

Chemistry 210
“Organic Chemistry I”
Summer Semester 1999
Dr. Somnath Sarkar

Examination #3
“Elimination Reactions
Structure, Synthesis and Reactions of Alkenes and alkynes.”

Friday, July 23, 1999, 8:40 – 9:40

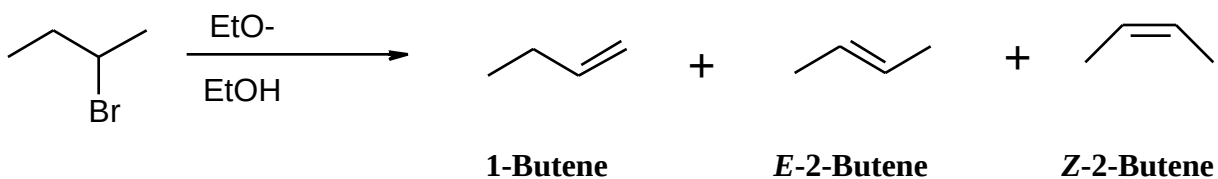
Name:

Question 1. Elimination	12	
Question 2. Elimination (MC #1)	16	
Question 3. Addition Reaction of alkene (News # 8)	14	
Question 4. Structure and Synthesis of alkenes (MC #2)	16	
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Question 6. Reactions of Alkenes (MC #3)	16	
Question 7. Mechanism of electrophilic addition	12	
Total	100	
Multiple Choice Points and Percentage:		

Question 1. Elimination. (12 points)

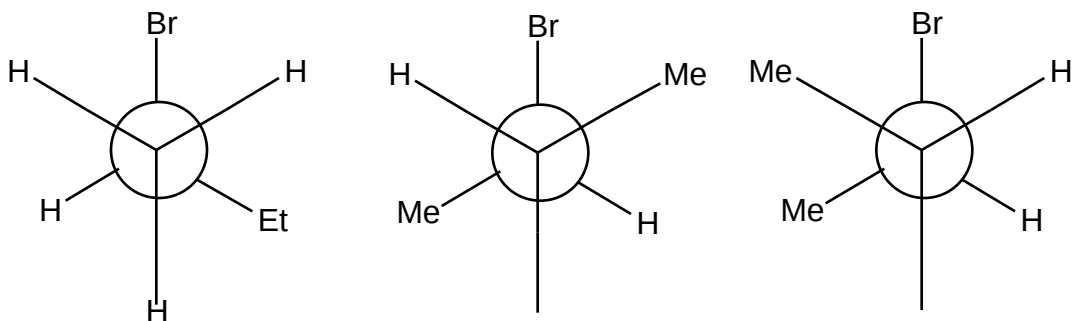
- a. The E2 elimination of 2-bromobutane with ethoxide can provide three possible products in different amounts. Write down the structure of these three elimination products. Name these three products. Use *E* (*trans*) or *Z* (*cis*) in your nomenclature as necessary.

6 points



- b. Draw the three Newman Projection diagrams for the *anti*-periplanar conformation of the substrate which would lead to these three products.

6 points



Question 2. Elimination. (16 points)

E-Q1 What is the rate limiting step of the E1 reaction?

- a Homolysis of a C-X bond(X carries a partial negative charge)
- b. Heterolysis of a C-X bond to form a carbanion
- c. Heterolysis of a C-X bond to form a carbenium ion**
- d. Heterolysis of a C-X bond to form a carbon radical
- e. Homolysis of a C-X bond to form a carbenium ion

E-Q19 Which type of E2 elimination is the only one possible for chlorocyclohexane

- a. Cl equatorial and *syn*-periplanar elimination
- b. Cl equatorial and *anti*-periplanar elimination
- c. Cl axial and *syn*-periplanar elimination
- d. Cl axial and *anti*-periplanar elimination**
- e. This option is not used

E-Q18 Which product is formed in the HBr elimination from (2S,3S)-2-bromo-3-phenylbutane?

- a. (E)-2-phenyl-2-butene**
- b. (Z)-2-phenyl-2-butene
- c. (E)-3-methyl-3-phenyl-1-butene
- d. (Z)-3-methyl-3-phenyl-1-butene
- e. This option is not used

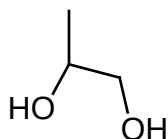
E-Q2 Which statement best describes the relative reactivities of the alkyl halides in E1 reaction?

- a. One-step reaction without transition state
- b. One-step reaction with 1 transition state
- c. One-step reaction with 2 transition state
- d. Two-step process with 1 intermediate and 1 transition state
- e. Two-step reaction with 1 intermediate and 2 transition state**

Question 3. Electrophilic Addition Reaction. (12 points)

The article “NEW USES FOR OLD DRUGS” (*Fort Worth Star-Telegram*, November 19, **1998**) talked about the serendipitous discovery of the hair-growth promotion by the drug minoxidil which was originally introduced as a high blood pressure drug. The drug is applied topically by rubbing a solution of minoxidil in a mixture of ethanol and propylene glycol directly on the body. Lets consider propylene glycol and the general synthesis of glycols.

- a. The IUPAC name for propylene glycol is **1,2-propane diol**. Provide the structure.

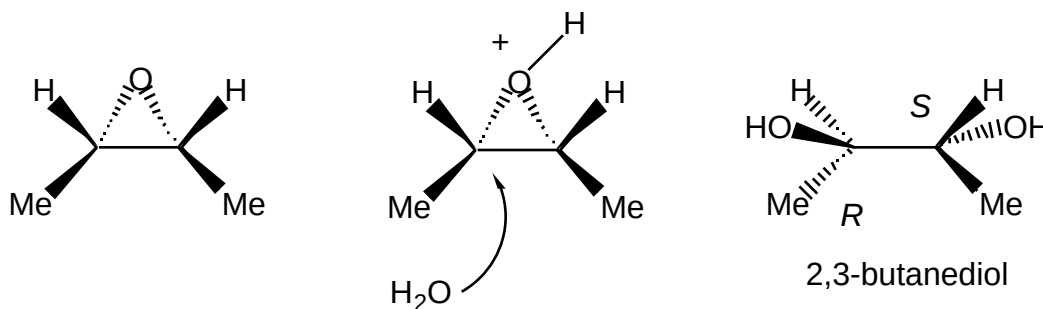


3 points

- b. Vicinal diols can be synthesized in several different ways. One of the ways to do it is to treat an alkene with **MCPBA** to make the epoxide and then open the epoxide ring with water under acidic condition. Consider the compound *Z*-2-butene.

Show the structure of the epoxide where the oxygen is attached to the back face of the alkene. With two arrows, indicate how the epoxide ring is opening and write down the structure of the product with proper stereochemistry. Make sure, that you consider the stereochemistry of the ring opening. What should be the IUPAC name of this compound (see how 1,2-propane diol is named)? Assign *R* and *S* configuration to these stereocenter.

2 + 4 + 2 + 4 points



Question 4. Structure and Synthesis of Alkenes. (16 points)

E-Q3 What is the hybridization of the C-atom in ethene?

- a. sp^3
- b. sp^2**
- c. sp
- d. Pure s
- e. Pure p

E-Q15 Identify the alkene with the lowest molar heat of hydrogenation.

- a. Ethene
- b. propene
- c. 2,3-dimethyl-1-butene
- d. trans-2-pentene
- e. 2,3-dimethyl-2-butene**

E-Q24 What conditions are best for the dehalogenation of bromine from vicinal dibromides

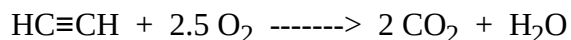
- a. Zn in acetic acid**
- b. Zn in hydrochloric acid
- c. Zn in acetone
- d. Zn in alcohol
- e. Zn in toluene

E-Q26 In the dehydration of an alcohol with concentrated sulfuric acid, which reaction step is the rate limiting step?

- a. Protonation of alcohol
- b. Elimination of water from protonated alcohol**
- c. Unimolecular elimination of hydroxide from alcohol
- d. Elimination of proton
- e. This option is not used

Question 5. Reactions of alkynes, News Item # 9 (14 points)

- a. Your reading of the article “A SEISMIC RESTORATION FOR SAN FRANCISCO OPERA” (*International Herald Tribune*, August 15, **1997**) brought up the topic of acetylene torch. Provide a stoichiometric equation for the complete combustion of acetylene. (3 points)



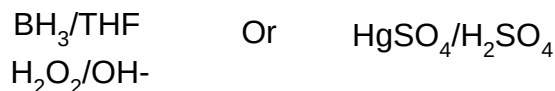
- b. If you burn acetylene in the regular atmosphere and without an additional oxygen stream, then the burning is quite different. The flame is much less hot and there is a lot of thick black smoke produced. What kind of combustion might be happening? Name one of the products that may be forming.

(2 points)

Incomplete combustion, CO and C are formed.

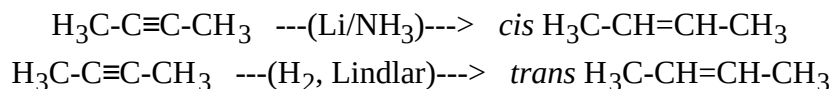
- c. In industry, acetylene is a central commodity. Acetylene is the starting material for many chemicals that are produced in large scale. Acetaldehyde, $\text{H}_3\text{C}-\text{CH}=\text{O}$, is made from acetylene. Provide the reagents that you would use to convert acetylene to acetaldehyde?

(3 points)



- c. 2-Butyne can be reduced in the *cis* or *trans* form depending upon the reagent used in the process. Provide the products of the following reduction with proper stereochemistry.

(6 points)



Question 6. Reactions of Alkenes. (16 points)

EQ3 Which product is formed in the peroxide catalyzed hydrobromination of 1-methylcyclohexene?

- a. 1-bromo-1-methylcyclohexane
- b. 1-bromo-2-methylcyclohexane**
- c. 3-bromo-1-methylcyclohexane
- d. 4-bromo-1-methylcyclohexane
- e. 5-bromo-1-methylcyclohexane

EQ5 Which one of the following statements about the Markonikov rule is **not** true ?

- a. When HX adds to an asymmetrical alkene, the protonation leads to the most stable carbocation intermediate.
- b. In Markonikov's additions, the alkene C-atom with the most H atoms will be protonated.
- c. When HX adds to an asymmetrical alkene, the halogen attaches to the most substituted alkene C atom.
- d. When HX adds to an asymmetrical alkene, the halogen attaches to the least substituted alkene C atom.**

EQ11. How does borane exist in THF solution?

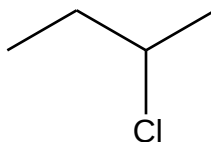
- a. As the monomer BH_3
- b. As the dimer B_2H_6
- c. As the trimer B_3H_9
- d. As the complex between borane and THF**
- e. As the complex between diborane and THF

EQ20 Which of the reagents is the best electrophile?

- a. Bromide, Br^-
- b. Bromine, Br_2
- c. Tribromide, Br_3^-
- d. Bromine radical, $\text{Br}^\cdot$
- e. Bromine cation, Br^+**

Question 7. Mechanism of electrophilic addition, hydrohalogenation. (12 points)

- a Write the product for the reaction of HCl with 1-butene. 3 points



- b. Will you expect an enantiomerically pure compound or a racemic mixture? Justify your answer by explaining it in a few sentences. 3 points

Racemic mixture, because the nucleophile is equally accessible from the top or the bottom phase of the intermediate carbenium ion.

- c. Draw an activation energy diagram for this reaction. Show the structure of the intermediate and indicate the rate determining step. 6 points

Look up your notes, p. 2, chapter 8.