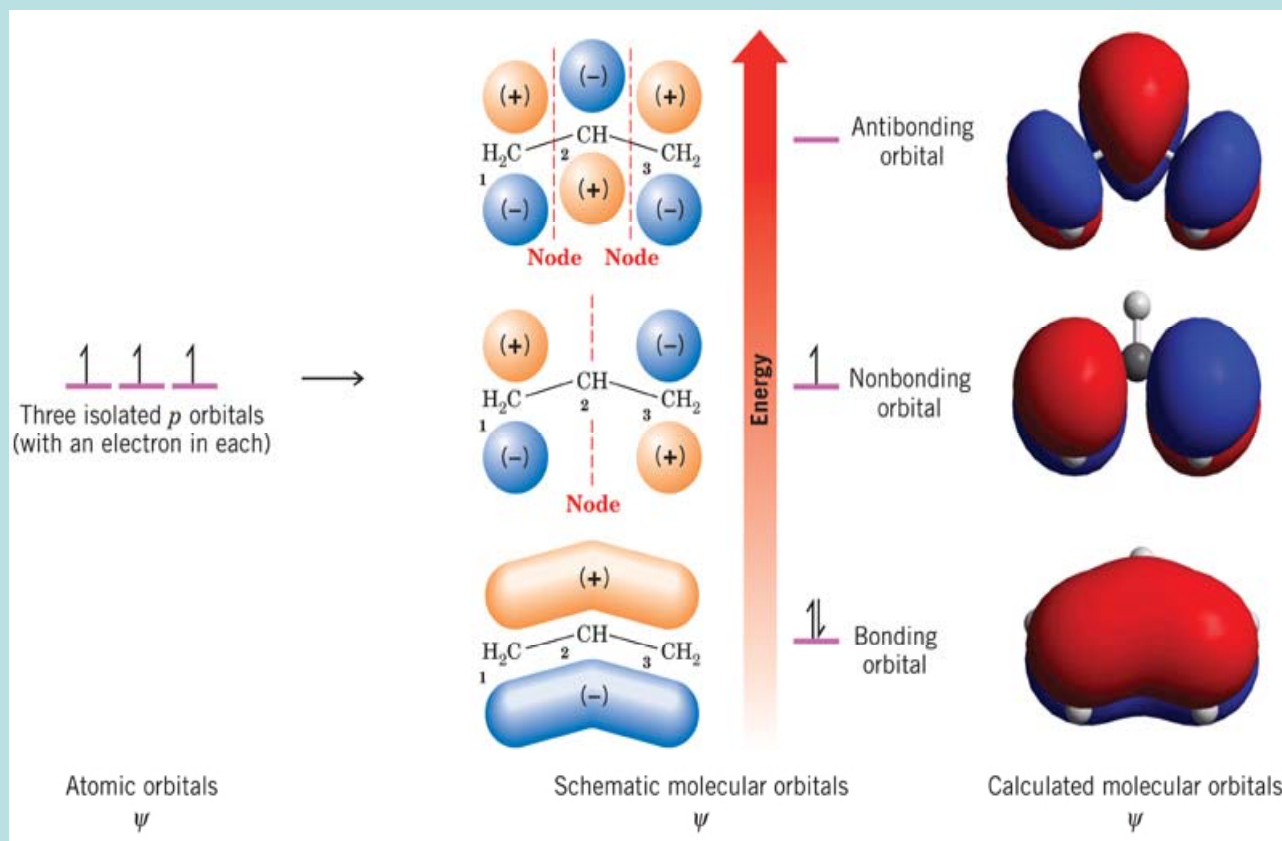


Nevertheless, representations like A and B are often used because they employ the more traditional depiction of covalent bonds, which make for easier accounting of electrons.

Resonance theory predicts a **symmetrical structure** for the simple allyl radical.

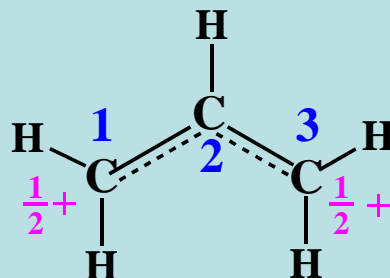
The Allyl Radical

Hybridization of the three atomic orbitals to form three π orbitals



Symmetry of the Allyl Cation

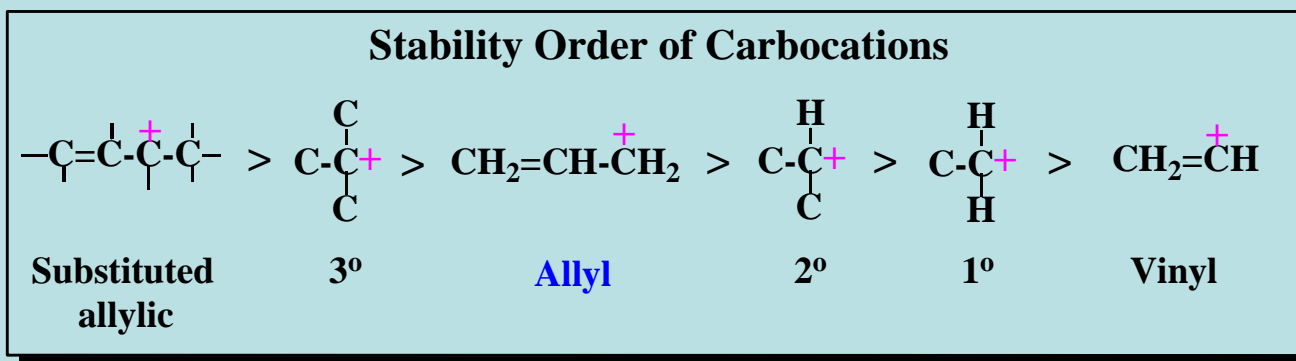
The hybrid structure below indicates the **symmetrical structure** of the allyl cation:



This structure implies (1) equivalent carbon-carbon bonds with a bond order of one and one half and (2) an equal distribution of the positive charge between the terminal carbons, C_1 and C_3 .

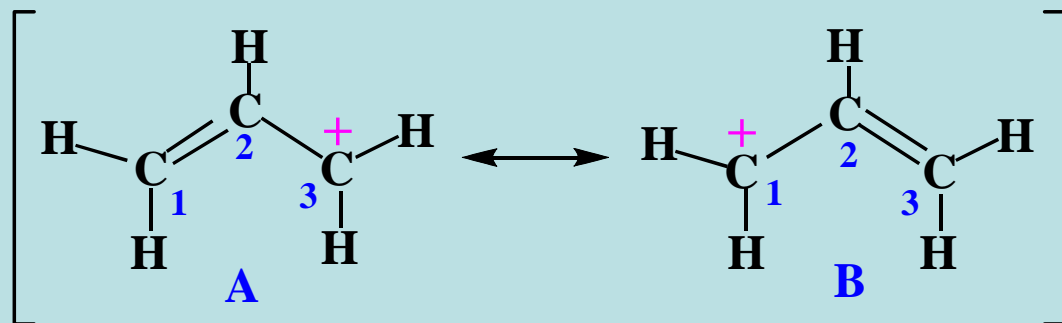
The Allyl Cation

The **allyl cation**, $\text{CH}_2=\text{CH}-\text{CH}_2^+$, is a very stable carbocation, almost as stable as a tertiary carbocation.



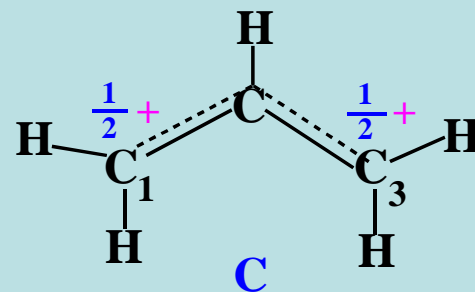
Resonance Theory Description of the Allyl Cation

Resonance theory describes the allyl cation as a **hybrid** of the two equivalent resonance structures **A** and **B**:



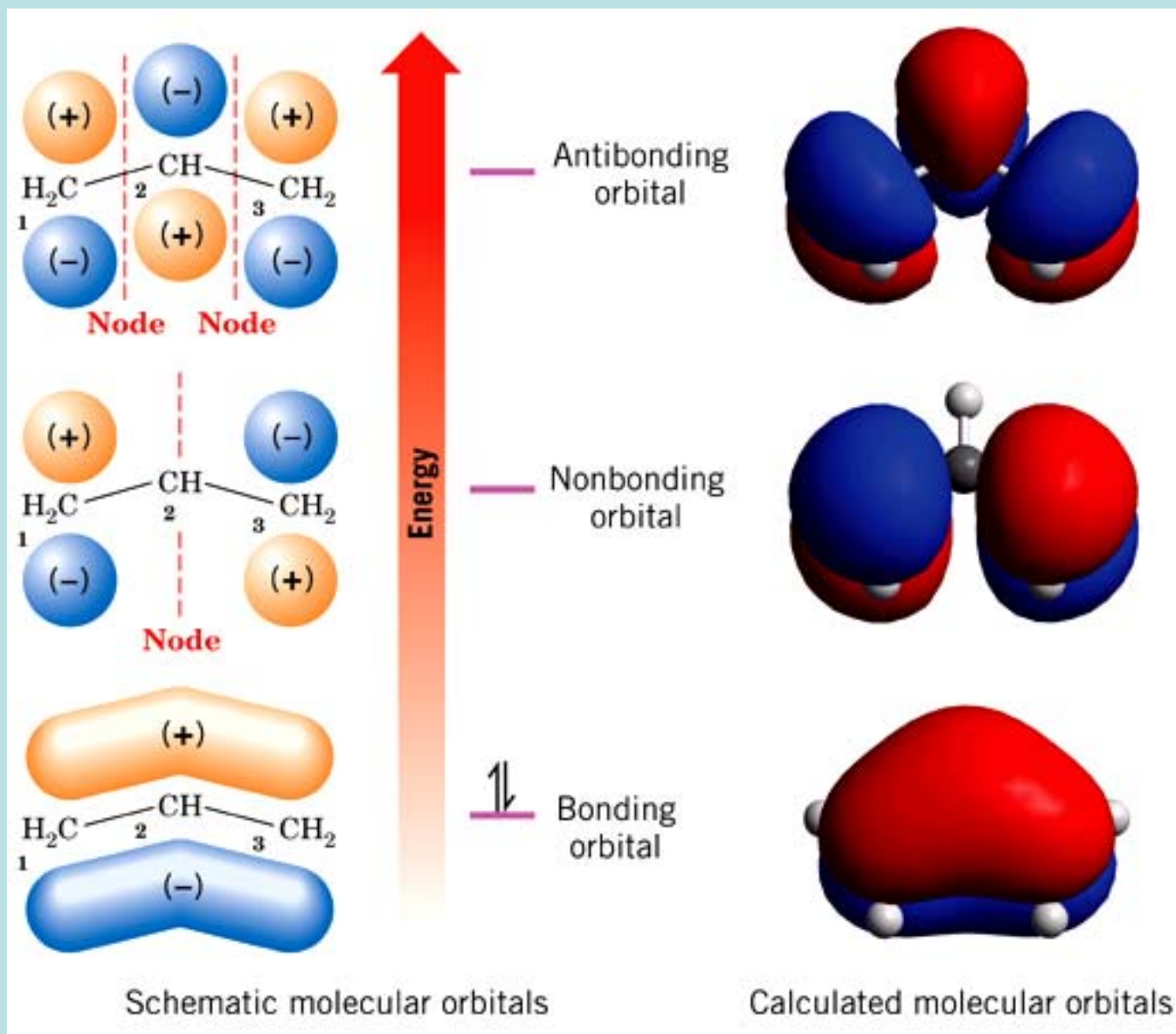
In the drawing of structures **A** and **B**, the interconversion is limited to the moving of pairs of electrons. The positions of the nuclei are fixed.

The **hybrid C** is symmetrical in the simple allyl cation, with the positive charge distributed equally between C_1 and C_3 . The carbon-carbon bonds are equivalent and have a bond order of one and one half.



The stability and reactivity of allyl-type cations are explained by resonance theory. The **hybrid** is **lower in energy** than either contributing resonance structure of the allyl cation, with the degree of stabilization due to resonance called **resonance energy**.

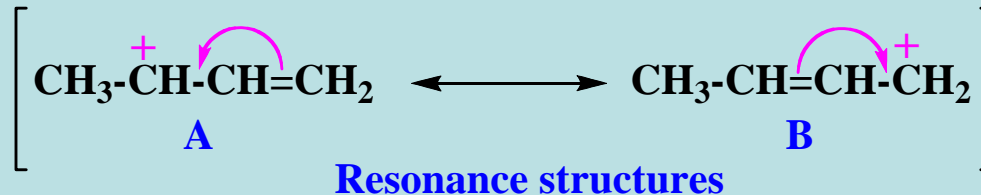
The π Molecular Orbitals of the Allyl Cation



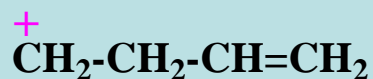
Rules for Writing Resonance Structures

The **resonance concept** gives insight into the reactivity and stability of organic structures.

- (1) Resonance structures exist only on paper. They provide a picture of the location of **valence-level electrons** within a structure. When two or more electronic representations can be written, they are called **resonance structures**, and are connected by double-headed arrows (\longleftrightarrow). The real molecule is a **hybrid** of all the resonance structures.
- (2) In writing a set of resonance structures, only the electrons are moved. **The positions of the nuclei remain the same.**

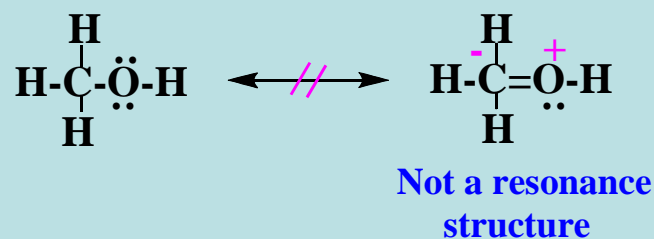


A and B interconvert by moving an electron pair.



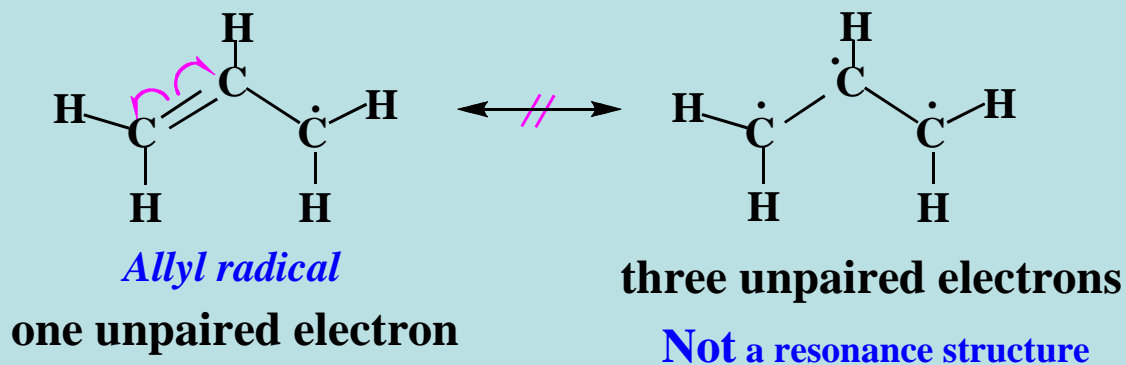
Not a resonance structure.
It is a **structural isomer**
formed by shifting an H.

(3) Resonance structures must be **proper Lewis structures**. The valency rules must be followed.

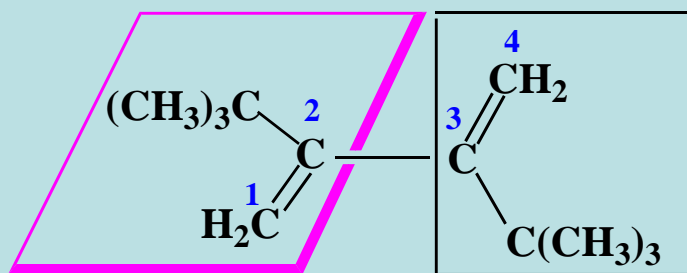


There are too many valence electrons around the C atom, which is limited to five bonds.

(4) All resonance structures must have the same number of **unpaired electrons**.



- (5) All atoms that are part of a delocalized electron system must be in a plane, or nearly in a plane.

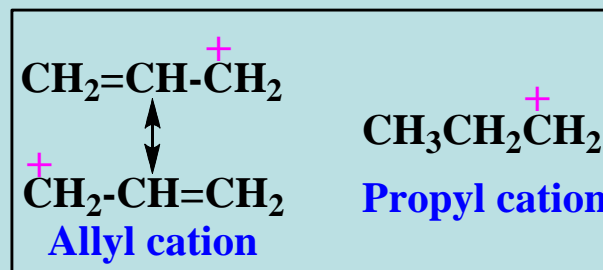


2,3-Di-*tert*-butyl-1,3-butadiene

This 1,3-butadiene acts like a nonconjugated diene because the two double bonds lie in **different planes**. The large *tert*-butyl groups impose a twist around the C₂-C₃ bond.

- (6) The energy of the **hybrid** (the real molecule) **is lower** than the energy of any single resonance structure.

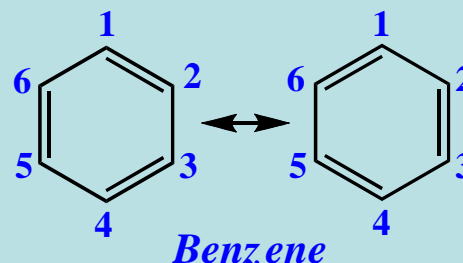
The energy of the allyl cation might be predicted to be similar to the propyl cation, since both seem to be 1° carbocations.



However, because of delocalization of charge in the allyl case, it would be an appreciably more stable ion.

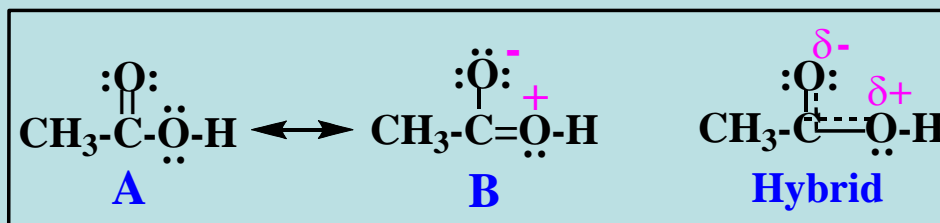
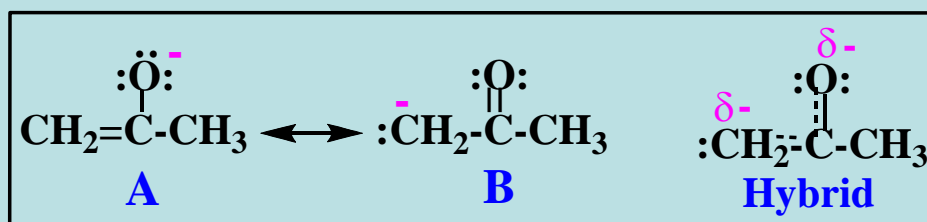
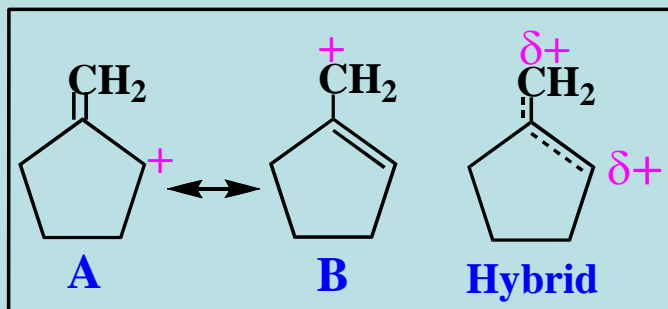
(7) Equivalent resonance structures make equal contributions to the hybrid and typically afford a **large resonance stabilization**.

In benzene, the two **resonance structures** at right are equivalent. There is a very large calculated resonance stabilization of about **152 kJ/mol** in benzene relative to the hypothetical cyclic polyene 1,3,5-cyclohexatriene (the name for each of the resonance forms **if** the double bonds were fixed in position).



(8) Nonequivalent resonance structures make unequal contributions to the hybrid. The more stable a structure, the more it contributes to the hybrid.

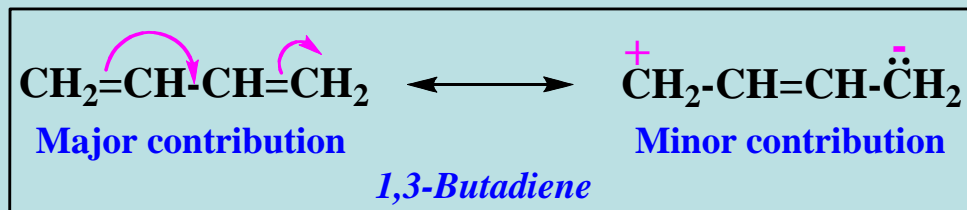
In each example below, structure **A** makes the larger contribution to the hybrid.



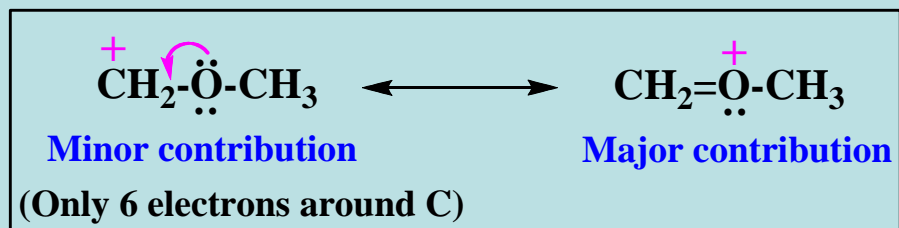
Estimating the Relative Stabilities of Resonance Structures: Some Guidelines

- (1) **The more covalent bonds** in a structure, **the more stable** it is.

Electrons are stabilized when they form covalent bonds. Alternatively, separating charges (creating positive and negative charges) by localizing a pair of electrons on one atom, raises the energy of a structure.

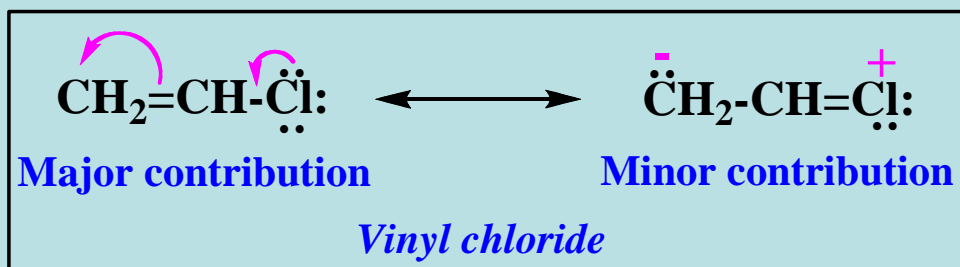


- (2) **Structures where all the atoms have a complete valence shell** of electrons **are especially stable** (octet rule) and make a major contribution to the hybrid.



Relative Stabilities of Resonance Structures, Continued

- (3) **Charge separation decreases stability** even when the number of covalent bonds remains the same.



in-class Quiz #4

- The first step of HBr addition to 1,3-butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ results in the formation of a carbocation. Draw this carbocation intermediate, all of its resonance structures, and the resonance hybrid.