Organic Chemistry: CHEM 231B

Spring 2003 - Whittier College

Problem Set #3

Due April 10 at 12:00 pm

1. When (5R) 1,5-diethylcyclopentene is reacted, first with borane in tetrahydrofuran and subsequently with hydrogen peroxide, sodium hydroxide in water, two products, Compounds A & B, are observed by NMR in a 55:45 ratio, respectively. When (3R) 1,3-diethylcyclopentene is reacted, first with Diisopropylborane in tetrahydrofuran and subsequently with hydrogen peroxide, sodium hydroxide in water, two products, Compounds C & D, are observed by NMR in a 95:5 ratio, respectively. (11 pts)

1a. Draw a graphical representation for each reaction. What general reaction is occurring? (1 pt)

1b. What are the structures of A & B? (1 pts)

1c. What are the structure of C & D? (1 pts)

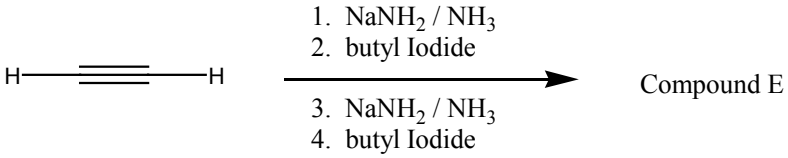
1d. What is (are) the reaction mechanism(s) for formation of the product(s)? Include a drawing of any important transition states. (4 pts)

1e. Using your mechanism, explain why there is a preference for the formation of A over B. (1 pt)

1f. Using your mechanism, explain why there is a preference for the formation of C over D? (1 pt)

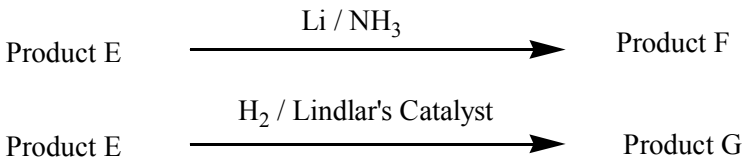
1g. Why do you see a difference in selectivity (A over B versus C over D) between the two different starting materials? (2 pt)

2. Bob conducted the following four reactions on ethyne. (9 pts)

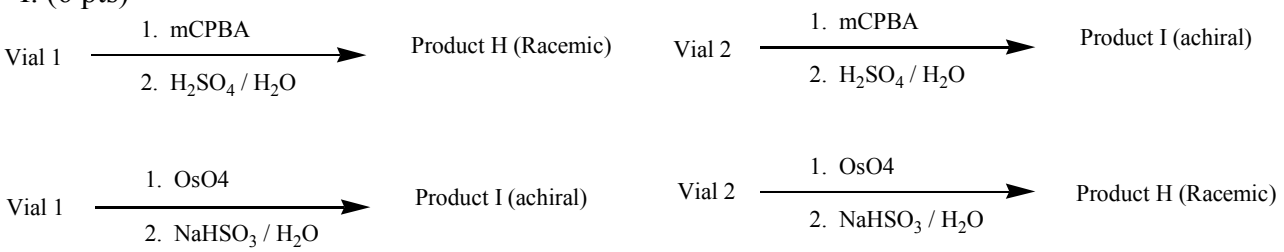


2a. What is compound E? (1 pt)

2b. Bob started the following two reactions in his laboratory.

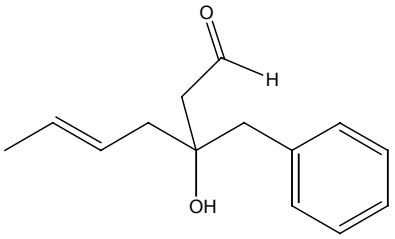


However, since Bob is a little disorganized, he mistakenly confused the vials that contained each reaction. Instead of asking for help he just continued on with the following reactions. Please help Bob identify which vial came from which product (either F or G). Also, Identify products F - I. (6 pts)



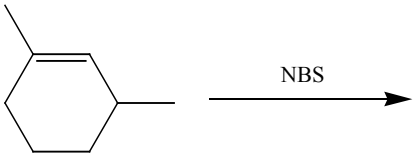
2c. Other than doing chemical tests, could he have differentiated the two products in an alternative manner? Explain thoroughly. (2 pts)

3. Conduct a retrosynthetic analysis for the problem below. Investigate at least three different methods to make the desired molecule; the various methods do not have to be completely correct (they need to be real reactions but do not have to go all the way to the desired starting material), but rather should show that you have thought of alternative routes. Choosing the best route, show the synthetic scheme you would use to make the desired molecule. (8 pts = 6 for retro, 2 for synthesis)



From any compound with three carbons or less or a simple substituted benzene compound

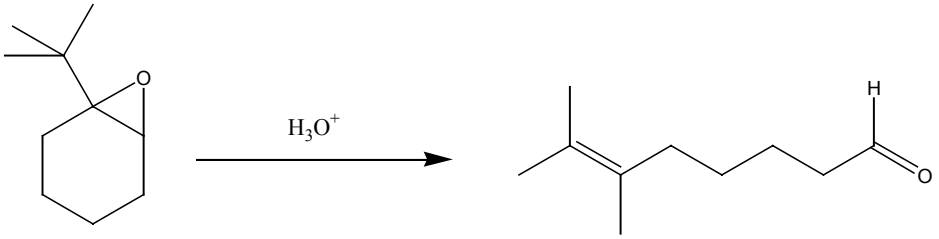
4. Consider the free radical bromination of 1,3-dimethyl cyclohexene with NBS. (7 pts)



5 possible products

4a. What are the five possible products? (2 pts)
4b. Write two mechanisms that explains the formation of two of these products (1 mechanism for each product) (4 pts).
4c. Which of the five products is the major product? Explain. (1 pts)

5. Write a mechanism that accounts for the formation the product from the following reaction. (5 pts)



6. Have a firm grasp on all of the reactions we covered since the last test: (priceless)
   1. Halogenation of alkenes
   2. Hydroboration of alkenes
   3. Oxymercuration of alkenes
   4. Cis dihydroxylation of alkenes
   5. Ozonolysis of alkenes
   6. Oxymercuration of alkynes
   7. Hydroboration of alkynes
   8. Synthesis of alkynes
   9. Reaction of bases with terminal alkynes and subsequent reactions
   10. Reduction of alkynes
   11. Free radical bromination of allylic carbons using N-bromo succinimide
   12. Sn2 and Sn1 reactions of allylic halides and other allylic leaving group compounds.
   13. Bonus: know all reactions that we have covered the entire year.