

## CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

# Hour Examination #3

Wednesday, November 11<sup>th</sup>, 2015

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	Solutions
Student Signature	N/A

## Instructions & Scoring

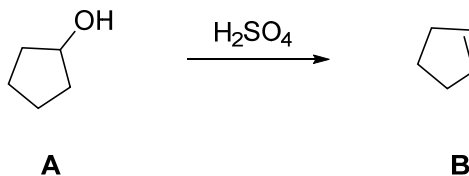
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes (on official paper) and your plastic model kit. No electronic resources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

Problem	Points Earned	Points Available
I		30
II		20
III		18
IV		16
V		16
TOTAL		100

Questions, **Required Information**, **Supplementary Information**

**Problem I.** Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, 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.

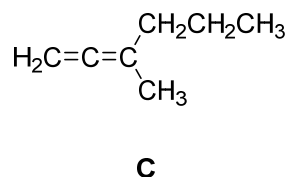
- (1)       D       Which of the following statements is not true regarding the conversion of compound **A** to compound **B**, depicted below?



- (a) this reaction proceeds through a carbocation intermediate
- (b) sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a catalyst for the reaction
- (c) tosic acid (TsOH) would also be an effective catalyst for the reaction
- (d) hydrochloric acid (HCl) would also be an effective catalyst for the reaction
- (e)  $\text{POCl}_3$  + pyridine would also convert **A** to **B**

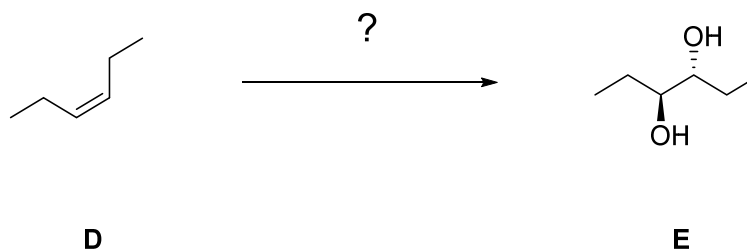
Acids with a good nucleophile as the counteranion will attack the carbocation intermediate.

- (2)       B       Which of the following statements is true regarding compound **C**?



- (a) compound **C** is too strained to exist
- (b) compound **C** is named 3-methyl-1,2-hexadiene
- (c) compound **C** has three carbon atoms that are  $sp^2$  hybridized
- (d) compound **C** is a structural isomer of cyclohexene
- (e) none of the above statements is true

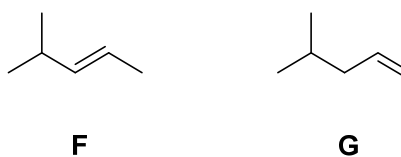
- (3)     A     Which of the following stepwise reactions will carry out the conversion of **D** to **E**?



- (a) 1. OsO<sub>4</sub>; 2. NaHSO<sub>3</sub>, H<sub>2</sub>O  
 (b) 1. mCPBA; 2. H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O  
 (c) 2. mCPBA; 2. NaOH, H<sub>2</sub>O  
 (d) both (b) and (c) will carry out this conversion  
 (e) (a), (b), and (c) will all carry out this conversion

Symmetrical, *cis*-alkenes (e.g., **D**) will afford a meso product (e.g., **E**) upon dihydroxylation with syn addition (e.g., by use of osmium tetroxide). Symmetrical, *cis*-alkenes will afford a pair of enantiomers as products upon dihydroxylation with anti addition (e.g., by epoxidation followed by hydrolysis). Symmetrical, *trans*-alkenes will afford a pair of enantiomers as products upon dihydroxylation with syn addition. Symmetrical, *trans*-alkenes will afford a meso product upon dihydroxylation with anti addition.

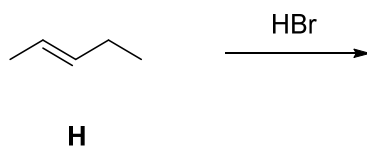
- (4)     D     Which of the following statements is true and most complete in its comparison of compounds **F** and **G**?



- (a) compound **F** has fewer constitutional/structural isomers than **G**  
 (b) compound **F** has a less negative heat of hydrogenation than **G**  
 (c) compound **F** has a slower rate of hydrogenation on Pd-C than **G**  
 (d) statements (b) and (c) are both true  
 (e) statements (a), (b), and (c) are all true

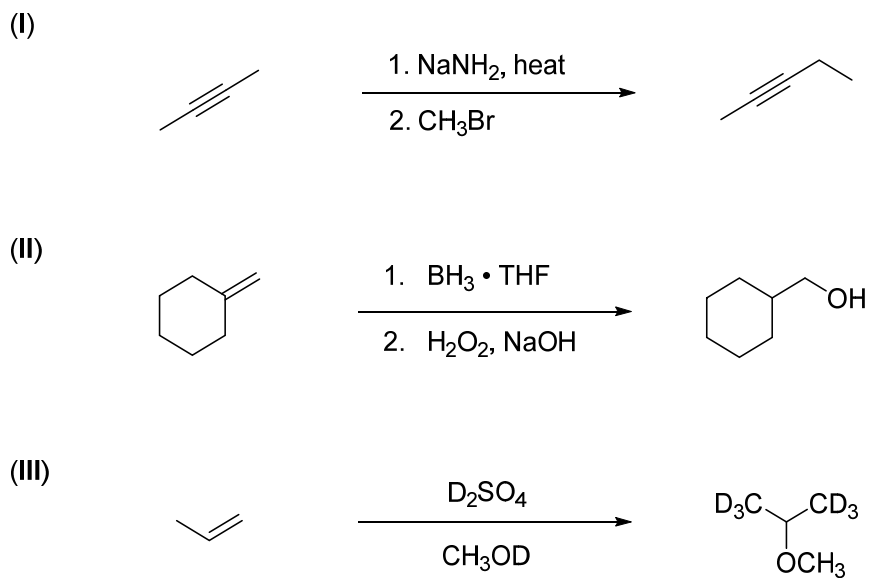
(5)       D      

Which of the following statements is true and most complete in its description of the addition of HBr to compound **H**?



- (a) the reaction proceeds via a bridged bromonium intermediate
- (b) the product mixture will include multiple constitutional isomers
- (c) this product mixture will include multiple stereoisomers
- (d) statements (b) and (c) are both true
- (e) statements (a), (b), and (c) are all true

(6)       E       Which of the following reactions will proceed as drawn to afford the indicated product in good yield?

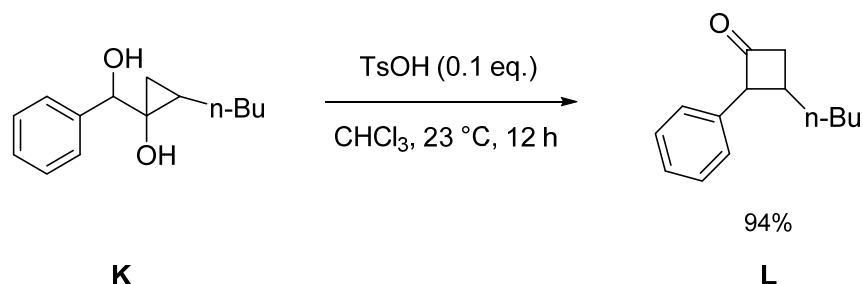


- (a) only reaction I will proceed as drawn  
 (b) only reaction II will proceed as drawn  
 (c) only reaction III will proceed as drawn  
 (d) only reactions II and III will proceed as drawn  
 (e) reactions I, II, and III will all proceed as drawn

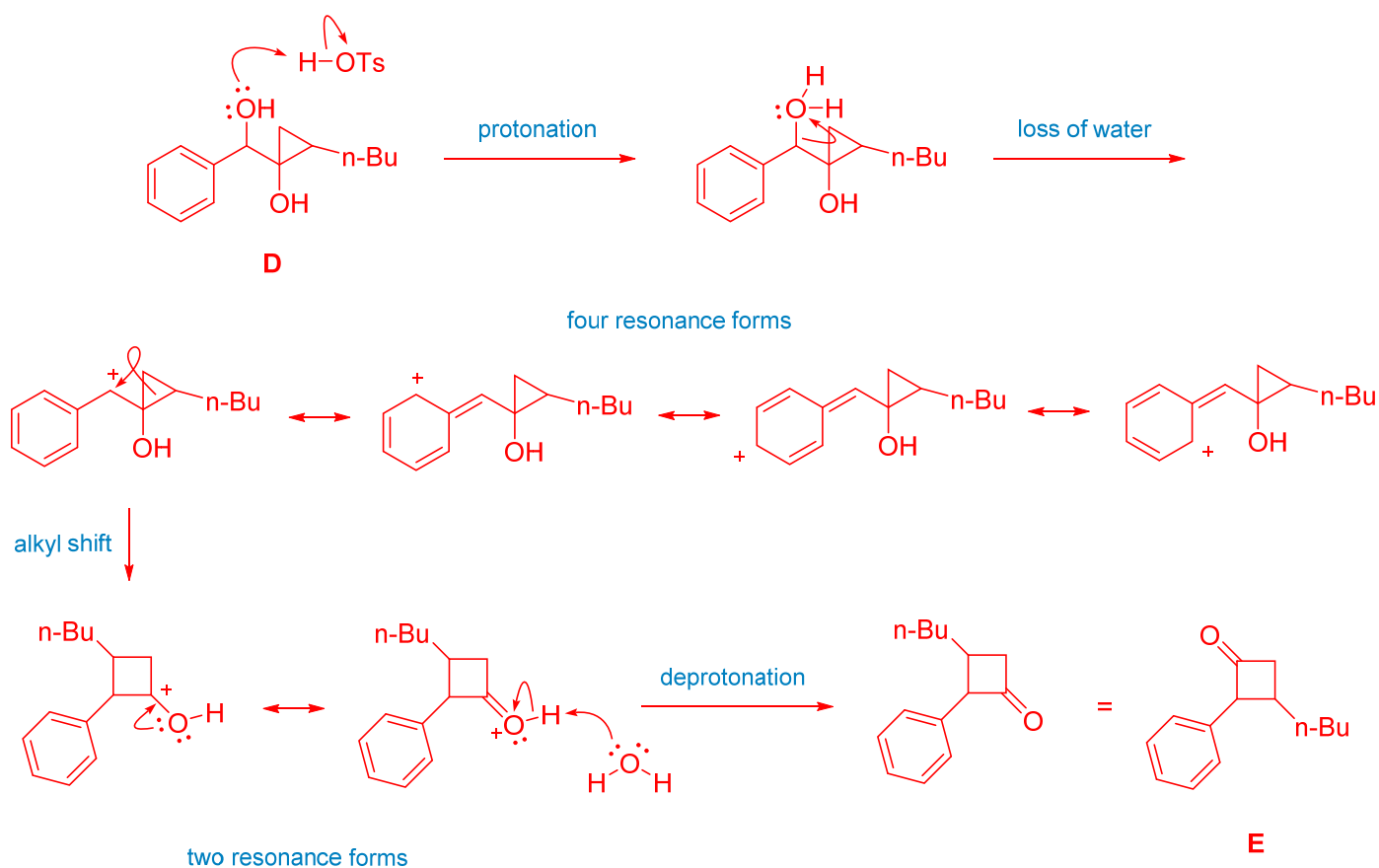
Reaction I proceeds by generation of the acetylide via the alkyne zipper reaction. Reaction II is straightforward. Reaction III proceeds by exchange of the hydrogens of the terminal carbons following protonation/deprotonation by the deuterated solvent.

**Problem II. Mechanism (20 points total).**

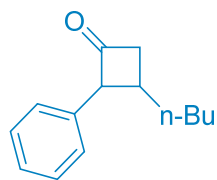
Part 1. (16 points) Draw a sensible mechanism for the formation of **L** from **K** in chloroform with *para*-toluenesulfonic acid (TsOH,  $pK_a < -4$ ) as a catalyst. Remember to use proper “curved arrow notation” to account for the redistribution of electrons in the making and breaking of bonds. Show all intermediates in the reaction and any significant resonance forms that account for the stability of these intermediates. Do not worry about accounting for stereochemistry.



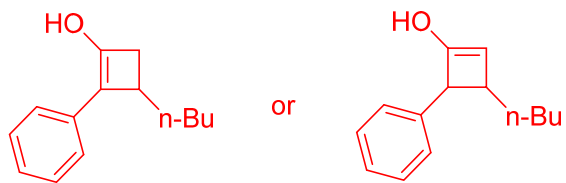
Ref: Walsh. *J. Am. Chem. Soc.* **2009**, *131*, 6516–6524



Part 2. (4 points) In the labeled box on your answer sheet, draw the structure of a tautomer of compound L.

**L**

keto tautomer



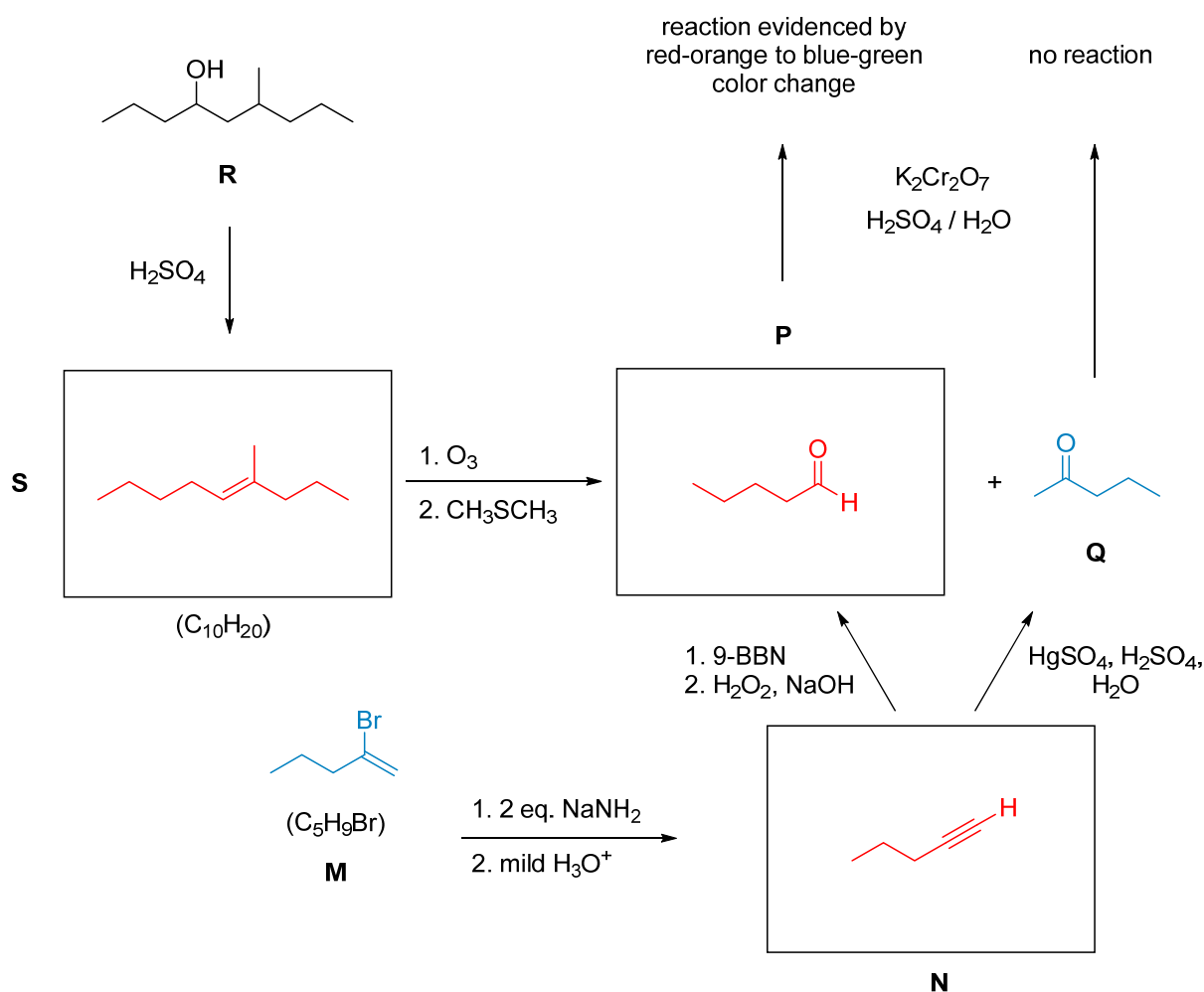
enol tautomers

Other tautomers, not keto–enol pairs, are also possible.

**Problem III.** (18 points) Roadmap Problem. Provide structures for compounds **S**, **P**, and **N**—note the eschewal of alphabetical order on the answer sheet—given the information listed below.

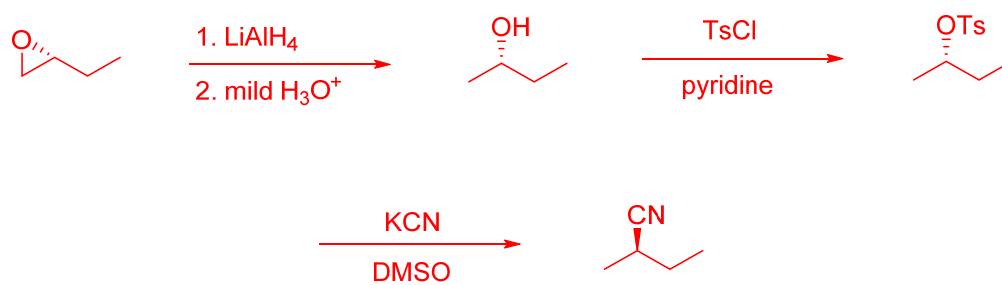
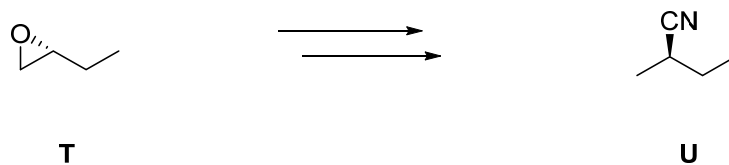
Compound **M** has the molecular formula  $C_5H_9Br$  and no stereoisomers. Heating **M** with 2 equivalents of sodamide, followed by acidic workup, yields compound **N**. Treatment of **N** with 9-borabicyclo[3.3.1]nonane followed stepwise with alkaline hydrogen peroxide affords compound **P**. Treatment of **N** with aqueous mercuric sulfate and sulfuric acid affords compound **Q**. Upon treatment of **P** and **Q** with aqueous acidic dichromate, compound **P** reacts to form a blue-green solution while the solution with **Q** remains red-orange, indicative of no reaction.

When compound **R**, a mixture of stereoisomers of 6-methyl-4-nonanol, is heated with a drop of sulfuric acid, compound **S** is isolated in decent yield. Compound **S** is a hydrocarbon of molecular formula  $C_{10}H_{20}$ . When **S** is subjected to ozonolysis and reductive workup, compounds **P** and **Q**—our old friends from the above paragraph—are the lone two organic products.

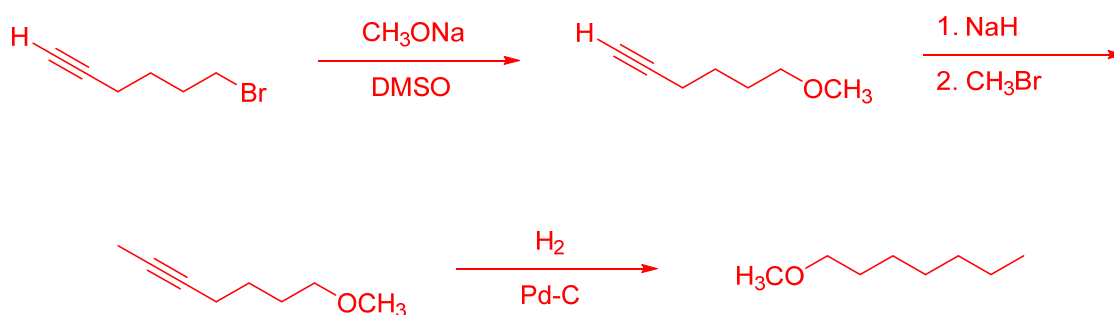
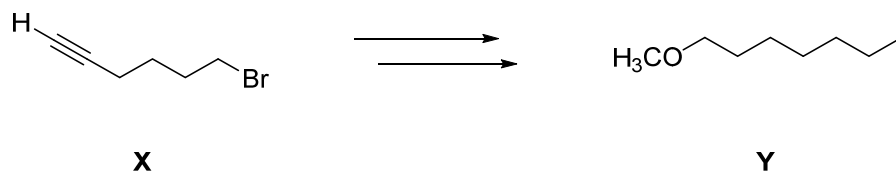




**Problem IV. Synthesis (16 points).** Outline a synthesis—i.e, a sequence of reactions—to prepare compound **U** from compound **T** using any other reagents and starting materials you wish.



**Problem V.** Synthesis (16 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **Y** from compound **X** using any other reagents and starting materials you wish.



Order matters: (i) the alkyl bromide must be used to generate the ether by Williamson ether synthesis prior to generation of the acetylide anion, and (ii) the acetylide anion must be generated prior to hydrogenation of the alkyne.