

## 14.1: STABILITY OF CONJUGATED DIENES- MOLECULAR ORBITAL THEORY

### OBJECTIVES

After completing this section, you should be able to

1. write a reaction sequence to show a convenient method for preparing a given conjugated diene from an alkene, allyl halide, alkyl dihalide or alcohol (diol).
2. identify the reagents needed to prepare a given diene from one of the starting materials listed in Objective 1, above.
3. compare the stabilities of conjugated and non-conjugated dienes, using evidence obtained from hydrogenation experiments.
4. discuss the bonding in a conjugated diene, such as 1,3-butadiene, in terms of the hybridization of the carbon atoms involved.
5. discuss the bonding in 1,3-butadiene in terms of the molecular orbital theory, and draw a molecular orbital for this and similar compounds.

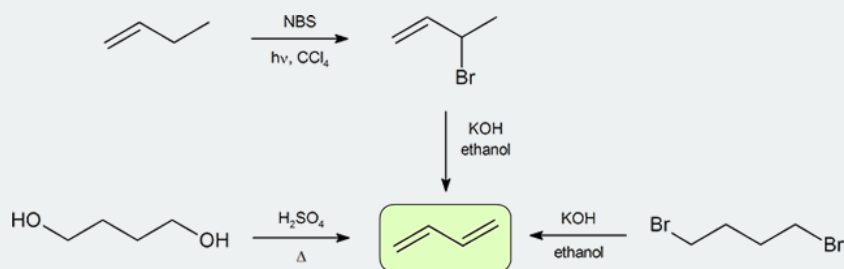
### KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- delocalized electrons
- node

### STUDY NOTES

The two most frequent ways to synthesize conjugated dienes are dehydration of alcohols and dehydrohalogenation of organohalides, which were introduced in the preparation of alkenes (Section 8.1). The following scheme illustrates some of the routes to preparing a conjugated diene.



The formation of synthetic polymers from dienes such as 1,3-butadiene and isoprene is discussed in Section 14.6. Synthetic polymers are large molecules made up of smaller repeating units. You are probably somewhat familiar with a number of these polymers; for example, polyethylene, polypropylene, polystyrene and poly(vinyl chloride).

As the hydrogenation of 1,3-butadiene releases less than the predicted amount of energy, the energy content of 1,3-butadiene must be lower than we might have expected. In other words, 1,3-butadiene is more stable than its formula suggests.

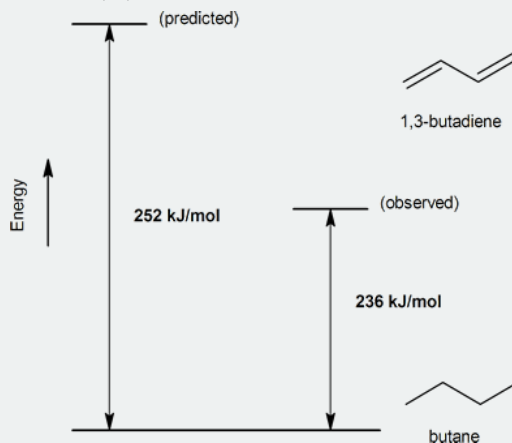


Figure 14.1: Energy diagram for the hydrogenation of 1,3-butadiene (not to scale).

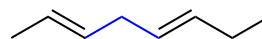
Some university-level general chemistry courses do not introduce the subject of molecular orbitals. If you have taken such a course, or forgotten what is meant by the term “molecular orbital,” combine a review of [Section 1.11](#) with your study of this section.

## CONJUGATED VS. NON-CONJUGATED DIENES

Dienes are compounds which contain two double bonds. These dienes can be non-conjugated (the two double bonds are separated by at least one  $sp^3$  hybridized atom). Conjugated dienes have the two double bonds separated by a single bond. Conjugated dienes have properties and reactivity which are distinctly different than non-conjugated dienes. Determining if double bonds are conjugated represents an important skill in organic chemistry.



**3,5-Octadiene**  
(Conjugated)



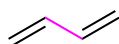
**2,5-Octadiene**  
(Non-Conjugated)



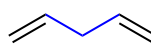
**1,3-Cyclohexadiene**  
(Conjugated)



**1,4-Cyclohexadiene**  
(Non-Conjugated)



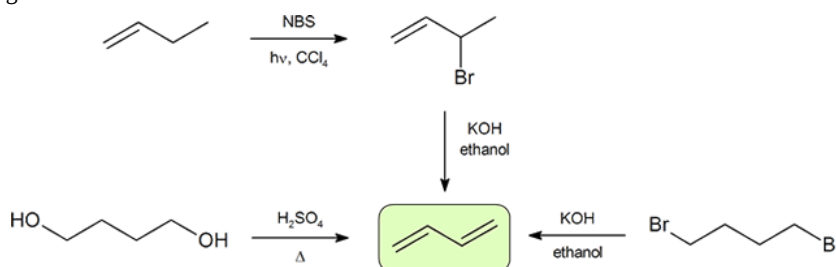
**1,3-Butadiene**  
(Conjugated)



**1,4-Pentadiene**  
(Non-Conjugated)

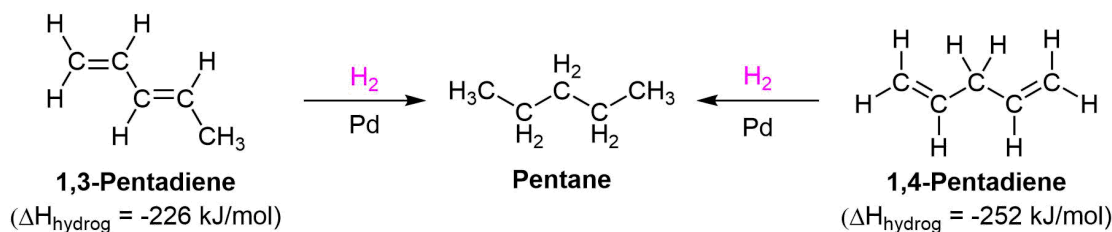
## SYNTHESIS OF DIENES

Conjugated dienes can be prepared using many of the methods used for the preparation of alkenes previously discussed (**Sections 11-7, 11-8, 11-9, and 11-10**). A convenient method starts with the free radical halogenation of the allylic carbon of an alkene using NBS. The resulting halide can then be reacted with a strong base to result in E2 elimination and create a diene product. The compound, 1,3-butadiene, is the simplest conjugated diene and has an important use in the synthesis of polymers which will be discussed in [Section 14.6](#). Many simple dienes, such as 1,3-butadiene and isoprene, can be prepared industrially by the double dehydration of alcohols and the double dehydrohalogenation of organohalides.

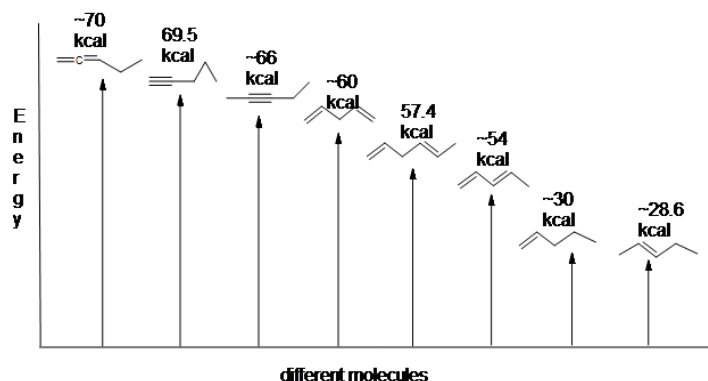


## STABILITY OF CONJUGATED DIENES

Conjugated dienes are known to be more stable than non-conjugated dienes as shown by their experimentally determined heats of hydrogenation. In **Section 7-6**, it was shown that as alkenes become more stable, they contain less energy, and therefore release less heat during hydrogenation. Experiments have shown that conjugated dienes have a lower heat of hydrogenation (-226 kJ/mol) than non-conjugated dienes (-251 kJ/mol). Using the differences in heats of hydrogenation the stabilization energy in conjugated dienes can be estimate to be roughly 25 kJ/mol.

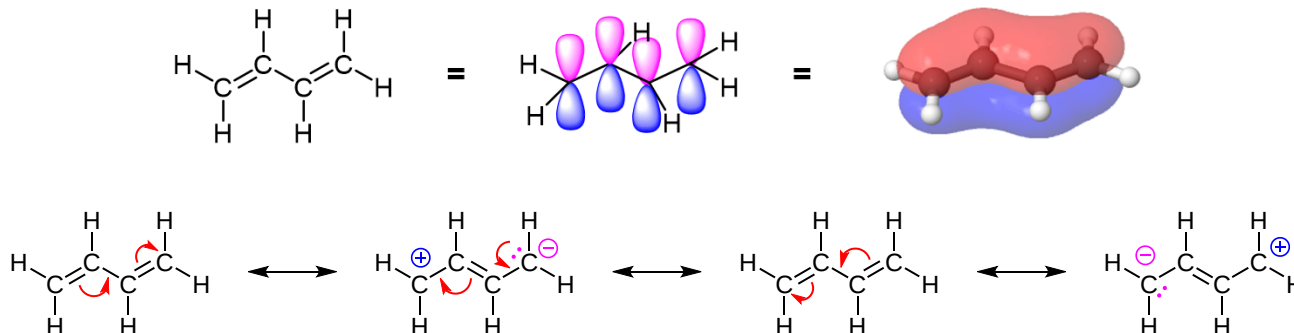


Here is an energy diagram comparing different types of bonds with their heats of hydrogenation to show relative stability of each molecule:

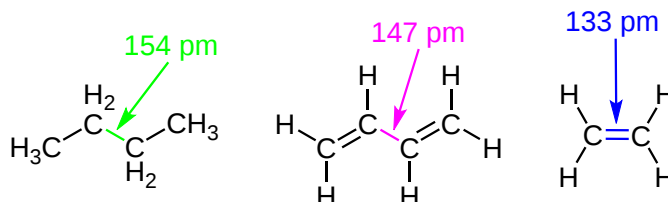


The stabilization of dienes by conjugation is less dramatic than the aromatic stabilization of benzene. Nevertheless, similar resonance and molecular orbital descriptions of conjugation may be written.

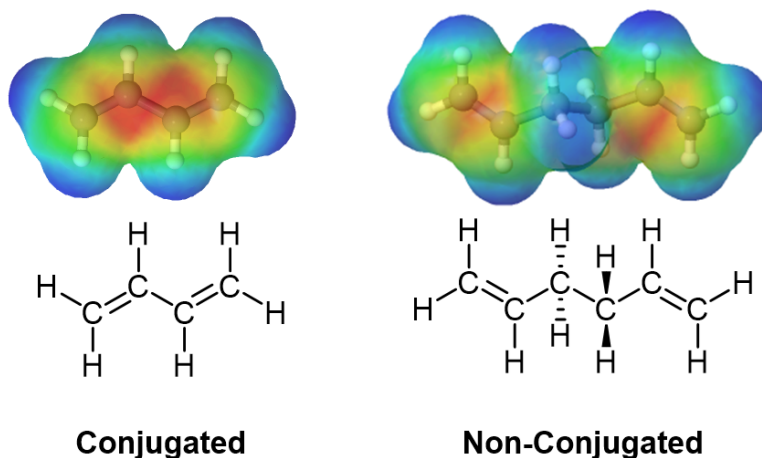
Each alkene carbon in 1,3 dienes are  $sp^2$  hybridized and therefore have one unhybridized  $p$  orbital. The four  $p$  orbitals in 1,3-butadiene overlap to form a conjugated system which can be represented by the resonance forms shown below. This delocalization of charges stabilizes conjugated diene making them more stable than non-conjugated dienes.



Evidence of conjugation in 1,3 dienes is seen in the single bond being stronger and shorter (147 pm) than an ordinary alkane C-C bond (154 pm). The resonance hybrid of a 1,3-butadiene shows this bond to contain significant double bond character with its bond length being roughly the average of a single and double bond.

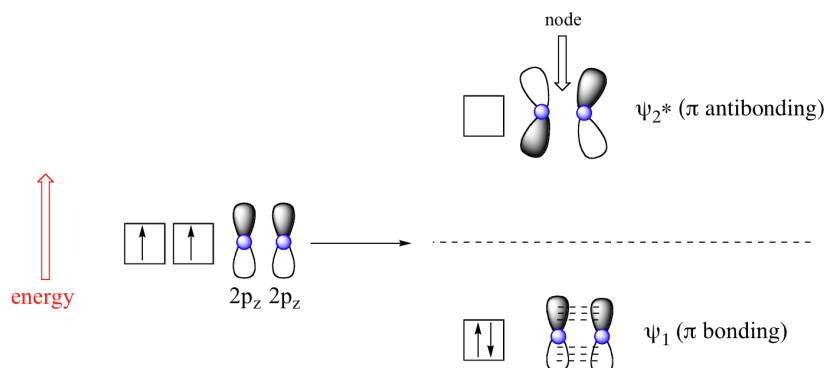


The delocalized electron density of a 1,3 diene can be seen when viewing an electrostatic potential maps. In conjugated dienes, it is observed that the pi electron density overlap (shown in red) is closer together and delocalized in conjugated dienes, while in non-conjugated dienes the pi electron density is located completely on the double bonds.

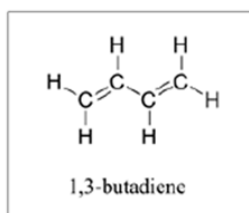


### MOLECULAR ORBITALS OF 1,3 DIENES

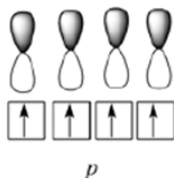
According to MO theory discussed in [section 1-11](#), when a double bond is non-conjugated, the two atomic  $2p_z$  orbitals combine to form two **pi ( $\pi$ ) molecular orbitals**, one a low-energy  $\pi$  bonding orbital and one a high-energy  **$\pi$ -star ( $\pi^*$ ) anti-bonding molecular orbital**. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi ( $\Psi$ ) instead of  $\pi$ . In the bonding  $\Psi_1$  orbital, the two (+) lobes of the  $2p_z$  orbitals interact constructively with each other, as do the two (-) lobes. Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital. In the higher-energy anti-bonding  $\Psi_2^*$  orbital, the (+) lobes of one  $2p_z$  orbital interacts destructively with the (-) lobe of the second  $2p_z$  orbital, leading to a node between the two nuclei and overall repulsion. By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy  $\Psi_1$  orbital when the molecule is in the ground state.



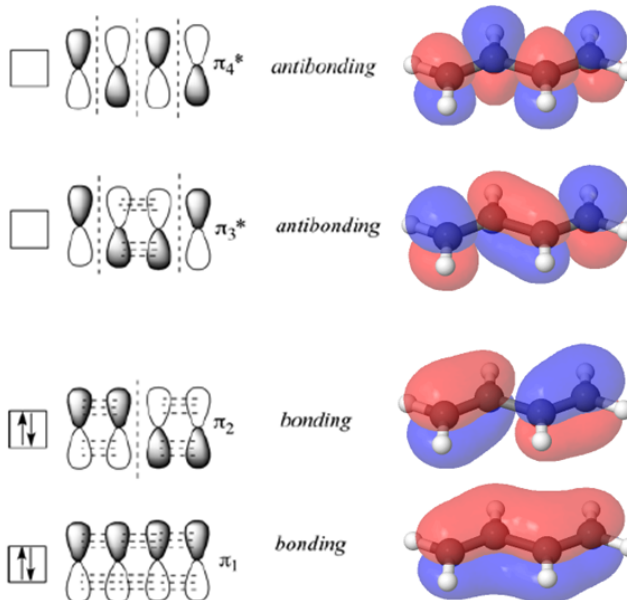
With a conjugated diene, such as 1,3-butadiene, the four  $2p$  atomic orbitals combine to form four pi molecular orbitals of increasing energy. Two bonding pi orbitals and two anti-bonding  $\pi^*$  orbitals. The combination of four pi molecular orbitals allow for the formation of a bonding molecular orbital that is lower in energy than those created by an unconjugated alkene. The 4 pi electrons of 1,3-butadiene completely fill the bonding molecular orbitals giving the additional stability associated with conjugated double bonds.



### atomic orbitals



### molecular orbitals



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