

Exam Booklet No.

## CHEM 2410 – Organic Chemistry 1 – Fall 2017

Instructors: Paul Bracher &amp; Erin Witteck

# Hour Examination #1

Wednesday, September 20<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

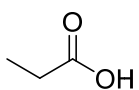
## Instructions & Scoring

- 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.

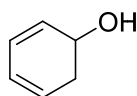
Problem	Points Earned	Points Available
I		60
II		10
III		10
IV		10
V		10
TOTAL		100

**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 two 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.

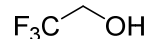
(1)     A     Which of the following compounds is the strongest Brønsted–Lowry acid?



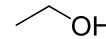
(A)



(B)



(C)

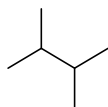


(D)

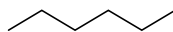
We generally evaluate the relative strength of acidity in a set of compounds by analyzing the relative stability of their conjugate bases. Here, all of the conjugate bases have a negative charge on an oxygen atom, but for the conjugate base of **A**, the negative charge is stabilized by virtue of being delocalized between two oxygen atoms by a resonance effect. Looking at a  $pK_a$  table is also useful for seeing just how much more acidic a typical carboxylic acid is than a typical alkyl alcohol.

Where you've seen it: Very similar to Fall 2016 Exam #1 Problem I-3, as well as Summer 2016 Exam #1 Problem I-5.

(2)     B     Which of the following compounds has the highest boiling point?



(A)



(B)



(C)

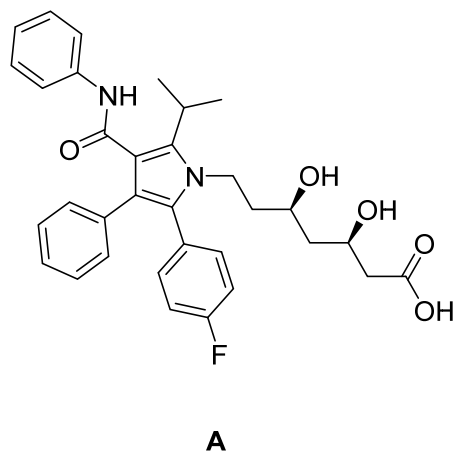


(D)

For evaluating the boiling points of alkanes, in general, the boiling point will be higher for compounds of greater mass and greater cylindrical (vs. spherical or branched) shape. Both of these traits lead to an electron cloud of greater surface area, which leads to stronger intermolecular interactions (with London forces as the predominate type).

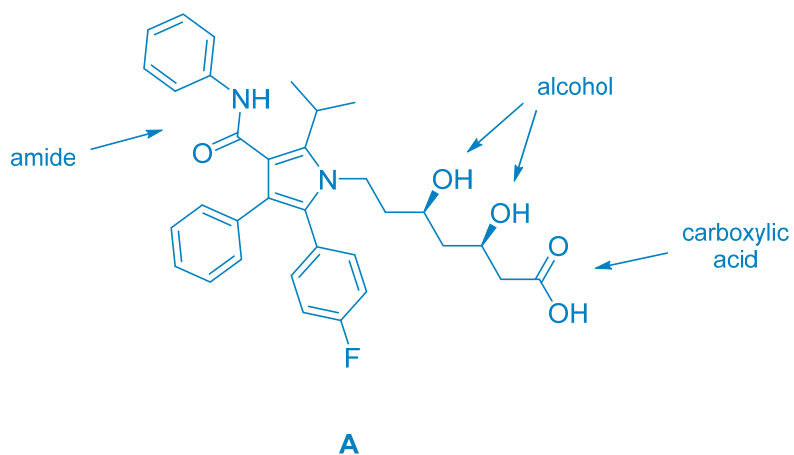
Where you've seen it: Format identical to Fall 2016 Exam #1 Problem I-6. MC version of explanation required on Fall 2016 Exam #1 Problem IV. Also see Summer 2016 Exam #1 Problem I-14.

(3)     D     Which functional group is not present in compound **A**?



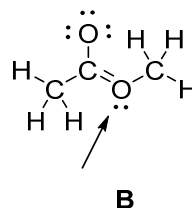
- (A) alcohol
- (B) amide
- (C) carboxylic acid
- (D) ester

The pertinent functional groups are labeled below:



Where you've seen it: Summer 2016 Exam #1 Problem I-1.

- (4)       <sup>C</sup> What is the formal charge on the oxygen atom that is labeled with an arrow in the Lewis structure of methyl acetate (**B**) drawn below? All hydrogen atoms and lone pairs have been drawn explicitly—there are no missing implicit hydrogen atoms or lone pairs.

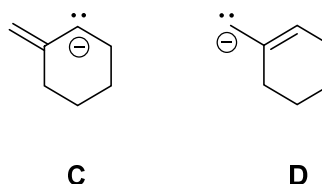


- (A) -1  
 (B) 0  
 (C) +1  
 (D) this Lewis structure is invalid because a second-row element has too many bonds

A formal charge for an atom is calculated by subtracting the number of electrons in lone pairs on that atom and half the number of electrons involved in valence bonds to that atom from the number of valence electrons expected of that element. Here, the calculation is  $6$  (expected valence electrons on oxygen)  $- 2$  (electrons in the single lone pair on that oxygen)  $- \frac{1}{2} \cdot 6$  (for the three pairs of electrons involved in the  $2 \sigma + 1 \pi$  bond to that oxygen atom) = a formal charge of  $+1$ .

Where you've seen it: Tests similar knowledge to Summer 2016 Exam #1 Problem I-4 and other problems on the exam and quiz archive.

- (5)       <sup>A</sup> What term best describes the relationship of structures **C** and **D**?

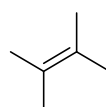


- (A) resonance forms  
 (B) constitutional/structural isomers  
 (C) conformational isomers  
 (D) *cis/trans* isomers

This is a standard example of resonance. For each structure, the atom bearing the lone pair is adjacent to an atom with an unhybridized  $p$  orbital into which you can “push” the lone pair. Both structures have the same molecular formula and charge, also consistent with resonance forms.

Where you’ve seen it: Format identical to Fall 2016 Exam #1 Problem I-12. Summer 2016 Exam #1 Problem I-15.

(6)     C     Which choice correctly and most completely describes the bonding in compound E?



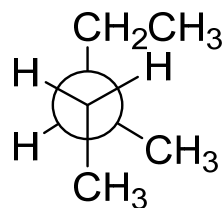
**E**

- (A) all C–C–C bond angles are approximately  $120^\circ$
- (B) all H–C–H bond angles are approximately  $109.5^\circ$
- (C) both statements A and B are correct
- (D) neither statement A nor statement B is correct

Both of the central carbon atoms are  $sp^2$ -hybridized and unstrained, so all C–C–C bond angles are approximately  $120^\circ$ . All H atoms are bonded to  $sp^3$ -hybridized carbon atoms, so all H–C–H bond angles are approximately  $109.5^\circ$

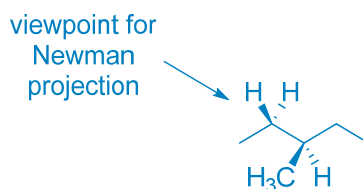
Where you’ve seen it: Similar to Summer 2016 Exam #1 Problem I-2. Tests similar knowledge to that required for Fall 2016 Exam #1 Problem I-16.

(7)      **B**      The Newman projection drawn below represents which of the following?



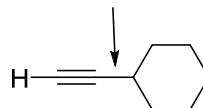
- (A) the most-stable staggered conformation of 2,3-dimethylbutane with respect to the C2–C3 bond
- (B) the most-stable staggered conformation of 3-methylpentane with respect to the C2–C3 bond
- (C) a staggered conformation of 2,3-dimethylbutane, but not the most stable with respect to the C2–C3 bond
- (D) a staggered conformation of 3-methylpentane, but not the most stable with respect to the C2–C3 bond

The corresponding skeletal structure is below. Converting to a skeletal structure makes it clear the compound is 3-methylpentane. The projection shown is of the most stable conformation, as any rotation of the C2–C3 bond places the C2 methyl group closer to the ethyl group on C3.



Where you've seen it: Very similar to Fall 2015 Exam #1 Problem I-3 and Fall 2016 Exam #1 Problem I-20.

- (8)      **B**      What orbitals form the bond between the carbon atom of the ring and the carbon atom of the adjoined ethynyl group in ethynylcyclohexane (**F**)? The bond is labeled with an arrow in the structure below.



- (A) two  $sp$  orbitals  
(B) one  $sp$  orbital and one  $sp^3$  orbital  
(C) one  $sp$  orbital, one  $sp^3$  orbital, and one  $p$  orbital  
(D) one  $sp$  orbital, one  $sp^3$  orbital, and two  $p$  orbitals

The bond is a single  $\sigma$  bond. Since it is between an  $sp$ -hybridized atom and  $sp^3$ -hybridized atom, these are the hybrid atomic orbitals used to construct the bond.

Where you've seen it: Format identical to Fall 2017 Quizzes #1 Problem I-1 and Fall 2016 Exam #1 Problem I-1, Summer 2016 Exam #1 Problem I-7.

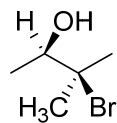
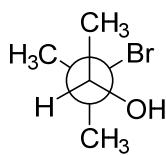
- (9)      **B**      Which of the following statements is the most correct and complete?

- (A)  $\text{CH}_3\text{S}^-$  is a stronger base than  $\text{CH}_3\text{O}^-$   
(B) the element sulfur is less electronegative than oxygen  
(C) both statement A and statement B are correct  
(D) none of the above statements are correct

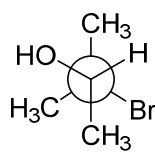
$\text{CH}_3\text{SH}$  is a stronger acid than  $\text{CH}_3\text{OH}$  (due to a "size/element effect"), so  $\text{CH}_3\text{S}^-$  (the conjugate base) must be a weaker base than  $\text{CH}_3\text{O}^-$ . Sulfur is also less electronegative than oxygen ( $\chi = 2.6$  vs. 3.4, respectively, on the Pauling scale). This difference might seem counterintuitive but is a classic example of how size ( $3p$  vs.  $2p$  orbital bearing the negative formal charge) predominates over electronegativity when comparing atoms from the same group. Also, the  $pK_a$  table included with the exam is very useful for evaluating statement (A).

Where you've seen it: Similar to parts of previous problems in exam and quiz archive and discussed extensively in Fall 2017 on class discussion forum.

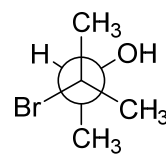
- (10)     D     Which of the following Newman projections is an accurate representation of compound **G**?

**G**

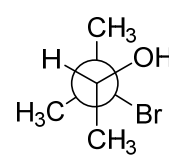
(A)



(B)

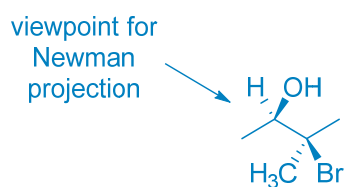


(C)



(D)

Here's the viewpoint corresponding to choice (D):

**G**

Where you've seen it: Format identical to Fall 2016 Exam #1 Problem I-8, Summer 2016 Exam #1 Problem I-16.



(11)       D       Which of the following is not a valid name for an alkane based on the IUPAC system of nomenclature?

- (A) 4-ethyl-3,3-dimethylheptane
- (B) 3-ethyl-4,4-dimethylheptane
- (C) 4,4-dipropylheptane
- (D) 3-ethyl-2,2-dimethylbutane

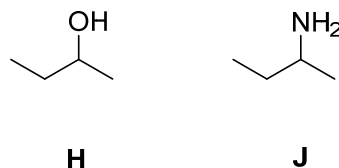
The structure corresponding to 3-ethyl-2,2-dimethylbutane is properly named 2,2,3-trimethylpentane.



"3-ethyl-2,2-dimethylbutane"

Where you've seen it: Similar to ruling out choice (A) in Summer 2016 Exam #1 Problem I-20.

(12)       C       Which of the following statements best describes the relative Brønsted–Lowry acidity and basicity of compounds **H** and **J**?

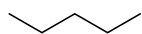


- (A) compound **H** is the stronger acid and the stronger base
- (B) compound **J** is the stronger acid and the stronger base
- (C) compound **H** is the stronger acid, compound **J** is the stronger base
- (D) compound **J** is the stronger acid, compound **H** is the stronger base

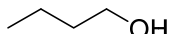
The stronger acid is the compound that is most easily deprotonated. That is compound **H**, as the negative charge in the conjugate base is more favorably borne by a (more electronegative) oxygen atom vs. a (less electronegative) nitrogen atom. The stronger base is similarly easy to explain by either the availability of the lone pairs (O stabilizes its lone pairs better than N) or by the relative stability of the conjugate acids, which in either case places the positive formal charge on N (less electronegative) vs. O with all other factors essentially equal (hybridization, orbital size, etc.) The  $pK_a$  table included in the exam booklet is very helpful here, as well.

Where you've seen it: Format identical to Fall 2016 Exam #1 Problem I-5.

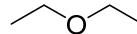
- (13)     C     Rank the following compounds in order of increasing solubility in water (i.e., from the least soluble to the most soluble).



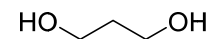
K



L



M



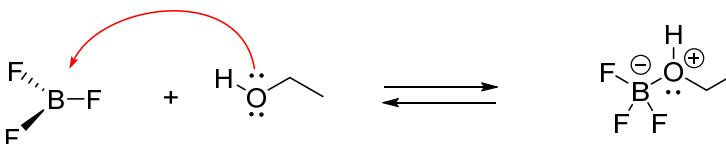
P

- (A)  $K < L < M < P$   
 (B)  $P < L < M < K$   
 (C)  $K < M < L < P$   
 (D)  $P < L < K < M$

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. **K** is nonpolar. **M** is polar but cannot donate hydrogen bonds. **L** can participate in hydrogen bonding. **P** can hydrogen bond more extensively.

Where you’ve seen it: Similar to Fall 2016 Exam #1 Problem I-6, Fall 2014 Exam #1 Problem IV-1

- (14)     C     Which of the following statements regarding the reaction drawn below is correct?

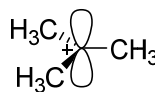
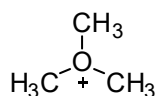


- (A) the hybridization of the boron atom is  $sp^3$  in the reactant and product  
 (B) the curved arrow is wrong—it should point toward the oxygen atom  
 (C) the alcohol reacts as a Lewis base and nucleophile  
 (D) the boron atom in the product should not have a  $-1$  formal charge

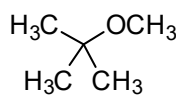
The alcohol does indeed react as a Lewis base, which is synonymous with the term “nucleophile”. As for the other choices: (a) the hybridization of the boron atom in boron trifluoride on the reactants side is  $sp^2$ ; (b) the curved arrow is correct; (d) the boron atom in the product is correct as drawn with a formal charge of  $-1$ .

Where you’ve seen it: Essentially identical to Summer 2016 Exam #1 Problem I-13. Very similar to Fall 2016 Exam #1 Problem I-2.

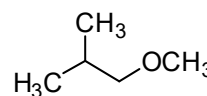
- (15)     D     Which of the following compounds is formed when methoxide ( $^-\text{OCH}_3$ ) reacts as a Brønsted–Lowry base with trimethylcarbenium cation (**Q**)?

**Q**

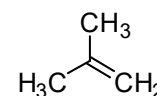
(A)



(B)



(C)



(D)

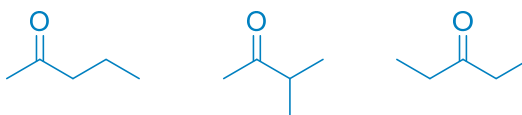
If methoxide reacts as a Brønsted–Lowry base, it must remove a proton from **Q**. This process generates choice (D).

Where you've seen it: Nearly identical to Fall 2016 Exam #1 Problem I-15.

- (16)     C     How many different isomers of  $\text{C}_5\text{H}_{10}\text{O}$  are ketones? Recall that ketones have a carbonyl group substituted with two alkyl groups, so do not include aldehydes in your count.

- (A) one  
(B) two  
(C) three  
(D) four

Start by “using” a carbon and oxygen in a double bond since you are told the compounds must be ketones. That leaves  $\text{C}_4\text{H}_{10}$ , which can only be made by one or more saturated alkyl groups (no other functionality is possible). Since ketones must have two alkyl groups, you are limited to a pair of 1C & 3C or 2C & 2C. The possibilities are limited and can be sketched out quickly knowing that only one type of methyl (1C), one type of ethyl (2C), and two types of propyl (3C) groups exist:



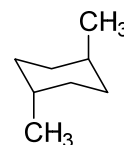
There are three isomers that fit the specifications. Note that having a methyl group “on the left” and propyl “on the right” is an equivalent structure to methyl on the right and propyl on the left.

Where you've seen it: Format identical to Fall 2016 Exam #1 Problem I-9.

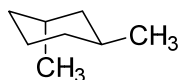
- (17)     D     Which of the following structures represents the most stable conformation of *cis*-1,4-dimethylcyclohexane?



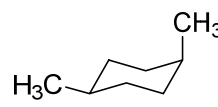
(A)



(B)



(C)

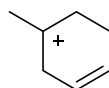
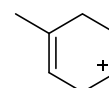


(D)

Structures (A) and (B) are *trans*-1,4-dimethylcyclohexane, not *cis*-1,4-dimethylcyclohexane. Structure (C) is *trans*-1,3-dimethylcyclohexane. Structure (D) is *cis*-1,4-dimethylcyclohexane in its most stable conformation. One methyl group must be in an axial position in either chair conformation.

Where you've seen it: Format identical to Fall 2016 Exam #1 Problem I-11. Similar to Summer 2016 Exam #1 Problem I-11.

- (18)     D     What statement is correct regarding cations **R** and **S**?

**R****S**

- (A) cation **R** has two  $sp^2$ -hybridized atoms  
 (B) cation **S** has 12 hydrogen atoms  
 (C) structures **R** and **S** are resonance forms  
 (D) none of the above statements are correct

Both structures have three  $sp^2$ -hybridized atoms: the carbon atoms in the  $\pi$  bond and the carbon atom bearing the +1 formal charge. Each structure has 11 hydrogen atoms. Structures **R** and **S** are not resonance forms because a hydrogen atom must move to interconvert between the two structures.

Where you've seen it: Format identical to Fall 2016 Exam #1 Problem I-7. Similar to Summer 2016 Exam #1 Problem I-9.

- (19)      **B** For all isomers of  $C_9H_{18}$  that are alkanes, what is the largest locant number that appears in at least one of their systematic IUPAC names?
- (A) 4  
(B) 5  
(C) 6  
(D) 7

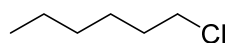
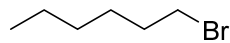
To be an alkane of molecular formula  $C_nH_{2n}$ , the compound must be a cycloalkane. (The only other compounds of this molecular formula are alkenes (with one  $\pi$  bond). Approach the problem by trying to place methyl substituents (smallest group possible so you're not 'wasting' atoms) on rings of different sizes, starting with the biggest ring size possible. The highest locant numbers for each possible ring size are:

cyclononane  
methylcyclooctane  
1,4-dimethylcycloheptane  
1,3,5-trimethylcyclohexane  
1,1,2,5-tetramethylcyclopentane (stop here as max locant # on cyclobutane is 4)

The winning compounds are 1,3,5-trimethylcyclohexane and 1,1,2,5-tetramethylcyclopentane, which have 5 as their largest locant.

Where you've seen it: Similar approach needed for Fall 2016 Exam #1 Problem I-10, Summer 2016 Exam #1 Problem I-12, Summer 2016 Exam #1 Problem III-2.

(20)       <sup>C</sup> What concept/property best explains the difference in melting points of compounds **T** and **U**?

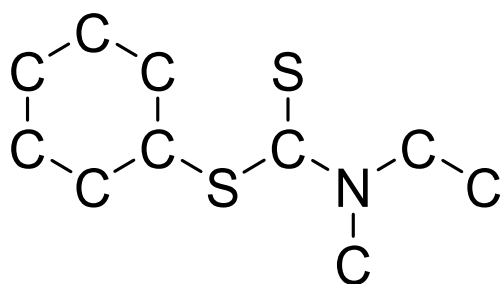
m.p. =  $-94\text{ }^{\circ}\text{C}$ **T**m.p. =  $-85\text{ }^{\circ}\text{C}$ **U**

- (A) net dipole moment
- (B) electronegativity
- (C) polarizability
- (D) symmetry

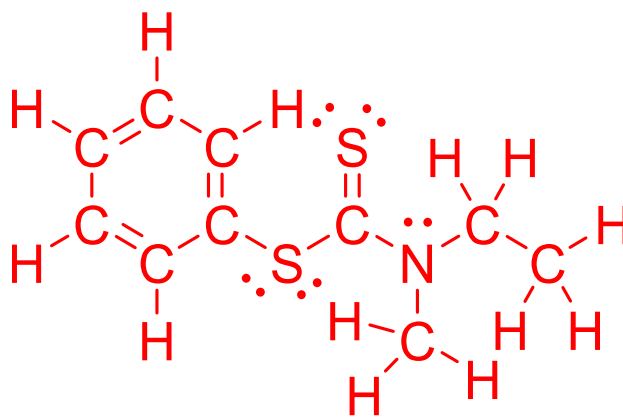
Note that  $-85^{\circ}\text{C}$  is a higher temperature than  $-94^{\circ}\text{C}$ . Cl has a higher electronegativity than Br, so compound **T** should have a higher dipole moment. But the higher dipole moment does not explain the data since **T** has a lower melting point despite having a larger dipole moment. Br has a larger, more polarizable electron cloud than Cl. This difference should lead to higher-magnitude London forces in **U**, which could explain why **U** has a higher melting point than **T**.

Where you've seen it: Very similar to Summer 2016 Quiz #1 Problem IV-1. Similar to Fall 2014 Exam #1 Problem IV-3, Summer 2016 Exam #1 Problem I-19.

**Problem II.** Lewis Structure (10 points). Complete the Lewis structure for compound **V** that has been started on your answer sheet. The compound has the molecular formula  $C_{10}H_{13}NS_2$ . The structure includes an aromatic ring, an ethyl group, and a methyl group. It is not a thiol (i.e., it does not contain a sulfhydryl group). All atoms in the structure (aside from hydrogen) have full octets and your structure should not have any formal charges. Explicitly include—i.e., draw out—all hydrogens, bonding pairs, and lone pairs on your Lewis structure.



**V**



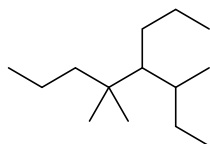
Where you've seen it: Format identical to Exam #1 Problem II in Fall 2014, 2015, and 2016 and Summer 2016 as well as Fall 2013 Exam #1 Problem III.

Grading and partial credit:

- +1 correct double bonds in aromatic ring
- +1 correct number of protons on aromatic ring
- +1 lone pairs on S1
- +1 lone pairs on S2
- +1 C=S bond order is two for S2
- +1 lone pair on nitrogen
- +1 methyl is completely correct
- +1 ethyl group is completely correct
- +1 no labeled formal charges and structure drawn by student is consistent with no formal charges
- +1 entire Lewis structure is correct

(Do not award half-points)

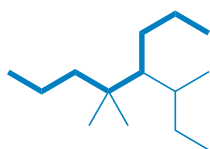
**Problem III.** Alkanes and Substituted Alkanes (10 points). Provide the IUPAC name for compound **W**. You need not worry about stereochemistry as no information about the three-dimensional structure of the molecule is indicated.

**W**

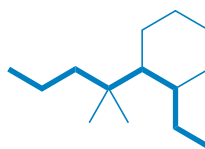
**3,5,5-trimethyl-4-propyloctane**

Compound **W** has two chains of eight carbon atoms. These are the longest chains possible. The parent chain is chosen using number of substituents as a tiebreaker. One chain has three substituents (1 *sec*-butyl and 2 methyls) while the other has four (1 ethyl and 3 methyls). The tie is broken and the latter chain is declared the parent. Finally, the chain is numbered right-to-left to assign the lowest locant number possible (3 for methyl if right-to-left vs. 4 for methyl if left-to-right).

longest chains - both 8 carbons



worse - 3 substituents



better - 4 substituents

Where you've seen it: Format identical to Fall 2014 Exam #1 Problem III-1, Fall 2016 Exam #1 Problem III, Summer 2016 Exam #1 Problem III-1.

Grading and partial credit:

Base Responses

- +10 for 3,5,5-trimethyl-4-propyloctane
- +6 for 5-*sec*-butyl-4,4-dimethyloctane
- +5 for 2,3-diethyl-4,4-dimethylheptane

Then, if any of the above parent structures have additional errors, subtract the following from the base:

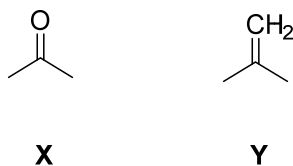


- 2 if chain numbered in wrong direction but the rest is consistent
- 2 if groups are miscounted (di- vs. tri-) but the rest is fine
- 1 if substituents are listed out of alphabetical order (e.g., propyl before trimethyl) but the rest is consistent
  
- 1 for each wrong substituent
- 1 for including stereochemistry/cyclo
- 1 if a comma used instead of a dash or vice versa
- 1 if a number was omitted or added incorrectly
- 1 spelling error (e.g., 'prophyl' instead of 'propyl')

Charity (use only if the response is not close enough to funnel into the first three base responses, funnel maximum = +4):

- +2 for octane
- +2 for having #,#-dimethyl, where # is any number between 3 and 6

**Problem IV.** Explanation (10 points). Of acetone (**X**) and isobutylene (**Y**), which has the higher boiling point? Write the letter of your answer in the box on the answer sheet and provide a brief explanation (of no more than three sentences) for your choice. Answers of more than three sentences will receive a maximum score of three points.



Compound **X** has the higher boiling point.

Higher boiling points are typically associated with compounds that participate in stronger intermolecular interactions. Compound **X** has a much higher dipole moment than **Y**, giving it stronger intermolecular interactions and a higher boiling point. The difference in mass is negligible.

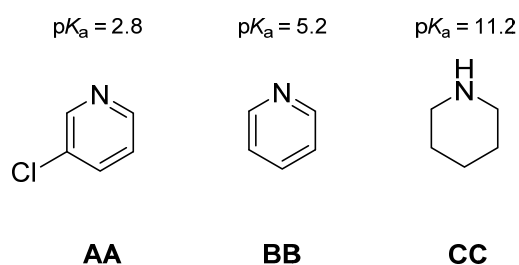
Where you've seen it: Format identical to Fall 2016 Exam #1 Problem IV. Similar multiple choice and free response questions in archive.

Grading and partial credit:

- +3 for "**X**" in the box
- +7 main explanation is that **X** has dipole-dipole interactions
  - 2 for any incorrect mention of size/mass/resonance/branching in addition to dipole-dipole interactions
  - 1 for each additional mention of an effect beyond dipole-dipole interactions

- +2 main explanation is that **X** has a higher mass/size/polarizability/resonance/electronegativity but no mention of dipole-dipole interactions
- +2 for any mention of intermolecular forces

**Problem V.** Explanation (10 points). The  $pK_a$  values for the conjugate acids of compounds **AA**, **BB**, and **CC** are provided below. In the box on your answer sheet, write which compound is the strongest base. Then, in no more than four sentences, provide an explanation for the relative basicity of these compounds that is consistent with the given  $pK_a$  data.



( $pK_a$  values are for the conjugate acids)

**Compound CC** is the strongest base. We know this empirically, as it has the weakest conjugate acid (highest  $pK_a$ ) of the three compounds.

We can analyze the trend in acidity by going “down the list” of element, hybridization, resonance, and inductive effects. The electron pair that is the most basic on each compound is a lone pair on a nitrogen atom, so we do not expect significant differences in terms of element effects. Note that they also all have the same charge (no formal charge). In terms of hybridization effects, the lone pair on **CC** is located in an  $sp^3$ -hybridized orbital while those on **BB** and **AA** are in  $sp^2$ -hybridized orbitals. Electrons in orbitals with more  $s$ -character are better stabilized, explaining why the lone pair on **CC** is more basic—it is more available.

There appear to be no significant differences between **AA** and **BB** in terms of hybridization or resonance effects, but the presence of the electron-withdrawing chlorine atom on **AA** explains why **AA** is a weaker base than **BB**—the chlorine atom withdraws negative charge density from nearby atoms, including the nitrogen, rendering it less available to serve as a base.

Where you’ve seen it: Very similar to Summer 2016 Quiz #1 Problem IV-2. Closely related to Fall 2017 Quizzes #1 Problem I-2. Also similar to Fall 2014 Exam #1 Problem IV-2, Summer 2016 Exam #1 Problem IV-1.

Grading and partial credit:

In the interest of fairness, all students were awarded full credit (+10) because many students interpreted the problem as asking them to use the given  $pK_a$  data as the explanation for why **CC** is more basic than **BB** than **AA**.