CHEM 2410 – Principles of Organic Chemistry I – Summer 2016

Instructor: Paul Bracher

Hour Examination #3

Monday, June 13th, 2016

9:00–10:30 a.m. in Macelwane Hall 342

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use one letter-sized sheet of handwritten notes (on "official" paper) and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		60
II		7
III		17
IV		16
TOTAL		100

Questions, Required Information, Supplementary Information

Special Instructions

Please Make Sure to Do the Following Before Starting Your Exam

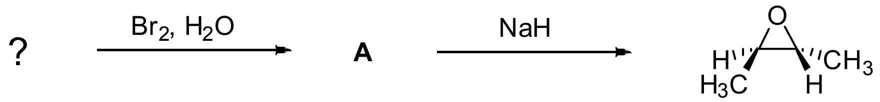
1. Both print your name and sign the front of the answer sheet in the appropriate boxes.
2. Also print your name at the top of the back of the answer sheet.
3. Enter your SLU Banner ID on the front of the answer sheet and bubble the corresponding numbers.
4. Do not check the "Hold for Pick-Up" box on the back of the answer sheet unless you want your graded sheet withheld from the distribution pile and handed back to you privately.

Please Make Sure to Do the Following After Completing Your Exam

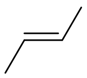
1. Ensure that all of your selected circles are darkened completely.
2. Turn in your note sheet with your name and this exam number (#3) in the appropriate space.

Problem I. Multiple choice (60 points total; +5 points for a correct answer, +2 points for answering with the letter "E", and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

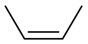
(1) ___A___ What starting material, when subjected to the following sequence of reactions, will form compound **B** as the major product?



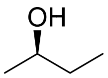
B



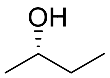
(A)



(B)

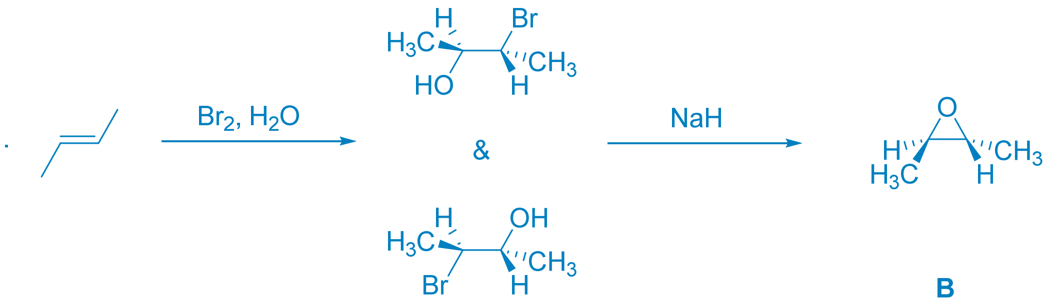


(C)



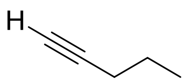
(D)

The epoxide **B** is formed from the intramolecular, S_N2-like attack within a deprotonated halohydrin. The deprotonated hydroxyl group and departing bromide must be oriented anti to each other (as in the structure of the enantiomers **A**, shown below). Since halohydrin formation from an alkene occurs with anti stereochemistry, we must begin with the alkene shown below, choice (A):

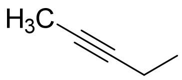


A

(2) ___D___ Which of the following statements is <u>not</u> true regarding the alkynes **C** and **D**?



C

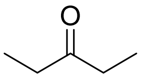


D

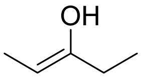
(A) compound **D** has a higher pK_a than compound **C**
(B) the hydration of **C** is more difficult than **D** and requires an extra reagent
(C) compound **C** can be used to synthesize pentanal ($CH_3CH_2CH_2CH_2CHO$)
(D) none of the above (i.e., all of the above statements are true)

Statements (A), (B), and (C) are all true.

(3) ___B___ Which of the following term(s) accurately describes the relationship of **E** and **F**?



E



F

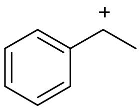
(I) constitutional/structural isomers
(II) stereoisomers
(III) tautomers

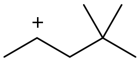
(A) only term **II** accurately describes the relationship of **E** and **F**
(B) only terms **I** and **III** accurately describe the relationship of **E** and **F**
(C) only terms **II** and **III** accurately describe the relationship of **E** and **F**
(D) terms **I**, **II**, and **III** all accurately describe the relationship of **E** and **F**

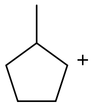
E and **F** are keto/enol tautomers. These are constitutional isomers, not stereoisomers.

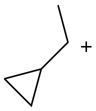
(4) C

Which of the following carbocations is likely to be observed to rearrange via a hydride shift but <u>not</u> an alkyl shift?


(A)


(B)


(C)


(D)

Carbocation (A) is unlikely to rearrange at all. If carbocation (B) undergoes a hydride shift such that the formal charge shifts to the adjacent secondary position, it will undergo a faster methyl shift to produce a tertiary carbocation. Choice (D) is likely to undergo an alkyl shift to expand the ring and relieve some of its ring strain. Choice (C) is likely to undergo a hydride shift to form the tertiary carbocation, which is then unlikely to rearrange further.

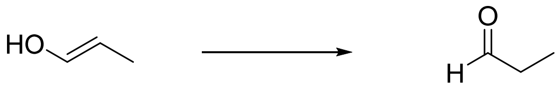
(5) D

Compound **G** has no double or triple bonds, and a molecular formula of $C_9H_{13}Br_2N_3O_4$. How many rings does the compound have?

(A) less than two
(B) two
(C) three
(D) more than three

A quick calculation of Ω, the # of rings and π bonds, gives $\Omega = (2+9\times2+3\times1+4\times0-13-2)/2=8/2= 4$. Since the compound has no double or triple bonds, and hence, no π bonds, it must have four rings.

(6) ____A____ Which of the following term(s) most accurately and completely describe(s) the conversion of **H** and **J**?

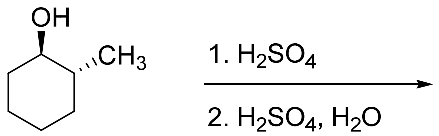


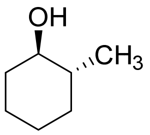
H **J**

(A) the mechanism for this conversion in acidic water proceeds via a resonance-stabilized carbocation
(B) the mechanism for this conversion in basic/alkaline water proceeds via a resonance-stabilized carbocation
(C) both the mechanisms for this conversion in acid and base proceed via resonance-stabilized carbocations
(D) neither the mechanism for this conversion in acid nor base proceeds via a resonance-stabilized carbocation

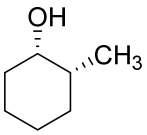
This reaction is enol–keto tautomerization. In aqueous acid, the reaction proceeds by protonation of the π bond (to form a resonance-stabilized carbocation) followed by deprotonation of the hydroxyl group. In aqueous base, the reaction proceeds by deprotonation of the hydroxyl group (to form a resonance-stabilized carbanion) followed by protonation at the distil carbon.

(7) ____D____ What is the major product expected of the following reaction sequence?

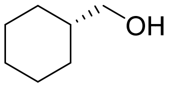




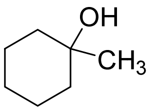
(A)



(B)

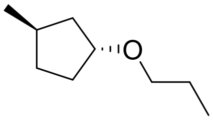


(C)

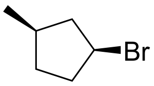


(D)

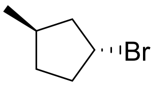
(8) C What alkyl bromide would be the best choice to synthesize compound **K** in one step?



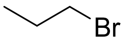
K



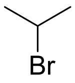
(A)



(B)



(C)



(D)

In the Williamson ether synthesis, you generally choose to form the ether by the reaction of a more-substituted alkoxide with a less-substituted alkyl halide. In this manner, you maximize the rate of the productive S_N2 reaction relative to undesired E2 reaction.

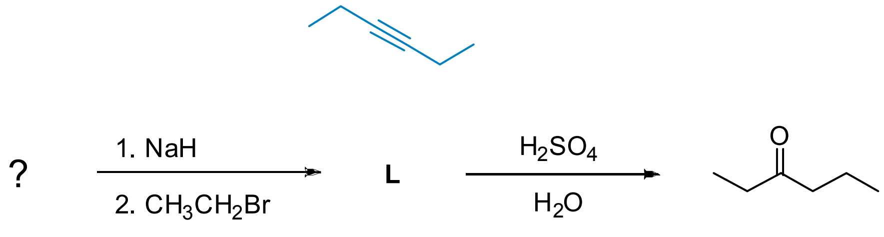
(9) D Which of the following products will be observed for the following reaction?

(A) 1-chloropentane
(B) (*R*)-2-chloropentane
(C) (*S*)-2-chloropentane
(D) both (*R*)-2-chloropentane and (*S*)-2-chloropentane

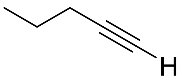
The reaction proceeds by Markovnikov addition. The terminal carbon is preferentially protonated to generate the more-stable secondary carbocation. This carbocation is then attacked from either face by chloride. One face generates the *R* stereoisomer, while attack of the other face of the carbocation generates the *S* stereoisomer.

(10) B

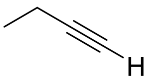
What starting material, when subjected to the following sequence of reactions, will form compound **M** as the major product?



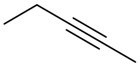
M



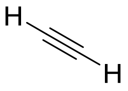
(A)



(B)



(C)

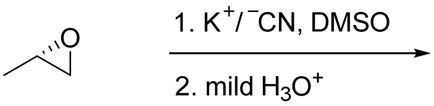


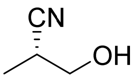
(D)

See the intermediate **L**, above.

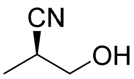
(11) C

What is the major product expected of the following reaction?

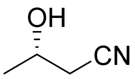




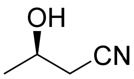
(A)



(B)



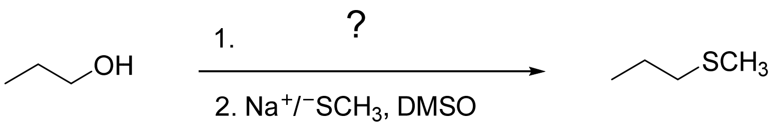
(C)



(D)

The opening of the epoxide takes place under basic conditions (no acid present), so the cyanide (a good nucleophile) attacks the less-substituted carbon. No reaction takes place at the middle carbon, so its stereochemistry does not change.

(12) B Which of the following reagents <u>cannot</u> be used for the following synthesis, where starting material **N** is converted into **P**?

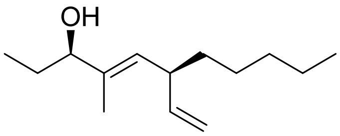


N **P**

(A) PBr_3
(B) $POCl_3$, pyridine
(C) $SOCl_2$, pyridine
(D) TsCl, pyridine

Choices (A), (C), and (D) all convert the hydroxyl group (a poor leaving group) into a good leaving group, in preparation for the S_N2 reaction in step 2. Choice (B) generates an alkene from the starting material.

Problem II. Alkenes (7 points). Provide the systematic IUPAC name for compound **Q**.

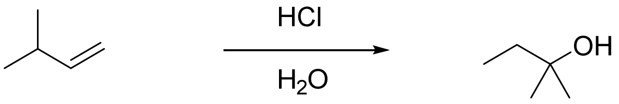


Q

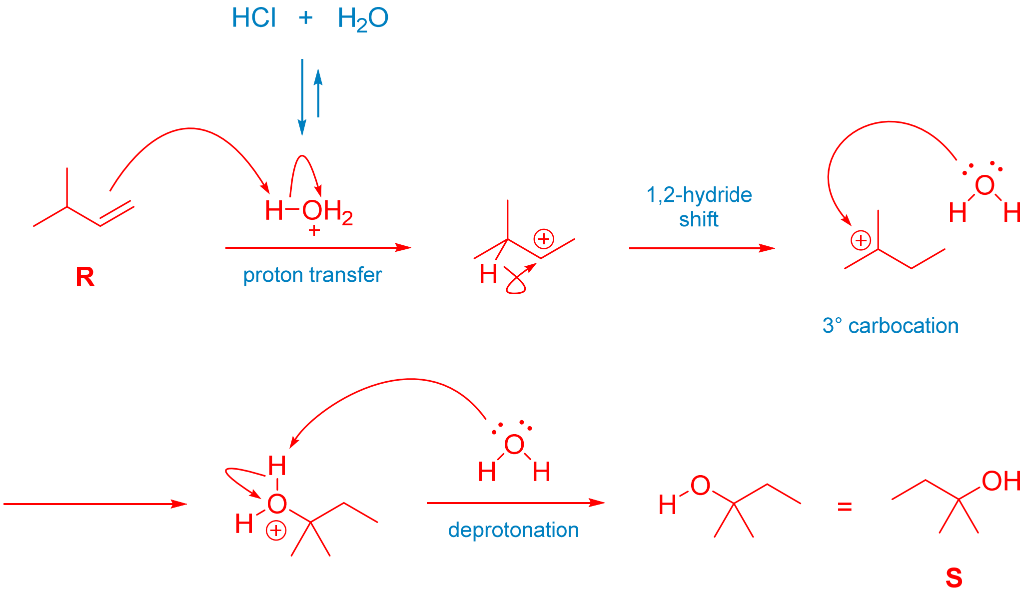
(3*R*,4*E*,6*S*)-4-methyl-6-pentyl-4,7-octadien-3-ol

The parent chain is the chain of carbons that contains the alcohol and both double bonds. You begin numbering the chain from the side closer to the alcohol, which takes precedence over the alkenes.

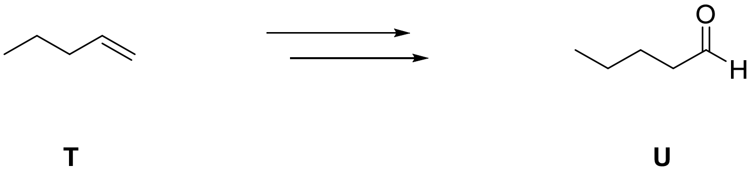
Problem III. Mechanism (17 points). Draw a sensible mechanism for the formation of **S** from **R** in aqueous, acidic solution. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all intermediates in the reaction and any significant resonance forms that account for the stability of these intermediates.

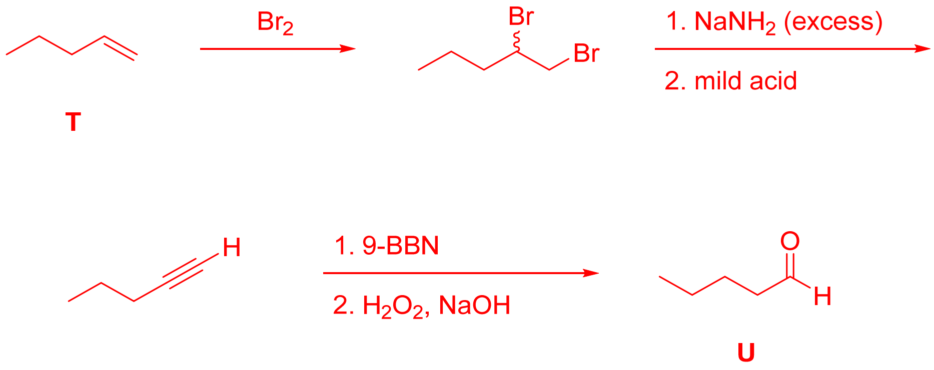


R **S**



Problem IV. Synthesis (16 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **U** using compound **T** as the starting material. You may use any other reagents and starting materials you wish.





If you had read ahead to Chapter 12, you would have known that a more direct route was available: