

CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Hour Examination #3

Wednesday, November 12th, 2014

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

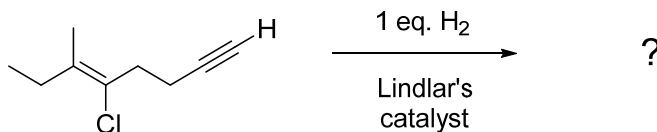
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes and your plastic model kit. No electronic resources are permitted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

Problem	Points Earned	Points Available
I		25
II		24
III		21
IV		10
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.

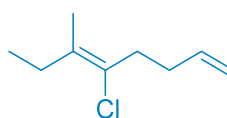
- (1) E What is the best name for the major product of the reaction shown below?



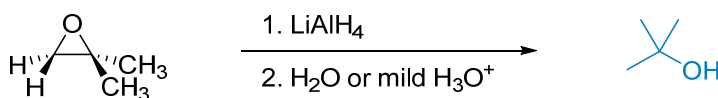
A

- (a) (3Z,7Z)-4-chloro-3-methyl-3,7-octadiene
 (b) (1Z,5Z)-5-chloro-6-ethyl-1,5-heptadiene
 (c) (1E,5Z)-5-chloro-6-methyl-1,5-octadiene
 (d) (1Z,5E)-5-chloro-6-methyl-1,5-octadiene
 (e) (Z)-5-chloro-6-methyl-1,5-octadiene

Major product:



- (2) A Which of the following compounds would you expect to observe as the major product of the following reaction?

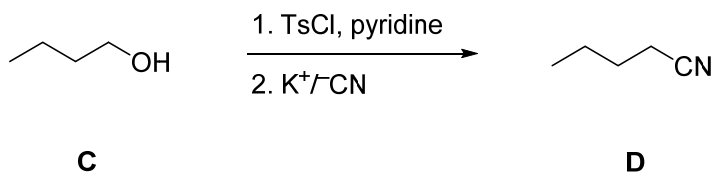


B

- (a) 2-methyl-2-propanol
 (b) 2-methyl-1-propanol
 (c) 2-methoxypropane
 (d) 1-methoxypropane
 (e) 2-methyl-propane

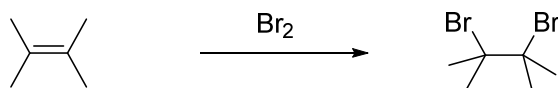
These are strongly basic conditions and the epoxide is opened by the delivery of hydride (H^-) to the less substituted/hindered carbon of the ring. The presence of weak acid instead of strong acid in the second step allows for protonation of the alkoxide without subsequent dehydration.

- (3) ^B What statement best describes the role of the first set of reagents in the following preparation of compound **D**?



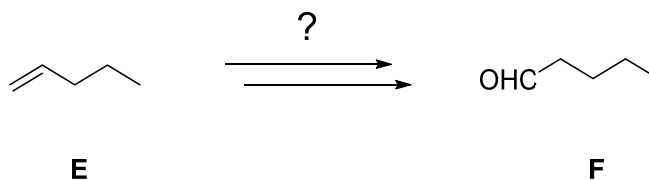
- (a) it prevents the formation of a primary carbocation
- (b) it converts the hydroxyl group into a good leaving group
- (c) it deprotonates the hydroxyl group to make the alkoxide
- (d) it gives an alkene intermediate by E2 elimination
- (e) it protonates the hydroxyl group which then leaves as water

- (4) ^C What statement does not accurately describe at least one step or aspect of the mechanism for the reaction drawn below?



- (a) a bromide anion serves as a nucleophile
- (b) the π bond on the alkene serves as a nucleophile
- (c) the addition of the Br groups takes place with syn geometry
- (d) an intermediate with a three-membered ring forms
- (e) the final product is saturated (degree of unsaturation = zero)

- (5) ^D Which of the following routes is the most appropriate to prepare pentanal (**F**) from 1-pentene (**E**)?

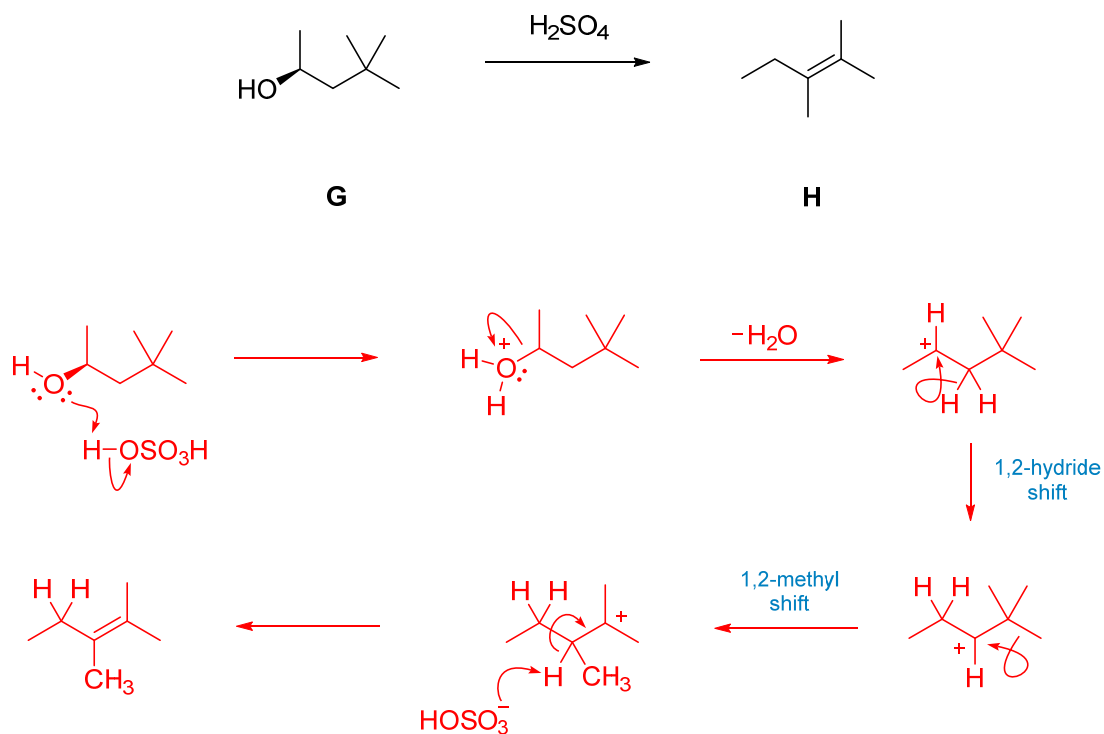


- (a)
$$\text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} \xrightarrow[\text{pyridine}]{\text{TsCl}} \xrightarrow[\text{tBuOH}]{\text{tBuOK}}$$
- (b)
$$\begin{array}{l} 1. \text{BH}_3 \cdot \text{THF} \\ 2. \text{H}_2\text{O}_2, \text{NaOH} \end{array} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \xrightarrow{\text{H}_2\text{SO}_4, \text{H}_2\text{O}}$$
- (c)
$$\text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} \xrightarrow[\text{H}_2\text{SO}_4, \text{H}_2\text{O}]{\text{K}_2\text{Cr}_2\text{O}_7}$$
- (d)
$$\begin{array}{l} 1. \text{BH}_3 \cdot \text{THF} \\ 2. \text{H}_2\text{O}_2, \text{NaOH} \end{array} \xrightarrow{\text{PCC}}$$
- (e)
$$\text{SOCl}_2 \xrightarrow{\text{pyridine}} \xrightarrow[2. \text{S}(\text{CH}_3)_2]{1. \text{O}_3}$$

Note that sequence (b) will produce the carboxylic acid instead of the aldehyde because dichromate is too strong of an oxidant.

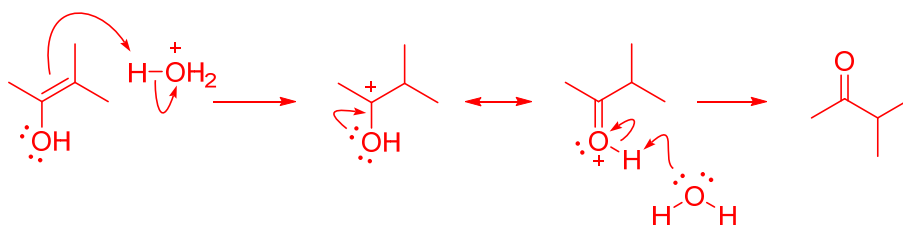
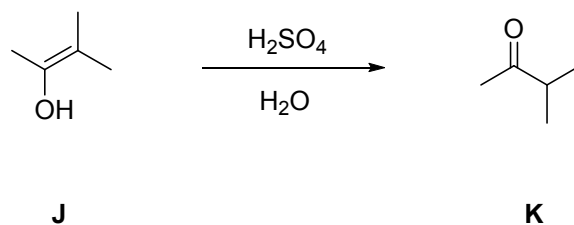
Problem II. Mechanisms (24 points).

(1) (16 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.



Note that the 1,2-hydride and 1,2-methyl shifts cannot be replaced by a single 1,3-methyl shift. The orbital overlap required for such a step is insufficient, since the C–C bond (filled σ orbital) is too far away from the empty unhybridized p orbital.

(2) (8 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.



This is the standard mechanism for acid-catalyzed keto–enol tautomerism. You will see this in spades next semester. Note that in water with strong acid present, H_3O^+ serves as the source of protons and H_2O serves as the base. Do not invoke strong bases (like hydroxide, HO^-) in your mechanisms when the conditions are strongly acidic.

Problem III. (21 points) Roadmap Problem. Provide structures for compounds **N** and **U**, as well as the reagents for the conversion of **M** → **N**. Do not write the structures of the other compounds on your answer sheet.

Compound **M** has the molecular formula C_6H_{10} . When **M** is treated with a set of reagents (that you must identify), it is converted to compound **N**. When **N** is subjected to ozonolysis with a reductive workup, compound **Q** is the only organic product. It has the molecular formula C_3H_6O and yields compound **T** ($C_3H_6O_2$) when treated with aqueous acidic dichromate. When **N** is treated with bromine in water, a racemic mixture of products with the molecular formula $C_6H_{13}BrO$ is produced. When a dilute solution of this racemic mixture is treated with sodium hydride, a racemic mixture of compound **U** of molecular formula $C_6H_{12}O$ is produced. On your answer sheet, provide structures for compounds **N** and **U** (only one enantiomer necessary) and the reagents for the conversion of **M** to **N** that are consistent with these data.

The best way to work this problem is to work backwards, and compound **Q** seems to be the ideal place to start. You can calculate the number of rings and π bonds for **Q** and find that $\Omega = 1$. We know that ozonolysis with reductive workup typically produces aldehydes and ketones from alkenes, so it would make sense that **Q** is either 1-propanal or 2-propanone. From these two choices, propanal makes the most sense because it would oxidize to a carboxylic acid, propanoic acid (**T**), upon treatment with dichromate while 2-propanone would not react at all.

So, at this point, we think we have the identity of **Q**. Since **Q** is the only organic fragment produced from ozonolysis of **N**, it makes sense that **N** is a symmetrical alkene. Since **Q** is propanal, **N** should be either *cis*- or *trans*-3-hexene. To decide between these two stereoisomers, we can observe that bromohydrin formation followed by treatment with base generates a racemic mixture. We know that this sequence of reagents typically makes epoxides. Finally, we must recognize that these reagents would turn *cis*-3-hexene into a meso epoxide while *trans*-3-hexene would be converted into a racemic mixture of epoxides (**U**). Thus, **N** must be *trans*-3-hexene.

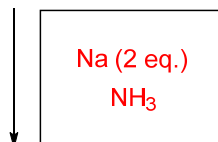
The last piece of the puzzle is to figure out how **N** was synthesized. We can calculate $\Omega = 2$ for the molecular formula of **M**. It makes the most sense for **M** to be the alkyne 3-hexyne. How do we convert 3-hexyne into *trans*-3-hexene? By treatment with sodium metal in ammonia.

The last remaining work for this problem is to fill in all of the blanks and double-check the compounds to make sure their structures are consistent with the reported data.

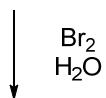
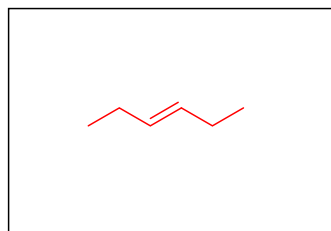


M
(C₆H₁₀)

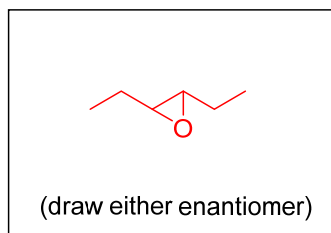
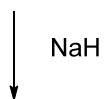
(reagents?)



N

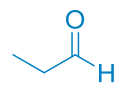


R
C₆H₁₃Br
(racemic mixture)

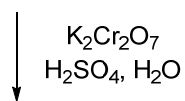


U
(C₆H₁₂O)

1. O₃
2. S(CH₃)₂

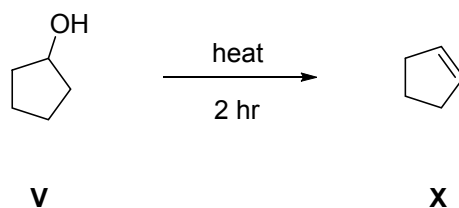


Q
(C₃H₆O)
(only organic compound)



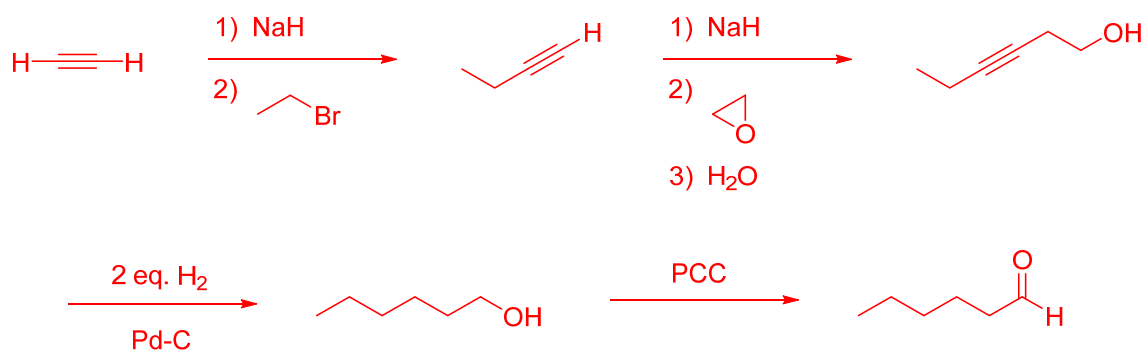
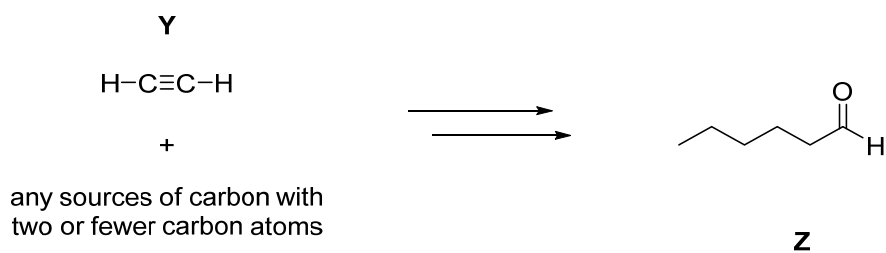
T
(C₃H₆O₂)
(only organic compound)

Problem IV. Explanations (10 points). Your orgo lab TA hands you a bottle of cyclopentanol and asks you to synthesize cyclopentene. You pour some of the cyclopentanol into a round-bottomed flask, attach a condenser, and heat the compound using the maximum setting on your heating mantle. Name two things you can add or do to maximize your percent yield of **X** by the end of your two-hour lab period. (Note: there are more than two correct answers)



- Add a nonaqueous acid, like H_2SO_4 or TsOH , as a catalyst for the reaction
- Affix a distillation apparatus to remove the lower-boiling alkene product as it is produced to drive the equilibrium right by Le Chatelier's Principle
- Add a drying agent to remove water and shift the equilibrium right by Le Chatelier's Principle
- Add POCl_3 /pyridine as a dehydrating agent

Problem V. Synthesis (20 points). Provide a synthetic route—i.e, a sequence of reactions—to produce hexanal (**Z**) from acetylene (**Y**) and any reagents you need so long as no synthon/reagent supplies more than two carbon atoms (of the six) in the final product.



or

