Exam Booklet No.

CHEM 2410 – Organic Chemistry 1 – Fall 2017

Instructors: Erin Whitteck & Paul Bracher

## Hour Examination #3

#### Wednesday, November 15<sup>th</sup>, 2017

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 a plastic model kit. No electronic resources or note sheets are permitted, and you may not communicate with others.
- Your exam answer sheet may be copied or scanned.
- The examination room may be monitored by audio, photo, and/or video recording.

| Problem | Points<br>Earned | Points<br>Available |
|---------|------------------|---------------------|
| 1       |                  | 60                  |
|         |                  | 6                   |
|         |                  | 12                  |
| IV      |                  | 12                  |
| V       |                  | 10                  |
| TOTAL   |                  | 100                 |

## **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 <u>print</u> your name and <u>sign</u> the front of the answer sheet <u>and this exam booklet</u> in the appropriate boxes.
- 2. Also print your name at the <u>top</u> of the <u>back</u> of the answer sheet.
- 3. Enter your SLU Banner ID number on the front of the answer sheet and <u>bubble</u> the corresponding numbers. <u>Failure to do this correctly will result in the loss of 2 points.</u>
- 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, data tables, and scratch paper to the proctors. You may not remove these items from the exam room.

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**Problem I.** Multiple Choice (60 points total). Correct answers score +3 points, answers of 'E' score +1 point, and incorrect answers score 0 points. Questions filled with zero or multiple responses will 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. For all questions that ask you to name or count compounds or products, include all distinct compounds that not interconvertible under ambient conditions (i.e., include or count different constitutional isomers and stereoisomers separately, but not different conformations that can interconvert).

(1) <u>A</u>

How many products will be generated in significant yield in the following reaction? Count different stereoisomers as different products.



(A) one product(B) two products(C) three products(D) four products

While addition of  $H_2$  could occur to either face of the  $\pi$  bond, both cases generate the identical product:



Note that the product, 2-methylhexane, is an alkane with no stereogenic carbon atoms (or double bonds or rings), so no stereoisomers are possible. This hydrogenation reaction yields only one product.

Where you've seen it: Identical format to Fall 2015 Quiz <sup>#</sup>4 Problem I-2. Addition of H<sub>2</sub> to alkenes covered in Fall 2017 Lecture 30. Some elements from Fall 2015 Quiz <sup>#</sup>4 Problem I-4 and Fall 2016 Exam <sup>#</sup>3 Problem I-6.

(2) B Which of the following statements is true about the reaction in question #1?

- (A) both carbon atoms of the C=C bond are oxidized
- (B) both carbon atoms of the C=C bond are reduced
- (C) one carbon atom is oxidized, one carbon atom is reduced
- (D) this is not an oxidation/reduction reaction

The addition of H<sub>2</sub> to the  $\pi$  bond results in the replacement of a carbon–carbon bond of each carbon atom of the alkene with a carbon–hydrogen bond. As H ( $\chi$  = 2.1) is a less electronegative element than C ( $\chi$  = 2.5), the carbon atoms in the starting material are both reduced during this reaction. The H<sub>2</sub> is a reductant. It reduces the alkene and the hydrogen atoms in H<sub>2</sub> are both oxidized in the process.

Where you've seen it: Fall 2016 Exam <sup>#</sup>3 Problem I-7. Elements of Fall 2017 Quiz <sup>#</sup>3 Problem I-6.

(3) B What product is formed in highest yield from the reaction of compound A with excess hydroiodic acid?



The cleavage of ethers by hydroiodic acid begins with protonation of the ether's oxygen atom (which makes it a good leaving group), followed by nucleophilic attack by I<sup>-</sup>. Remember that  $S_N 1$  and  $S_N 2$  reactions cannot occur on  $sp^2$ -hybridized carbon atoms. Our initial cleavage product is:



Now the question is whether this initial product can react with another equivalent of HI. While the initial product does have a hydroxyl group (–OH), it is bonded to an  $sp^2$ -hybridized carbon atom, so further S<sub>N</sub>1 or S<sub>N</sub>2 substitution is not possible.

Where you've seen it: Fall 2017 discussion section the week of October 30<sup>th</sup> (ether cleavage), Fall 2017 Lecture 28 (roadmap problem with ether cleavage). Mechanism discussed in Chapter 9 lectures. Ether cleavage was also covered in Fall 2016 Exam <sup>#</sup>3 Problem I-17.



Carbocation rearrangements by 1,2-hydride and 1,2-alkyl shifts are most likely to occur when such a shift is possible and it leads to a carbocation that is more thermodynamically stable than the original. In the case of (A), (C) and (D), there are no 1,2-shifts possible to generate a more stable carbocation. In the case of (B), a 1,2-hydride shift converts the secondary carbocation to a more-stable tertiary carbocation:



Where you've seen it: Very similar to Summer 2016 Quiz <sup>#</sup>3 Question 2. Similar to Summer 2016 Exam <sup>#</sup>3 Problem I-4. Fall 2017 Lecture 33 practice problem.

(5) C Which of the following sequences of reactions is the best choice to convert compound **B** to compound **C**?



#### Only pathway (C) accomplishes the synthesis:



Where you've seen it: Format similar to Fall 2016 Exam #3 Problem I-13.

# (6) C Which of the following statements is correct regarding the conversion of **D** to **E** depicted in the scheme below?



- (A) HCl is a catalyst for this reaction
- (B) the reaction proceeds via a chloronium intermediate where the Cl atom is temporarily in a bridged, three-membered ring
- (C) as shown, this addition follows Markovnikov's Rule
- (D) the conversion of **E** back to **D** is accomplished in high yield by treatment with potassium *tert*-butoxide (KOtBu)

Let's evaluate each statement one at a time. Statement (A) is incorrect, as HCl is not a catalyst in this reaction—it is a stoichiometric reagent because one equivalent is consumed per molecule of starting material. Statement (B) is incorrect, as the intermediate is a carbocation generated by protonation of the alkene. Statement (C) is correct, as Markovnikov's Rule states that when HX is added to an alkene, the X group/atom will bond to the more-substituted carbon of the double bond in the starting material. Statement (D) is incorrect, as when **E** is treated with a bulky, strong base, the major product will be the less-substituted alkene because the corresponding  $\beta$ -hydrogens leading to this product are more available (less sterically hindered) for the bulky base to access:



Where you've seen it: Similar to Fall 2015 Exam #3 Problems I-1 and I-5



Only sequence (D) will accomplish the synthesis:



Where you've seen it: Format identical to Fall 2017 Quiz <sup>#</sup>3 Problem I-1. Fall 2017 Lecture 30: Markovnikov vs anti-Markovnikov hydration of an alkene to generate an alcohol that can then be converted to another functional group.

(8) A What is the IUPAC name for compound **H**?



Н

- (A) (7Z)-8-bromo-7-tert-butyl-2-methylnon-7-en-2-ol
- (B) (7*E*)-8-bromo-7-*tert*-butyl-2-methylnon-7-en-2-ol
- (C) (2Z)-2-bromo-3-tert-butyl-8-methylnon-2-en-8-ol
- (D) (2*E*)-2-bromo-3-*tert*-butyl-8-methylnon-2-en-8-ol

The parent chain is the longest chain that contains all of the carbons involved with the alcohol and the alkene groups. It is nine carbons long, so this is a nonenol:



In numbering chains, alcohols take priority. Number the chain in the direction that gives the OH group the lower locant number:



Since the higher-priority groups are on the same side of the double bond, it is a *Z*-alkene. Naming all of the substituents on the chain and putting them in alphabetical order gives:

(7Z)-8-bromo-7-tert-butyl-2-methylnon-7-en-2-ol

Where you've seen it: Format identical to Fall 2017 Quiz <sup>#</sup>3 Problem I-2. Similar to Question <sup>#</sup>5 on Fall 2013 Practice Hour Exam <sup>#</sup>3. Fall 2017 Lecture 25 (*E* vs. *Z* alkenes) and Tegrity video for nomenclature of alkenes. Also Summer 2016 Quiz <sup>#</sup>3 Problem II.

(9) B

Rank the following compounds in order of their heats of complete/exhaustive hydrogenation to an alkane with excess  $H_2$  and Pd/C as a catalyst. List the least exothermic first and the most exothermic last.





Μ

J

(A) J < K < L < M</li>
(B) J < K < M < L</li>
(C) M < L < J < K</li>
(D) L < M < K < J</li>

Κ

Heats of hydrogenation of alkenes are always exothermic. They will be of a greater magnitude for alkynes than alkenes because the alkynes have an extra  $\pi$  bond to hydrogenate. In differentiating between the two alkynes, we must remember that alkyl substituents stabilize  $\pi$  bonds, so  $\pi$  bonds with greater alkyl substitution will release less energy upon hydrogenation (by virtue that they started out as more stable). Here, this means that the hydrogenation of **M** will be less exothermic than the hydrogenation of **L**. Alkenes **J** and **K** differ in being *trans* and *cis* isomers. The *cis* isomer is less stable—in a higher state of potential energy—due to steric repulsion of the larger alkyl groups being placed in closer proximity relative to the *trans* isomer. Correspondingly, the *cis*-alkene releases more energy upon hydrogenation than the *trans*-isomer.

Where you've seen it: Fall 2016 Exam <sup>#</sup>3 Problem I-21, Fall 2013 Practice Hour Exam <sup>#</sup>3 Problem I-ii, Fall 2015 Hour Exam <sup>#</sup>3 Problem I-4. Covered in Fall 2017 Lecture 33.



The "tiny drop" of sulfuric acid suggests only a catalytic amount is needed. In acidic conditions, the mechanism involves protonation of the epoxide's oxygen atom followed by nucleophilic attack of ethanol on the more-substituted carbon of the epoxide. This will result in geometric inversion at the carbon atom that is attacked:



Where you've seen it: Very similar to Summer 2016 Quiz <sup>#</sup>3 Question 5 and Fall 2016 Exam <sup>#</sup>3 Problem I-15. Acid-catalyzed opening of an epoxide was covered in Fall 2017 discussion section the week of October 30<sup>th</sup> and Lecture 24. Summer 2016 Quiz <sup>#</sup>3 Question 5.

(11) C Which of the following statements about the reaction shown below is true?



- (A) the mechanism of this reaction is E1
- (B) TsOH converts –OH to –OTs, which is a better leaving group
- (C)  $\Delta H^{\circ}$  is positive for this reaction
- (D) addition of TsOH shifts the equilibrium further to the right

Let's evaluate each statement. Statement (A) is false—the mechanism of this reaction is certainly not E1, as that would require the generation of a very unstable primary carbocation. Statement (B) is also false—tosic acid (TsOH) is a strong acid like sulfuric acid that will protonate the hydroxyl group. Tosyl chloride (TsCl) is the reagent required to generate the alkyl tosylate. Statement (C) is true. You can calculate the  $\Delta H^{\circ}$  for this reaction by Hess's Law using the bond dissociation energy (BDE) table at the end of this exam:

Broken: C–H and C–O; Formed: O–H and C=C.

ΔH° = +410 + 350 - 460 - (611-350) = +39 kJ/mol

Finally, statement (D) is false. TsOH is a catalyst. Adding more TsOH will not shift the equilibrium—it will only help the reaction reach equilibrium faster.

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Where you've seen it: Fall 2017 Lecture 26 clicker question regarding the role of TsOH in a dehydration. Somewhat similar to Fall 2016 Exam <sup>#</sup>3 Problem I-3.



Reaction (A) is flawed because an aryl bromide is not a good electrophile for substitution by an alkoxide. Reaction (B) is flawed because tertiary alcohols are too hindered for conversion to alkyl bromides by PBr<sub>3</sub>. Reaction (C) works—the hydroxyl group is protonated, leaves as water to generate a carbocation that rearranges by a 1,2-alkyl shift, which then is then deprotonated to yield the alkene shown. Reaction (D) is flawed because base-catalyzed hydrolysis of that epoxide gives the opposite stereochemistry to the product shown.

Where you've seen it: Fall 2017 discussion section week of October 30<sup>th</sup>. Fall 2017 Quiz <sup>#</sup>3 Question 1. Fall 2017 Lecture 24 clicker question. Format identical to Fall 2015 Quiz <sup>#</sup>4 Problem I-6. Reaction (D) identical to Summer 2016 Quiz <sup>#</sup>3 Question 4.

(13) <u>B</u>

Which of the following terms accurately describes the stereochemistry of the product(s) of this reaction?



- (A) one meso compound
- (B) one achiral compound that is not meso
- (C) a racemic mixture of enantiomers
- (D) two diastereomers

This is a standard hydrochlorination of an alkene that proceeds by Markovnikov's Rule to generate 1-chloro-1-ethylcyclopentane:

The product has an internal plane of symmetry (and is thus achiral) and has no stereocenters, so it is not a meso compound.

Where you've seen it: Material covered in Fall 2017 Lecture 25 Slides 29–32. Compounds that are achiral and not meso covered extensively in a series of clicker questions in Fall 2017 Lecture 19.

(14) <u>A</u>

Which of the following compounds is  $\underline{not}$  a product of ozonolysis of compound **P**?

(B)



(C)



(A)

Ρ



(D)

?

Ozonolysis with reductive workup cleaves carbon–carbon double bonds to produce two carbonyl containing compounds. Let's draw in all of the implied hydrogen atoms on the double bonds and cleave them:



All of the fragments are present in the product mixture except fragment (A).

Where you've seen it: Fall 2015 Quiz #4 Problem I-5. Fall 2016 Exam #3 Problem I-11. Also various roadmap problems from the archive.

(15) D Which of the following alkenes is the <u>best</u> starting material to synthesize **Q**, 3-ethylcyclopentanol. without regard for stereochemistry?



We know alkenes can be converted to alcohols by simple acid-catalyzed hydration or by hydroboration– oxidation. Either of these reactions performed on (A) and (B) will not yield **Q**. We can make **Q** from (C) but we have a selectivity problem. The fact that both sides of the alkene in (C) have similar alkyl substitution means that we will get a mixture of 3-ethylcyclopentanol and 2-ethylcyclopentanol from either reaction. However, compound (D) is an excellent substrate to synthesize **Q**. While we can't easily control which carbon of its C=C bond will be hydroxylated, due to the symmetry of (D), hydroxylation of either carbon produces the same product. Thus, (D) is the best choice of starting material.

Where you've seen it: Essentially identical to Fall 2016 Exam #3 Problem I-8. Similar to Smith 5<sup>th</sup> edition's 10.48d.



The mechanism for this reaction is drawn below. Note that the second bromine adds to the same bromine as the first because the second carbocation intermediate can be stabilized by a resonance effect when the cation is adjacent to the first added bromine atom.

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Where you've seen it: Fall 2017 Lecture 28 Slides 19–26 extensively discuss the reaction and its mechanism.



Hydration of a terminal alkyne catalyzed by acid yields a methyl ketone following tautomerization of the initial product, an enol:



Where you've seen it: Fall 2017 discussion section problem and other multiple choice questions in archive.

(18) C What is the major product **U** generated when compound **T** is treated with pyridinium chlorochromate (PCC) with dichloromethane as the solvent?



PCC will oxidize primary alcohols to aldehydes and secondary alcohols to ketones. It does not react with tertiary alcohols. Here, **T** has a tertiary alcohol and a primary alcohol. The former is untouched while the latter is oxidized to an aldehyde, yielding compound (C).

Where you've seen it: Fall 2017 Lecture 31 Slides 29–34 and various problems in the exam archive.

(19) A Rank the following compounds from <u>highest to lowest</u> boiling point. List the compound with the highest boiling point first.

ОН

I



Ш





Ш

IV

(A) IV > I > III > II
(B) II > I > III > IV
(C) IV > III > I > II
(D) III > I > II > IV

Higher boiling points correspond to stronger intermolecular interactions. Compound (II) is a nonpolar alkane that will have relatively weak intermolecular interactions and the lowest boiling point. The other three compounds all have hydroxyl groups capable of hydrogen bonding. Compound (IV) will have the highest boiling point as it has an extra OH group compared to (I) and (III). While (I) and (III) both have 1 OH group and are isomers with the same mass, (I) will have the higher boiling point as it has a larger surface area than (III), and will thus benefit from net stronger induced dipole—induced dipole interactions (London forces) than for (III). The strength of intermolecular hydrogen bonding for (III) is also reduced by steric hinderance.

Where you've seen it: Very similar to Fall 2016 Exam #3 Problem I-2.



This reaction is clearly a syn addition to the alkene as the carbon backbone is drawn identically in both the starting material and product and the two added functional groups point in the same direction. Syn dihydroxylation is accomplished by cold, dilute basic potassium permanganate (or oxidations with OsO<sub>4</sub>). Thus, reaction (A) will produce **W**, as well as its enantiomer. Reactions (B) and (C) result in an anti-addition to produce a diastereomer of **W**.

Where you've seen it: Very similar to Fall 2015 Exam <sup>#</sup>3 Problem I-3 and Fall 2016 Exam <sup>#</sup>3 Problem I-22. Covered in detail in Fall 2017 Lecture 32.

**Problem II.** Explanation (6 points). HBr adds faster to the C=C bond of compound **BB** than compound **AA**. On your answer sheet, explain why compound **BB** reacts faster than **AA** in this reaction using drawings and a maximum of one sentence.



One-sentence explanation:

The addition of HBr to an alkene proceeds by a two-step mechanism. In the endothermic first step, the  $\pi$  bond is protonated to generate a carbocation intermediate. In the exothermic second step, the carbocation intermediate is attacked by bromide. Here, the addition of HBr to **BB** is faster because the rate-determining endothermic first step is faster since the carbocation intermediate of **BB** is more stable as it is stabilized by a resonance effect while that of **AA** is not.



#### Partial credit:

| +6 (full)  | Drew resonance forms of starting alkenes to show <b>BB</b> is more nucleophilic.   |
|------------|--|
| +4         | Correct explanation, and drawings of reaction occurring between <b>AA</b> and/or <b>BB</b> and HBr but no drawings of resonance forms  |
| +3         | Explanation includes stability of intermediate and describes resonance but does not explicitly mention resonance   |
| +1         | Explanation that resulting intermediate of <b>BB</b> is more stable, but no mention of resonance   |
| -1         | Any small errors (incorrect formal charges, wrong curved arrows etc.)  |
| +0 points: | Protonation of oxygen favors reaction of <b>BB</b><br>Electronegative oxygen destabilizes <b>BB</b><br>Bond dissociation energy for <b>BB</b> is less than <b>AA</b><br><b>BB</b> can hydrogen bond<br>Electronegative oxygen makes the carbocation of <b>BB</b> more positive |

Where you've seen it: Discussed in relation to the mechanism in problem solving session in Fall 2017 Lecture 26. Similar to Fall 2017 Quiz <sup>#</sup>3 Problem I-7 and Fall 2016 Exam <sup>#</sup>3 Problem I-16.

**Problem III.** Roadmap Problem. (12 points) Identify compounds/reagents **CC**, **DD**, and **JJ** in the reaction scheme below. Do not write the structures of the other compounds on your answer sheet.

Unknown compound **CC**, with molecular formula  $C_4H_6$ , reacts with reagent(s) **DD** to produce **FF**. **FF** reacts with  $Br_2$  to form a single organic product, **HH**, of molecular formula  $C_4H_8Br_2$ . Compound **CC** reacts with reagent(s) **EE** to produce **GG**. **GG** reacts with  $Br_2$  to form a racemic mixture of two products, **KK** and **LL**, both of molecular formula  $C_4H_8Br_2$ . Compound **CC** reacts with excess HBr to produce **JJ**, also of molecular formula  $C_4H_8Br_2$ . Compounds **FF** and **GG** are stereoisomers of each other.

On your answer sheet, identify **CC**, **DD**, and **JJ**. Your proposals should be consistent with all of the data provided above. Do <u>not</u> provide the structures of other compounds/reagents.



The best way to work this roadmap problem—or any roadmap—is to start from the position where you have the most information. Here, there are a lot of unknowns. So, let's focus on one of the few things we do know: the common starting material (**CC**) has molecular formula  $C_4H_6$  and the products all have molecular formula  $C_4H_8Br_2$ . If we calculate the rings and  $\pi$  bonds (RAPB) for the products we get  $\Omega = 0$ . Thus, the products are saturated. We also find that **CC** has  $\Omega = 2$ .

So far, we have only seen Br<sub>2</sub> as a reagent for reactions with alkenes. If we use that as the seed of an educated guess, it would make sense to guess that **FF** and **GG** are alkenes of molecular formula C<sub>4</sub>H<sub>8</sub>. As the products **HH**, **JJ**, **KK**, and **LL** all have two added Br atoms relative to **CC**, it makes sense to guess that the Br<sub>2</sub> step was a dibromination and that **DD** and **EE** would both be reagents that hydrogenate **CC** (add H<sub>2</sub> to it) to make **FF** and **GG**, respectively. Combined, this hydrogenation/dibromination sequence explains how two H atoms and two Br atoms were added to **CC** to make the four products.

So, where are we? There are only four carbons in **CC**, so there are a limited number of possibilities for arranging  $\Omega$ =2. Let's go ahead and draw them out:



If we are adding H<sub>2</sub> and Br<sub>2</sub> to **CC** to generate the products, it makes sense that the two elements of unsaturation ( $\Omega$ =2) for **CC** are two  $\pi$  bonds (and no rings). None of the compounds with rings make sense because how are we going to add 2 H atoms and 2 Br atoms to get the molecular formulas of the final products? It makes much more sense that both elements of unsaturation are  $\pi$  bonds, to which H<sub>2</sub> and Br<sub>2</sub> are added.

Turning to options (I)–(IV), only (II) jibes with all the observations. We have two options for hydrogenating internal alkynes (H<sub>2</sub>/Lindlar to give *cis*, Na/NH<sub>3</sub> to give *trans*), while hydrogenation of all the other compounds is going to lead to identical products. Then, we know that anti addition of Br<sub>2</sub> to an alkene is going to yield product(s) of different stereochemistry depending on whether the alkene is *cis* or *trans*. We must simply determine which isomer (*cis* or *trans*) leads to the meso and racemic products. Since dibromination by Br<sub>2</sub> is an anti addition, *trans*-2-butene must be **FF** (leading to the meso product) and *cis*-2-butene must be **GG** (leading to the racemic mix of products). Circling back, that means **DD** must be Na/NH<sub>3</sub> and **EE** must be H<sub>2</sub>/Lindlar catalyst.

We complete the picture by predicting **GG**, the product of addition of 2 equivalents of HBr to 2-butyne, which is 2,2-dibromobutane. Recall that following the first addition of HBr, the second proton adds to generate the carbocation on the same carbon to which the first bromine added, as this carbocation will be stabilized by a resonance effect (as shown in Problem I-16).

Grading and Partial Credit:

| full credit: | +4 | for each correctly filled box   |
|--------------|----|---|
| сс           | +4 | (full credit), even if bond angles of alkyne are incorrect:   |
|              | +1 | any alkyne or correct number of RAPB (no more than +1 total for this part)  |
| DD           | +3 | 1. Na, 2. NH <sub>3</sub>   |
|              | +2 | NaNH <sub>2</sub> , H <sub>2</sub> and Lindlar catalyst, NaNH <sub>3</sub> , NH <sub>3</sub>  |
|              | +1 | $H_2$ and $NH_3$ , $H_2$ and Pd/C, Lindlar catalyst, $Na^+$ and $NH_3$ , 2 equiv of $H_2$ , $NH_2$ and $H_2O$ , or missed compound spelling |
|              | 0  | NaOH, LiAlH <sub>4</sub> , NaH, H <sub>2</sub> SO <sub>4</sub> , mCPBA, Br <sub>2</sub> and CCl <sub>4</sub> , NaNH <sub>2</sub> and HBr    |
| 11           | +2 | 2,3-dibromobutane   |
|              | +1 | for any isomer of C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub>   |

Where you've seen it: Format and concept very similar to Fall 2017 Quiz <sup>#</sup>3 Problem II and similar format on many previous exams. Elements similar to Summer 2016 Quiz <sup>#</sup>3 Question 8.

**Problem IV.** Synthesis (12 points). Provide a synthetic route—i.e, a sequence of reactions—to produce a racemic mixture of *trans*-1,2-cyclohexanediol (**NN** + **PP**) from bromocyclohexane (**MM**) and any reagents you wish. Draw each synthetic intermediate in the boxes in the template on your answer sheet and provide the necessary reagents above/below the reaction arrows. (Note: There are multiple correct answers. If you choose to complete this synthesis in fewer than three steps, just cross out any unused arrows and boxes.) Please do <u>not</u> draw curved arrows; we are not asking for mechanisms.



The targets are a pair of enantiomers that you should recognize as the products of dihydroxylation of cyclohexene with anti-addition to the double bond. The only sequence of reactions we know to accomplish this transformation is epoxidation of the alkene followed by hydrolysis:



Now the question is whether we can make cyclohexene from the starting material (**MM**). Fortunately, we can do this in one step by an E2 reaction with strong base:



We finish by putting all of the reagents and intermediates in sequence in the "forward direction" on the template:



#### Grading and Partial Credit:

+12 (full) synthesis matches key or different (but appropriate) base is substituted in first step or RCOOOH is used instead of *m*CPBA

- -1 if no cation/anion
- -1 if elimination of an alcohol with H<sub>2</sub>SO<sub>4</sub> is not anhydrous
- -1 if opening of epoxide is only done with water, does not include acid or base
- -1 if steps are not numbered (1.*m*CPBA; 2. H<sub>2</sub>O in NaOH or H<sub>2</sub>SO<sub>4</sub>)
- +7 points if the reaction sequence includes substitution with NaOH, elimination with POCl<sub>3</sub> in pyridine, then dihydroxylation with KMnO<sub>4</sub> or OsO<sub>4</sub>
- +6 maximum if synthesis is incorrect but some steps are reasonable

Where you've seen it: Identical format to Format identical to Fall 2017 Quiz #3 Problem III. Anti dihydroxylation of cyclohexene covered extensively in in-class practice problem in Fall 2017 Lecture 32. **Problem V.** Mechanism (10 points). Draw a sensible mechanism for the isomerization of **QQ** to **RR** in aqueous base. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all intermediates in the reaction and any significant resonance forms that account for the stability of these intermediates. Use the template provided on your answer sheet and draw one structure in each empty box.



In basic conditions, enol–keto tautomerization proceeds with deprotonation as the first step. The strongest base present is hydroxide. Deprotonation of **QQ** generates an anion that is stabilized by a resonance effect. In the second step, the resonance-stabilized anion is protonated at the carbon atom to generate the keto tautomer. Note that the source of the proton is neutral water, as under basic conditions,  $H^+$  or  $H_3O^+$  are not available (if present, they are present at really really really low concentrations such that invoking them in the mechanism is wrong as their low concentrations would make the protonation step too slow to be productive).

Grading and Partial Credit:

- +1 for each correct curved arrow (+6 points total)
- for each incorrect additional arrow per step
- +2 for each correct intermediate resonance form (+4 total)

Where you've seen it: Format identical to Format identical to Fall 2017 Quiz <sup>#</sup>3 Problem IV. The arrowpushing mechanism for base-catalyzed keto-enol tautomerization was the only item presented on Fall 2017 Lecture 29 Slide 10, which was explained in detail for two minutes of that lecture. The subject was also a key part of the clicker question on Fall 2017 Lecture 31 Slide 7—which was pulled from Fall 2016 Exam <sup>#</sup>3 Question 19—and the base-catalyzed mechanism was repeated in full on Slide 9 of that lecture. This time, the discussion of the clicker question and mechanism was an investment of roughly 5 minutes of the lecture. The acidcatalyzed mechanism was asked in Fall 2017 Exam 3 Problem II-2, so it makes sense you'd want to be ready for the base-catalyzed mechanism too.

|                 |                   | -  |    |           | _                   |        |                        | -  |    |           |                     |          |                 |        |                |             |        |     |                 |                        | - | _  |        |              |        |            |        |
|-----------------|-------------------|----|----|-----------|---------------------|--------|------------------------|----|----|-----------|---------------------|----------|-----------------|--------|----------------|-------------|--------|-----|-----------------|------------------------|---|----|--------|--------------|--------|------------|--------|
| He <sup>~</sup> | helium<br>4.003   | 10 | Ne | neon      | 20.180<br><b>18</b> | Ar     | <b>argon</b><br>39.948 | 36 | Ϋ́ | krypton   | 83.798<br><b>54</b> | Xe       | xenon           | 131.29 | å<br>A         | radon       | (222)  | 118 | 0g<br>0         | oganesson<br>(294)     |   | 71 | Lu     | lutetium     | 174.97 | 6 <b>5</b> | 3      |
|                 |                   | 6  | щ  | fluorine  | 18.998<br>17        | ບ      | chlorine<br>35.45      | 35 | Br | bromine   | /9.904<br>53        | _        | iodine          | 126.90 | °<br>Ơ         | astatine    | (210)  | 117 | Ts              | tennessine<br>(294)    |   | 70 | γb     | ytterbium    | 173.05 |            |        |
|                 |                   | 80 | 0  | oxygen    | 15.999<br><b>16</b> | S      | sulfur<br>32.06        | 34 | Se | selenium  | 52                  | Ъ        | tellurium       | 127.60 | <sup>1</sup> C | polonium    | (209)  | 116 | 2               | livermorium<br>(293)   |   | 69 | Ta     | thulium      | 168.93 |            | 212    |
|                 |                   | 7  | Z  | nitrogen  | 14.007<br>15        | ٩      | phosphorus<br>30.974   | 33 | As | arsenic   | ,4.922<br>51        | Sb       | antimony        | 121.76 | "<br>"         | bismuth     | 208.98 | 115 | ğ               | moscovium<br>(290)     |   | 68 | ц      | erbium       | 167.26 |            |        |
|                 |                   | 9  | ပ  | carbon    | 12.011<br>14        | Si     | silicon<br>28.085      | 32 | Ge | germanium | /2.631<br>50        | Sn       | ţi              | 118.71 | ہ م<br>م       | lead        | 207.2  | 114 | Ŧ               | flerovium<br>(289)     |   | 67 | Ч      | holmium      | 164.93 | ι<br>Γ     | 2      |
|                 |                   | 2  | В  | boron     | 10.81<br>13         | A      | aluminum<br>26.982     | 31 | Ga | gallium   | 69./23<br>49        | <u>_</u> | indium          | 114.82 | ⊒ ⊢            | thallium    | 204.38 | 113 | ЧN              | nihonium<br>(286)      |   | 99 | D      | dysprosium   | 162.50 | , t        | 5      |
|                 |                   |    |    |           |                     |        |                        | 30 | Zn | zinc      | 48<br>48            | S        | cadmium         | 112.41 | ° Å            | mercury     | 200.59 | 112 | C               | copernicium<br>(285)   |   | 65 | Ъb     | terbium      | 158.93 | 10         | 20     |
|                 |                   |    |    |           |                     |        |                        | 29 | Cu | copper    | 63.546<br>47        | Ag       | silver <b>(</b> | 107.87 | ΔII            | 2 pool      | 196.97 | 111 | Rg              | roentgenium<br>(282)   |   | 64 | Вd     | gadoliníum   | 157.25 | s<br>د     | 5      |
|                 |                   |    |    |           |                     |        |                        | 28 | ïZ | nickel    | 46                  | Pd       | palladium       | 106.42 | ° <b>t</b>     | platinum    | 195.08 | 110 | Ds              | darmstadtium<br>(281)  |   | 8  | Eu     | europium     | 151.96 | ،<br>۲     | ſ      |
|                 |                   |    |    |           |                     |        |                        | 27 | ပိ | cobalt    | 45                  | Rh       | rhodium         | 102.91 | : <b>-</b>     | iridium     | 192.22 | 109 | Ę               | meitnerium<br>(278)    |   | 62 | Sm     | samarium     | 150.35 |            | 7      |
|                 |                   |    |    |           |                     |        |                        | 26 | Fe | iron      | 44                  | Ru       | ruthenium       | 101.07 | č              | osmium      | 190.23 | 108 | Hs              | hassium<br>(277)       |   | 61 | Pm     | promethium   | (145)  | ŝ          | 222    |
|                 |                   |    |    |           |                     |        |                        | 25 | Mn | manganese | 54.938<br><b>43</b> | ц        | technetium      | (98)   | ه<br>۲۵        | rhenium     | 186.21 | 107 | Вh              | bohrium<br>(270)       |   | 60 | PN     | neodymium    | 144.24 | 26         | כ      |
|                 |                   |    |    |           |                     |        |                        | 24 | ۍ  | chromium  | 42                  | Вo       | molybdenum      | 95.95  |                | tungsten    | 183.84 | 106 | Sg              | seaborgium<br>(269)    |   | 59 | Pr     | praseodymium | 140.91 | ן<br>ק     | 0      |
|                 |                   |    |    |           |                     |        |                        | 23 | >  | vanadium  | 50.942<br><b>41</b> | qN       | niobium         | 92.906 | ° r            | tantalum    | 180.95 | 105 | Db              | dubnium<br>(268)       |   | 58 | С<br>С | cerium       | 140.12 | ک<br>۲     | =      |
|                 |                   |    |    |           |                     |        |                        | 22 | Ξ  | titanium  | 4/.86/<br>40        | Zr       | zirconium       | 91.224 | μţ             | hafnium     | 178.49 | 104 | Rf              | rutherfordium<br>(267) |   | 57 | La     | lanthanum    | 138.91 |            | נ<br>נ |
|                 |                   |    |    |           |                     |        |                        | 21 | Sc | scandium  | 44.956<br><b>39</b> | 7        | yttrium         | 88.906 | *              | lanthanides |        |     | **<br>actinides |                        |   |    | *      | lantnanides  |        | *          |        |
|                 |                   | 4  | Be | beryllium | 9.01<br>12          | Ы<br>В | magnesium<br>24.305    | 20 | S  | calcium   | 40.0/8<br><b>38</b> | Sr       | strontium       | 87.62  | å              | barium C    | 137.33 | 88  | Ra              | radium<br>(226)        |   |    |        |              |        |            |        |
| - T             | hydrogen<br>1.008 | m  | := | lithium   | 6.94<br><b>11</b>   | Na     | 22.990                 | 19 | ¥  | potassium | 39.05<br>37         | Rb       | rubidium        | 85.468 | ک ۽            | Cesium      | 132.91 | 87  | Ţ               | francium<br>(223)      |   |    |        |              |        |            |        |
|                 |                   |    |    |           |                     |        |                        |    |    |           |                     |          |                 |        |                |             |        |     |                 |                        | - |    |        |              |        |            |        |

awrenciur ۲

nobelium ۶

> nendelevíur (258)

fermium (257)

insteiniun

aliforniun

berkelium

americium Am

olutonium Pu

> eptuniu (237)

uranium 238.03

rotactinium

231.04

thorium 232.04

 $\mathop{Ac}\limits_{actinium}$ 

\*\* actinides

(243)

(244)

g curium (247)

(252)

(251)

(247)

(266)

(259)



#### **Bond Dissociation Energies (BDEs)**

| Average Bond Dissociation Energies, D (kJ/mol) <sup>a</sup> |                  |            |     |      |           |      |                  |              |                  |  |  |  |  |
|---|------------------|------------|-----|------|-----------|------|------------------|--------------|------------------|--|--|--|--|
| н—н   | 436 <sup>a</sup> | С—Н        | 410 | N—H  | 390       | О-Н  | 460              | F-F          | 159 <sup>a</sup> |  |  |  |  |
| н—с   | 410              | С—С        | 350 | N-C  | 300       | О-С  | 350              | Cl—Cl        | 243 <sup>a</sup> |  |  |  |  |
| H-F   | 570 <sup>a</sup> | C-F        | 450 | N-F  | 270       | O-F  | 180              | Br — Br      | 193 <sup>a</sup> |  |  |  |  |
| H-Cl  | 432 <sup>a</sup> | C-Cl       | 330 | N-Cl | 200       | O-CI | 200              | I—I          | 151 <sup>a</sup> |  |  |  |  |
| H-Br  | 366 <sup>a</sup> | C-Br       | 270 | N—Br | 240       | O—Br | 210              | S—F          | 310              |  |  |  |  |
| H—I   | 298 <sup>a</sup> | C-I        | 240 | N-I  |           | O-I  | 220              | S-Cl         | 250              |  |  |  |  |
| H-N   | 390              | C-N        | 300 | N-N  | 240       | O-N  | 200              | S—Br         | 210              |  |  |  |  |
| н-о   | 460              | C-O        | 350 | N-O  | 200       | 0-0  | 180              | s—s          | 225              |  |  |  |  |
| H—S   | 340              | C—S        | 260 | N-S  | . <u></u> | o—s  | <u> </u>         |              |                  |  |  |  |  |
| Multipl   | e coval          | lent bonds |     |      |           |      |                  |              |                  |  |  |  |  |
| C=C   | 611              | C≡C        | 835 | C=O  | 732       | 0=0  | 498 <sup>a</sup> | $N \equiv N$ | 945 <sup>a</sup> |  |  |  |  |

<sup>a</sup> Exact value

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#### 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.