Chapter 20 – Dienes, Conjugated Systems, and Pericyclic Reactions
Lecture Outline

I. Stability of Conjugated Dienes

A. **Conjugation** refers to molecules that contain two or more adjacent double bonds.

1. Dienes are compounds that contain two C=C bonds.

2. An unconjugated diene is one in which the double bonds are separated by two or more single bonds.

3. Conjugated diene = C=C's are separated by 1 single bond

a. The simplest diene is 1,3-butadiene.

4. A cumulated diene is one in which the double bonds share an sp-hybridized carbon.

B. Table 20.1 gives the heats of hydrogenation for several alkenes and conjugated dienes.

Table 20.1 Heats of Hydrogenation of Several Alkenes and Conjugated Dienes

Name	Structural Formula	ΔH° kJ (kcal)/mol
1-Butene		−127 (−30.3)
1-Pentene		−126 (−30.1)
cis-2-Butene		−120 (−28.6)
trans-2-Butene		−115 (−27.6)
1,3-Butadiene		−237 (−56.5)
trans-1,3-Pentadiene		−226 (−54.1)
1,4-Pentadiene		−254 (−60.8)

2. Let's estimate the heat of hydrogenation in the following manner:

1 + H2 → 1 + heat released

a. ΔH for 1-butene is

-127 kJ/mol.

b. Theoretically, all we're doing to make 1,3-butadiene is adding another double bond. So what if we said we were hydrogenating two moles of 1-butene??

That means....

ΔH = (-127 kJ/mol) 2 = -254 kJ/mol.

2 1 + 2H2 → 2 1 ΔH = -254 kJ/mol

3. In nature, we see that ΔH for 1,3-butadiene is -237 kJ/mol, a difference of 17 kJ/mol than what we predicted. We can reach one conclusion from this: conjugation provides an extra stability to the molecule.

4. If you do this calculation for other conjugated systems, you'll find the same result: conjugated dienes are more stable by between 15-20 kJ/mol of energy.

5. compound containing conjugated double bonds are more stable than unconjugated molecules.

6. Where does this stability come from?

a. In a conjugated system, each C contains a p-orbital that is used to form a double bond. That means that 4π electrons are delocalized among the 4p-orbitals. → leads to increased stability.

7. Figure 20.2 on pg. 813 gives the molecular-orbital (MO) explanation of what's going on here:

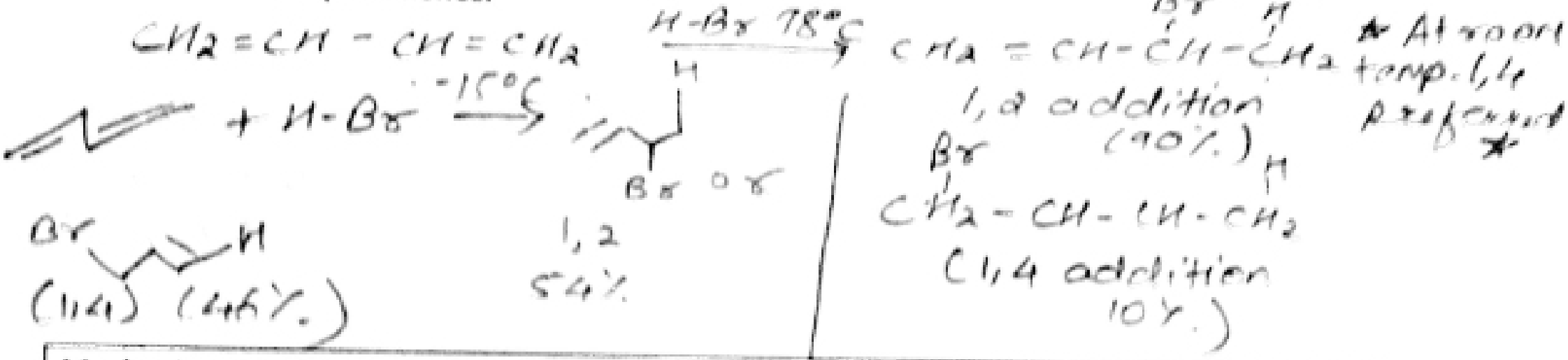
a. In order to create a π-bond, you have to have overlapping p-orbitals that are parallel (we can't use the sp^2-hybridized orbitals to create the π-bonds).

b. The situation that gives the most stable molecule in the one in which all the pink orbitals are overlapped with each other, and likewise with the blue.

c. As more nodes (places in which electrons will NOT reside at) are introduced into the model the less likely that π-bonds will form (but anti-bonding bonds will!)

II. Electrophilic Addition to Conjugated Dienes

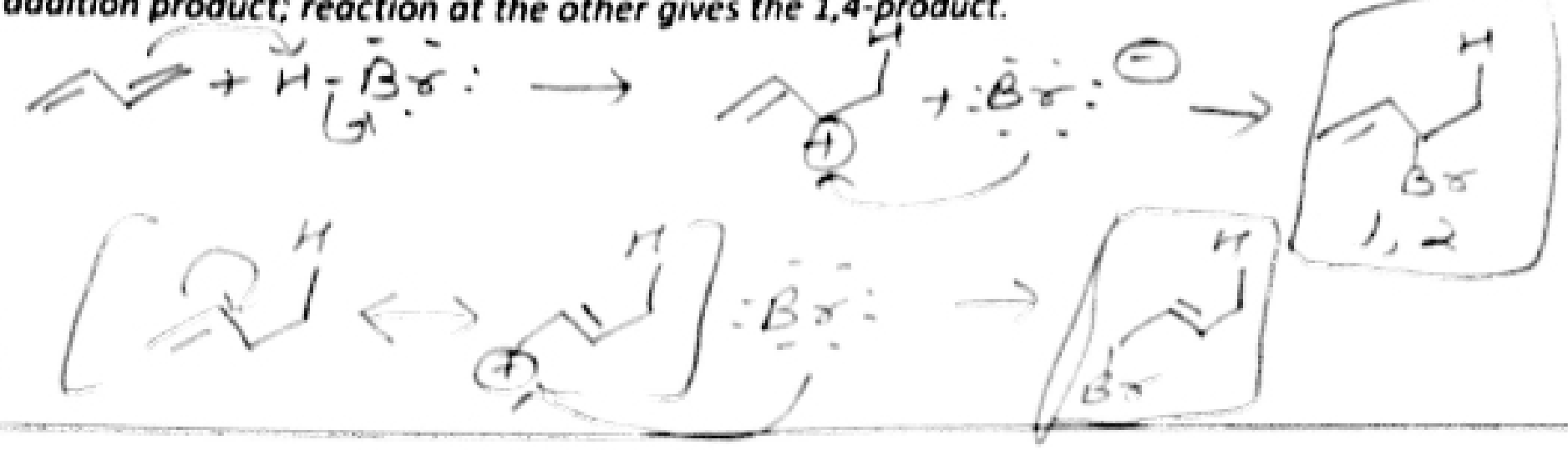
A. Conjugated dienes undergo two-step nucleophilic addition reactions just like simple alkenes.



Mechanism #1: 1,2- and 1,4-Addition to a Conjugated Diene

Step 1: *Electrophilic addition is initiated by reaction of a terminal carbon of one of the double bonds with HBr to give an allylic carbocation intermediate, which can be best represented as a resonance hybrid of two contributing structures. Formation of this very stable cation is the rate-determining step.*

Step 2: *Reaction of bromide at one of the carbons bearing partial positive charge gives the 1,2-addition product; reaction at the other gives the 1,4-product.*



B. Let's summarize the observations found in the mechanism:

1. 1,2 addition predominated over 1,4 addition typically, at lower temperatures. 1,2 product was out.