| Exam Booklet No. |
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## CHEM 2410 – Organic Chemistry 1 – Fall 2016

**Instructors: Paul Bracher & Erin Whitteck**

# Hour Examination #3

Wednesday, November 9th, 2016

6:10–8:10 p.m. in the Lecture Halls at Saint Louis University

| | |
|---|---|
| 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 may use one letter-sized sheet of hand-written notes (on the "official" template) and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be copied or scanned.
- The examination room may be photographed or videotaped.

| Problem | Points Earned | Points Available |
|---|---|---|
| I | | 66 |
| II | | 4 |
| III | | 9 |
| IV | | 9 |
| V | | 12 |
| TOTAL | | 100 |

**Questions, Required Information, Supplementary Explanation, Grading Notes, Where You've Seen It**

# Examination Instructions

**DO NOT TURN THE PAGE ON THIS BOOKLET UNTIL DIRECTED BY A PROCTOR TO BEGIN**

## Please Make Sure to Do the Following Before Starting Your Exam

1. Both print your name and sign the front of the answer sheet and this exam booklet in the appropriate boxes.

2. Also print your name at the top of the back of the answer sheet.

3. Enter your SLU Banner ID number on the front of the answer sheet and bubble the corresponding numbers. Failure to do this correctly will result in the loss of 2 points.

4. Write the serial number of this exam booklet on your answer sheet in the appropriate box.

5. Check the "Hold for Pick-Up" box on the back of the answer sheet if you want your graded sheet withheld from the distribution pile on Monday and handed back to you privately. Checking this box will delay your receipt of your graded exam.

## Please Make Sure to Do the Following After Completing Your Exam

1. Ensure that all of your selected circles are darkened completely.

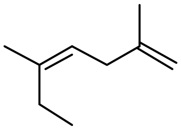
2. Submit your answer sheet, exam booklet, and scratch paper to the proctors. You may not remove these items from the exam room.

3. Turn in your note sheet with your name and Banner ID written clearly in the appropriate space. Your note sheet will be returned to you on Monday.

**DO NOT TURN THE PAGE ON THIS BOOKLET UNTIL DIRECTED BY A PROCTOR TO BEGIN**

**Problem I.** Multiple Choice (66 points total). Correct answers score +3 points, answers of 'E' score +1 point, and incorrect answers score 0 points. For each question, select the best and most complete answer of the choices given. Bubble the answer, darkly, in the space provided on the answer sheet.

(1) D What is the IUPAC name of compound **A**?



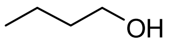
**A**

(A) (*E*)-3,6-dimethyl-3,6-heptadiene
(B) (*Z*)-3,6-dimethyl-3,6-heptadiene
(C) (*E*)-2,5-dimethyl-1,4-heptadiene
(D) (*Z*)-2,5-dimethyl-1,4-heptadiene

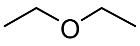
The parent chain is the longest sequence of carbon atoms. The chain is numbered starting from the side closest to the first double bond. In compound **A**, the alkene on the right has no *E*/*Z* designation (since one *sp*$^2$ carbon has two hydrogens) while the left alkene is *Z*, because the higher priority groups are *cis* relative to each other.

Where you've seen it: Lecture 24 Chapter 10 Slides Slide 9; Connect homework Chapter 10 problems 2 and 3; Smith problems 38, 39, and 40; Fall 2014 Quiz $^{\#}$4 Problem I-1; Fall 2014 Hour Exam $^{\#}$3 Problem I-1.

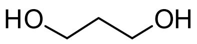
(2) D Rank the following compounds in order of increasing solubility in water (i.e., from the least soluble to the most soluble).



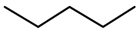
**B**



**C**



**D**



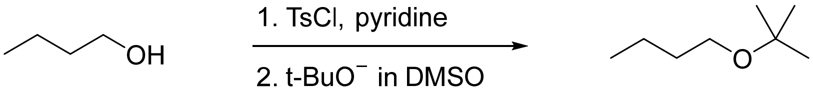
**E**

(A) **B** < **C** < **D** < **E**
(B) **E** < **C** < **D** < **B**
(C) **E** < **D** < **C** < **B**
(D) **E** < **C** < **B** < **D**

The solubility of a compound will increase as the intermolecular forces in which the compound participates more closely resemble those of the solvent (“like dissolves like”). Here, water molecules are strong dipoles capable of hydrogen bonding. **E** is nonpolar. **C** is polar but cannot donate hydrogen bonds. **B** can hydrogen bond. **D** can hydrogen bond more extensively.

Where you’ve seen it: Chapter 9 Smith problems 43 and 44; Connect HW; Fall 2013 Hour Exam $^{\#}$2 Problem 1-4.

(3) A __________ What statement best describes the role of the reagents TsCl and pyridine in the following preparation of compound **G**?



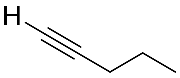
**F** **G**

(A) to convert the hydroxyl group into a good leaving group
(B) to protonate the hydroxyl group such that water can leave
(C) to avoid the formation of an unstable primary carbocation
(D) to improve yield by disfavoring the competing E1 reaction

This example is a Williamson ether synthesis. The first step, TsCl + pyridine, converts the hydroxyl group (a terrible leaving group) into a tosylate group (a great leaving group). The second step substitutes the tosylate group with a *tert*-butoxy group by an $S_N2$ reaction in DMSO (a polar, aprotic solvent that is often used for $S_N2$ reactions). Note: you would expect a substantial amount of E2 side product for this reaction.

Where you’ve seen it: <u>very similar</u> to Fall 2014 Hour Exam $^{\#}$3 Problem I-3.

(4) B Which of the following statements is not true regarding the alkyne **H**?



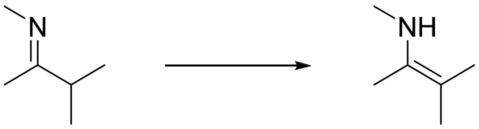
**H**

(A) compound **H** has a p$K_a$ between 20 and 30
(B) compound **H** reacts with $Hg(OAc)_2$, $H_2SO_4$, and $H_2O$ to generate an aldehyde
(C) compound **H** is an isomer of cyclopentene
(D) none of the above (i.e., all of the above statements are true)

Let's evaluate each statement one-by-one. Statement (A) is true, as terminal alkynes have p$K_a$ values around 25. Statement (B) is false. Terminal alkynes are hydrated by $Hg(OAc)_2$, $H_2SO_4$, and $H_2O$ to form ketones, not aldehydes. To make an aldehyde from a terminal alkyne, you need to use hydroboration–oxidation. Statement (C) is true. Both compound **H** and cyclopentene are five-carbon hydrocarbons with two elements of unsaturation. You can calculate the molecular formulas of each to be $C_5H_8$—or draw out the full Lewis structures and count the atoms.

Where you've seen it: very similar to Fall 2015 Quiz $^{\#}$4 Problem I-4; Summer 2016 Exam 3; reiteration of aldehyde synthesis in Fall 2016 Lecture 30 Slide 2; Fall 2013 Hour Exam $^{\#}$3 Problem II-1; Fall 2014 Quiz $^{\#}$4 Problem IV; oxymercuration answer also found in Fall 2015 Hour Exam $^{\#}$3 Problem III roadmap; Fall 2016 Lecture 32 Slide 18 in-class problem.

(5) D Which of the following most accurately and completely describes the relationship of compounds **J** and **K**?



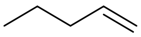
**J** **K**

(A) tautomers
(B) constitutional isomers
(C) different molecules
(D) all of the above

The enamine/imine relationship is another form of tautomerization. Tautomers are molecules that differ in the positioning of a hydrogen atom across a double bond or longer π system. Tautomers are constitutional isomers (as they have the same molecular formula but a different connectivity of atoms/bonds), and isomers are always different molecules.

Where you've seen it: Chapter 11 Connect HW; similar to Summer 2016 Hour Exam #3 Problem I-3.

(6) B Which of the following statements is correct regarding compound **L**?



**L**

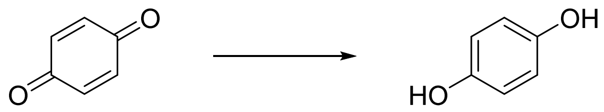
(A) compound **L** forms two products upon reaction with $H_2$, Pd/C
(B) compound **L** forms two products upon reaction with *m*CPBA
(C) compound **L** is named (*E*)-1-pentene
(D) compound **L** is named (*E*)-4-pentene

Compound **L** is named 1-pentene. The lowest locant is given to the first point of unsaturation. The *E*/*Z* designations are not utilized since the alkene is only monosubstituted. Hydrogenation occurs with syn addition of $H_2$ across either side of the double bond, and this does not result in two products. Hydrogenation of **L** produces only pentane. Whereas, syn addition of oxygen across the double bond with *m*CPBA can occur to either face and produces two products (that are enantiomers):

Where you've seen it: similar to Fall 2015 Quiz #4 Problem I-1; Fall 2015 Quiz #4 Problem I-2 (the mCPBA answer regarding two products); Chapter 10 slides and "Chapter 10 – Nomenclature of Alkenes" Tegrity video.

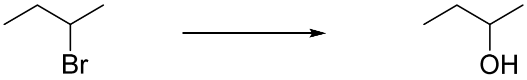
(7) C Which of the following reactions is not an oxidation or reduction reaction?

(A)

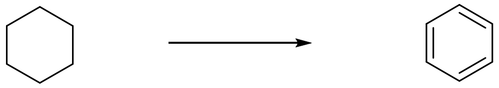


(B)

(C)



(D)

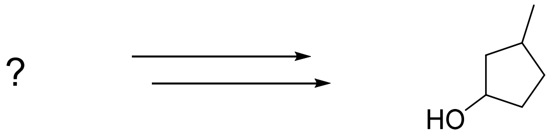


Oxidation reactions involve an increase in the number of C–Z bonds or a decrease in the number of C–H bonds in the organic molecule. Reduction reactions involve an increase in the number of C–H bonds or a decrease in the number of C–O bonds. The only reaction that does not involve a change in the number of C–Z or C–H bonds is (C). Choice (A) is a hydrogenation—a reduction. Choice (B) is a reduction. Choice (D) is a dehydrogenation—an oxidation. Choice (C) is a substitution reaction, which is not a type of redox reaction.

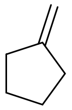
Where you've seen it: Lecture 28 Slide 4 clicker question and Chapter 12 Connect HW Question 1.

(8) D

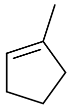
Which of the following substrates is the best choice of starting material to synthesize compound **M** as efficiently as possible?



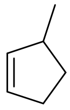
**M**



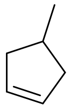
(A)



(B)



(C)



(D)

Choices (A) and (B) make it impossible to functionalize the correct carbon atom. It is impossible to control the selectivity of addition to the double bond in (C) because both carbon atoms have the same substitution. And while this is also the case in (D), the symmetry of the molecule makes both carbons equivalent—addition of the OH group to either carbon during hydration gives the desired product.

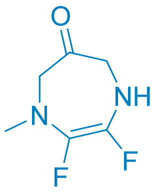
Where you've seen it: Connect HW Chapter 10 Question 21; importance of symmetry re-emphasized in Fall 2016 Lecture 31 Slide 8 in-class problem.

(9) A

Compound **N** has no triple bonds and its molecular formula of $C_6H_8F_2N_2O$. Which of the following could accurately describe **N**?

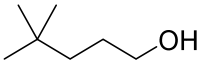
(A) compound **N** could have 1 C=C, 1 C=O bond, and 1 ring
(B) compound **N** could have 2 C=O bonds
(C) compound **N** could have 2 C=C bonds and 2 rings
(D) none of the above (i.e., it is impossible for **N** to have a structure described by any of the above)

A quick calculation of $\Omega$, the # of rings and $\pi$ bonds (RAPB), gives $\Omega = (2+6\times2+2\times1+1\times0-8-2)/2=6/2= 3$. Since the compound has no triple bonds, these three elements must be alkenes or rings. We can immediately eliminate choice (C) because it has RAPB = 4. Choice (B) can also be eliminated. Although we can't exclude it because it has too many elements of unsaturation (as 2<3), compound **N** only has one oxygen atom, so it is impossible to have two C=O bonds. Choice (A) is perfectly acceptable, as it has RAPB = 3 and there is nothing disqualifying. Here's one valid Lewis structure (of many possibilities) that meets all of the criteria:

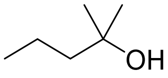


Where you've seen it: Summer 2016 Hour Exam $^{\#}$3 Problem I-5.

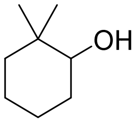
(10) ___C___ Which of the following substrates is <u>most likely</u> to undergo an alkyl migration (carbocation rearrangement) upon treatment with sulfuric acid?



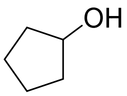
(A)



(B)



(C)

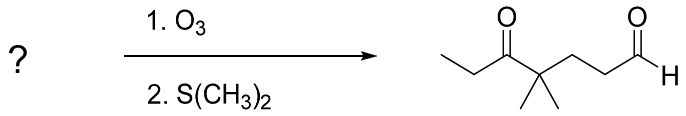


(D)

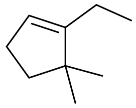
Choice (A) is unlikely to generate a carbocation, because departure of the protonated hydroxyl group would generate a highly unstable primary carbocation. Choice (B) will generate a tertiary carbocation that cannot rearrange to anything more stable. Choice (D) will generate a secondary carbocation that cannot undergo an alkyl or hydride shift to a more stable cation. Choice (C) would produce a secondary carbocation next to a quaternary center. A 1,2-methyl shift could occur to generate a tertiary carbocation. Therefore, (C) would be most likely to rearrange.

Where you've seen it: Summer 2016 Quiz $^{\#}$3, Problem I-4; Fall 2016 CYOA 10/24+25; Fall 2016 Lecture 32 Slide 5 in-class problem.

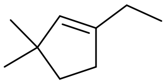
(11) A Which of the following substrates would give compound **P** upon ozonolysis?



**P**



(A)



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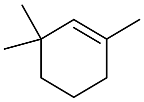
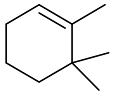
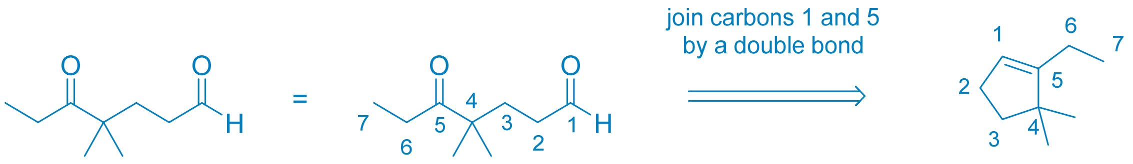


(C)



(D)

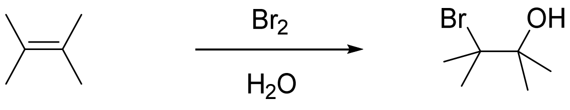
The key to this problem is to realize which two carbons are attached together in the original starting material. Ozonolysis cleaves C=C double bonds to produce two carbonyl groups. In the product, **P**, take both carbonyl carbons and join them together via a double bond. This then gives you the only choice being (A). How? Let's number our skeleton and paste it back together at the carbonyl groups:



**P**

Where you've seen it: Fall 2015 Hour Exam $^{\#}$3; similar to Fall 2015 Quiz $^{\#}$4 Problem I-5 but much easier; Fall 2013 Hour Exam $^{\#}$3 Problem III **N**→**Q**.

(12) C What statement does <u>not</u> accurately describe at least one step or aspect of the mechanism for the reaction drawn below?

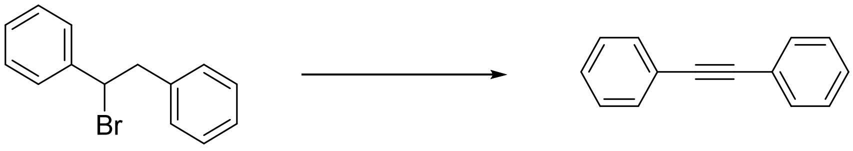


(A) water serves as a nucleophile
(B) the π bond on the alkene serves as a nucleophile
(C) each equivalent of $Br_2$ consumed generates two molecules of product
(D) this is a type of reduction–oxidation reaction

The π bond initially serves as a nucleophile to attack $Br_2$. Water attacks the bromonium intermediate to form the product. The reaction increases the number of bonds to C–X and C–O, so this is an oxidation reaction. Each equivalent of $Br_2$ contributes one Br atom to the product. The other bromine from $Br_2$ is converted to the byproduct HBr.

Where you've seen it: very similar to Fall 2014 Hour Exam $^{\#}$3 Problem I-4; $Br_2$ as an oxidant in Lecture 30 clicker question; Fall 2014 Quiz $^{\#}$4 Problem I-5.

(13) D Which of the following sequences of reactions will convert **Q** to **R**?



**Q** **R**

(A) $\xrightarrow{Br_2}\xrightarrow[NaNH_2]{\text{excess}}$

(B) $\xrightarrow{NaH}\xrightarrow{H-C\equiv C-H}\xrightarrow{NaH}$

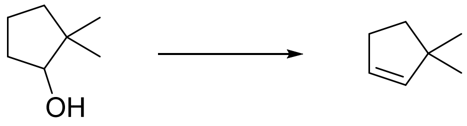
(C) $\xrightarrow[H_2O]{H_2SO_4}\xrightarrow[H_2SO_4,\ H_2O]{K_2Cr_2O_7}$

(D) $\xrightarrow[\textit{t}BuOH]{\textit{t}BuOK}\xrightarrow{Br_2}\xrightarrow[NaNH_2]{\text{excess}}$

The main method we discussed to synthesize alkynes was the formation of a dihalide which could undergo a double elimination to the corresponding alkyne.

Where you've seen it: Fall 2016 Lecture 27 slides 6 and 7; similar to Fall 2014 Hour Exam $^{\#}$3 Problem I-5.

(14) B Which of the following conditions is the best choice to convert **S** to **T**?



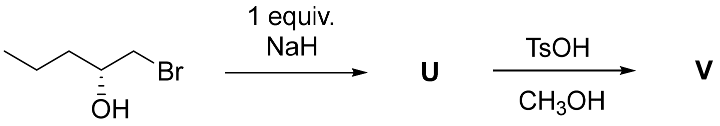
**S** **T**

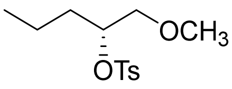
(A) $H_2SO_4$, heat
(B) 1. TsCl, pyridine; 2. *t*BuOK in *t*BuOH
(C) $PBr_3$
(D) $SOCl_2$, pyridine

Choices (C) and (D) generate alkyl halides, not alkenes. While $H_2SO_4$ will generate an alkene, in this case, the carbocation intermediate will undergo an alkyl shift to change the carbon backbone. Only (B), tosylation followed by E2 elimination, will generate **T** exclusively as the major product in good yield.

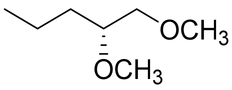
Where you've seen it: Chapter 9 CYOA; a review of these methods appeared in Fall 2016 Lecture 32 Slide 4.

(15) C What is the major product, **V**, expected of the following sequence of reactions? Compounds **U** and **V** both contain no bromine.

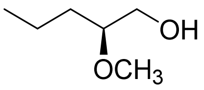




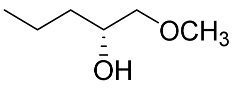
(A)



(B)



(C)



(D)

NaH deprotonates the alcohol. The alkoxide then forms the resulting epoxide (**U**). The epoxide is then opened under acidic conditions to form the corresponding ether. The ether is formed through inversion at the most-hindered carbon.

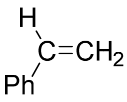
Where you've seen it: The opening exam-style problem covered in Fall 2016 Lecture 21 (21 October 2016); Summer 2016 Hour Exam #3 Problem I-1 (epoxide synthesis via halohydrin); Summer 2016 Quiz #3 Problem I-5 (epoxide opening in acid); Fall 2016 Lecture 32 Slide 7 in-class problem.

(16) B

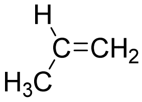
Which of the following alkenes reacts fastest with HBr? Note: Ph = a phenyl group (–$C_6H_5$).

$H_2C{=}CH_2$

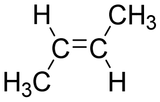
(A)


$\mathrm{H(Ph)C{=}CH_2}$

(B)


$\mathrm{H(H_3C)C{=}CH_2}$

(C)


$\mathrm{H(H_3C)C{=}C(CH_3)H}$

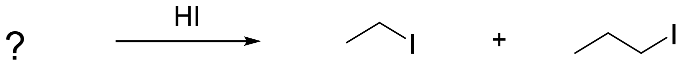
(D)

The more stable the carbocation intermediate, the faster the reaction due to decrease in the activation energy (by the Hammond Postulate). The most-stable carbocation intermediate will be (B) due to resonance stabilization that is not possible in the other choices.

Where you've seen it: The opening exam-style problem covered in Fall 2016 Lecture 21 (21 October 2016).

(17) D

Treatment of what ether with concentrated hydroiodic acid will produce alkyl iodides **W** and **X**?



**W** **X**

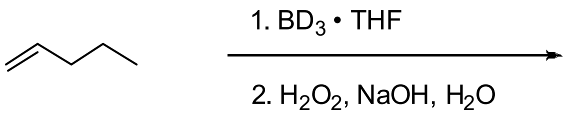
(A) diethyl ether
(B) ethyl methyl ether
(C) ethyl isopropyl ether
(D) ethyl propyl ether

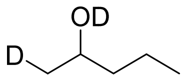
Ether cleavage in strong acid produces two alkyl halides.

Where you've seen it: This exact reaction was in the Lecture 26 in-class roadmap problem.

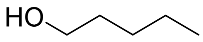
(18) C

What is the product of the following reaction? Note: D is just the isotope of hydrogen containing one neutron ($^2H$).

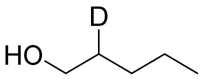




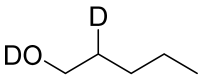
(A)



(B)



(C)



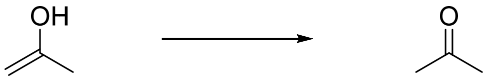
(D)

Deuteration (from the equivalent of $BD_3$) occurs at the more-hindered carbon, and the boron is added to less hindered carbon. Oxidation then yields the alcohol where the boron atom was attached.

Where you've seen it: CYOA Chapter 10 October 31/November 1st; very similar to Summer 2016 Quiz #3 Problem I-12; Fall 2016 Lecture 32 Slide 15 in-class problem.

(19) C

Which of the following statements most accurately and completely describes the conversion of **Y** to **Z**?



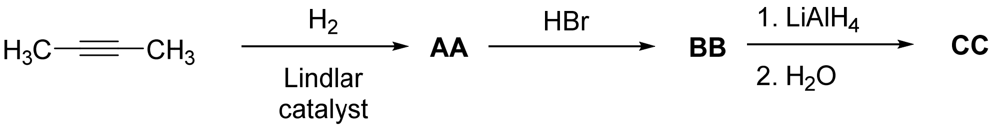
**Y** **Z**

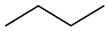
(A) the mechanism for this conversion in acidic water proceeds via a resonance-stabilized intermediate
(B) the mechanism for this conversion in basic/alkaline water proceeds via a resonance-stabilized intermediate
(C) the mechanisms for this conversion in both acid and base proceed via resonance-stabilized intermediates
(D) the mechanisms for this conversion in neither acid nor base proceed via a resonance-stabilized intermediates

This reaction is enol–keto tautomerization. In aqueous acid, the reaction proceeds by protonation of the π bond (to form a resonance-stabilized carbocation) followed by deprotonation of the hydroxyl group. In aqueous base, the reaction proceeds by deprotonation of the hydroxyl group (to form a resonance-stabilized anion) followed by protonation at the carbon adjacent to the carbonyl group. So, both mechanisms proceed through resonance-stabilized intermediates.

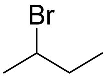
Where you've seen it: almost exactly the same as Summer 2016 Hour Exam #3 Problem I-6; both mechanisms were explicitly drawn out in Fall 2016 Lecture 31 Slide 10 in-class problem; the complete acid-catalyzed mechanism was asked as a free response question on Fall 2014 Hour Exam #3 Problem II-2.

(20) ____A____ What is the major product of the following sequence of reactions, compound **CC**?

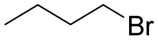




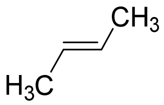
(A)



(B)

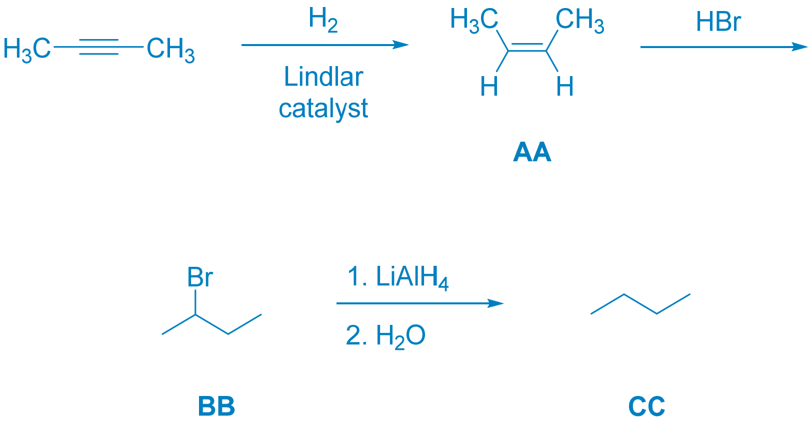


(C)



(D)

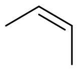
The reaction sequence is as follows:



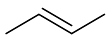
Where you've seen it: all of these reactions were covered separately in various lecture slides and problems throughout the unit.

(21) C

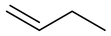
Rank the following compounds from <u>least</u> exothermic to <u>most</u> exothermic heat of hydrogenation (i.e., start with that will which release the least heat upon addition of $H_2$ and end with that which will release the most heat.)



**DD**



**EE**



**FF**

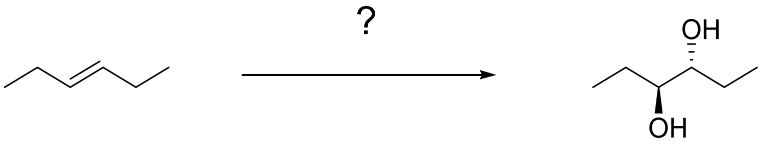
(A) **DD** ⟶ **EE** ⟶ **FF**
(B) **DD** ⟶ **FF** ⟶ **EE**
(C) **EE** ⟶ **DD** ⟶ **FF**
(D) **FF** ⟶ **DD** ⟶ **EE**

The most-stable alkene will release the least heat upon hydrogenation. **EE** is the most substituted and is *trans* and is therefore the most stable, releasing the least heat upon hydrogenation. **DD** is disubstituted but is *cis* making, it less stable by a steric effect. **FF** is the least substituted and is therefore the least stable and will release the most heat upon hydrogenation.

Where you've seen it: Fall 2013 Practice Hour Exam #3 Problem I-ii; Fall 2015 Hour Exam #3 Problem I-4; Fall 2016 Lecture 32 Slide 20 in-class problem.

(22) D

Which of the following sequences will carry out the conversion of **GG** to **HH**?



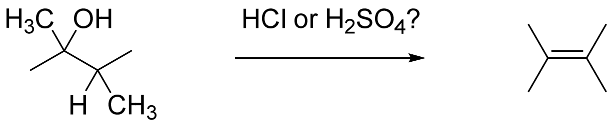
**GG** **HH**

(A) 1. $OsO_4$; 2. $NaHSO_3$, $H_2O$
(B) 1. mCPBA; 2. catalytic $H_2SO_4$, $H_2O$
(C) 2. mCPBA; 2. catalytic NaOH, $H_2O$
(D) both (B) and (C) will carry out this conversion

Symmetrical, *trans*-alkenes (e.g., **GG**) will afford a pair of enantiomers as products upon dihydroxylation with syn addition (e.g., by use of osmium tetroxide). Symmetrical, *trans*-alkenes will afford a meso product (e.g., **HH**) upon dihydroxylation with anti addition (e.g., by epoxidation followed by hydrolysis in either acid or base).

Where you've seen it: almost exactly the same as Fall 2015 Hour Exam $^{\#}3$ Problem I-3 except the starting material was swapped to *trans* instead of *cis*.

**Problem II.** Explanation (4 points). Consider the transformation drawn below. Would hydrochloric acid or sulfuric acid be a better reagent for this transformation? Circle your preferred reagent on your answer sheet, and in one sentence, explain your choice.



Circle the better reagent: HCl [✓ $H_2SO_4$]

One-sentence explanation:

Sulfuric acid is the better reagent because sulfate is not nucleophile, unlike chloride, and will not attack the intermediate carbocation will not to form chlorinated side products.

Where you've seen it: very similar to Fall 2015 Hour Exam $^{\#}3$ Problem I-1; discussed in relation to the mechanism in problem solving session in Lecture 26.

Grading and partial credit:

+1 point: $H_2SO_4$ is circled

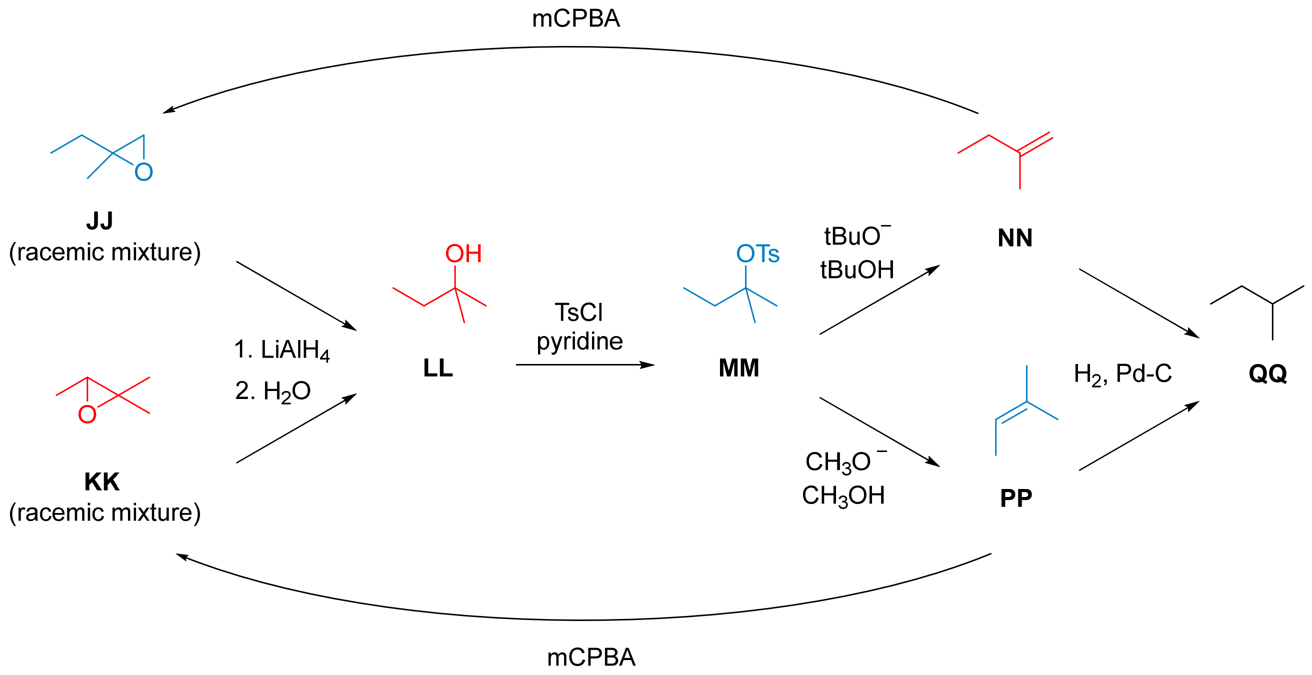
+3 points: full credit if the explanation is any of the following: HCl has water in it or $H_2SO_4$ has no/little water in it or $Cl^-$ is nucleophilic/reactive or sulfate is not nucleophilic/reactive

+0 points: one acid is stronger than the other (they are both orders of magnitude more acidic than a protonated hydroxyl group, so there is no significant effect from acid strength here)

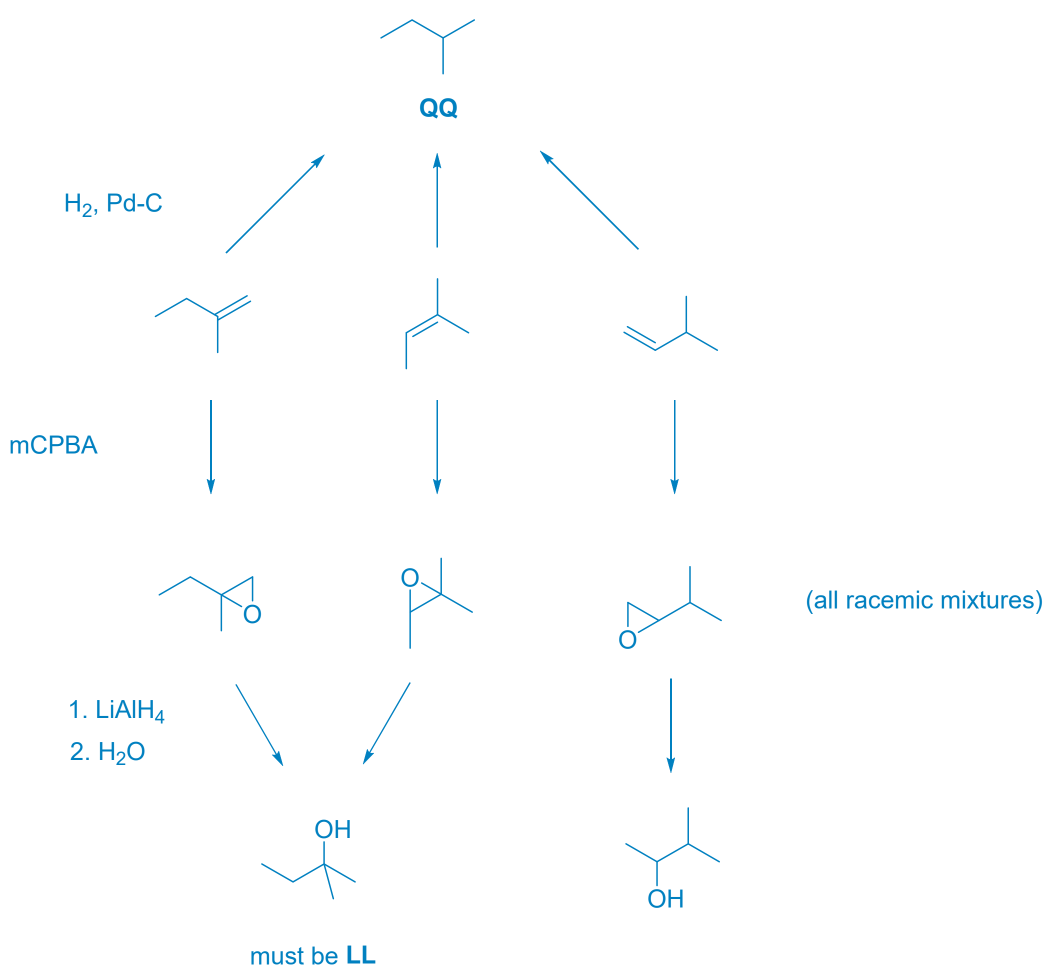
**Problem III.** Roadmap Problem. Provide structures for compounds **KK**, **LL**, and **NN** in the reaction scheme below. Do not write the structures of the other compounds on your answer sheet.

Compound **JJ** exists as a racemic mixture of enantiomers, as does compound **KK**. Compounds **JJ** and **KK** are constitutional isomers of each other. Upon treatment with lithium aluminum hydride ($LiAlH_4$) followed by quenching with water, compounds **JJ** and **KK** give the identical product, **LL**. Compound **LL** can be tosylated to form **MM**. Upon treatment with *tert*-butoxide, **MM** yields **NN** as the major product. However, when **MM** is treated with methoxide, **PP** is the major product. Catalytic hydrogenation of both **NN** and **PP** produce the identical product, methylbutane (**QQ**). When compound **NN** is treated with *meta*-chloroperbenzoic acid, the racemic mixture of **JJ** is produced. When compound **PP** is treated with *meta*-chloroperbenzoic acid, the racemic mixture of **KK** is produced.

On your answer sheet, provide structures of compounds **KK**, **LL**, and **NN** that are consistent with these data. Do not provide the structures of other compounds.



The best way to work this problem—or any roadmap—is to start from the position where you have the most information. Here, that is undoubtedly **QQ**, where you are given the Lewis structure for the compound. It makes sense that **NN** and **PP** would be alkenes for several reasons. First, they would be candidates for hydrogenation to **QQ**. Second, they are formed by what appears to be elimination reactions that do not require a super-strong base like $NaNH_2$ (suggesting **NN** and **PP** are alkenes, not alkynes). Finally, **NN** and **PP** react with *m*CPBA to form **JJ** and **KK**, respectively. The only things we've seen (so far) that react with *m*CPBA are alkenes. So what are the possibilities for **NN** and **PP**, given the structure of **QQ**?



(all racemic mixtures)

must be **LL**

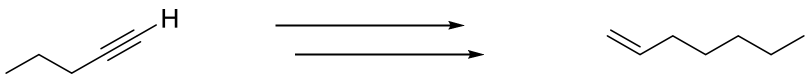
There are three candidate alkenes for **NN** and **PP**, but only two of them will be epoxidized and reduced with $LiAlH_4$ to the same product. So, this alcohol must be **LL**. The rest of the problem is filling in the blanks correctly and double-checking the answers to make sure their structures are consistent with the reported data.

Where you've seen it: very similar to Fall 2016 Lecture 31 Slide 4 in-class problem; Fall 2014 Hour Exam #3 Problem I-2 (epoxide reduction).

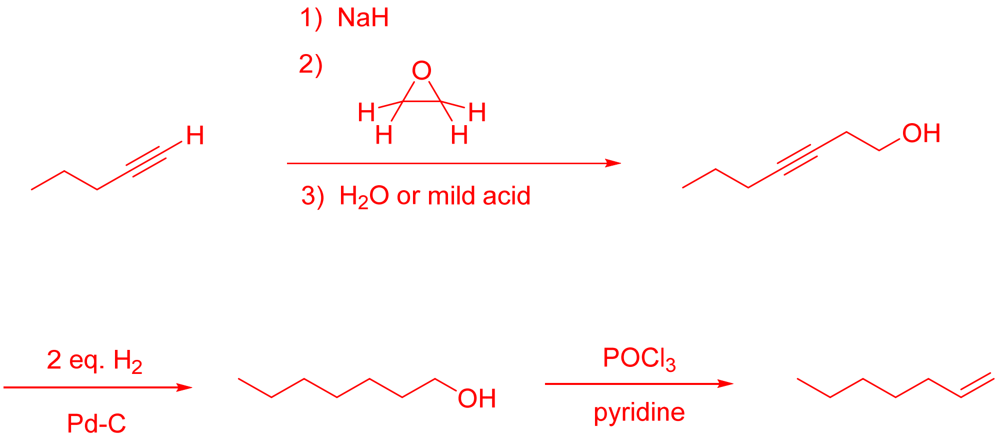
Grading and partial credit:

| | | |
|---|---|---|
| +3 points: | for each correct answer | |
| +1.5 points: | drawing **JJ** instead of **KK**<br>drawing **PP** instead of **NN** | (swapping answers) |
| +1 point: | drawing **NN** as any other alkene or alkyne that will be hydrogenated properly to **QQ** | |
| +0.5 points: | drawing **LL** as any alcohol that is not the correct answer | |

**Problem IV.** Synthesis (9 points). Provide a synthetic route—i.e, a sequence of reactions—to produce 1-heptene (**SS**) from 1-pentyne (**RR**) and any other starting materials or reagents you need that contain six or fewer carbon atoms.



**RR** **SS**



The first thing to notice is that the product has two extra carbons relative to the starting material. At this point in the semester, the only way we know how to add multiple carbon atoms is by alkylation of acetylide ions. Fortunately, the starting material is set up perfectly for this reaction.

Next, we know that **SS** can be produced exclusively by eliminating a good leaving group at the 1-position of heptane. We can install at leaving group at the 1-position by choosing to react the acetylide of **RR** with a two-carbon epoxide, then hydrogenating and tosylating the alcohol product. Converting the OH group to Cl (by $SOCl_2$/pyridine) or Br (by $PBr_3$) are also good alternatives.

Note that you must hydrogenate the alkyne before generating the alkene, else you will hydrogenate both.

Where you've seen it: this synthesis is very similar to many found in old exams and in examples worked in class and at CYOA this year; almost exactly like Fall 2014 Hour Exam #3 Problem V except shorter/easier; very similar to Fall 2016 CYOA 10/24+25 session; very similar to Fall 2016 Lecture 31 Slide 11 in-class problem.

Grading and partial credit:

| | |
|---|---|
| full credit | synthesis matches key<br>or student eliminates $H_2O$ using $H_2SO_4$ or 1. $PBr_3$ or $SOCl_2$, 2. strong base<br>or alkylates with ethyl bromide, then uses alkyne zipper, followed by Lindlar hydrogenation |
| +6 total | all correct except student eliminates $H_2O$ to form alkene prior to hydrogenation of alkyne |

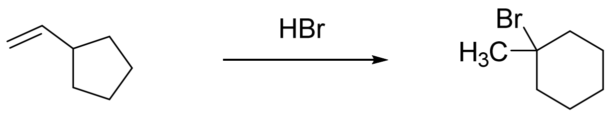
Small errors (give full credit then subtract points for the following):

| | |
|---|---|
| −2 points | student omits base to deprotonate acetylide |
| −1 point | student uses a base that is too weak (e.g., NaOH) |
| −0 points | student does not reacidify (let it slide) |
| −1 point | student forgets to write $H_2$ or Pd-C for hydrogenation, but has the other |
| −1 point | student alkylates acetylide with $BrCH_2CH_2Br$ or similar instead of epoxide (unless they explicitly use “excess” to avoid dialkylation) |
| −3 points | student alkylates acetylide with $BrCH_2CH_2OH$ or similar reagent containing a protic hydrogen (that will quench the carbanion) |
| −1 point | student omits pyridine with $POCl_3$ |

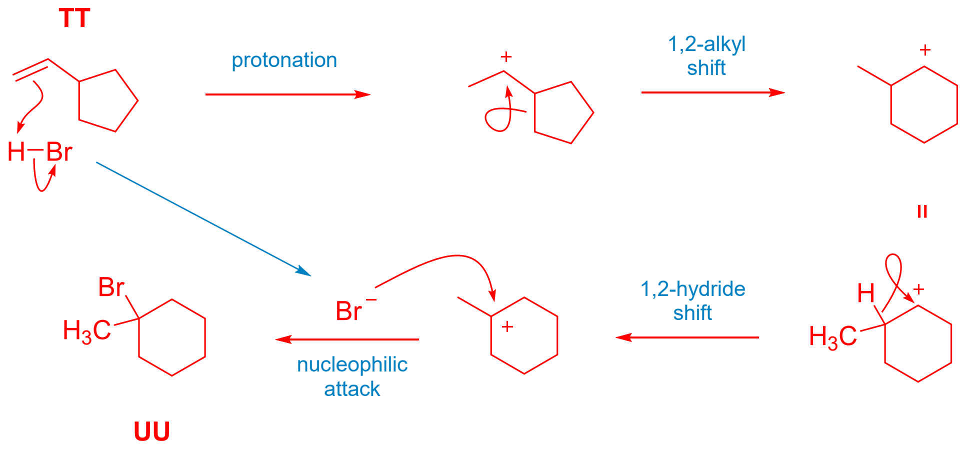
Charity partial credit (start at zero and add points for each of the following):

| | |
|---|---|
| +1 point | synthesis is a loss, but charity for any attempt at alkylation of acetylide |
| +1 point | synthesis is a loss, but charity for any attempt at hydrogenation of the alkyne |
| 0 points | synthesis is a loss, hydroboration–oxidation of the starting alkyne (no charity credit for this, as it is pretty illogical and unproductive) |

**Problem V.** Mechanism (12 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. Hint: This mechanism has four steps.



**TT** **UU**



Where you've seen it: similar to Fall 2016 Lecture 31 Slide 6 in-class problem; Fall 2016 CYOA 10/24+10/25; Fall 2013 Practice Hour Exam #3 Problem V; Summer 2016 Hour Exam #3 Problem III.

Grading and partial credit:

| | |
|---|---|
| +12 total | response matches key |
| +8 total | all correct except alkyl shift leads directly to tertiary carbocation |
| +8 total | HBr adds Markovnikov to alkene then alkyl shift is done like an $S_N2$ reaction to displace bromide and generate secondary carbocation, and all else is correct |

Piecewise partial credit (start at zero and add points for all the following):

+2 for correct initial protonation of alkene
+4 for correct alkyl shift ring expansion
+4 for correct hydride shift
+2 for correct bromide attack of carbocation

+1 incorrect protonation of alkene
+1 bromide attacks as a nucleophile somewhere but electrophile is wrong
+2 for ring-expanding alkyl shift but wrong (e.g., onto alkene directly or via bromonium)
+2 for a hydride shift but not the correct one

## Scratch Paper

You may rip this sheet out of the exam booklet, but you are responsible for turning it in at the end of the exam.

**Exam Booklet No.**