CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Hour Examination #1

Wednesday, September 16th, 2015

6:00–8:00 p.m. in Macelwane Hall 334

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.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes (on official paper) and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		30
II		16
III		14
IV		10
V		30
TOTAL		100

Questions, Required Information, Supplementary Information

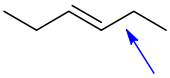
Problem I. Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) B What statement is <u>not</u> true of compound **A**?

A

(a) **A** has the highest boiling point of all its isomers
(b) **A** has the highest melting point of all its isomers
(c) **A** has 18 hydrogen atoms
(d) **A** is a saturated alkane
(e) **A** is an isomer of 4-methylheptane

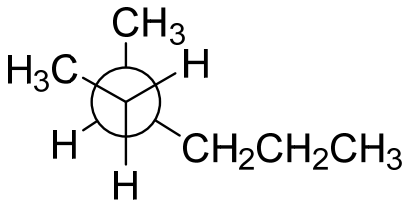
(2) D What type(s) of orbitals form the σ bond between the C2 and C3 carbon atoms in 3-hexene (**B**)? This bond is indicated with an arrow in the figure, below.



B

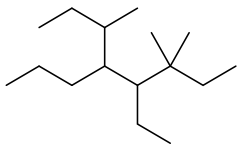
(a) sp^2 orbitals only
(b) sp^3 orbitals only
(c) *p* orbitals only
(d) both sp^2 and sp^3 orbitals
(e) sp^2, sp^3, and *p* orbitals

(3) A The Newman projection drawn below best represents which of the following?



(a) the most stable staggered conformation of 3-methylhexane
(b) the least stable staggered conformation of 3-methylhexane
(c) the most stable staggered conformation of 2-methylpentane
(d) the second-most stable staggered conformation of 2-methylpentane
(e) the least stable staggered conformation of 2-methylpentane

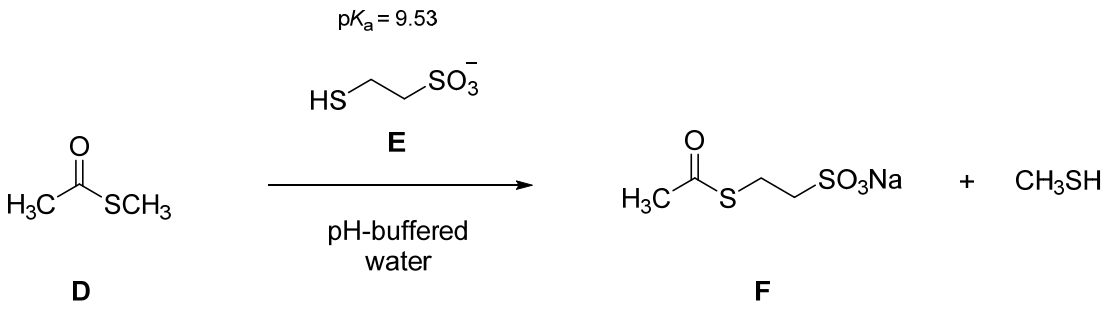
(4) C What is the systematic name of compound **C**?



C

(a) 5-ethyl-3,6,6-trimethyl-4-propyloctane
(b) 5-*sec*-butyl-4-ethyl-3,3-dimethyloctane
(c) 4-ethyl-3,3,6-trimethyl-5-propyloctane
(d) 4-*sec*-butyl-5-ethyl-6,6-dimethyloctane
(e) 4-ethyl-5-isobutyl-3,3-dimethyloctane

For question 5, consider the following reaction, the kinetics of which are governed by the stated rate law.



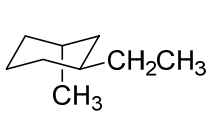
$$\text{rate} = k[^{-}SCH_2CH_2SO_3^{-}][\mathbf{D}]$$

- Note that the pK_a of thiol **E** is 9.53 and the concentration of the conjugate base of **E** appears in the rate law.

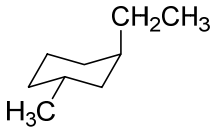
(5) E What effect will raising the pH from pH 3 to pH 4 have on the rate of this reaction, assuming the volume of the solution is held constant?

(a) the new rate will be approximately one-tenth the original rate
(b) the new rate will be approximately one-half of the original rate
(c) the rate will be approximately unchanged
(d) the new rate will be approximately double the original rate
(e) the new rate will be approximately 10 times the original rate

(6) A Which of the following structures represents the <u>most stable</u> conformation of *trans*-1-ethyl-3-methylcyclohexane?



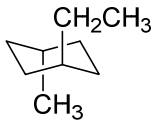
(a)



(b)

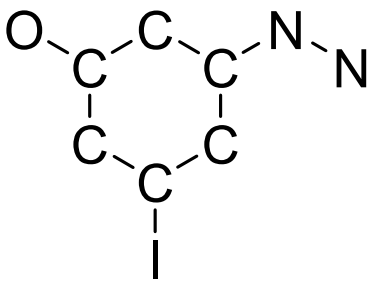
(c)

(d)

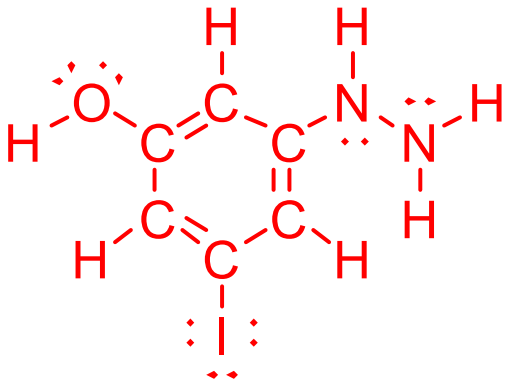


(e)

Problem II. Lewis Structure (18 points). Complete the Lewis structure for 3-hydroxy-5-iodophenylhydrazine (**G**) that has been started on your answer sheet. The compound has the molecular formula $C_6H_7IN_2O$ and no atom in the structure bears a formal charge. All atoms in the structure (aside from hydrogen) have full octets. All of the carbon atoms in the ring are sp^2-hybridized. Explicitly include—i.e., draw out—all hydrogens, bonding pairs, lone pairs, and non-zero formal charges on your Lewis structure.

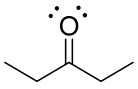


G



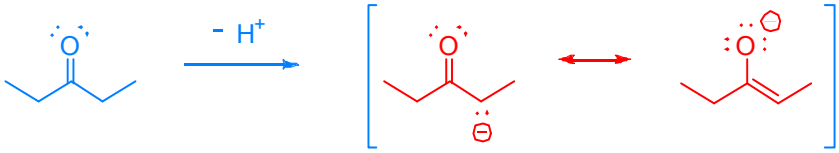
G

Problem III. Short Answers (14 points). Write your answers in the appropriate boxes on your answer sheet. Refer to the structure for 3-pentanone, compound **H**, below.

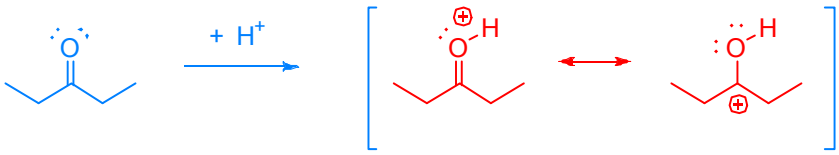


H

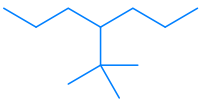
(1) (7 points) Draw the Lewis structure for the conjugate base of **H** (i.e., deprotonated 3-pentanone). If applicable, include all pertinent resonance structures for describing the electronic structure of the ion.



(2) (7 points) Draw the Lewis structure for the conjugate acid of **H** (i.e., protonated 3-pentanone). If applicable, include all pertinent resonance structures for describing the electronic structure of the ion.

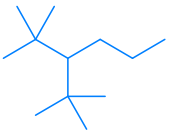


Problem IV. Isomers of Alkanes (10 points). Provide the systematic IUPAC name of the stable compound that is the smallest (by mass) acyclic, saturated hydrocarbon for which its systematic name contains the word "*tert*".



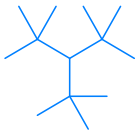
4-*tert*-butylheptane

$C_{11}H_{24}$



3-*tert*-butyl-2,2-dimethylhexane

$C_{12}H_{26}$

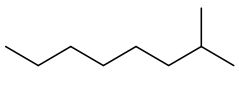


3-*tert*-butyl-2,2,4,4-tetraamethylpentane

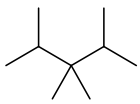
$C_{13}H_{28}$

Problem V. Explanations (30 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) (10 points) Of compounds **J** and **K**, which has the higher boiling point?



J

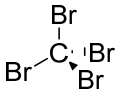


K

Compound **J**. Compounds **J** and **K** are isomeric alkanes with similar intermolecular forces. The less-branched structure of **J** will result in a greater surface area of exposed electron cloud for each molecule of **J** than **K**. Correspondingly, molecules of **J** will participate in stronger induced dipole–induced dipole (London or dispersion) forces and samples of **J** will have a higher boiling point.

(2) (10 points) Of tetrafluoromethane (**L**) and tetrabromomethane (**M**), which has the higher melting point?

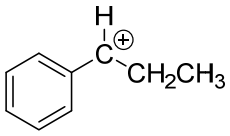
L



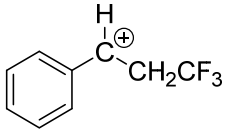
M

Compound **M**. Compounds **L** and **M** are structurally similar halocarbons with no net dipole moment. The key difference is that Br atoms have electron clouds that are considerably more polarizable than those for F atoms. This difference results in stronger induced dipole–induced dipole (London or dispersion) forces for samples of **M**, and correspondingly, a higher melting point.

(3) (10 points) Of carbocations **N** and **P**, which is more stable?



N



P

Carbocation **N**. While both of these carbocations are stabilized by a resonance effect due to the adjacent phenyl ring, the key difference is the presence of a methyl group (in **N**) vs. a trifluoromethyl group (in **P**). The electronegative fluorine atoms withdraw negative charge density from their neighboring atoms, exacerbating the positive charge borne by the carbon, and thus, destabilizing **P** by an inductive effect.