

Chemistry 210
“Organic Chemistry I”
Winter Semester 1999
Dr. Rainer Glaser

Examination #3

“Alkenes and Alkynes: Their Syntheses and Reactions.
Alcohols: Synthesis from Alkenes and Using Organometallics.”

Friday, April 16, 1999, 9:00 - 9:50

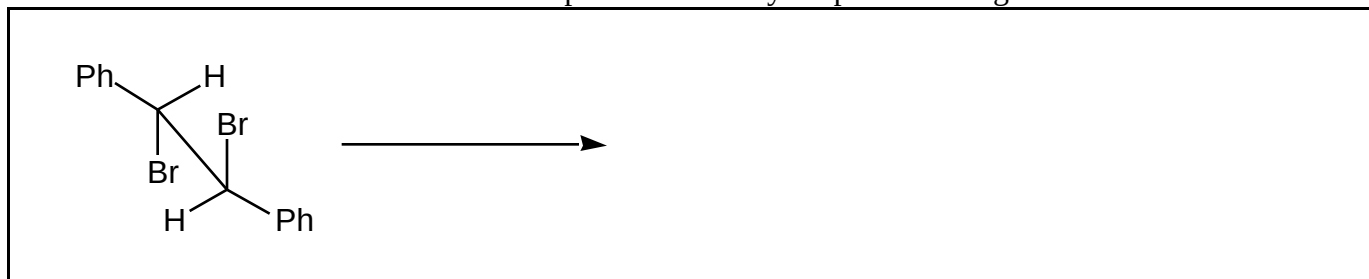
Name:

Question 1. Alkenes I. (incl. News #7)	12	
Question 2. Alkenes II.	16	
Question 3. Addition Reactions I. (incl. News #8)	14	
Question 4. Addition Reactions II.	16	
Question 5. Alkynes I. (incl. News #9)	12	
Question 6. Alkynes II.	16	
Question 7. Alcohol Synthesis with Organometallics.	14	
Total	100	
Multiple Choice Percentage Q2, Q4 and Q6.		

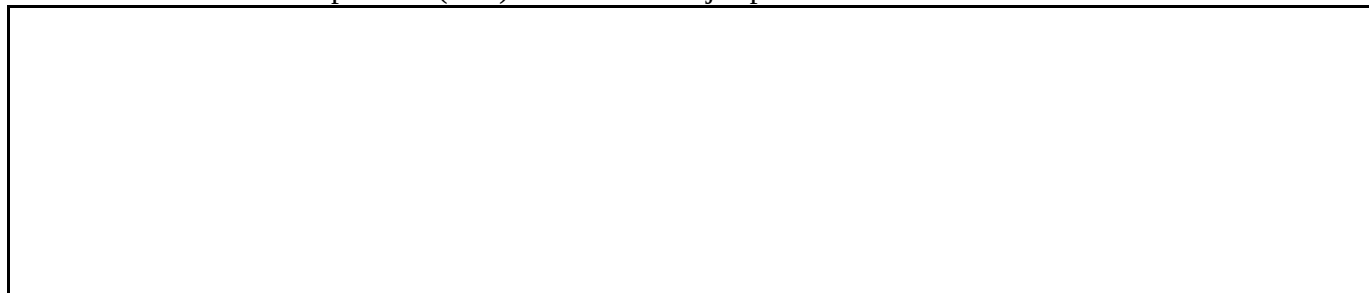
Question 1. Alkenes I: Preparations and Reactions. (12 points, 3 points each part)

(a) During your studies of the article "GASOLINE FALLS ON REFINERY STARTS" (*Bloomberg News*, September 8, **1997**), you learned that alkenes are produced in the chemical industry by way of **catalytic cracking**. The breaking down at elevated temperatures of large, high-boiling hydrocarbon molecules into smaller molecules is an _____ (endothermic, exothermic) process that proceeds via _____ (cations, anions, radicals) and requires _____ catalysts. These catalysts are porous minerals that contain _____ and aluminates. The principal applications of catalytic cracking are the production of high-octane gasoline and of propylene and butylene for polymerization.

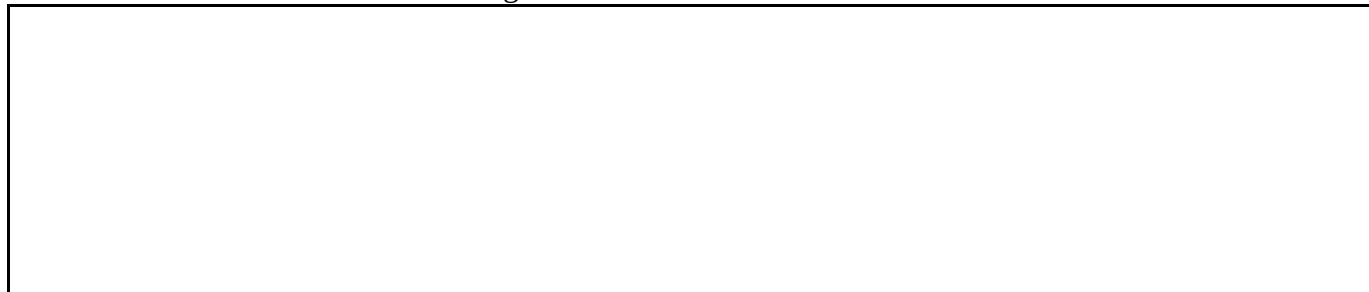
(b) Consider the **dehalogenation of the dibromide** shown. Provide a reagent that accomplishes this reaction and draw the structure of the product. Label your product using the *E/Z* nomenclature.



(c) **Electrophilic addition of HCl to propene**. Draw and mark the "Markovnikov" (M) and the "Anti-Markovnikov" product (AM). Circle the major product of the reaction.



(d) **Addition of dichlorocarbene to cis-butene**. Draw the product of this addition reaction. Indicate how dichlorocarbene can be generated.



Question 2. Alkenes II. (16 points)

E-Q2 How long is the C=C double bond in ethene? [Bond lengths in Angstroms.]

- a. 1.20
- b. 1.33
- c. 1.44
- d. 1.54
- e. 2.10

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

PE2-Q4 What is the name of the 8-membered ring hydrocarbon with 4 conjugated double bonds?

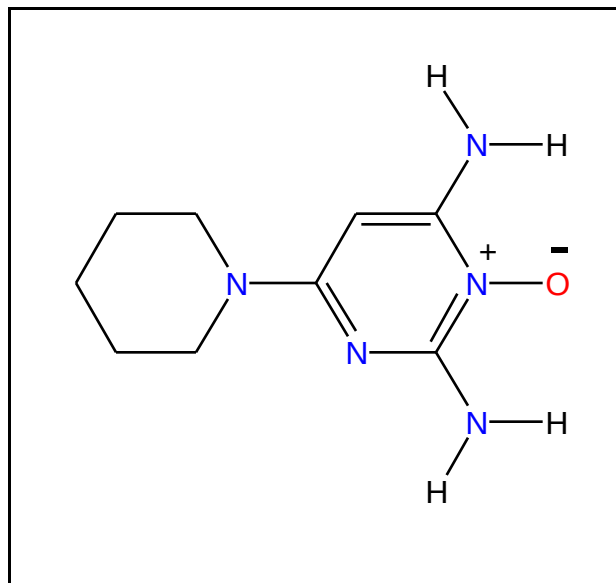
- a. 1,5-Cyclooctadiene
- b. 2,4,6,8-Cyclooctatetraene
- c. 1,2,3,4-Cyclooctatetraene
- d. 1,3,5,7-Cyclooctatriene
- e. 1,3,5,7-Cyclooctatetraene

PE-Q6 Which of the following compounds **cannot** exist as *cis/trans* or *E/Z* isomers?

- a. ClDC=CHD
- b. ClHC=CHD
- c. DHC=CHD
- d. ClHC=CD₂
- e. ClHC=CHBr

Question 3. Addition Reactions I. (14 points)

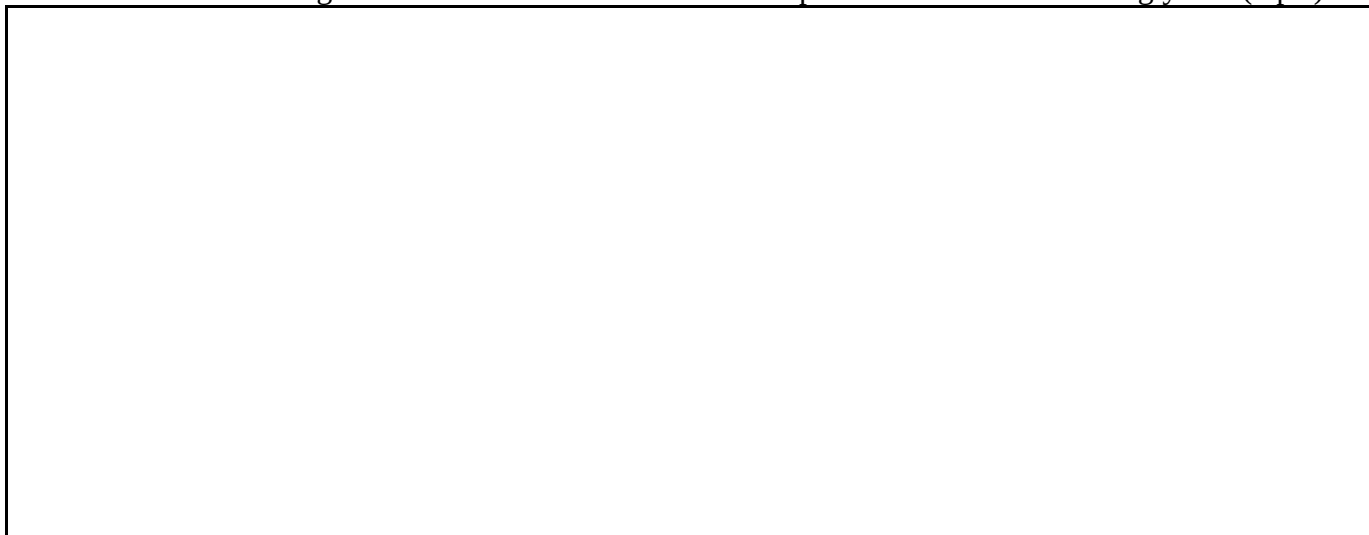
The article “NEW USES FOR OLD DRUGS” (*Fort Worth Star-Telegram*, November 19, **1998**) talked about the serendipitous discovery of the hair-growth promotion by the drug **minoxidil** which was originally introduced as a high blood pressure drug. The drug is applied topically by rubbing a solution of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



(a) Draw the structure of "propylene glycol" and provide an acceptable IUPAC name. (3 pts)



(b) Show the synthesis of "propylene glycol" by epoxidation of propene with MCPBA. Show the structure MCPBA and give its full name. Indicate how the epoxide is converted to the glycol. (7 pts)



(c) In the above structural drawing of minoxidil, circle every atom that can serve as a **hydrogen bond acceptor**. (4 points)

Question 4. Addition Reactions II. (16 points)

- E-Q3 What is the product of the peroxide-catalyzed hydrobromination of 1-methylcyclohexene?
- 1-bromo-1-methylcyclohexane
 - 2-bromo-1-methylcyclohexane
 - 3-bromo-1-methylcyclohexane
 - 4-bromo-1-methylcyclohexane
 - 5-bromo-1-methylcyclohexane
- E-Q9 The oxymercuration-demercuration (called oxymercuration for short) and the hydroboration-oxidation (or just hydroboration for short) complement each other well. Which one of the following statements is true?
- For non-terminal, asymmetrical alkenes, hydroboration and oxymercuration give the same anti-Markovnikov regiochemistry.
 - For non-terminal, asymmetrical alkenes, hydroboration and oxymercuration give the same Markovnikov regiochemistry.
 - In the case of terminal alkenes, hydroboration and oxymercuration both give alcohols with anti-Markovnikov regiochemistry.
 - In the case of terminal alkenes, the hydroboration gives primary alcohols, while oxymercuration gives secondary alcohols.
 - In the case of terminal alkenes, hydroboration and oxymercuration both give alcohols with Markovnikov regiochemistry.
- E-Q13 Which product is formed in the reaction of propene and BH_3 ?
- $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-BH}_2$. Monomer of alkylborane.
 - $(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-BH}_2)_2$. Dimer of alkylborane.
 - $(\text{CH}_3\text{-CH}_2\text{-CH}_2)_2\text{BH}$. Monomer of dialkylborane.
 - $[(\text{CH}_3\text{-CH}_2\text{-CH}_2)_2\text{BH}]_2$. Dimer of dialkylborane.
 - $(\text{CH}_3\text{-CH}_2\text{-CH}_2)_3\text{B}$. Monomer of trialkylborane.
- E-Q17 What product is formed by reaction of diazomethane and cyclobutylethene?
- diazocyclobutylethene
 - azocyclobutylethene
 - cyclobutylcyclopropane
 - cyclopentylethene
 - methylenecyclohexane

Question 5. Alkynes I. (12 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 the **acetylene torch**. Provide a stoichiometric equation for the complete combustion of acetylene. Also used in welding is a mixture of the tautomers methylacetylene and allene; provide their structures and IUPAC names. (3 pts)

Combustion of Acetylene:

Methylacetylene:

Allene:

(b) **Hydration of Propyne.** Specify the catalyst required. Draw the structures of the intermediate enol and of the final keto tautomer. Pay attention to regiochemistry. Name the product. (3 points)

(c) **Lithium-Ammonia Reduction of 2-Butyne.** Draw the structures of 2-butyne and of the product of its reduction with lithium-ammonia. Clearly indicate whether the product is *cis* or *trans*. Then provide the reaction mechanism of the reduction showing structures of all intermediates. (6 pts)

Overall Reaction:

Mechanism:

Question 6. Alkynes II. (16 points)

E-Q6 Alkynes contain two π -bonds. Which statement best describes how these π -bonds are formed?

- a. Each π -bond is formed by end-on C(p)-C(p) overlap.
- b. Each π -bond is formed by side-by-side C(p)-C(p) overlap.
- c. Each π -bond is formed by end-on C(sp)-C(sp) overlap.
- d. Each π -bond is formed by side-by-side C(sp)-C(sp) overlap.
- e. Each π -bond is formed by side-by-side C(s)-C(s) overlap.

E-Q7 How long is a C-C triple bond.

- a. 100 pm
- b. 120 pm
- c. 10 pm
- d. 12 pm
- e. 1.0 pm

E-Q17 In the presence of excess hydrogen bromide, what is the major product of the addition of HBr to 2-pentyne?

- a. 2-bromopentene
- b. 1-bromopentene
- c. 1,2-dibromopentane
- d. 2,2-dibromopentane
- e. 1,1-dibromopentane

E-Q26 With the aid of Lindlar's catalyst (quinoline and lead acetate) the hydrogenation of alkynes can be stopped at the stage of the alkene. Which formula is that of quinoline?

- a. $\text{C}_9\text{H}_8\text{N}$
- b. $\text{C}_9\text{H}_7\text{N}$
- c. $\text{C}_{10}\text{H}_7\text{N}$
- d. $\text{C}_{10}\text{H}_8\text{N}$
- e. $\text{C}_{10}\text{H}_9\text{N}$

Question 7. Alcohol Synthesis with Organometallics. (14 points)

(a) Provide syntheses for ethylmagnesium bromide, vinyl lithium, and ethynyllithium. In each case, draw the structures of the starting materials and the product and specify the solvent. (2 pts each)

Ethylmagnesium bromide:

Vinyl lithium:

Ethynyllithium:

(b) Show the mechanism of the Grignard reaction of propylmagnesium bromide with butanone. (4 pts)

(c) Suggest a synthesis of *tert.*-butanol that starts with a carboxylic acid derivative of your choice and employs Grignard chemistry. Draw starting material, all intermediates and the product. (4 pts)