CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Hour Examination #2

Wednesday, October 23rd, 2013
6:30–8:30 p.m.

Student Name (Printed)	
Student Signature	

Instructions & Scoring

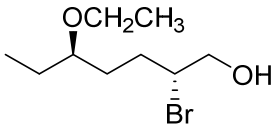
- You have two hours to complete this exam. The exam will end promptly at 8:30 pm.
- You are allowed access to two (2) letter-sized pages of handwritten notes and a molecular model kit. You may not share these materials.
- Partial credit will be awarded on problems 3, 4, and 5. Try not to leave blank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

Question	Points Earned	Points Available
1		15
2		25
3		25
4		20
5		15
TOTAL		100

Original Problems, Required Information in Answers, and Supplementary Explanation

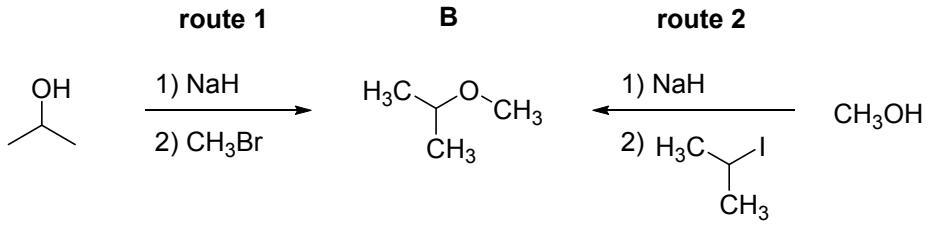
Problem 1. (15 points total, 3 points each) Determine whether the following five statements are true or false. Write out the full word "true" or "false" beside each statement; do not just write "T" or "F". If any part of the statement is false, the entire statement is false.

(i) _____ The proper IUPAC name of compound **A** is (2*R*,5*R*)-2-bromo-5-ethoxy-1-heptanol.

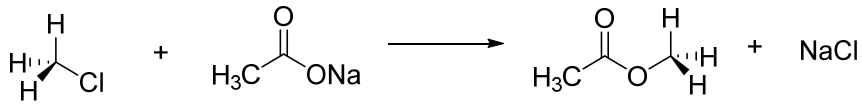


A

(ii) _____ To conduct a Williamson ether synthesis of isopropyl methyl ether (**B**), route 1 is a better choice than route 2 (see below).



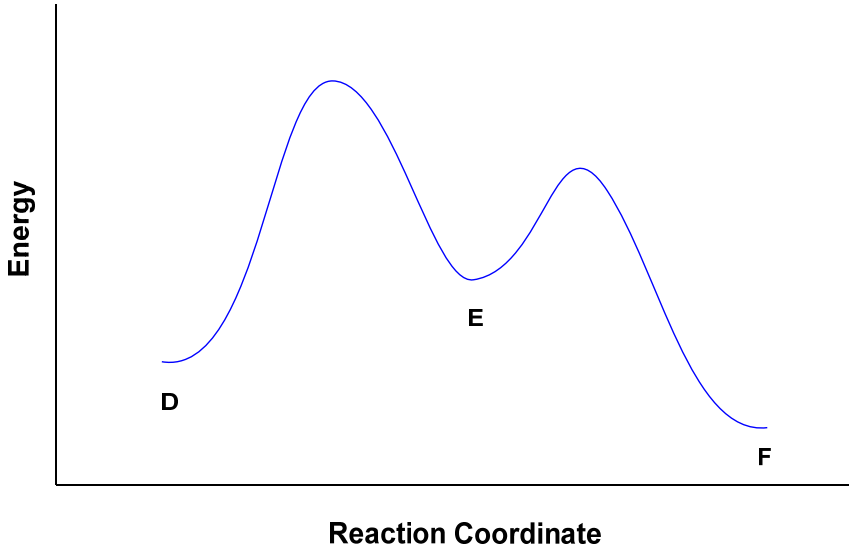
(iii) _____ For the following reaction, doubling the concentration of sodium acetate (**C**) in solution will double the rate of the reaction.



C

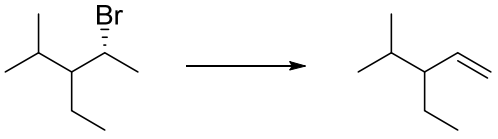
(iv) _____ The boiling point of 1-butanol is higher than the boiling point of diethyl ether.

(v) _____ The energy diagram below depicts the exothermic reaction of **D** to yield the product **F** *via* the transition state **E**.



Problem 2. (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.

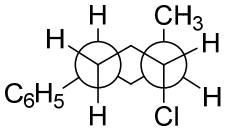
(i) _____ Which reagent and solvent pairing from the choices shown below would make the best selection to favor elimination of HBr from compound **G** to form product **H** and minimize any competing side reactions that would erode the yield?



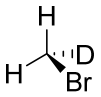
G **H**

(a) CH_3ONa in ethanol
(b) CH_3ONa in DMSO
(c) *tert*-BuONa in *tert*-butyl alcohol
(d) HCl in methanol
(e) HCl in DMSO

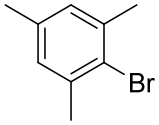
(ii) _____ Which alkyl halide will undergo heterolytic bond dissociation to form a carbocation that is stabilized by both hyperconjugation and a resonance effect as well?



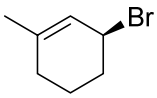
(a)



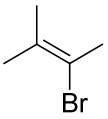
(b)



(c)

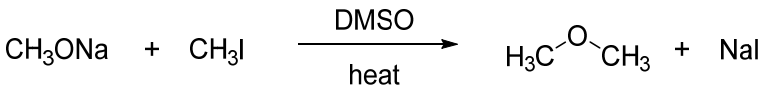


(d)



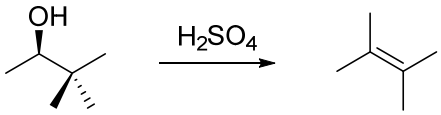
(e)

(iii) _____ In the following reaction, what orbital does the nucleophile attack?



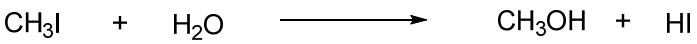
(a) the empty π bonding orbital of the C–I bond
(b) the σ* antibonding orbital of the C–I bond
(c) the σ* antibonding orbital of the C–O bond
(d) an unhybridized p orbital on carbon
(e) a lone pair on the negatively charged oxygen

(iv) _____ Which of the following is <u>not</u> a key step in the mechanism for the reaction drawn below.



(a) generation of a carbocation
(b) protonation of a hydroxyl group
(c) a 1,2-methyl shift
(d) deprotonation by a Brønsted–Lowry base
(e) all of the above are steps in the mechanism

(v) _____ Consider the following reaction and bond dissociation energies, then select the most correct statement of those given.

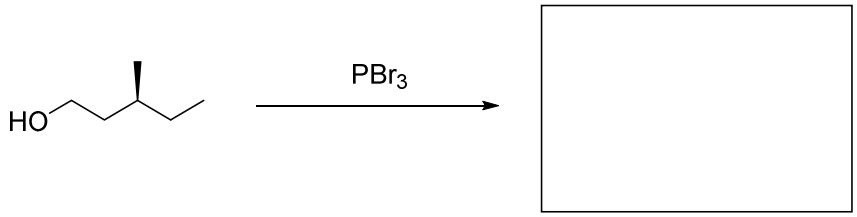


Bond	BDE (kJ/mol)
H–OH	498
CH_3–OH	389
H_3C–I	234
H–I	297

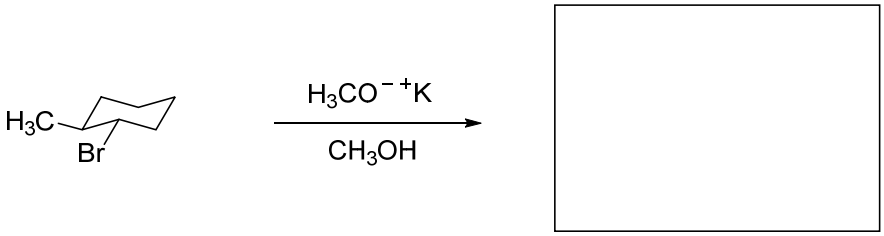
(a) the reaction is endothermic
(b) the reaction occurs in more than one step (i.e., there is more than one transition state along the path from starting materials to products)
(c) the equilibrium constant will increase with the addition of CH_3I
(d) both (a) and (b) are correct
(e) both (b) and (c) are correct

Problem 3. (25 points total, 5 points each) Reactions. The following chemical reactions are missing their starting materials or products. Write the missing compounds into the empty boxes below, as appropriate. For missing products, draw the single organic product that you expect to be produced in the highest yield among all of the possibilities. In some cases, there will be more than one correct answer that will merit full credit.

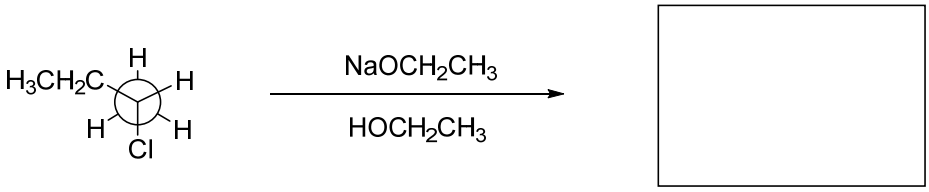
(i) (5 points)



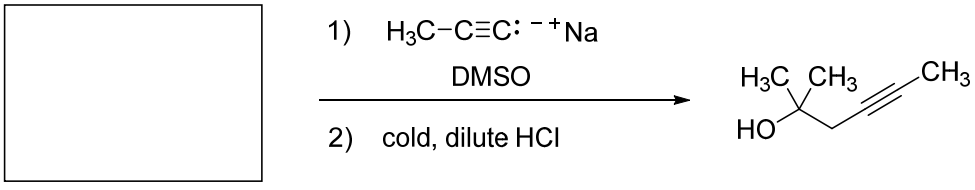
(ii) (5 points)



(iii) (5 points)

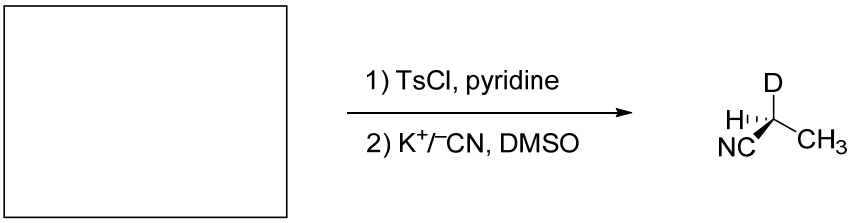


(iv) (5 points)



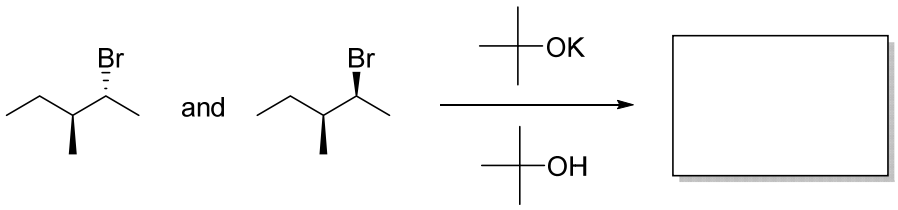
C_4H_8O

(v) (5 points)

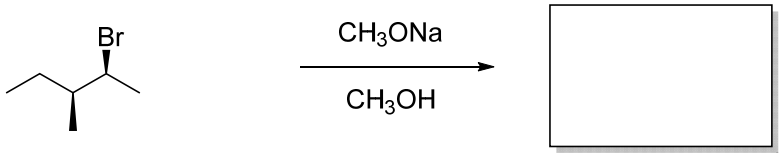


Problem 4. (20 points total). Competing reactions of 2-bromo-3-methylpentane.

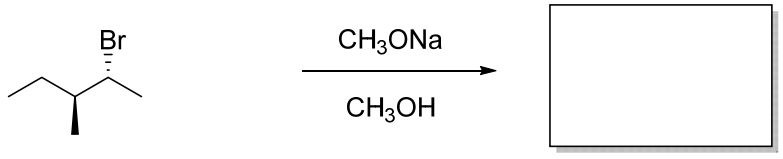
(i) (4 points) Treatment of both (2*R*,3*S*) and (2*S*,3*S*)-2-bromo-3-methylpentane with potassium *tert*-butoxide forms the same major product for both compounds. Draw a structure of this product in the box below.



(ii) (6 points) (2*R*,3*S*) and (2*S*,3*S*)-2-bromo-3-methylpentane react with sodium methoxide in methanol to produce different major products. Both products have the molecular formula C_6H_{12}, and they are diastereomers of each other. In the empty boxes below, draw the major product for each reaction.



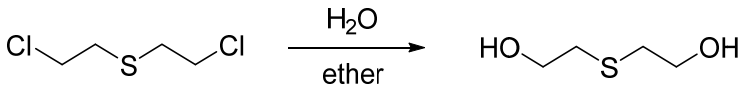
(2*S*,3*S*)-2-bromo-3-methylpentane



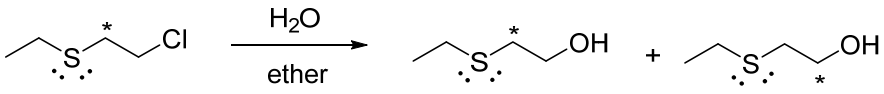
(2*R*,3*S*)-2-bromo-3-methylpentane

(iii) (10 points) Explain why (2*R*,3*S*)-2-bromo-3-methylpentane forms the product it does versus the other products in parts (i) and (ii). Your explanation must include some form of three-dimensional drawing.

Problem 5. (15 points total) Mustard agents like 2,2'-bis(chloroethyl) sulfide can react to crosslink the DNA in your cells and cause cell death. They were employed extensively in World War I as chemical weapons. These molecules also react quickly with water:



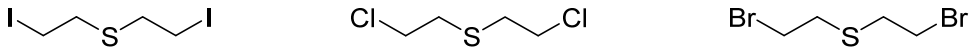
(i) (9 points) If one of the carbons of **J** is isotopically labeled with carbon-13 (*), the following product mixture is observed. The rate of the reaction does not depend on the concentration of water, only on the concentration of **J**. Propose a mechanism for the reaction of **J** with water that is consistent with these observations. Hint: It does not involve the formation of a carbocation.



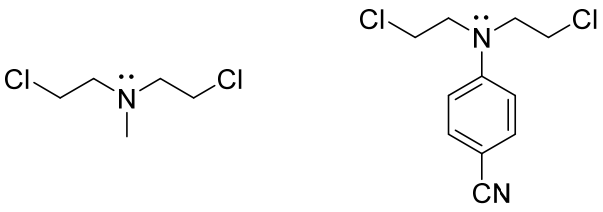
100% 50% 50%

J

(ii) (3 points) Circle which compound you would expect to react fastest with water.



(iii) (3 points) Circle which compound you would expect to react faster with water.



Problem 6. (0 points total) Qualitative grumpiness assessment.

(i) _____ Which of the following statements is funny?

(a) "Organic chemistry is hard; I am having alkynes of problems."
(b) "Professor S_N1 found the methyl halide hard to impress. She could never get a reaction from him."
(c) "Why does carbon always return his tuxedo rentals on time? To avoid formal charges"
(d) "Student #1: Hey man, do you know what reagent I should use to deprotonate an alcohol? Student #2: NaH, sorry, dude."
(e) All of the above.
(f) None of the above.
(g) How can you joke around like this after giving me the hardest orgo exam of my life?!
(h) Studying for this exam ruined my fall break; I am not in the mood to laugh.
(i) My beloved Cardinals are in the World Series and I am sitting here taking an orgo exam. =/
(j) (*R*)-2-chlorobutane
(k) (*S*)-2-chlorobutane