CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Quiz #4

Due: Saturday, November 8th, 2014

6:00 p.m. (in Monsanto Hall 103)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

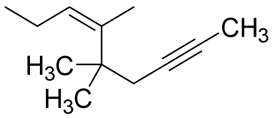
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. You must submit a hard copy of your answer sheet. Answer sheets submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		25
II		24
III		18
IV		13
V		20
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (25 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) A What is the best name for compound **A**?

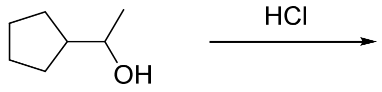


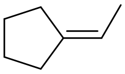
A

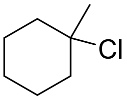
- (a) (6*Z*)-5,5,6-trimethyl-6-nonen-2-yne
- (b) (6*E*)-5,5,6-trimethyl-6-nonen-2-yne
- (c) (3*Z*)-4,5,5-trimethyl-3-nonen-7-yne
- (d) (5*Z*)-1,4,4,5-tetramethyl-5-octen-1-yne
- (e) (5*E*)-1,4,4,5-tetramethyl-5-octen-1-yne

You begin by finding the longest carbon chain that contains both the double and triple bond, then number from the side of the chain that gives the lower number to the first π bond.

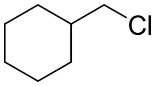
(2) C Which of the following compounds would you <u>least</u> expect to observe as a product of the following reaction?



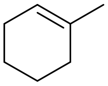

(a)

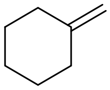


(b)



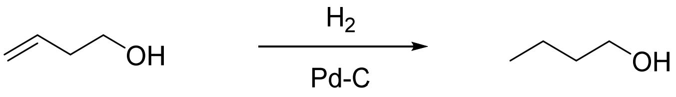
(c)


(d)


(e)

Begin by protonating the hydroxyl group so that it may leave as water to generate a carbocation. This carbocation is subject to attack by a nucleophile (e.g., Cl^- or H_2O), elimination, or rearrangement to a different carbocation. Compound **C** would not be present in any detectable yield because it would have to form by chloride attacking a primary carbocation, which is very unstable.

(3) B What statement best describes the role of Pd-C in the following reaction?

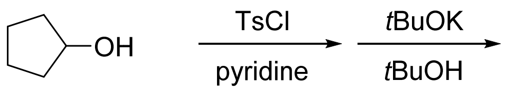


(a) it makes the reaction more exothermic and drives the equilibrium right
(b) it increases the rate of the reaction
(c) it prevents the hydroxyl group from serving as a nucleophile
(d) statements (a) and (b) are both correct
(e) statements (a), (b), and (c) are all correct

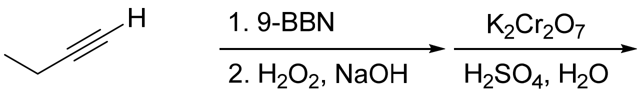
Pd-C is purely a catalyst for the reaction. As such, it simply lowers the activation barrier for the reaction, thereby increasing the rate. The Pd-C does not influence the equilibrium or relative stability of the reactants.

(4) ___D___ Which of the following reaction sequences does not generate a major product that contains a π bond?

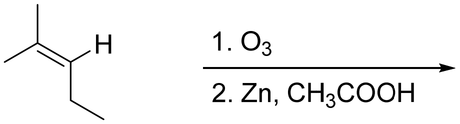
(a)



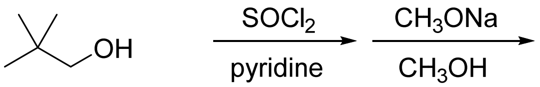
(b)



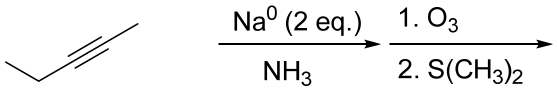
(c)



(d)

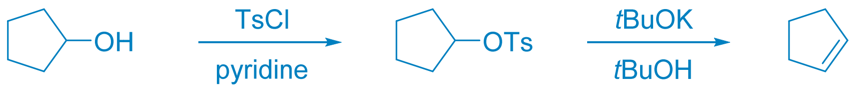


(e)



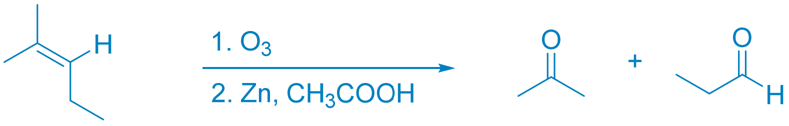
For choice D, the hydroxyl group could be converted to the chloride, but the reaction would probably be quite slow—substitution reactions at neopentyl groups are very, very sluggish. The elimination of HCl from the intermediate is impossible because there are no β hydrogens. This sequence would probably produce an ether as the product, if you waited long enough for it to form. Here are all of the intermediates and products expected from each sequence.

(a)

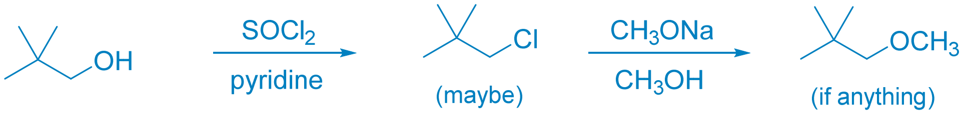


(b)

(c)

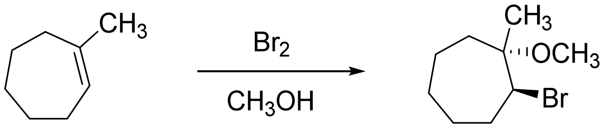


(d)



(e)

(5) B What statement does <u>not</u> accurately describe the following reaction?

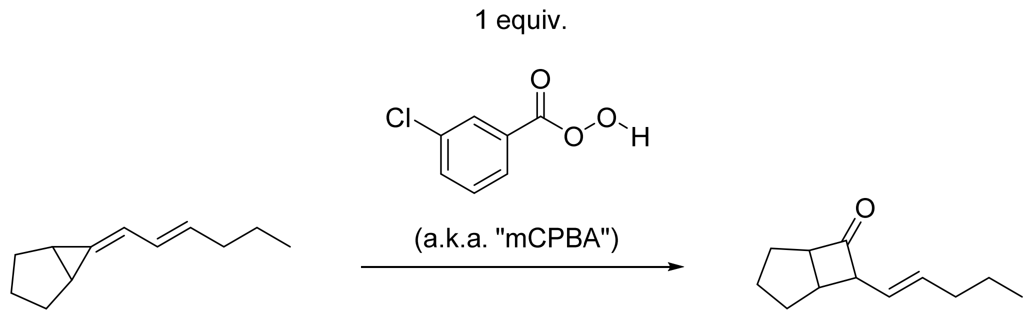


(a) H^+ and Br^- are byproducts of the reaction
(b) the reaction produces another diastereomer, not shown
(c) at least one carbon atom is oxidized
(d) at least one bromine atom is reduced
(e) the reaction mechanism involves a bridged bromonium intermediate

This reaction produces two enantiomers (only one of which is shown), not two diastereomers. HBr is a by-product, both carbon atoms of the alkene are oxidized, and both bromine atoms are reduced. The first step of the mechanism is formation of a bromonium ion.

Problem II. Mechanism (24 points).

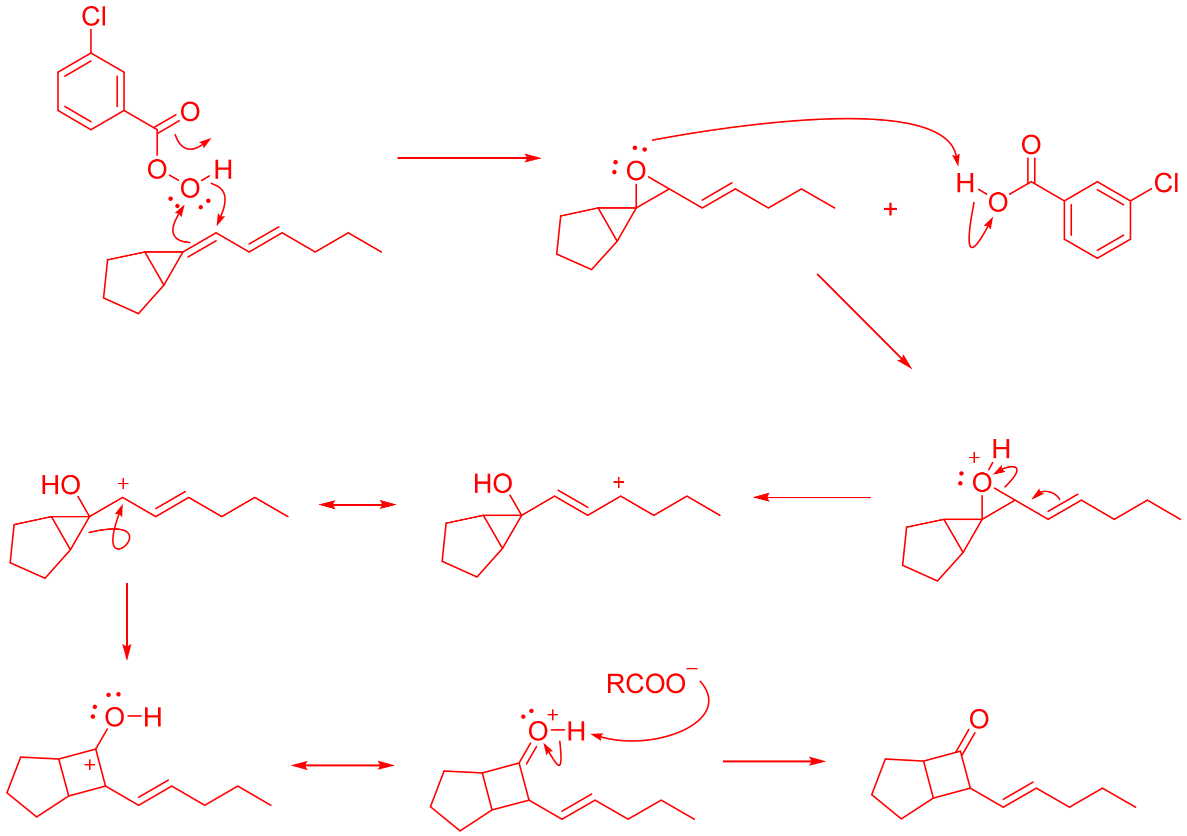
(1) (18 points) Draw a sensible mechanism for the following reaction. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reaction.



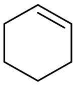
B **C**

61% yield

Ref: McCullough and Cohen. *Tet. Lett.* **1988**, *29*, 27–30.



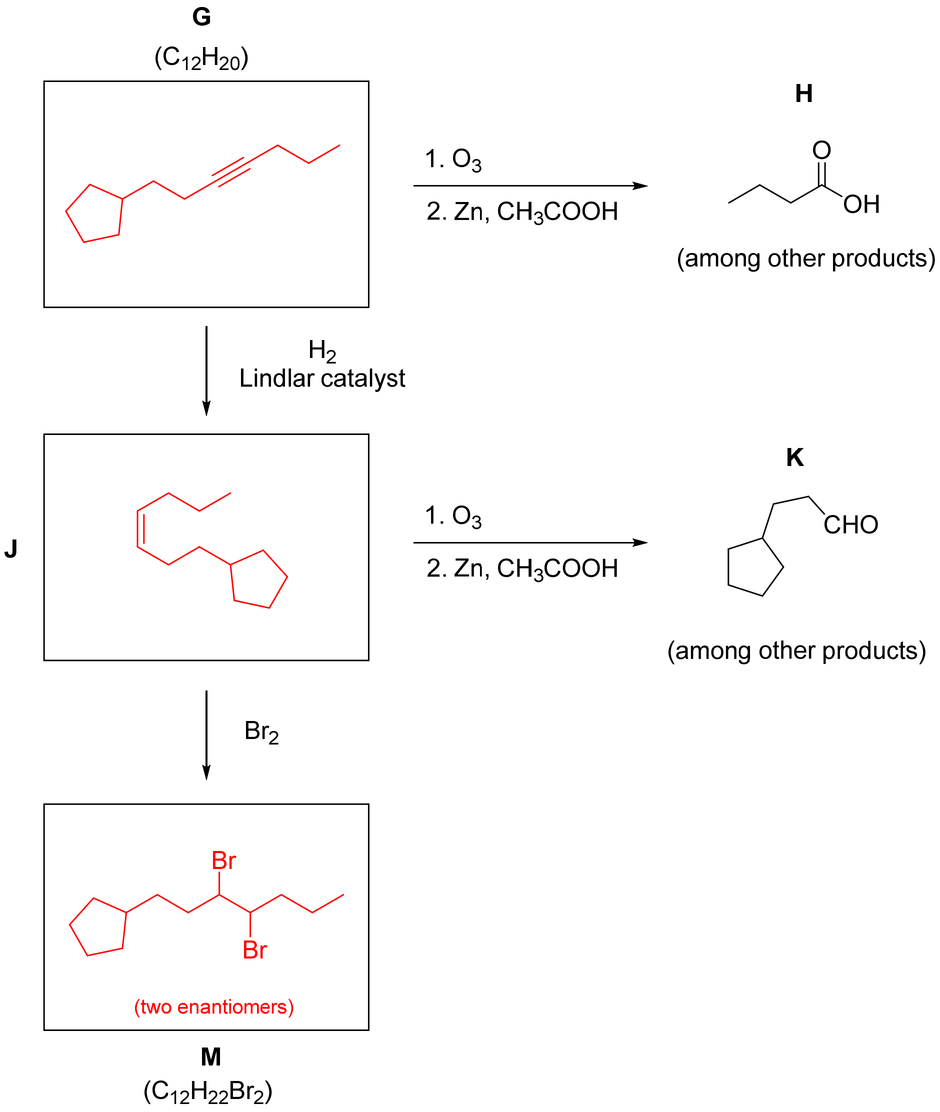
(2) (6 points) Which of the following three compounds would make the best choice as a solvent for this reaction? Write your choice in the box and explain your choice in three sentences or fewer.

NH_3	$CHCl_3$	
D	**E**	**F**
ammonia	chloroform	cyclohexene

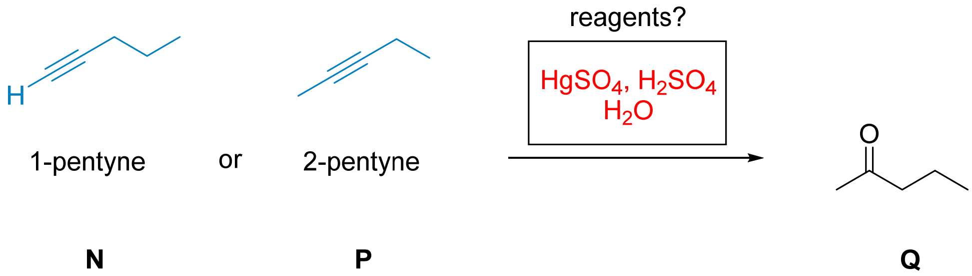
Compound **E** is the best choice of solvent. Compound **D** can react with the epoxide intermediate and compound **F** can react with the mCPBA to form an epoxide. Compound **E** is neither a strong nucleophile nor electrophile, and as such, will not lead to the formation of side products.

Problem III. (18 points) Roadmap Problem. Provide structures for compounds **G**, **J**, and **M** given the information listed below.

Compound **G** has the molecular formula $C_{12}H_{20}$. When **G** is subjected to ozonolysis with a reductive workup, compound **H** is one of the fragments isolated from the reaction. When compound **G** is treated with H_2 in the presence of Lindlar catalyst, compound **J** is formed. When **J** is subjected to ozonolysis with a reductive workup, compound **K** is one of the fragments isolated from the reaction. When compound **J** is treated with elemental bromine, the orange color disappears and yields a racemic mixture of product **M** with molecular formula $C_{12}H_{22}Br_2$. On your answer sheet, provide structures for compounds **G**, **J**, and **M** that are consistent with these data.

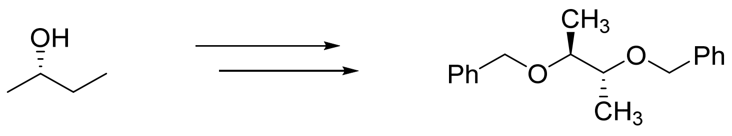


Problem IV. Explanations (13 points). Of compounds **N** and **P**, which is the better choice of starting material to synthesize 2-pentanone (**Q**)? Mark the letter of your selection in the box marked “choice” and the reagents required for the transformation in the box marked “reagents”

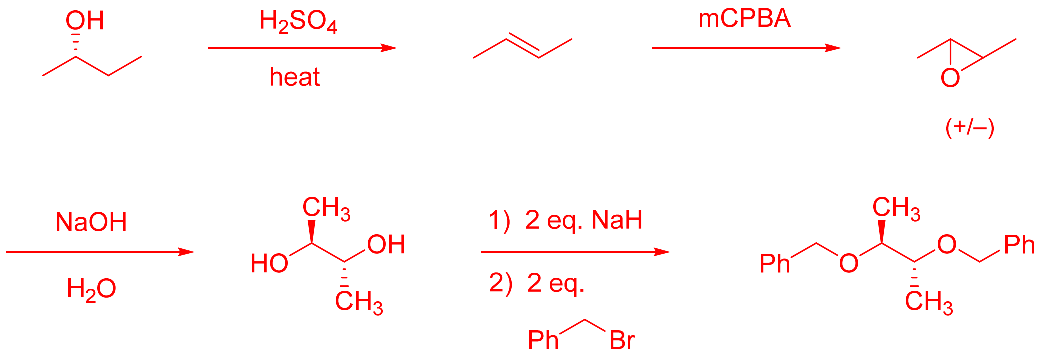


The two *sp*-hybridized carbons in the terminal alkyne (**N**) have different reactivities, so the desired product can be preferentially formed by favoring Markovnikov addition of water. In the case of the internal alkyne, both carbons are substituted with alkyl groups and there will be very little preference for adding the oxygen to the second or third carbon. This will lead to a mixture of the desired 2-pentanone but an almost equal quantity of undesired 3-pentanone. Thus, compound **N** is the better starting material, as it offers a more selective, less wasteful route to the target.

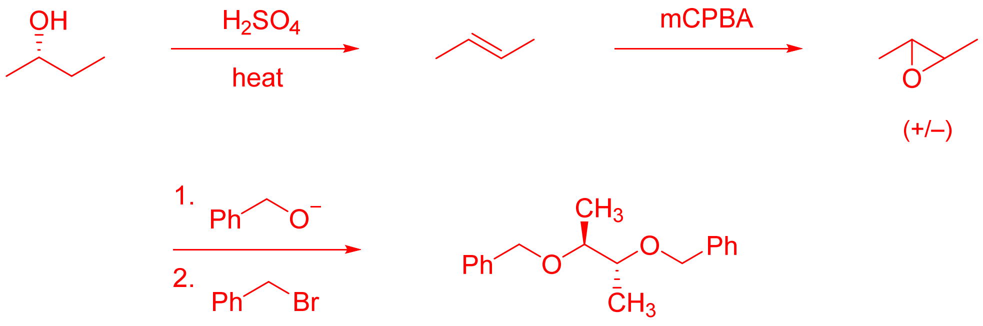
Problem V. Synthesis (20 points). Provide a synthetic route—i.e, a sequence of reactions—to produce compound **U** using (*S*)-2-butanol (**T**) as the starting material and any other compounds and reagents you wish. (Just don't violate the spirit of the problem by not using compound **T** as one of the sources of carbon atoms in **U**).



T **U**



or



Note that the following route is <u>not</u> favorable because S_N2 substitution on a secondary alkyl halide by a strong base will favor E2 elimination and generate undesired side product: