CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Hour Examination #3

Wednesday, November 20th, 2013
6:30–8:30 p.m.

Student Name (Printed)	Solutions
Student Signature	

Instructions & Scoring

- You have two hours to complete this exam. The exam will end promptly at 8:30 pm.
- You are allowed access to two (2) letter-sized pages of handwritten notes and a molecular model kit. You may not share these materials.
- Partial credit will be awarded on problems 2, 3, 4, and 5. Try not to leave blank answers.
- You may not access any electronic devices during the examination.
- Your examination may be photocopied.

Problem	Points Earned	Points Available
I		25
II		15
III		20
IV		24
V		16
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) C Which of the following statements about radical reactions is not correct?

(a) The stability of carbon radicals follows the trend 3° > 2° > 1°. (Tertiary radicals are more stable than secondary, which are more stable than primary.)

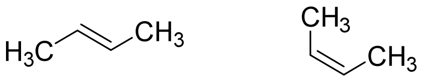
(b) Molecular oxygen is a diradical that can interfere with organic radical reactions

(c) Photochlorination is typically more selective than photobromination

(d) Allylic radicals like $H_2C{=}CH{-}CH_2^{\bullet}$ are stabilized by a resonance effect

(e) Initiation steps typically involve the homolysis of a covalent bond to generate unpaired electrons

(2) E Which of the follow statements about *trans*-2-butene (**A**) and *cis*-2-butene (**B**) is not correct?



A **B**

(a) Compounds **A** and **B** are diastereomers

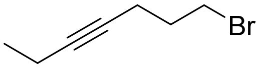
(b) Both **A** and **B** produce the same product upon reaction with H_2 in the presence of palladium metal on carbon (Pd-C)

(c) Both **A** and **B** produce the same product upon reaction with HBr in the *presence* of peroxides (HBr with ROOR)

(d) Both **A** and **B** produce the same product upon reaction with HBr in the *absence* of peroxides (HBr without ROOR)

(e) Compound **A** has a higher boiling point than compound **B**

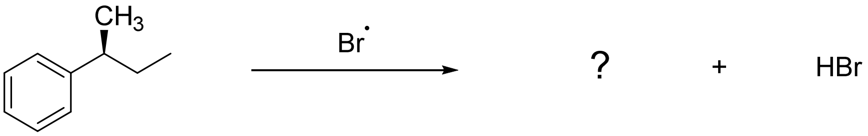
(3) B Which of the following reagents will <u>not</u> carry out a reduction reaction of compound **C**?



C

(a) Na / NH_3
(b) mCPBA
(c) H_2, Lindlar's catalyst
(d) $LiAlH_4$
(e) H_2, Pd-C

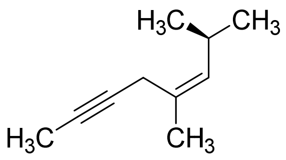
(4) D Which of the following statements best describes the predominant species formed when the most easily abstracted hydrogen atom is removed from compound **D** by a bromine radical?



D

(a) A chiral radical with a half-filled, unhybridized *p* orbital
(b) An achiral radical with a half-filled sp^3 orbital
(c) A chiral radical with a half-filled sp^2 orbital
(d) An achiral radical stabilized by a resonance effect
(e) A carbocation stabilized by a resonance effect

(5) ____D____ What is the IUPAC name of compound **E**?



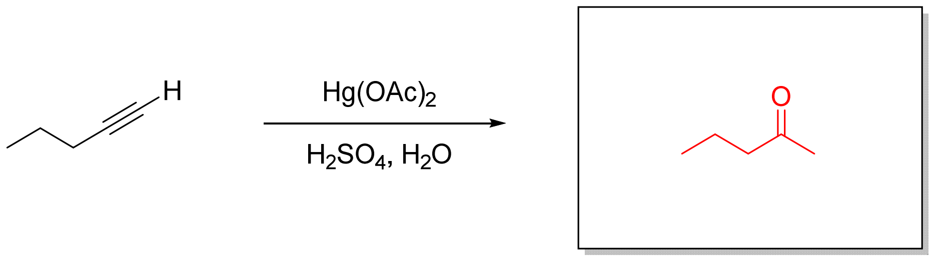
E

(a) (5*Z*,7*S*)-5,7-dimethyl-5-octen-2-yne
(b) (4*E*,7*S*)-1,4,7-trimethyl-4-heptenyne
(c) (2*S*,3*E*)-2,4,7-trimethyl-3-hepten-6-yne
(d) (*Z*)-5,7-dimethyl-5-octen-2-yne
(e) *cis*-1,4,7-trimethyl-4-hepten-1-yne

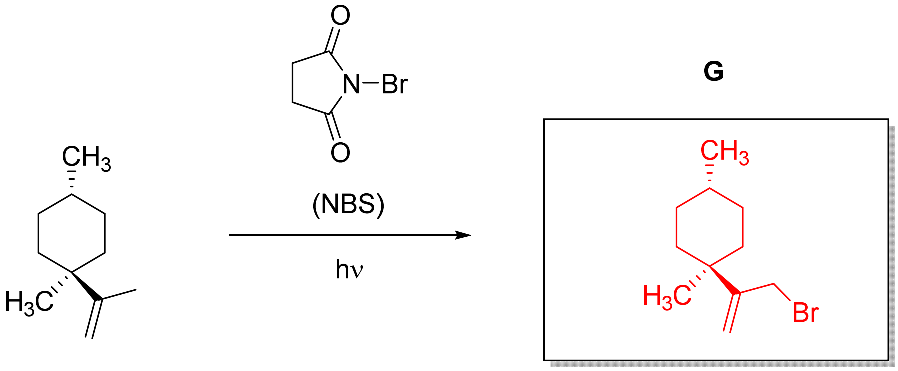
Problem II. (15 points total, 5 points each) Reactions. The following chemical reactions are missing their starting materials, reagents, or products. Write the missing compounds into the empty boxes below, as appropriate. In some cases, there will be more than one correct answer that will merit full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

(1) (5 points)

F

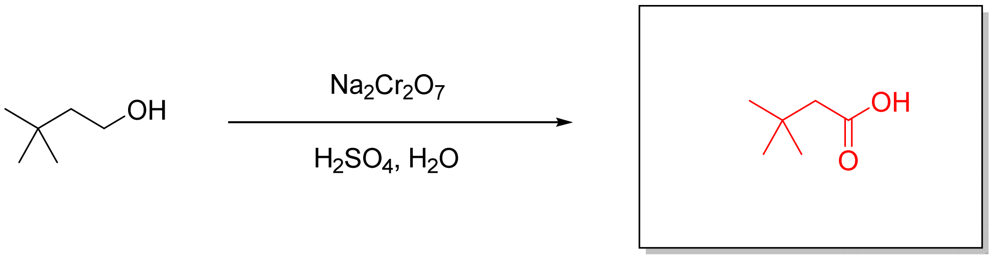


(2) (5 points)



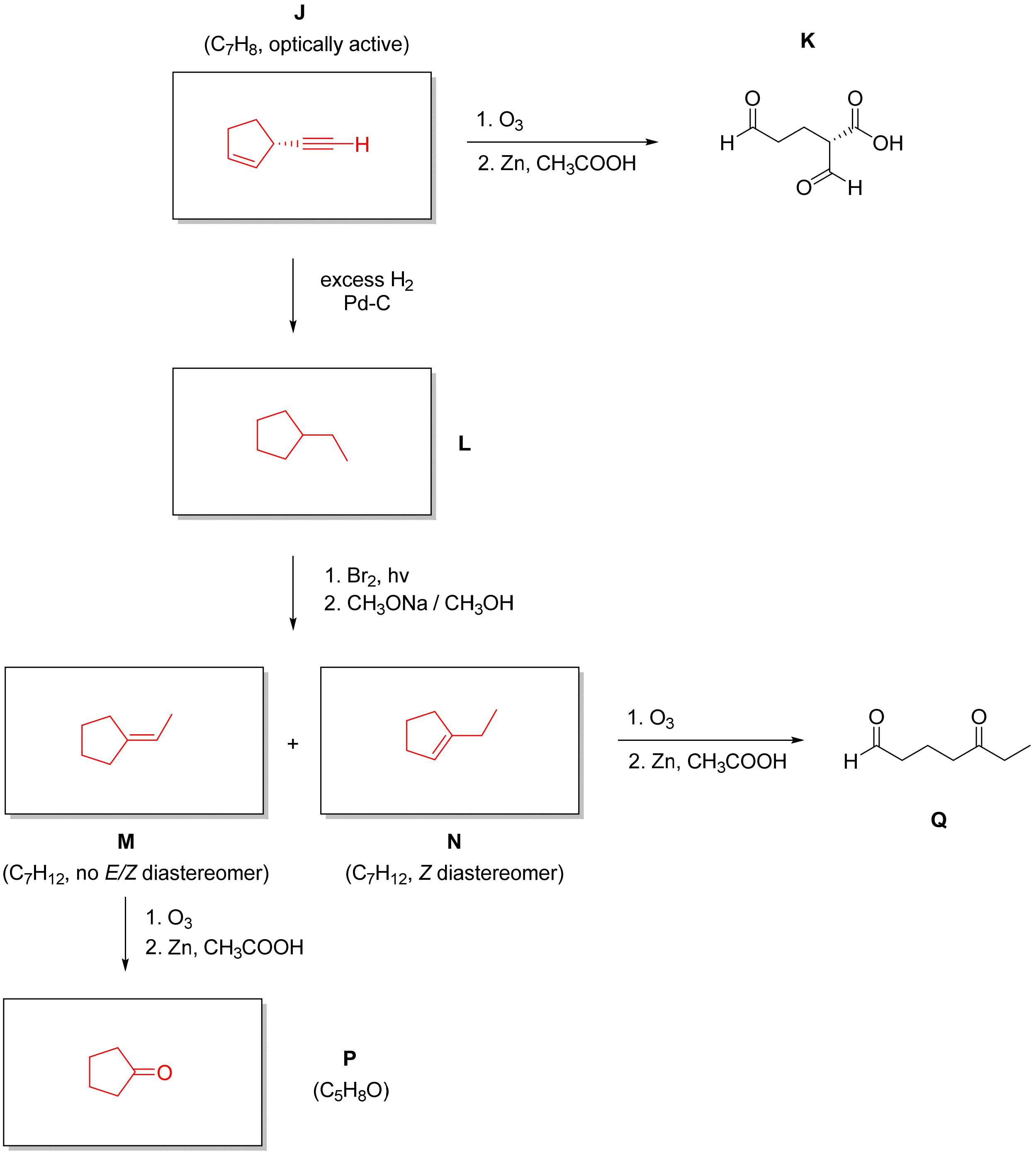
(3) (5 points)

H



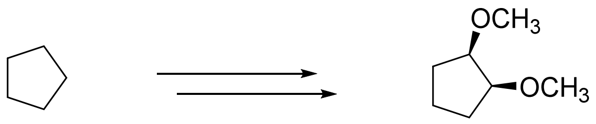
Problem III. (20 points total) Roadmap. Provide structures for compounds **J**, **L**, **M**, **N**, and **P** given the information listed below.

Compound **J** has the molecular formula C_7H_8. When **J** is subjected to ozonolysis with a reductive workup, compound **K** is the major fragment isolated from the reaction. When compound **J** is treated with excess H_2 in the presence of palladium on carbon, compound **L** is formed. Photobromination of **L** yields a single product that when treated with sodium methoxide in methanol yields the major products **M** and **N** (both having a molecular formula of C_7H_{12}). Compound **N** is a *Z* diastereomer, while compound **M** has no *E* or *Z* designation. When compound **M** is subjected to ozonolysis, the major fragment isolated is compound **P**, which has a molecular formula of C_5H_8O. When **N** is subjected to ozonolysis, compound **Q** is the product.

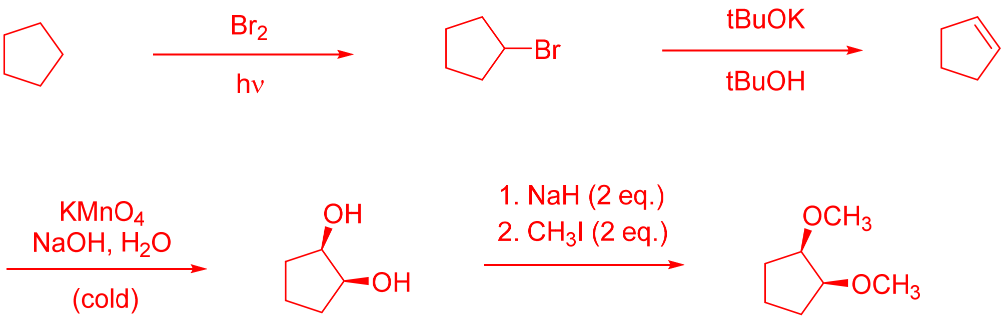


Problem IV. (24 points total) Synthesis. Write out efficient synthetic routes for the following transformations being sure to follow the instructions provided.

(1) (12 points) Outline a synthesis for the preparation of *cis*-1,2-methoxycyclopentane (**T**) from cyclopentane (**S**) and any other reagents you desire.

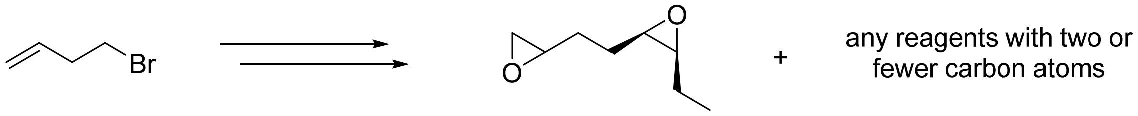


S **T**

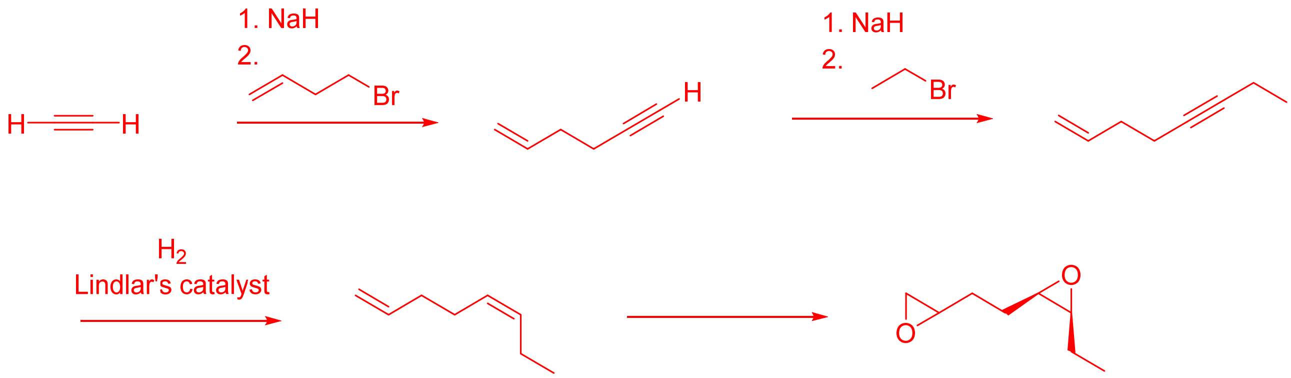


T

(2) (12 points) Outline a route for the preparation of compound **V** (below) from 4-bromo-1-butene (**U**) and sources of carbon with <u>two or fewer</u> carbon atoms. Use any other reagents and solvents you desire. You do not need to control the *R*/*S* stereochemistry of any single carbon in **V**.

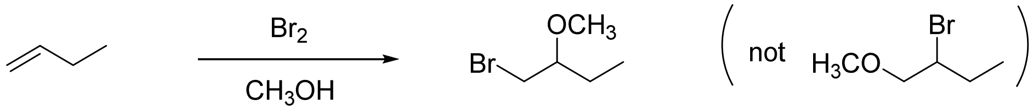


U **V**



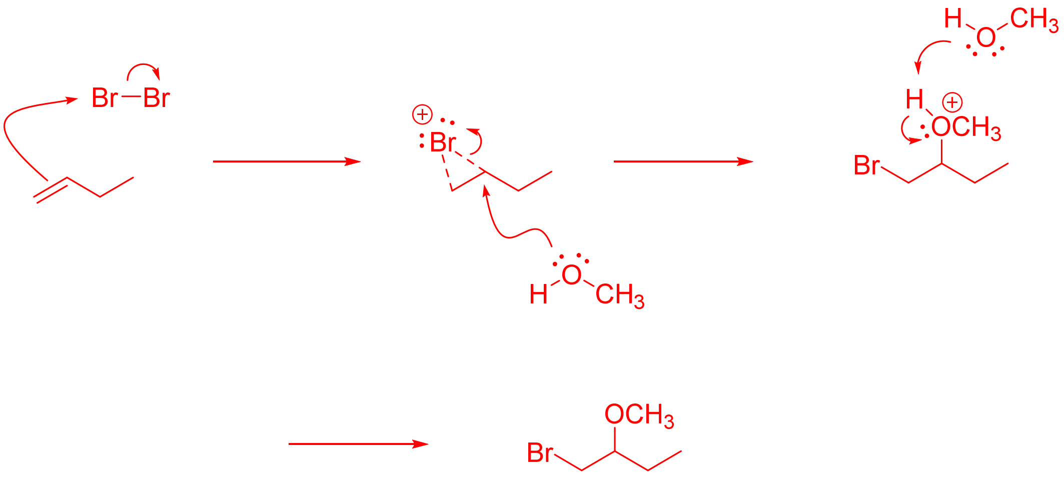
V

Problem V. (16 points total) Mechanism. Consider the following reaction where 1-butene (**X**) forms 1-bromo-2-methoxybutane (**Y**) when treated with one equivalent of elemental bromine in methanol as a solvent.



X **Y** **Z**

(1) (10 points) Draw a sensible mechanism for the transformation of **X** to **Y** using proper "curved arrow" notation to account for the redistribution of electrons.



(2) (4 points) Based on your mechanism, explain in four sentences or fewer why the methoxy group preferentially adds to the 2 position (as in **Y**) rather than the 1 position (as in **Z**). Feel free to draw a picture, if you wish.

This reaction proceeds through a bromonium intermediate, where a bromine atom with a positive formal charge is bridged between two carbon atoms (previously, of the alkene). The positive bromine atom will withdraw negative charge density from the neighboring carbons, and the more-substituted carbon will be able to donate more electron density because its resulting partial positive charge (δ^{+}) will be better stabilized. This greater partial positive charge and weaker C–Br bond on the secondary carbon makes it more electrophilic, so the methanol nucleophile attacks that carbon rather than the (less sterically hindered) primary carbon.