CHEM 2410 – Principles of Organic Chemistry I – Summer 2016

Instructor: Paul Bracher

Quiz #1

Due: Friday, May 27th, 2016

12:00 p.m. (to the mailbox outside Monsanto Hall 103)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

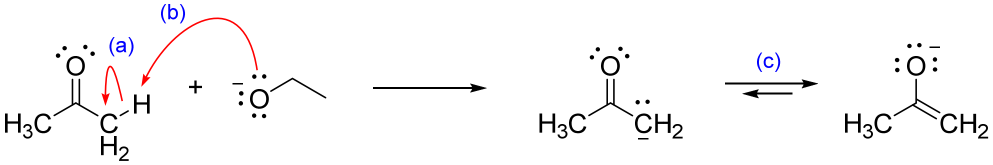
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. Submissions submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		60
II		10
III		14
IV		16
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (60 points total; +3 points for a correct answer, +1 points for answering with the letter "E",, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

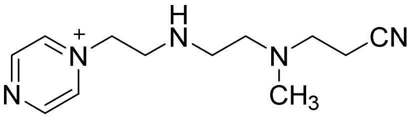
(1) C Which of the following statements best describes the use of the arrows labeled (a), (b), and (c) in the acid–base reaction depicted below?



(A) arrow (a) is used incorrectly
(B) arrow (b) is used incorrectly
(C) arrows (c) are used incorrectly
(D) arrows (a), (b), and (c) are all used incorrectly

Arrows (a) and (b) are used correctly. The arrows (c) are used incorrectly here. The arrows (c) should only be used to indicate an equilibrium that favors the right side over the left side. Here, a single double-headed arrow should be used for (c) to separate the two resonance forms drawn.

(2) C How many of the five nitrogen atoms in structure **A** are sp^2-hybridized?

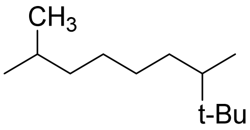


A

(A) 0
(B) 1
(C) 2
(D) 3

From left-to-right in **A**, the nitrogen atoms are sp^2-hybridized, sp^2-hybridized, sp^3-hybridized, sp^3-hybridized, and sp-hybridized.

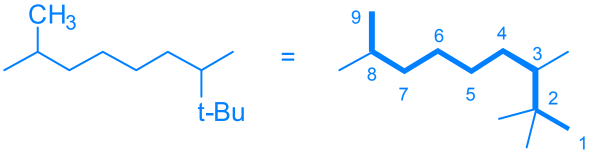
(3) D What is the systematic name of compound **B**?



B

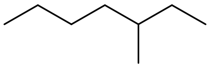
(A) 2-*tert*-butyl-7-methyloctane
(B) 7-methyl-2-*tert*-butyloctane
(C) 2-methyl-7-*tert*-butyloctane
(D) 2,2,3,8-tetramethylnonane

Remember to consider the full Lewis structure when finding the longest chain of carbon atoms. Here, this chain has nine carbon atoms and is numbered to give the second substituent the lowest locant (2 vs. 8) since the first substituents will have identical locants when the chain is numbered from either side.



Also, we are ignoring that C3 is a stereogenic center. This concept will be discussed later in the course.

(4) D Which of the following statements is <u>not</u> true of compound **C**.



C

(A) compound **C** is named 3-methylheptane
(B) compound **C** has a lower melting point than 2,2,3,3-tetramethylbutane
(C) compound **C** is a saturated hydrocarbon
(D) compound **C** has more 2° hydrogen atoms than 1° hydrogen atoms

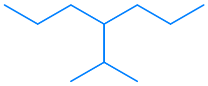
While compound **C** has four secondary carbons and three primary carbons, a full Lewis structure reveals that it has only 8 secondary hydrogens compared to 9 primary hydrogens.

(5) C How many carbon atoms are in the smallest (lowest mass), acyclic, saturated hydrocarbon that has the word "isopropyl" in its proper IUPAC

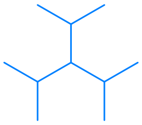
(A) 6 or fewer carbon atoms
(B) 7 or 8 carbon atoms
(C) 9 or 10 carbon atoms
(D) 11 or more carbon atoms

Perhaps the best approach to this problem is to start with an isopropyl group and keep adding carbons until the longest chain of carbons no longer passes through your isopropyl group. Possible structures include:

4-isopropylheptane

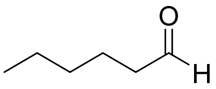


3-isopropyl-2,4-dimethylpentane

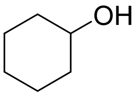


all are $C_{10}H_{22}$

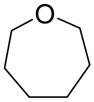
(6) B Of the following isomers of $C_6H_{12}O$, which has the <u>highest</u> boiling point?



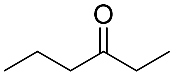
(A)



(B)



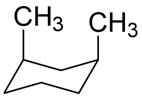
(C)



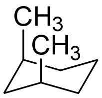
(D)

While all of these molecules have identical mass and are polar, cyclohexanol (B) can participate in hydrogen bonding, a particularly strong type of dipole–dipole interaction. Since this compound has the strongest intermolecular interactions of the four, the sample will have the highest boiling point.

(7) A What term best describes compounds **D** and **E**?



D

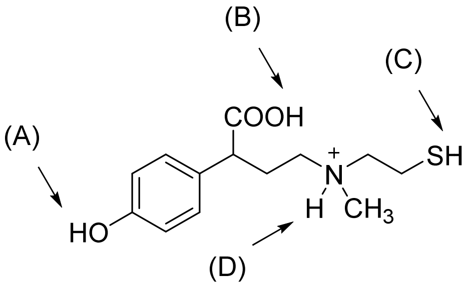


E

(A) identical
(B) constitutional isomers
(C) conformational isomers
(D) stereoisomers

If you attempt to name both structures, you will come up with *cis*-1,3-dimethylcyclohexane. It is a meso compound (internal plane of symmetry, achiral). Both structures represent the chair conformation in which the methyl groups are axial. The bottom line is that **D** and **E** represent identical compounds with the identical conformation. They are simply viewed from a different perspective for each drawing.

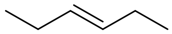
(8) B Which of the labeled hydrogen atoms is the most acidic in compound **F**?



F

The best approach to this problem is to look at a pK_a table, see roughly where each type of protic functional group appears, and then choose the proton with the lowest pK_a (which is the most acidic). Here, phenols (A) typically have pK_a ≈ 10, carboxylic acids (B) typically have pK_a ≈ 4–5, thiols (C) typically have pK_a ≈ 10–11, protonated amines (D) typically have pK_a ≈ 10–11. Thus, proton (B) is the most acidic. Note that even though the protonated amine at (D) has a positive charge that would be neutralized upon deprotonation, a neutral carboxylic acid is still a stronger acid. Charge alone does not determine acidity.

(9) C What type(s) of orbitals form the bond between the C3 and C4 carbon atoms in 3-hexene (**G**)?

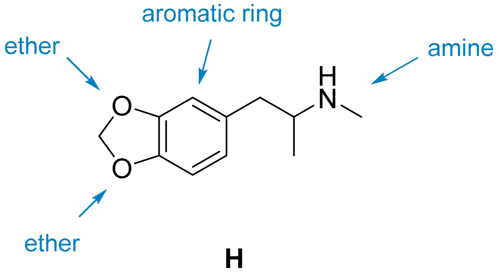


G

(A) *sp*^{2} orbitals only
(B) *sp*^{3} orbitals only
(C) *p* and *sp*^{2} orbitals
(D) *p* and *sp*^{3} orbitals

C3 and C4 are both *sp*^{2}-hybridized. The double bond between them comprises a σ bond and a π bond. The σ bond is made from the constructive interaction of two *sp*^{2} orbitals. The π bond is made from the constructive interaction of two unhybridized *p* orbitals.

(10) B Which of the following functional groups is not present in 3,4-methylenedioxymethamphetamine (**H**), a drug more commonly known as ecstasy?

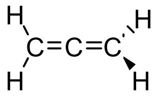


H

(A) amine
(B) alcohol
(C) ether
(D) aromatic ring

Compound **H** does not have a hydroxyl group (–OH) and is therefore not an alcohol. (See annotations above.)

(11) C What is the approximate value of the H–C–C bond angles in propadiene (**J**)?

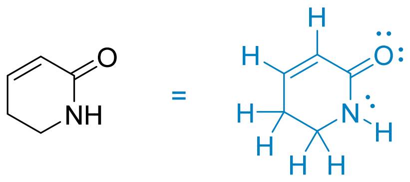


J

(A) 90°
(B) 109.5°
(C) 120°
(D) 180°

The terminal carbons (C1 and C3) that bear the hydrogen atoms are both *sp*^{2} hybridized. Thus, we expect them to have H–C–C bond angles close to 120°.

(12) D How many nonbonding pairs of valence electrons (i.e., lone pairs) are present in compound **K**?

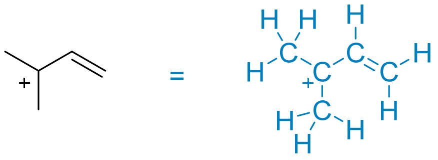


K

(A) 0
(B) 1
(C) 2
(D) 3

A more detailed Lewis structure for **K** is shown above. The molecule has three valence lone pairs of electrons.

(13) C How many carbon atoms are sp^2-hybridized in cation **L**?

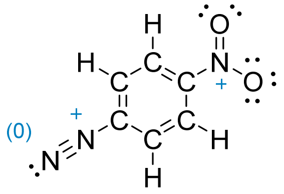


L

- (A) 0 or 1
- (B) 2
- (C) 3
- (D) 4 or 5

In the more-detailed Lewis structure of **L**, we see that the carbon atom labeled with the positive formal charge and the two carbons that are bonded to each other have three groups each (where a group equals a connection to one other atom or a lone pair). These three carbons are sp^2-hybridized. The two other carbons are each connected to four atoms, and thus, are sp^3-hybridized.

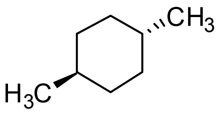
(14) D What is the net sum of the formal charges on all the nitrogen atoms in the following Lewis structure? All atoms, lone pairs, and bonding pairs have been drawn explicitly in this structure, but no charges or formal charges have been labeled.



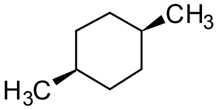
- (A) −1
- (B) 0
- (C) +1
- (D) +2

The formal charges on the three nitrogen atoms are labeled above. 0 + 1 + 1 = 2.

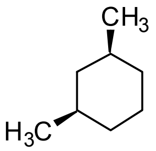
(15) D or B Which of the following isomers of C_8H_{16} will have the most exothermic heat of combustion? That is, if one mole of each compound is burned (completely), which will release the most heat?



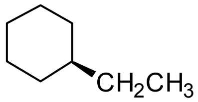
(A)



(B)



(C)

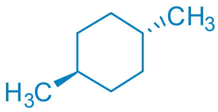


(D)

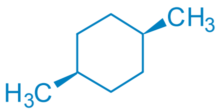
OK, I got more than I bargained for when I wrote this problem, but it is instructive in that it demonstrates the importance of comparing molecules with similar structures. The less similar the structures being compared, the more likely it is that multiple effects will come into play when judging the relative physical properties of the compounds.

All four of the compounds under consideration are isomers of C_8H_{16} that will generate 8 equivalents of CO_2 and 8 equivalents of H_2O when burned with 12 equivalents of oxygen gas (O_2). If the complete combustion of all four compounds produces identical sets of products (which must have the same relative energy), then the heat of combustion will be determined by the differences in relative stability (potential energy) of the starting materials. The compound that is least stable (i.e., most strained, with the highest potential energy) will liberate the most energy (heat) upon combustion (since it started with the most potential energy to begin with and all four compounds produce the same products).

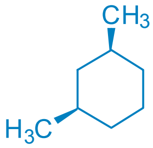
Let's begin by comparing (A), (B), and (C). All of these compounds have six membered rings with two methyl groups. If we draw them in their most stable conformations, we have:



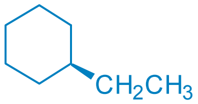
(A)



(B)



(C)



(D)

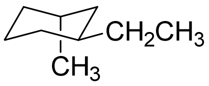
Note that for compound (B), either chair confirmation will have one methyl group in an axial position. Substituents in axial positions are associated with unfavorable steric interactions. All of the other compounds have a conformation where all of the substituents occupy less hindered equatorial positions. As a result, we might expect (B) to have the most exothermic heat of combustion.

But it actually only has a more exothermic heat of combustion relative to (A) and (C), the two other dimethylcyclohexanes. It turns out that (D) actually has a more exothermic heat of combustion than all of the others. In hindsight, this actually makes sense. Compound (D) differs from the other compounds in that (D) has one fewer C(3°)–H bond, three fewer C(1°)–H bonds, two fewer C(3°)–C(1°) bonds, one more C(3°)–C(2°) bond, one more C(2°)–C(1°) bond, and four more C(2°)–H bonds. When you add up the bond dissociation energies associated with these differences (Chapter 6), they account for the difference.

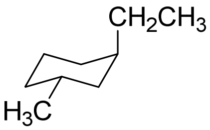
At the end of the day, this wasn't a good problem, but you should be able to recognize why (B) has the most exothermic energy of combustion for the set (A), (B), and (C), without including (D).

Refs: (a) Johnson, W.H.; Prosen, E.J.; Rossini, F.D. *J. Res. National Bureau of Standards*, **1947**, *39*, 49–52. National Bureau of Standards Research Paper RP1812. (b) Prosen, E.J.; Johnson, W.H.; Rossini, F.D. *J. Res. National Bureau of Standards*, **1947**, *39*, 174–175. National Bureau of Standards Research Paper RP1821. (c) Francis A. Carey, "Organic Chemistry" 5th edition, Chapter 3: "Conformations of Alkanes and Cycloalkanes".

(16) D Which of the following structures represents the <u>most stable</u> conformation of *cis*-1-ethyl-3-methylcyclohexane?



(A)



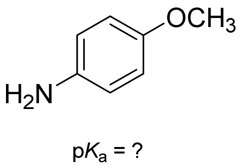
(B)

(C)

(D)

Choices (A), (B), and (C) aren't even *cis*-1-ethyl-3-methylcyclohexane. Choice (D) is *cis*-1-ethyl-3-methylcyclohexane, and the structure shown is also the most stable conformation of the molecule. Its other chair conformation—with both substituents in axial positions—is less stable.

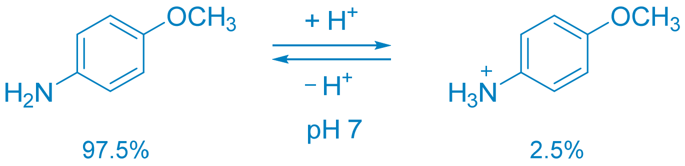
(17) ___B___ When a small sample of 4-methoxyaniline (**M**) is dissolved in aqueous solution buffered at pH 7, roughly 2.5% of the nitrogen atoms in the sample become protonated. Which of the following values is closest to the pK_a of (protonated) 4-methoxyaniline?



M

(A) 4.2
(B) 5.4
(C) 8.6
(D) 9.4

The equilibrium at play is:

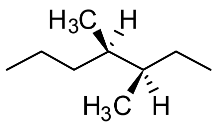


This problem is best approached using the Henderson–Hasselbalch equation, pH = pK_a + log ([A^-]/[HA]). The percent of A^- (deprotonated) plus the percent of HA (protonated) equals 100%, so pH = pK_a + log (x / (100 – x)). You can plug in pH = 7.0 and x = 97.5 to find pK_a = 3.4.

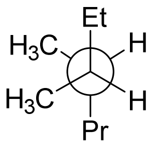
Note that an acid will exist in solution as 50/50 protonated/deprotonated when pH = pK_a. Here, you could have used the fact that 2.5% < 50% to immediately eliminate choices (C) and (D).

(18) A

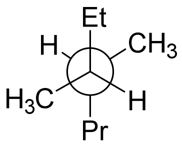
Which of the following Newman projections is an accurate representation of alkane **N**? "Et" is the abbreviation for an ethyl group (–CH_2CH_3). "Pr" is the abbreviation for a propyl group (–$CH_2CH_2CH_3$).



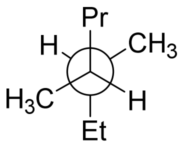
N



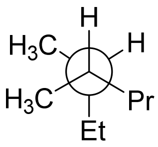
(A)



(B)

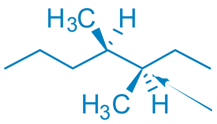


(C)



(D)

Here's the direction and carbon–carbon bond you're looking down:



N

(19) B

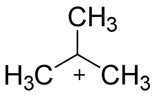
Which of the following is the most likely product of the heterolytic cleavage of the C–Br bond in compound **P**? (*t*-Bu = a *tert*-butyl group)

t-Bu–Br

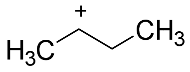
P

$Br^{\bullet}$

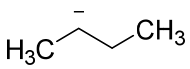
(A)



(B)



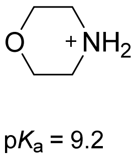
(C)

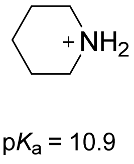


(D)

For heterolytic cleavage, one atom in the bond gets both electrons while the other gets none. It is almost always preferable for the more electronegative atom to get the pair of electrons. The electronegativity of bromine is higher than that of carbon.

(20) C Which of the following statements is central to explaining the difference in acidity between these two compounds?


pK_a = 9.2


pK_a = 10.9

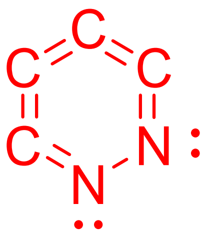
(A) the oxygen atom destabilizes the parent acid by a resonance effect
(B) the oxygen atom stabilizes the parent acid by a resonance effect
(C) the oxygen atom destabilizes the parent acid by an inductive effect
(D) the oxygen atom stabilizes the parent acid by an inductive effect

The species with the oxygen atom is more acidic (as it has a lower pK_a), so that cation must be destabilized relative to the other, thereby showing a stronger preference to relieve its charge by donating a proton. There are no p orbitals in the ring to support a resonance effect, but we know oxygen is more electronegative than carbon and will withdraw more electron density from its neighbors by an inductive effect. This effect exacerbates the charge on the nitrogen.

Problem II. Lewis Structure (10 points). Draw a Lewis structure for a molecular that is composed of 4 carbon atoms and 2 nitrogen atoms (and no other elements) with no formal charges in the structure.

$$:N\equiv C-C\equiv C-C\equiv N:$$

As this problem is written, the following structure also meets the given criteria (and would receive full credit at this point in the course), but it is too unstable to exist:



Problem III. Alkanes and Substituted Alkanes (14 points). Provide the systematic IUPAC names requested below.

(1) (7 points) Provide the IUPAC name for compound **Q**.

Q

4,4-diethyl-2,2-dimethylheptane

The longest chain has seven carbons (shown in bold) and the tiebreaker for deciding from what end to begin numbering it is that the locant for the first substituent will be 2 vs. 4.

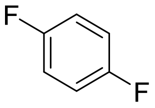
(2) (7 points) Provide the IUPAC name for an alkane that is an isomer of C_7H_{14} and has the number 2 in its name but not the number 1.

The fact that the molecule is of the formula C_nH_{2n} and is an alkane necessitates that the molecule will have a ring. Any cycloalkane ring with two or more alkyl substituents must have one of those substituents with a locant of 1. The only way to avoid having the 1 as a locant is for the molecule to be named with the ring as a substituent of a linear alkane. Here, the only way for that to occur is for a smaller ring to be a substituent of a larger linear alkane. Since the molecule here only has seven carbon atoms and a three-membered ring is the smallest cycloalkane possible, the molecule must be 2-cyclopropylbutane.

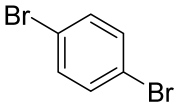
Note that 2-cyclobutylpropane is properly named isopropylcyclobutane, since the larger fragment takes precedence in terms of identifying the parent alkane.

Problem IV. Explanations (16 points). For each question posed below, write the letter of your answer in the box on the answer sheet and provide a brief explanation (of no more than four sentences) for your choice. You should draw out any relevant resonance forms if the concept factors into your explanation.

(1) (8 points) Of compounds **R** and **S**, which has the lower melting point?



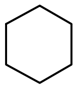
R



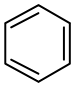
S

Compound **R**. Both compounds are symmetrical and have no net dipole moment, but the electron cloud for compound **S** is larger and more polarizable. As a result, the magnitude of the induced-dipole/induced-dipole (London) intermolecular forces in a sample of **S** will be greater than in a sample of **R**, and correspondingly, the melting point will be higher.

(2) (8 points) Of compounds **T** and **U**, which has the <u>lower</u> pK_a?



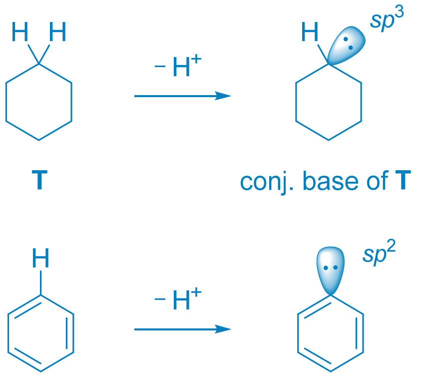
T



U

Compound **U**. The compound with the lower pK_a will be the stronger acid. The best way to gauge this acidity is by looking at the relative stability of the conjugate bases that result from removal of a proton from either compound. Here, the lone pair left behind on cyclohexane is located in an sp^3 orbital, whereas the lone pair left behind on benzene will be located in an sp^2 orbital. Orbitals will higher *s*-character are better at stabilizing negative charge density because s orbitals are more penetrating, and favorably place the (negative) electron density closer to the (positively charged) nucleus. Since the lone pair and residual negative charge are better stabilized for the conjugate base of **U** than **T**, **U** is a stronger acid and will have the lower pK_a.

Note that a resonance does not play a significant factor here. The lone pair in the conjugate base of **U** is in an sp^2 orbital that is perpendicular to the *p* orbitals in the π system of the aromatic ring. Orthogonal orbitals have no ability to delocalize electron density. Furthermore, while compound **U** does have two trivial resonance forms, its conjugate base has the same two resonance forms, so there is no significant difference that would help stabilize the conjugate base relative to the parent acid.



U conj. base of **U**