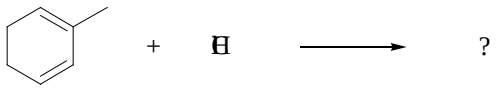
Problem Set #3

Chemistry 3231
September 18, 2001

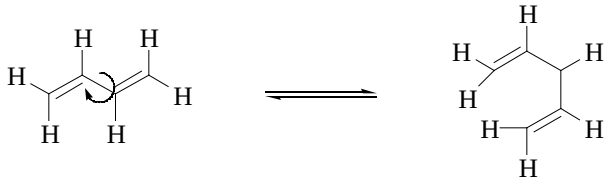
1. HCl adds to diene **1** below, giving both kinetic (1,2) and thermodynamic (1,4) products.



1

   (a) Write the mechanism and products for this reaction, indicating which product is the kinetic one and which is the thermodynamic one.
   (b) Draw a free energy vs. reaction coordinate diagram in accord with the observations that the 1,2-product is formed faster, but that the 1,4-product is more thermodynamically stable.
   (c) Be sure to do problem 11.19 in Jones.

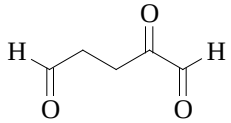
2. The two most stable conformers of 1,3-butadiene are shown below. The barrier for rotation about the central single bond is approx. 5 kcal/mol in going **2** → **3**. The *s-cis* conformer (**3**) is about 3 kcal/mol less stable than the *s-trans* (**2**).



2 **3**

   (a) Construct a free energy vs. bond rotation diagram for **2** → **3**. Indicate on the diagram the position of the transition state, and use models to draw a good picture of the transition state structure.
   (b) Why do the two most stable conformers have all four carbons in the same plane?
   (c) Why is the barrier to rotation around the central C-C single bond (**2** → **3**) slightly higher than for a "normal" C-C single bond (as in ethane, for example)?
   (d) Is the conversion from **2** → **3** faster/slower/same compared to the conversion of **3** → **2**?

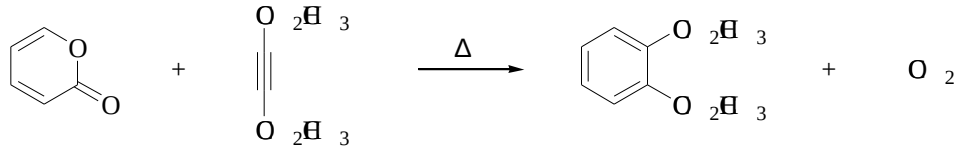
3. Myrcene, $C_{10}H_{16}$, is found in oil of bay leaves. It can be catalytically hydrogenated to yield 2,6-dimethyloctane. On ozonolysis followed by Zn/HOAc treatment, myrcene yields formaldehyde, acetone, and 2-oxopentanedial (**4**).



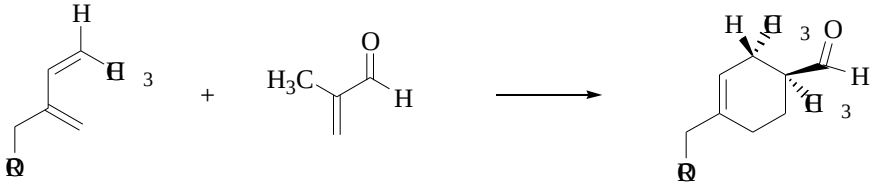
4

Deduce the structure of myrcene, and formulate all the reactions, showing starting material and products.

4. Propose a mechanism to explain the following reaction. (HINT: The Diels-Alder reaction is reversible.)



5. Diene **5** undergoes a Diels-Alder reaction with methacrolein (**6**), yielding endo product **7** (ref: Roush, et al. *J. Am. Chem. Soc.* **1997**, *119*, 7402).



5 **6** **7**

(a) Draw a detailed picture of the diene and dienophile in the transition state. Make sure that your picture accounts for the formation of product 7.
(b) What controls the stereochemistry of the reaction (endo vs. exo)?
(c) Explain the regioselectivity of the above reacion ("ortho" vs. "meta" regiochemistry).