CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Quiz #2

Due: Friday, September 12th, 2014

6:00 p.m. (in 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.

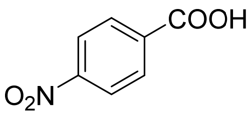
Problem	Points Earned	Points Available
I		30
II		20
III		14
IV		36
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) B

When a small sample of 4-nitrobenzoic acid (**A**) is dissolved in an aqueous solution buffered at pH 3.0, what percentage of the carboxyl groups (–COOH) will be deprotonated once an equilibrium has been established? Assume the pH of the solution does not change significantly over the course of the experiment.



pK_a = 3.4

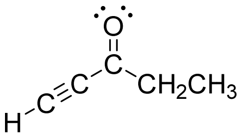
A

(a) 10%
(b) 28%
(c) 40%
(d) 60%
(e) 72%

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 = 3.0 and pK_a = 3.4, then solve for x to find x = 28.

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 3.0 < 3.4 to immediately eliminate choices (d) and (e).

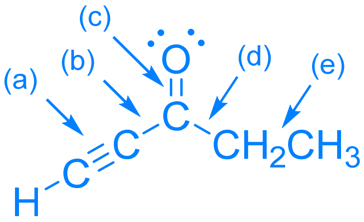
(2) F Which of the following pairs of orbitals do not interact to form any of the σ bonds in compound **B**, shown below.



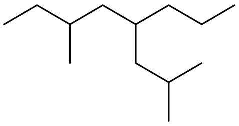
B

(a) an *sp*-hybridized orbital with an *sp*-hybridized orbital
(b) an *sp*-hybridized orbital with an sp^2-hybridized orbital
(c) an sp^2-hybridized orbital with an sp^2-hybridized orbital
(d) an sp^2-hybridized orbital with an sp^3-hybridized orbital
(e) an sp^3-hybridized orbital with an sp^3-hybridized orbital
(f) all of the above pairs of orbitals interact to form bonds in **B**

All five types of bonds are found in **B**:



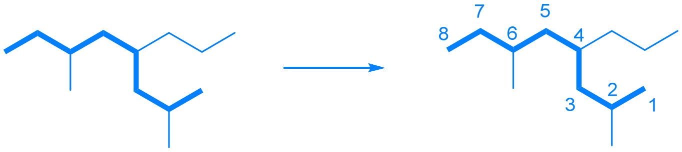
(3) A What is the systematic name of compound **C**?



C

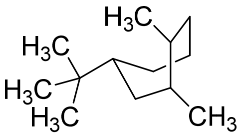
(a) 2,6-dimethyl-4-propyloctane
(b) 3-methyl-5-isobutyloctane
(c) 5-isobutyl-3-methyloctane
(d) 4-isobutyl-6-methyloctane
(e) 3,7-dimethyl-5-propyloctane

The first step is to identify the parent chain, which is the longest contiguous chain of carbons. There are three chains of eight carbons in alkane **C**. To break the tie among these chains, we pick the one (bolded) that has the most substituent groups (3):



Next, we number the chain from the end that gives the first substituent group on the chain the lowest locant number (here: 2 for methyl vs. 3 for methyl had we numbered starting on the opposite end). Next, we name the substituents, identify their locants on the chain, group them, and alphabetize them to give: 2,6-dimethyl-4-propyloctane. Note that "di-" "tri-", "tetra-", "penta-", etc. are ignored for alphabetizing the groups. The prefixes "*sec*-" and "*tert*-" are also ignored, but "iso-" does count for alphabetization.

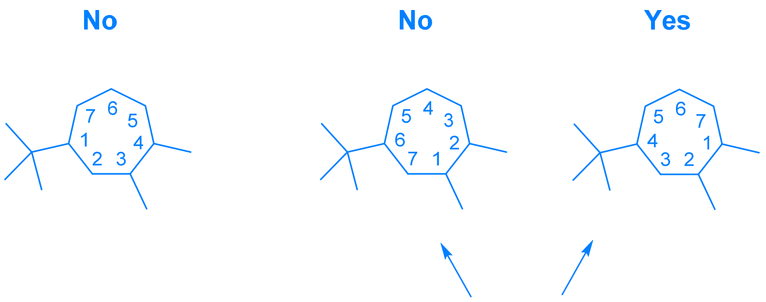
(4) C What is the systematic name of compound **D**?



D

(a) 1-*tert*-butyl-3,4-dimethylcycloheptane
(b) 1,2-dimethyl-4-*tert*-butylcycloheptane
(c) 4-*tert*-butyl-1,2-dimethylcycloheptane
(d) 1,2-dimethyl-6-*tert*-butylcycloheptane
(e) 3,4-dimethyl-1-isobutylcycloheptane

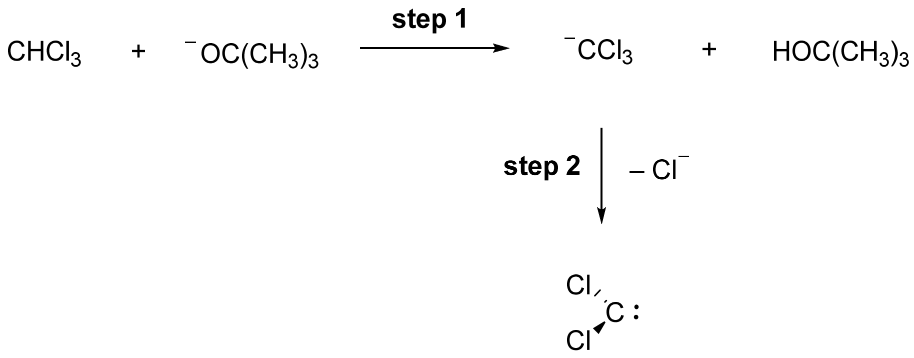
To name a substituted cyclic alkane, you first identify the size of the ring. Here, it is seven carbons, so we have a cycloheptane. Next, we number the ring to give the first substituent the lowest number (always a 1) and the second substituent the lowest number possible. If we start from the *tert*-butyl group, the closest methyl would be at the 3 position. If we start numbering at a methyl, the next methyl would be at a 2 position. We start at the methyl group shown and number in the direction shown so that the *tert*-butyl group is at the 4 position, not 6:



both numberings give the second substituent a lower locant number, but the right scheme is correct based on the tie-breaker of assigning the third substituent the lower locant number

Note that we are ignoring stereochemistry here. That will be covered in Chapter 5 of our text.

For questions 5 and 6, consider the following sequence of reactions.



(5) D In the first step, $CHCl_3$ is serving as

(a) a Brønsted–Lowry acid
(b) a Lewis acid
(c) a nucleophile
(d) both (a) and (b)
(e) (a), (b), and (c)
(f) none of the above

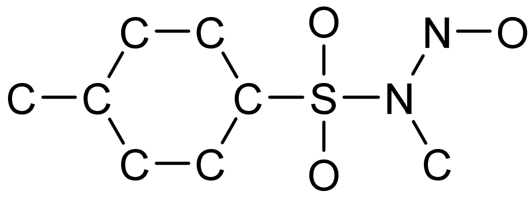
Chloroform is donating H^+ in this reaction, so it is serving as a Brønsted–Lowry acid and (a) is correct. All Brønsted–Lowry acids are also Lewis acids, so (b) is correct. Lewis acids are electrophiles (electron pair acceptors), not nucleophiles (electron pair donors), so (c) is incorrect.

(6) B What is the formal charge on the carbon atom in $:CCl_2$, the molecule drawn as the product of the second step?

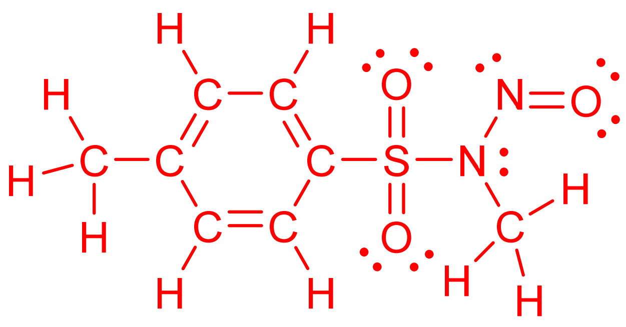
- (a) −1
- (b) 0
- (c) +1
- (d) this is an impossible "Rhode Island" carbon

The formal charge for an atom is calculated by subtracting the number of electrons the atom "owns" in the Lewis structure from the number of valence atoms expected for that element. We expect carbon ([He]$2s^2 2p^2$) to have four valence electrons. In the structure, it owns both of the electrons in the lone pair and one from each of the two covalent bonds to chlorine. The corresponding formal charge on carbon is zero (4−4 = 0).

Problem II. Lewis Structure (20 points). Complete the Lewis structure for compound **E**, shown below, which when treated with base, produces the highly explosive compound diazomethane (CH_2N_2). The compound has the molecular formula $C_8H_{10}N_2O_3S$. All of the hydrogen atoms in **E** are bonded to carbon atoms. Among other features, the compound has an aromatic ring and one atom with "expanded valence" that is surrounded by more than an octet of electrons. Explicitly include—i.e., draw out—all hydrogens, bonding pairs, lone pairs, and non-zero formal charges on your Lewis structure. The molecule has been started on your answer sheet.

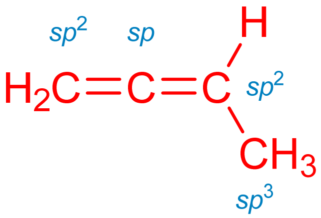


E

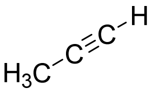


E

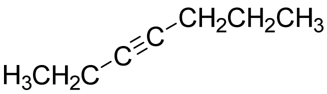
Problem III. Short Answer (14 points). Among all neutral (uncharged) organic molecules in which every carbon atom possesses a full octet of valence electrons, draw the structure of the smallest (by mass) compound that possesses at least one *sp*-hybridized carbon atom, one sp^2-hybridized carbon atom, and one sp^3-hybridized carbon atom. Your structure should not have any bond angles that deviate far from the ideal values for any particular hybridization of carbon.



Problem IV. Explanations (36 points). For each question posed below, write the letter of your answer in the box on the answer sheet and provide a brief explanation (no more than four sentences) for your choice. You should draw out any relevant resonance forms, if the concept factors into your explanation.



F



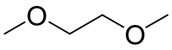
G

(1) (9 points) Of compounds **F** and **G**, which is the stronger acid?

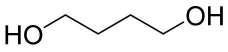
Compound **F** is the stronger acid. The relative acidity of two compounds is best judged by assessing the relative stability of the conjugate bases. The more stable (or less unstable) the conjugate base, the better we can expect the parent compound to serve as an acid. In compound **F**, the most acidic hydrogen is that of the terminal alkyne, as the anion of the conjugate base is located in a *sp*-hybridized orbital on carbon. In compound **G**, deprotonation can only occur from sp^3-hybridized carbons. While the carbanion can be delocalized by resonance, none of the resonance forms is as favorable as the single structure for the conjugate base of **F**. The extra negative charge density on the conjugate base of **F** is better stabilized by virtue of being held in an orbital with more *s*-character than for the conjugate base of **G**, since *s* orbitals are more penetrating than *p* orbitals and favorably place negative charge closer to the positively charged nucleus.

(2) (9 points) Of compounds **F** and **G**, which has the higher boiling point?

Higher boiling points are indicative of stronger intermolecular forces. The functional groups present in **F** and **G** are similar, and there is no large difference in the polarity of the molecules or bonds within the molecules. The key difference between the molecules is that **G** has additional methylene ($–CH_2–$ groups). This difference gives **G** a larger electron cloud with more surface area, enabling the generation of stronger London (induced dipole–induced dipole) forces between molecules.



H

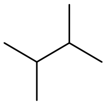


J

(3) (9 points) Of compounds **H** and **J**, which has the higher boiling point?

Higher boiling points are indicative of stronger intermolecular forces. Compounds **H** and **J** are isomers with the exact same number and type of atoms, but a different arrangement of bonds. The hydroxyl groups present in **J** enable hydrogen bonding—a particularly strong type of dipole–dipole interaction—among molecules. Similarly strong forces are absent among molecules of **H**, so we can expect **J** to have the higher boiling point.

K



M

(4) (9 points) Of compounds **K** and **M**, which has the higher boiling point?

Both **K** and **M** lack polar bonds, so London (induced dipole–induced dipole) forces are the dominant intermolecular force for both compounds. While **K** and **M** are isomers of each other and have the same mass, the less-branched (more cylindrical vs. spherical) structure of **K** gives its electron cloud more surface area than that of **M**. The greater surface area provides more opportunity for the induction of dipoles, so the London forces among molecules of **K** are greater, leading **K** to have a higher boiling point than **M**.