CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Practice Hour Examination #3

Solutions Key

Student Name (Printed)	Solutions
Student Signature	

Please also write your name on the back of the exam

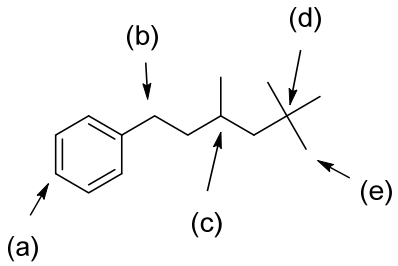
Scoring

Problem	Points Earned	Points Available
I		25
II		15
III		20
IV		20
V		20
TOTAL		100

Original Problems, Required Information in Answers, and Supplementary Explanation

Problem I. (25 points total, 5 points each) For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided.

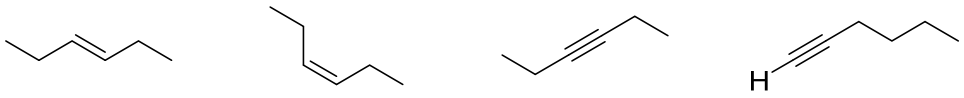
(1) B Which of the following arrows points to the easiest hydrogen atom(s) for a bromine radical ($Br^{\bullet}$) to abstract from compound **A**?



A

The most easily abstracted hydrogen will be the one that leaves behind the most stable carbon radical. Here, abstraction of (b) generates a benzylic radical stabilized by a resonance effect. Note that abstraction of the hydrogen at (a) will not generate a resonance-stabilized radical, and that there are no hydrogens at (d)—a quaternary carbon.

(2) A Rank the following compounds in descending order of enthalpy (ΔH) of hydrogenation (i.e., least exothermic to most exothermic when hydrogenated completely) per mole of substrate.

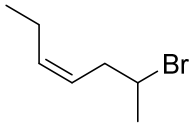


B **C** **D** **E**

(a) **B** > **C** > **D** > **E**
(b) **E** > **D** > **C** > **B**
(c) **E** > **D** > **B** > **C**
(d) **D** > **E** > **B** > **C**
(e) none of the above

The alkynes rank highest because there are two π bonds that are hydrogenated per molecule. The most stable π bonds will liberate less energy upon hydrogenation. Thus, the amount of liberated energy decreases with increasing substitution and *cis* double bonds liberate more energy than similar *trans* bonds.

(3) D Which of the following reagents will not oxidize compound **F**?

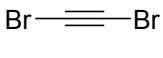


F

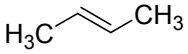
(a) Br_2
(b) mCPBA
(c) OsO_4
(d) $LiAlH_4$
(e) 1. O_3, 2. Zn, CH_3COOH

Br_2 oxidizes the double bond to generate a vicinal alkyl dihalide. mCPBA oxidizes the double bond to generate an epoxide. Osmium tetraoxide oxidizes the double bond to a vicinal diol. Ozonolysis oxidizes the compound to two aldehyde fragments. Lithium aluminum hydride reduces the compound by replacing the bromine atom with a hydrogen.

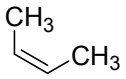
(4) D Which of the following compounds has the highest net dipole moment?



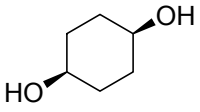
(a)



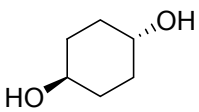
(b)



(c)

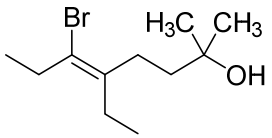


(d)



(e)

(5) A What is the IUPAC name of compound **G**?

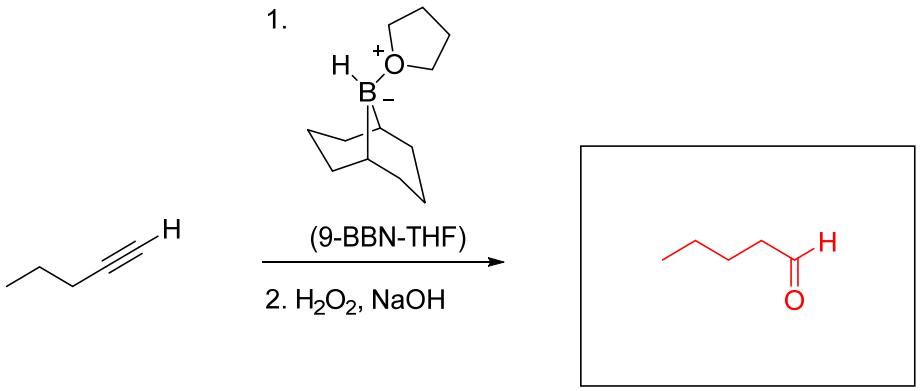


G

(a) (Z)-6-bromo-5-ethyl-2-methyl-5-octen-2-ol
(b) (*Z*)-3-bromo-4-ethyl-7-hydroxyl-7,7-dimethylheptene
(c) (*E*)-3-bromo-4-ethyl-7-hydroxyl-7,7-dimethylheptene
(d) (*Z*)-5-bromo-4-ethyl-1,1-dimethyl-4-hepten-1-ol
(e) (*E*)-5-bromo-4-ethyl-1,1-dimethyl-4-hepten-1-ol

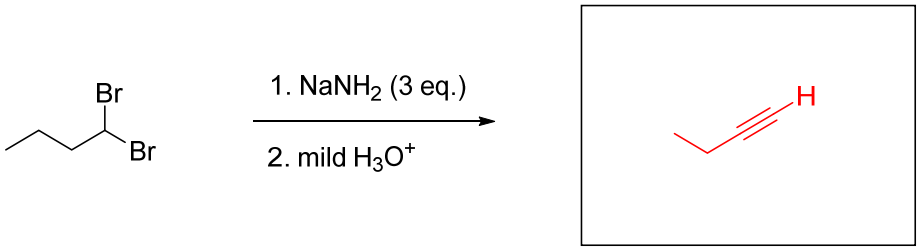
Problem II. (15 points total, 5 points each) Reactions. The following chemical reactions are missing their starting materials, reagents, or products. Write the missing compounds into the empty boxes below, as appropriate. In some cases, there will be more than one correct answer that will merit full credit.

(1) (5 points)



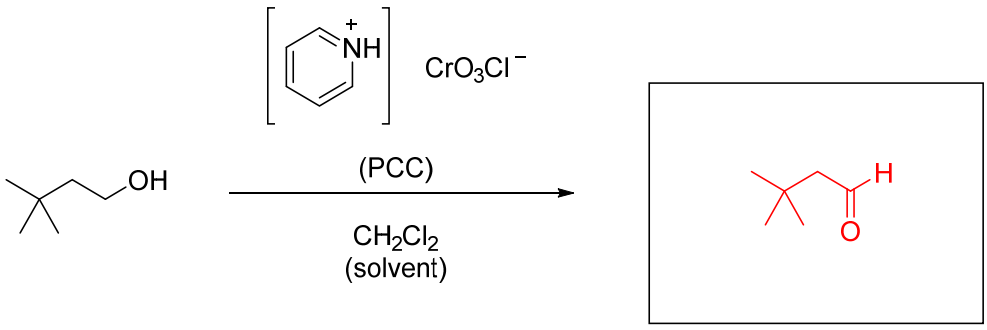
Note that BH_3 and equivalent reagents (e.g., B_2H_6 or BH_3-THF) should not be used on terminal alkynes because they tend to add twice and lead to mixtures of products. A bulky borane should be used, like 9-BBN or Sia_2BH.

(2) (5 points)



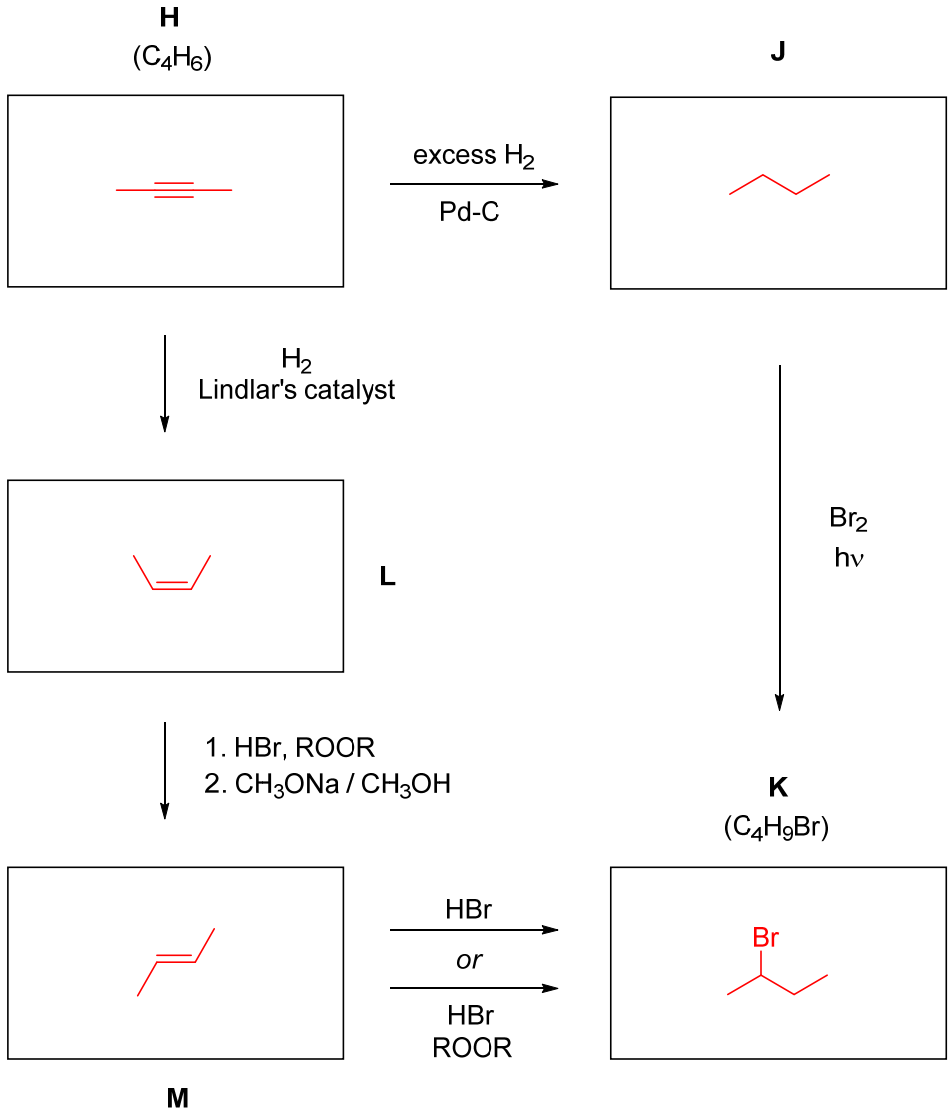
Note that three equivalents of $NaNH_2$ are required because upon production of the alkyne, the terminal hydrogen (pK_a ~ 25) will be deprotonated by an equivalent of base. Treatment with acid in the second step protonates the acetylide to form the terminal alkyne.

(3) (5 points)



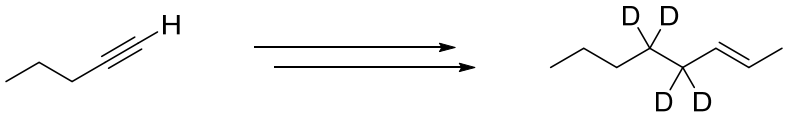
Problem III. (20 points total) Roadmap. Provide structures for compounds **H**, **J**, **K**, **L**, and **M** given the clues listed below.

Compound **H** has the molecular formula C_4H_6. When **H** is treated with excess H_2 in the presence of palladium on carbon, compound **J** is formed. Photobromination of **J** yields the major product **K**, with molecular formula C_4H_9Br. When compound **H** is hydrogenated in the presence of Lindlar's catalyst, compound **L** is the major product. Treatment of **L** with HBr in the presence of peroxides, followed by reaction with methoxide in methanol, yields **M**. The reaction of **M** with HBr—either in the presence of peroxide or not—yields compound **K**. Provide structures for compounds **H**, **J**, **K**, **L**, and **M**. All five compounds have different structures, but not necessarily different molecular formulas.

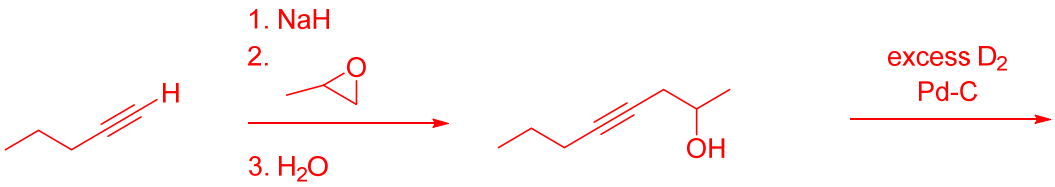


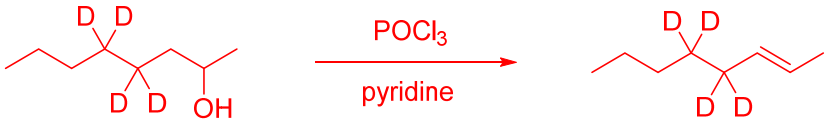
Note that the steps from **L**→**M**→**K** eliminate the possibility of **H** = 1-butyne.

Problem IV. (20 points total) Synthesis. Write out an efficient synthetic route for the preparation of compound **P** from the indicated starting material and any other reagents you wish.



P





P

Problem V. (20 points total) Mechanism. Write out a sensible mechanism for the following transformation.