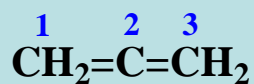


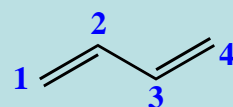
Alkadienes and Other Polyunsaturated Hydrocarbons

Hydrocarbons may contain more than one carbon-carbon double or triple bond. They also may have combinations of double and triple bonds. If the multiple bonds are separated by just one single bond, the compounds contain **conjugated systems**.

Examples

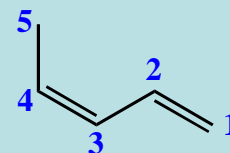


1,2-Propadiene



1,3-Butadiene

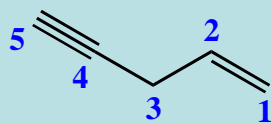
CONJUGATED



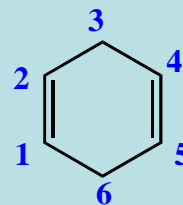
(3Z)-1,3-Pentadiene

(*cis*-1,3-Pentadiene)

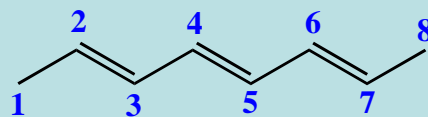
CONJUGATED



1-Pentene-4-yne



1,4-Cyclohexadiene



(2E,4E,6E)-2,4,6-Octatriene

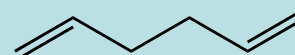
(*trans, trans, trans*-2,4,6-Octatriene)

CONJUGATED

CATEGORIES OF POLYENES

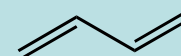
Isolated dienes have double bonds electronically isolated from each other (separated by two or more single bonds).

EXAMPLES



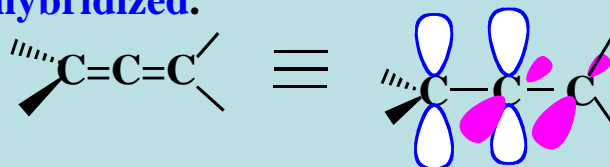
1,5-Hexadiene

Conjugated dienes have double bonds connected by just one single bond:

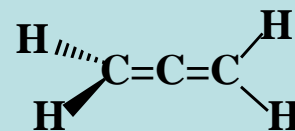


1,3-Butadiene

Cumulenes contain two double bonds that have a common central carbon that is **sp hybridized**.



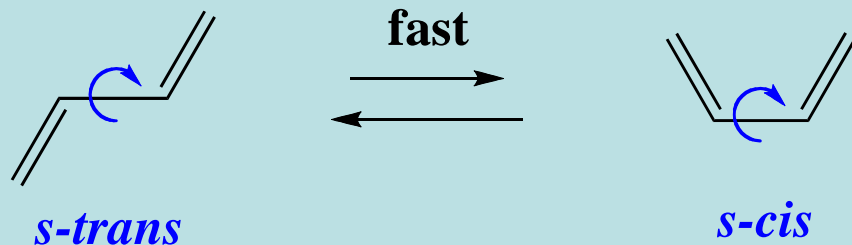
A "cumulated" system



Allene
(1,2-Propadiene)

Conformations of 1,3-Butadiene

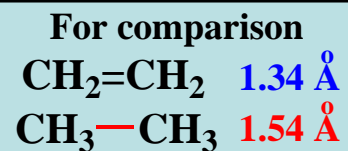
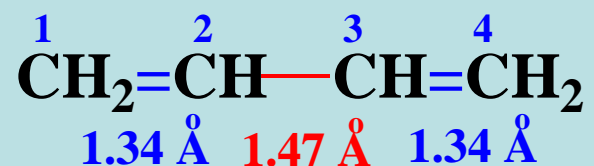
Rotation around the C₂-C₃ bond in 1,3-butadiene leads to different conformations, including two different planar conformations. In these two planar conformations, overlap of the p-atomic orbitals is maintained leading to extended π -systems. The two planar conformations (*s-cis* and *s-trans*) are more stable than the nonplanar conformations.



These two conformations rapidly interconvert by rotation around the single bond. The more stable *s-trans* dominates in the equilibrium at room temperature.

1,3-Butadiene: Bonding in a Conjugated Diene

The C-C bond lengths in 1,3-butadiene have been measured:



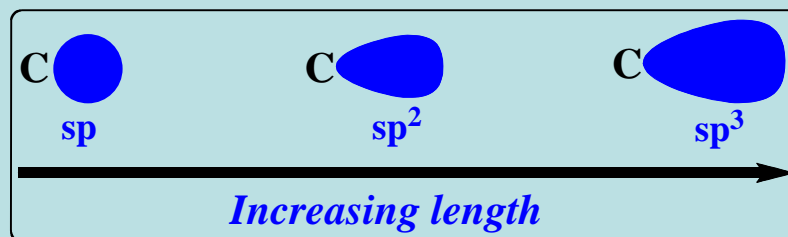
The carbon-carbon double bonds are within experimental error the same length as the bond in ethene. But the C₂-C₃ bond is much shorter than the C-C bond in ethane.

One interpretation of this difference is based on the **different hybridizations at C**, and the type of hybrid orbital projected out from carbon as shown in the following table.

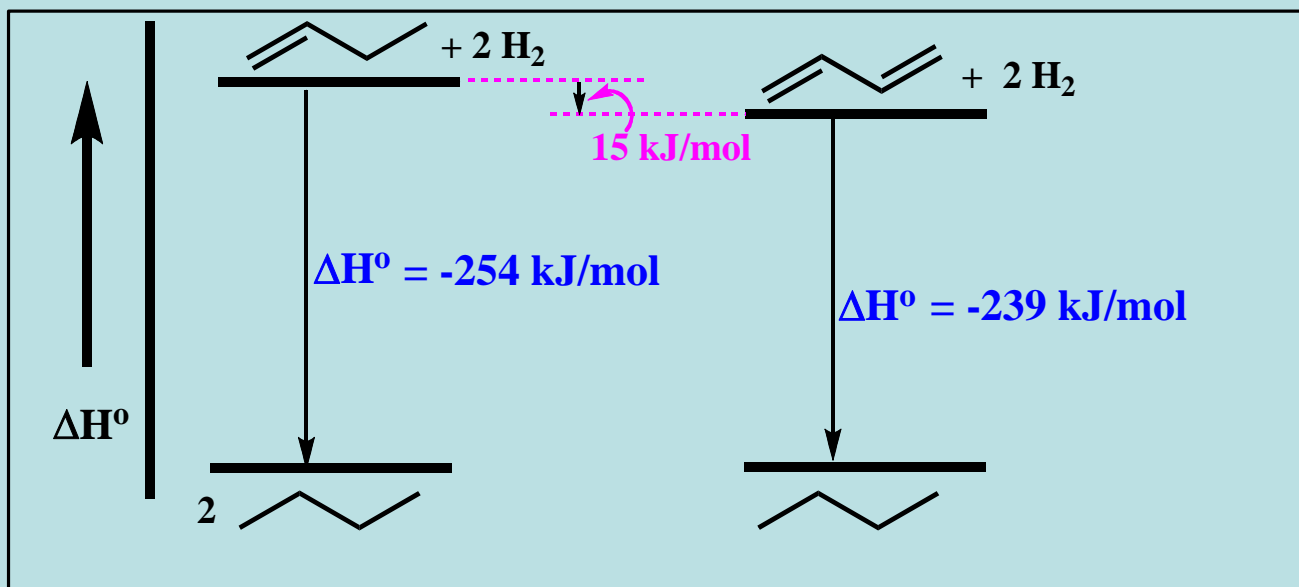
Effect of Hybridization on C-C Bond Length

Compound	Hybridization States of Bonding Carbons	Bond Length (Å)
$\text{H}_3\text{C}-\text{CH}_3$	sp^3--sp^3	1.54
$\text{CH}_2=\text{CH}-\text{CH}_3$	sp^2--sp^3	1.50
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	sp^2--sp^2	1.47
$\text{HC}\equiv\text{C}-\text{CH}_3$	$sp--sp^3$	1.46
$\text{HC}\equiv\text{C}-\text{CH}=\text{CH}_2$	$sp--sp^2$	1.43
$\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$	$sp--sp$	1.37

The varying lengths of the carbon-carbon single bonds reflect the different lengths of the hybrid atomic orbitals projected by the carbon atoms.



Heats of Hydrogenation Reveal Extra Stability in Conjugated Dienes



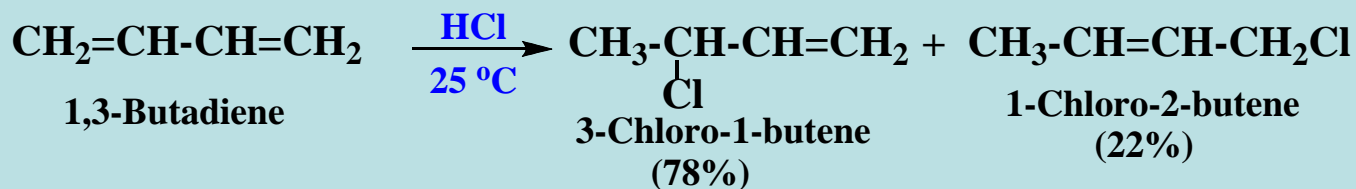
Possible Sources of the Extra Stability in Conjugated Dienes

- (1) The **shorter** C₂-C₃ bond provides a **stronger bond** that stabilizes the conjugated diene.
- (2) The small amount of **additional delocalization** of the π -electrons stabilizes the conjugated diene.

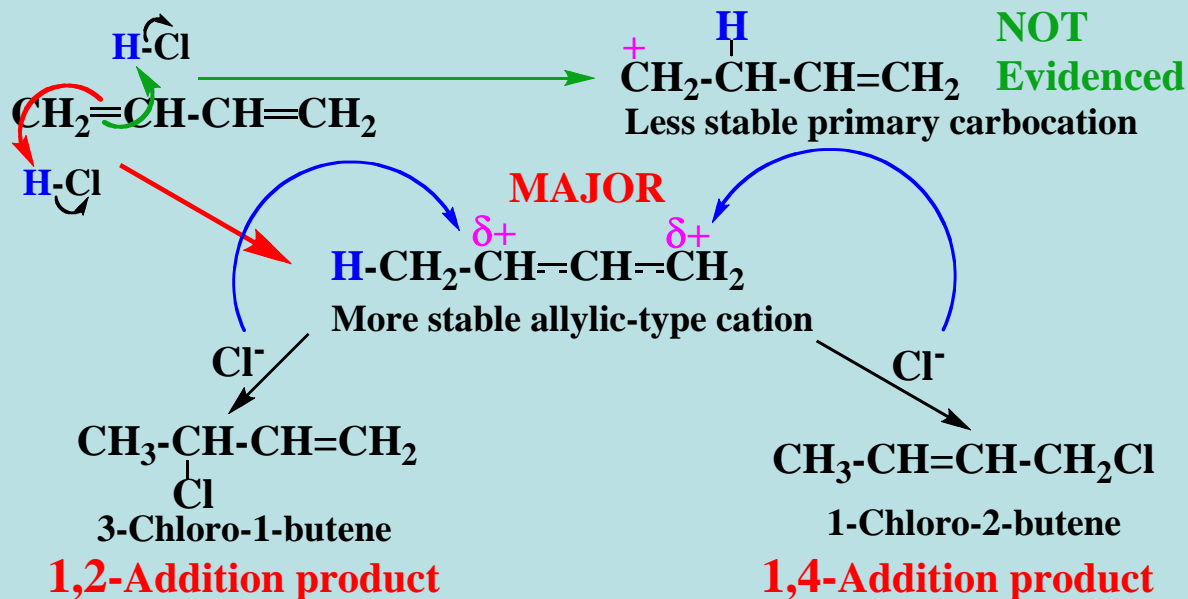
This extra stability of conjugated dienes is also revealed in a comparison of the electronic absorption spectra (ultraviolet-visible spectroscopy) of hydrocarbons of these types.

Electrophilic Attack on Conjugated Dienes: 1,2- and 1,4-Addition

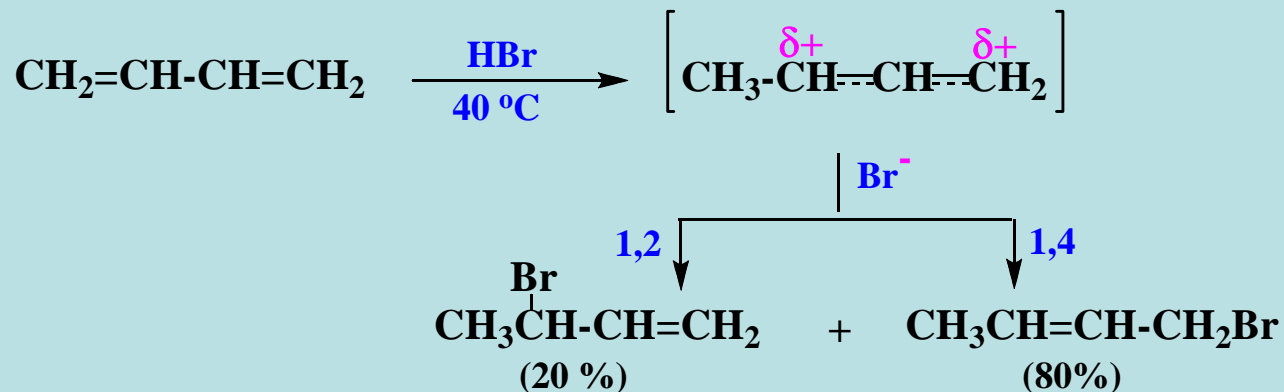
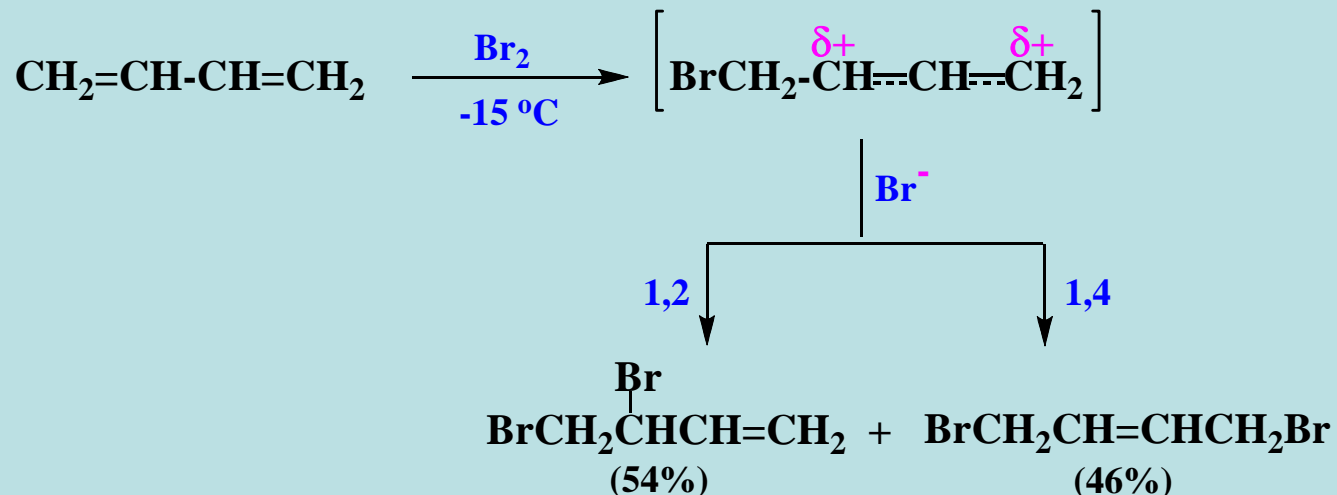
Conjugated dienes display a more complicated mode of electrophilic addition than simple alkenes. Typically, more than one product is formed.



Formation of the above two products, and absence of $\text{ClCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, could have been predicted by consideration of the **carbocation intermediates**.

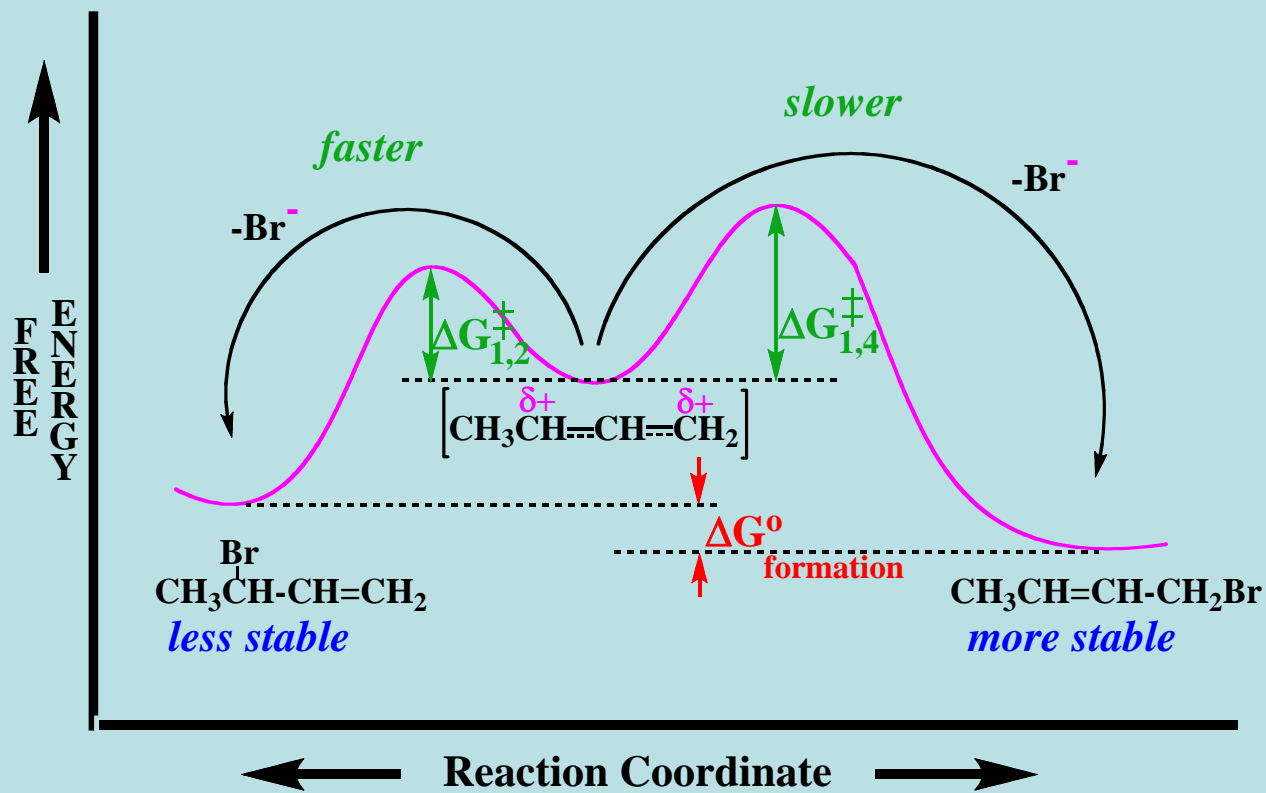


Other Examples of Competing 1,2- and 1,4-Additions



But if this reaction is carried out at **-80 °C**, the ratio of products is exactly **reversed**. And, on warming this cold reaction product up to 40 °C, it equilibrates to the 20:80 ratio that would have formed at 40 °C.

Energetics of the Product-Forming Steps



Under conditions of **thermodynamic control**, the product mixture is determined by the difference in the standard free energies of formation of the products: $\Delta G^\circ_{\text{formation}}$

Under conditions of **kinetic control**, the product mixture is determined by the **relative rates of product formation**. The more rapid formation of the 1,2-addition product is because the energy of activation required there ($\Delta G_{1,2}^\ddagger$) is less than that required for 1,4-addition ($\Delta G_{1,4}^\ddagger$).