2. To recap, 1,2-addition happens at a faster rate than 1,4-addition, and if the reaction was irreversible, that's the product that we would observe (1,2-addition).

3. If the reaction IS reversible, eventually you form 1,4. That is what will predominate

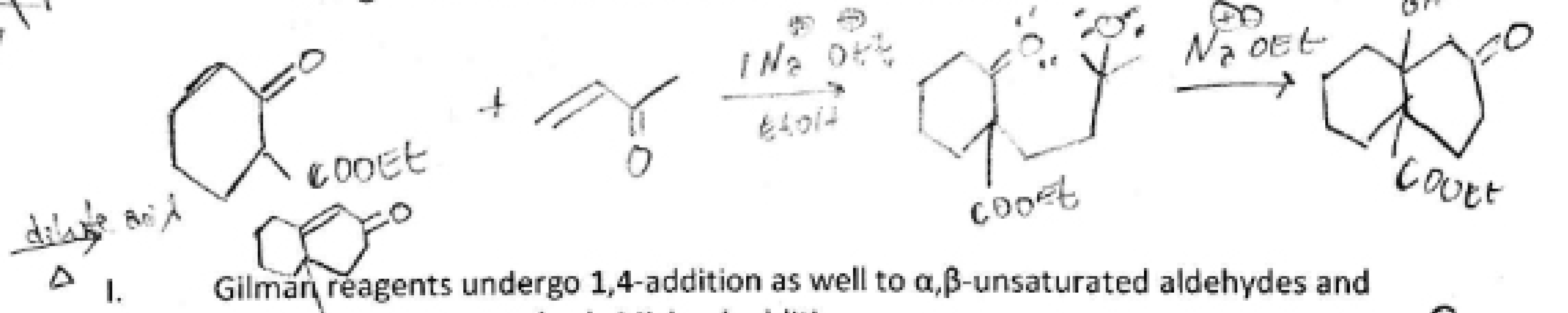
4. Remember that I said earlier that C=O bonds are thermodynamically stronger than C=C bonds.

5. Under conditions of thermodynamic control the 1,4 product is the most stable product.

H. A Michael reaction with an α,β-unsaturated ketone followed up with an intramoelcular aldol reaction is useful in synthesizing 2-cyclohexenones.

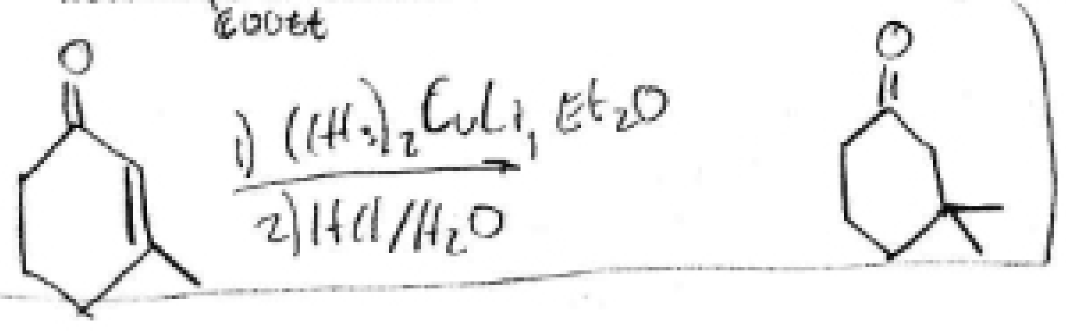
WON'T BE ON EXAM

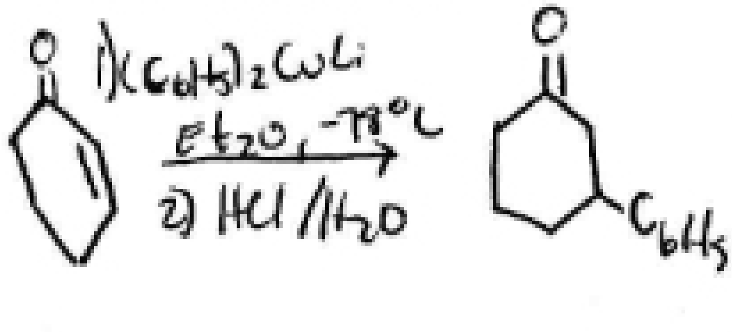
1. An important example of this is treating a cyclic ketone, β-ketoester, or β-diketone with an α,β-unsaturated unsaturated ketone in the presence of a base catalyst – this forms a cyclohexanone ring fused to the original ring. This reaction is called the **Robinson annulation**.



COOEt

I. Gilman reagents undergo 1,4-addition as well to α,β-unsaturated aldehydes and ketones in a reaction that's Michael addition-esque.





End-of-Chapter Problems: 18, 19, 21, 22, 24, 27, 28, 29, 31, 32, 33, 34, 35, 36, 38, 39, 44, 45, 46, 47, 49, 53, 54, 56, 59, 61.

* * Grignard + organolithium add to carbonyl carbon

* Gilman go $\boxed{1,4}$. Add to double bond

Chapter 20 – Dienes, Conjugated Systems, and Pericyclic Reactions

Lecture Outline

I. Stability of Conjugated Dienes

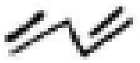
A. **Conjugation** refers to molecules that contain two or more adjacent double bonds.

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

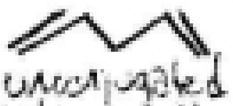
2. An unconjugated diene is one in which the double bonds are separated by two or more single bonds.

3. Conjugated diene : C=C bonds are separated by 1 single bond

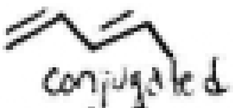
a. The simplest diene is 1,3-butadiene.



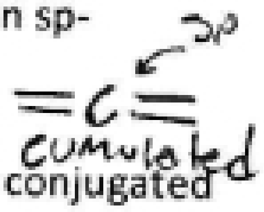
4. A cumulated diene is one in which the double bonds share an sp-hybridized carbon.



unconjugated



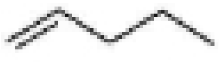
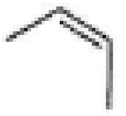
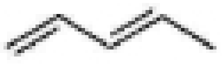
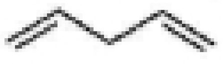
conjugated



cumulated

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)

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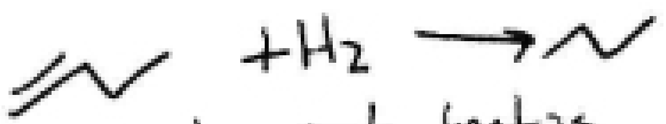

how much heat is released during this?

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

   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??

ΔH = -237 KJ/mol

Why the difference in energies?

   That means....
   ΔH = (-127 KJ/mol) 2 = -254 KJ/mol

ΔH = -254 KJ/m

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 here ~17 KJ. This stability means it's a bit harder to react.

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. From this we can generalize that compounds containing double bonds are more stable than unconjugated molecules.

6. Where does this stability come from?

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

Review ? for exam

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).