

Chemistry 210
“Organic Chemistry I”
Fall Semester 2000
Dr. Rainer Glaser

Examination #3

“Alkenes and Alkynes. Structure, Synthesis and Reactions.”

Friday, November 17, 2000, 9:00 - 9:50

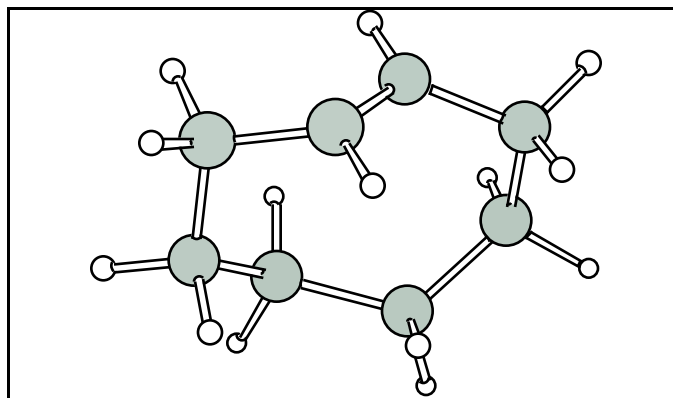
Name:

Answer Key

Question 1. Alkenes I. Preps & Properties.	20	
Question 2. Alkenes II. Addition Reactions. (VC #8)	20	
Question 3. Alkenes III. Oxidations. (News #8)	20	
Question 4. Alkynes I. Preps & Properties. (VC #9)	20	
Question 5. Alkynes II. Reactions.	20	
Total	100	

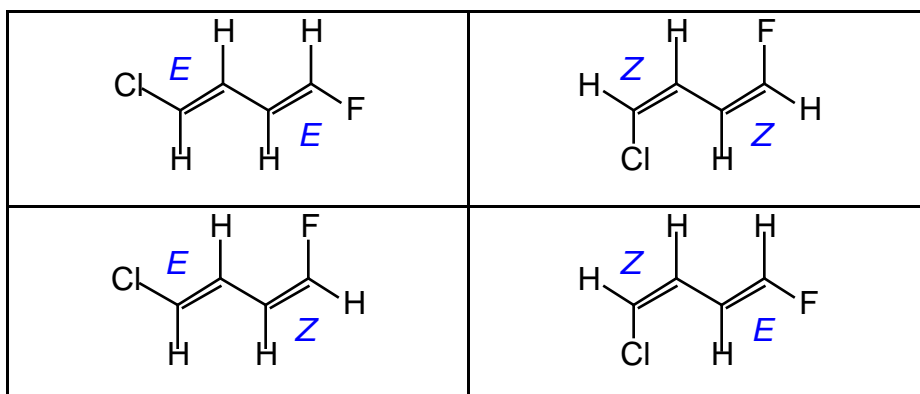
Question 1. Alkenes I. Preparations & Properties. (20 points)

(a) The molecular model is shown of a cyclic alkene. This molecule is _____ (*cis*, *trans*). Provide a suitable IUPAC name of the molecule. (3 points)



Name: *E* or *trans*-cyclooctene

(b) Draw Lewis structures of the 4 stereoisomers of 1-chloro-4-fluorobutadiene and indicate for each double bond whether it is *E* or *Z*. (8 points)



(c) Alkene synthesis by way of elimination from secondary alkyl halides employs bulky bases to reduce competition by nucleophilic substitution. Provide the name and the structure of one base that is typically used for this purpose. (3 points)

many choices
most likely responses include
TEA, triethylamine, $\text{N}(\text{C}_2\text{H}_5)_3$
Diisopropylamine, $\text{HN}(\text{C}_3\text{H}_7)_2$

(d) Circle the alkene with the lowest heat of hydrogenation (the most stable alkene). (3 points)

(1) *cis*-2-butene (2) ***trans*-2-butene** (3) butene (4) 2-methylpropene

(e) Alkenes can be prepared by the reduction of dibromides. This elimination of bromine can be accomplished with two kinds of reagent/solvent combinations. (3 points)

Reagent 1: NaI in acetone.

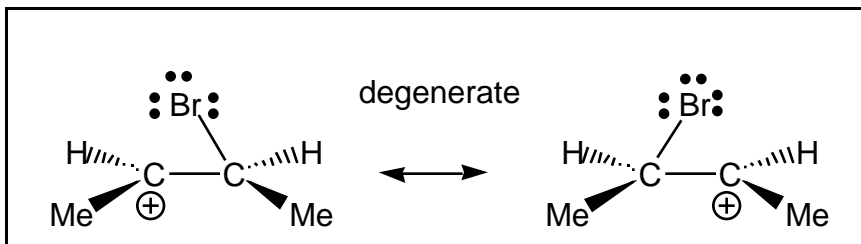
Reagent 2: Zn in acetic acid.

Dibromide needs to be _____ (geminal or **vicinal**).

Question 2. Alkenes II. Addition Reactions. (20 points)

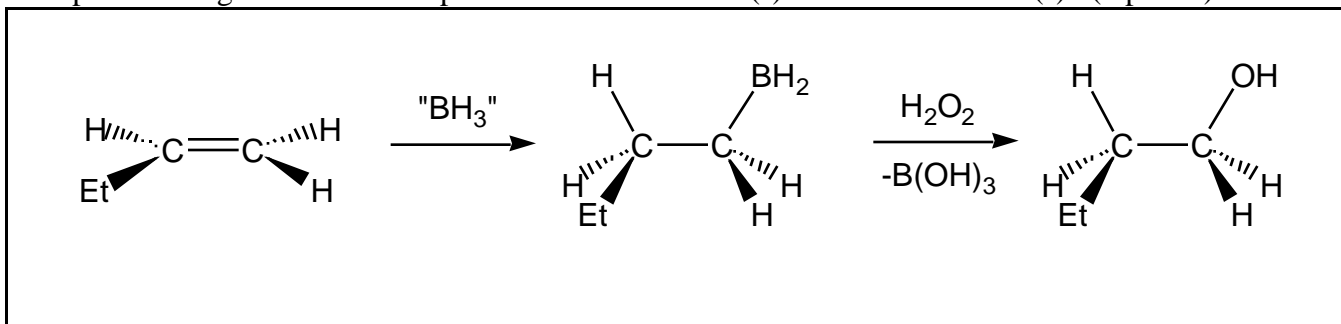
(a) Consider the catalytic hydrogenation of *cis*-butene to butane (name of product). Suggest a suitable catalyst for the heterogeneous catalytic hydrogenation: Pd or Pt. The hydrogenation will be _____ (endothermic, **exothermic**). (3 points)

(b) The bromination of *cis*-butene results in 2,3-dibromobutane. The two Br atoms will be added in a *trans* fashion because the reaction goes via a “bromonium ion”. In the

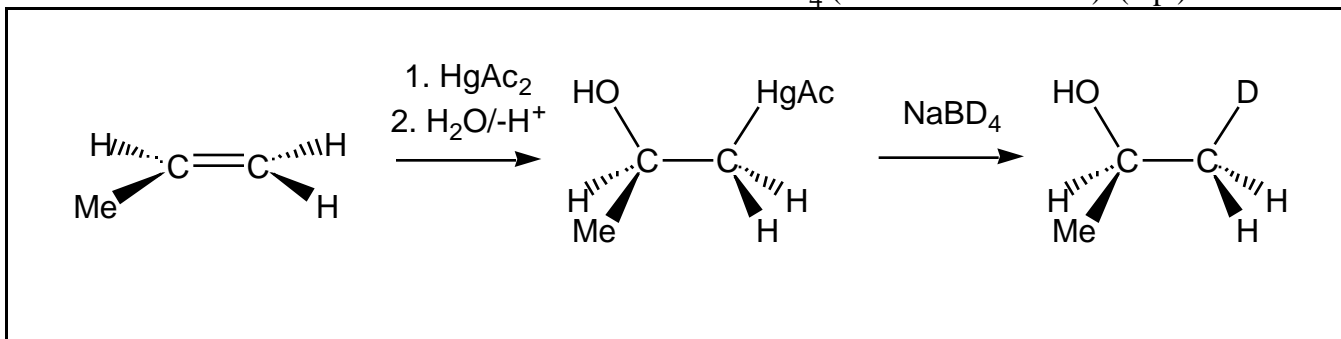


bromonium ion, one Br _____ (**cation**, radical, anion) is bonded to 2 C-atoms but there are only 2 electrons to form these 2 “C-Br bonds”. Draw the resonance forms that describe this “bromonium ion” and draw all lone pairs on Br. Indicate whether the resonance forms are degenerate or not. (6 p.)

(c) Suggest a preparation of butanol (the primary alcohol) from butene (a terminal alkene). Provide the structures of butene and of butanol. Specify all reagents needed. If the reaction involves several steps, then provide reagents for each step and draw the structure(s) of the intermediate(s). (6 points)



(d) Show the oxymercuration/demercuration reaction of propene. The reaction exhibits _____ (**Markovnikov**, anti-Markovnikow) regiochemistry. Draw the structures of the organomercurial alcohol and of the alcohol obtained after reduction with NaBD₄ (note the deuterium!) (5 p.)



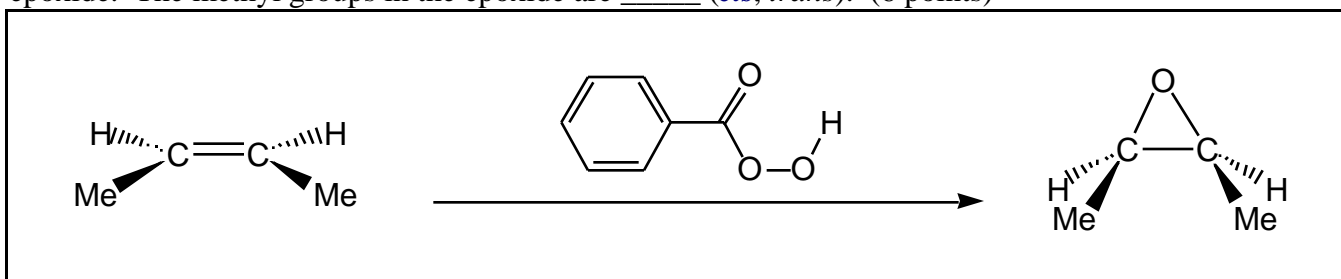
Question 3. Alkenes III. Oxidations. (20 points)

The article “NEW USES FOR OLD DRUGS” (*Fort Worth Star-Telegram*, Nov. 19, **1998**) talked about minoxidil. The drug is applied by rubbing a solution of minoxidil in ethanol and propylene glycol directly on the body. So, let’s consider some aspects of diols.

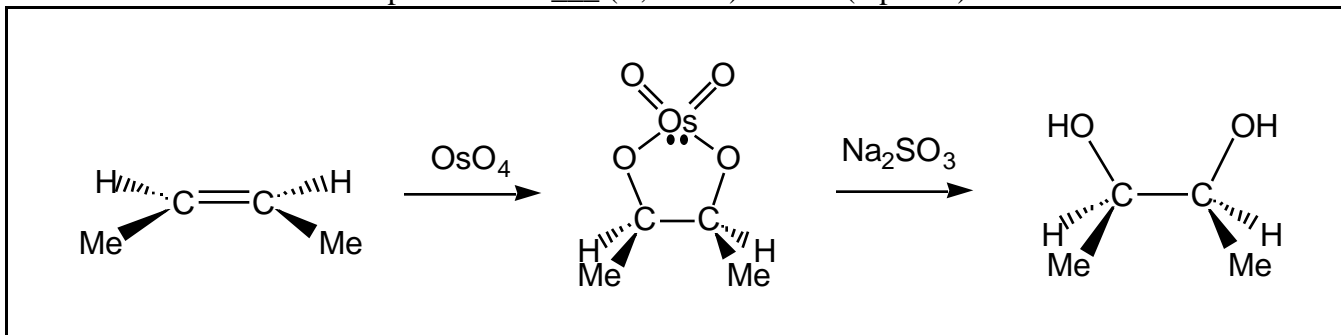
(a) Draw the structures of “propylene”, of “glycol”, and of “propylene glycol” and provide acceptable IUPAC names. (6 points)

Propylene $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$	Glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	Propylene Glycol $\text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_2(\text{OH})$
IUPAC: propene	IUPAC: 1,2-ethanediol	IUPAC: 1,2-propandiol

(b) Consider the epoxidation of *cis*-butene with perbenzoic acid. *Cis*-butene is ___ (*E* or *Z*) butene. Draw the structure of *cis*-butene. Draw the structure of perbenzoic acid. Draw the structure of the epoxide. The methyl groups in the epoxide are ___ (*cis*, *trans*). (6 points)



(c) Consider the oxidation of *cis*-butene with osmium tetroxide. Draw the structures of *cis*-butene, of the osmate ester, and of the product diol. Provide a reducing reagent for the reduction of the cyclic osmate ester to the diol. The product diol ___ (is, **is not**) chiral. (6 points)



(d) Hydrolysis of the epoxide generated in (b) yields a diol. What is the relationship between this diol and the diol formed in (c)? (1) Structure Isomers, (2) Enantiomers, or (3) **Diastereoisomers**? (2 points)

Question 4. Alkynes I. Preparations & Properties. (20 points)

(a) Identify the general formula of acyclic alkynes. (2 points)

- (1) C_nH_{2n+4} (2) C_nH_{2n+2} (3) C_nH_{2n} **(4) C_nH_{2n-2}** (5) C_nH_{2n-4}

(b) Identify the bond length of the C—C bond in alkynes. (2 points)

- (1) 1.10 Å **(2) 1.20 Å** (3) 1.30 Å (4) 1.40 Å (5) 1.50 Å

(c) Which orbital description best describes the C—H bond in acetylenes? (2 points)

- (1) C(s)—H(s) **(2) C(sp)—H(s)** (3) C(sp²)—H(1s) (4) C(sp³)—H(1s)

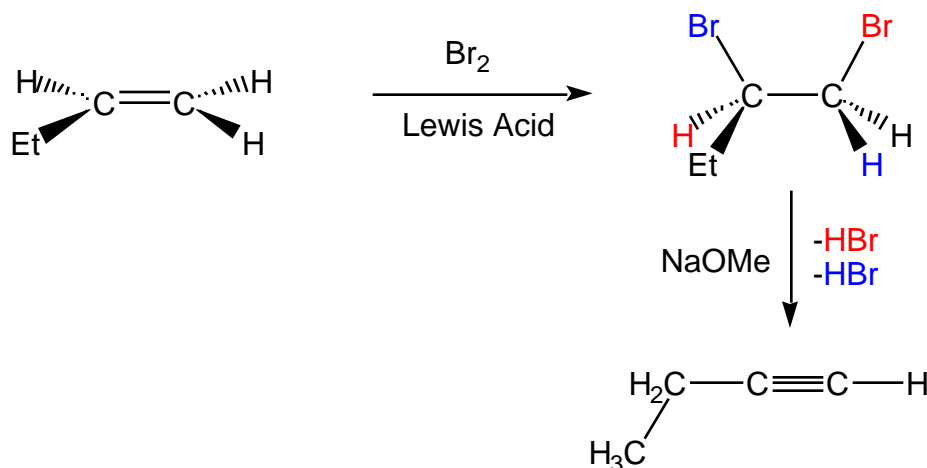
(d) Which base is best used for the deprotonation of a terminal acetylene? (2 points)

- (1) NaOH **(2) NaNH₂** (3) NaCH₃ (4) NaBH₄

(e) The acetylide $CH_3-C \equiv C^- Na^+$ is treated with bromopropane. Draw the organic product of this reaction and name it using IUPAC nomenclature (VC #9). The reaction mechanism of this reaction is SN₂. The inorganic product of this reaction is NaBr. (6 points)



(f) Suggest a synthesis of butyne from butene. Draw the structures of the starting material, give the reagents needed in each step and draw the products obtained in each step. (6 points)



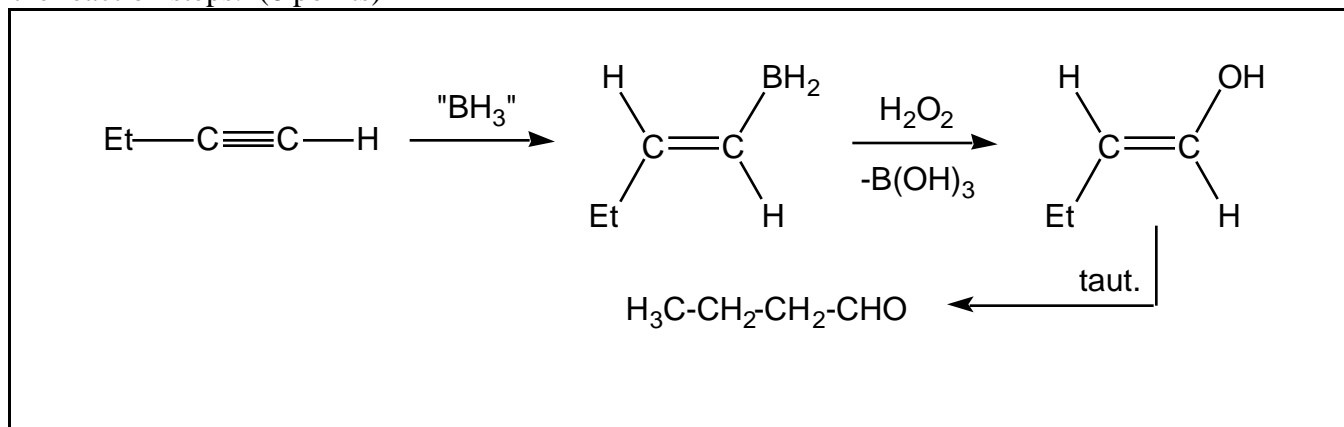
Question 5. Alkynes II. Reactions. (20 points)

(a) Butyne is hydrated in the presence of the catalyst HgSO_4 and a product **A** is obtained. This product **A** undergoes a rearrangement to the final product **B**. This rearrangement is a tautomerization.

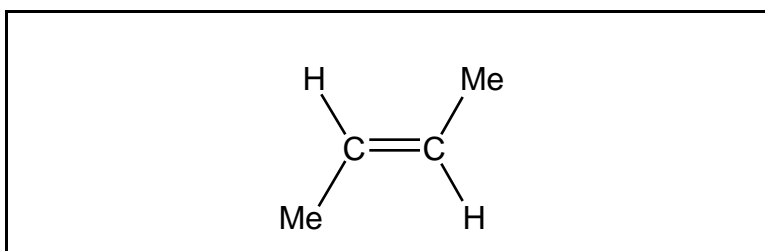
Draw the structures of butyne and of compounds **A** and **B**. (6 points)

Butyne	Compound A	Compound B
$\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$	$\text{H}_3\text{C}-\text{CH}_2-\text{C}(\text{OH})=\text{CH}_2$	$\text{H}_3\text{C}-\text{CH}_2-\text{CO}-\text{CH}_3$

(b) Show how butanal, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$, can be prepared from butyne via hydroboration. Draw the starting material and the products of all reaction steps. Give the reagents needed to accomplish each of the reaction steps. (6 points)



(c) 2-butyne is treated with lithium metal in liquid ammonia. Draw the structure of the product and clearly indicate its stereochemistry. (4 points)



(d) 2-butyne is treated with an excess of HBr . Draw the structure of the final product. (4 points)

