

Chemistry 125 Sixth Examination
February 27, 2006

Name _____

1. (3 min) The heat of hydrogenation of ethene (C_2H_4) is -32.7 kcal/mole. The heats of hydrogenation of the four acyclic isomers of C_4H_8 are listed below (in kcal/mole). Draw the structure of each of these four isomers and connect each with with a line to the appropriate heat of hydrogenation. [Don't worry about the difference between -28.4 and -28.6 .] No explanation necessary.

-27.6

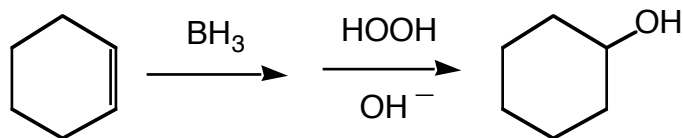
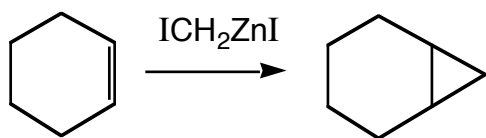
-28.4

-28.6

-30.3

2. (1 min) Explain in a few words why ethylene polymerization using a titanium "Ziegler/Natta" catalyst gives a higher density product than polymerization with a free-radical catalyst. Don't discuss mechanism, just structure.

3. (8 min) Superficially the following two transformations seem entirely different, but each transformation involves **TWO** important steps that are quite similar between the two transformations (a concerted reaction counts as a single step). Draw curved-arrow mechanisms for the relevant steps of each reaction to make the analogy clear.



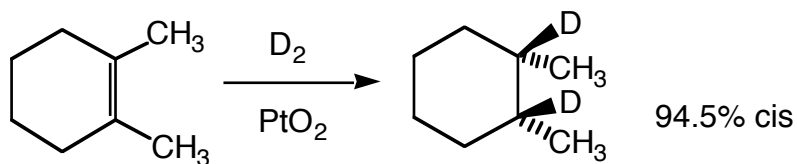
4. Cite **DIFFERENT KINDS** of **EXPERIMENTAL EVIDENCE** to support each of **FOUR** (4 only) the following five assertions. That is, for each assertion you choose you should cite one kind of experimental evidence, but you may not use the same type of evidence for more than one assertion. Be as specific as you can with your example.
- A. (4 min) The transition state structure for the initial step of Br_2 addition to an alkene differs in different solvents.
 - B. (4 min) The initial step for Br_2 addition to an alkene involves attack at both alkene carbon atoms.
 - C. (4 min) A bromonium ion may be bridged, but not symmetrically bridged.
 - D. (4 min) A bromonium ion may be made sufficiently stable to determine its x-ray crystal structure.
 - E. (4 min) The hydroxymercuration/ NaBH_4 reduction sequence with an alkene can yield a different hydration product from that obtained by treatment with acid and water.

(red means not in 2010)

(Continue your answer on following page, if necessary)

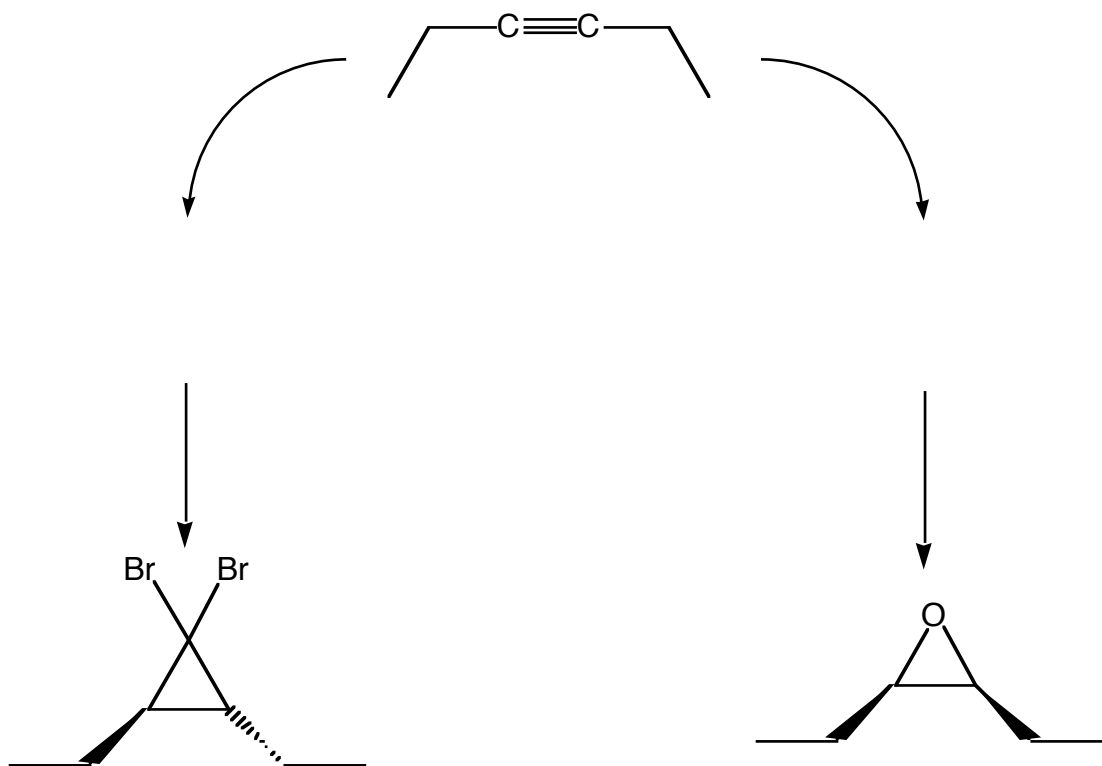
Answer to question 4 (cont)

5. On page 439 the textbook illustrates the following transformation:



- A. (5 min) Explain in terms of the reaction mechanism why it is reasonable that the product should be cis. Clearly drawn figures are essential to a convincing explanation.
- B. (1 min) What is curious about the book's statement "In this example D_2 is used so we can see the stereochemical outcome of the reaction"?
- C. (5 min) Why might someone have studied the reaction with D_2 , given that with a different metal catalyst (Pd) the product is predominantly trans.

6. (6 min) 3-hexyne could be converted in **two steps** into either trans-1,1-dibromo-2,3-diethylcyclopropane or into cis-2,3-diethyloxirane. Show the sets of reagents needed for each of the **four transformations**. *NO MECHANISMS NECESSARY*, just indicate the reagents and the structure of the intermediate compound for each transformation.



7. (5 min) Having learned that the allylic π system of O_3 forms two bonds at once to an alkene, as shown below, one might think to try the same thing with the apparently analogous boron compound (assuming it exists). Explain **in terms of the orbitals involved** why this might not be such a good idea.

