

## CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

# Hour Examination #1

Wednesday, September 17<sup>th</sup>, 2014

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	Solutions
Student Signature	N/A

## Instructions & Scoring

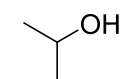
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes and your plastic model kit. No electronic resources are permitted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

Problem	Points Earned	Points Available
I		30
II		18
III		18
IV		34
TOTAL		100

Questions, **Required Information**, **Supplementary Information**

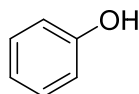
**Problem I.** Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

- (1)       <sup>D</sup> Which of the following compounds will not be deprotonated (to *any* extent) by Sodium methoxide ( $\text{CH}_3\text{O}^-/\text{Na}^+$ )? The  $\text{p}K_a$  of each compound is listed below, and the  $\text{p}K_a$  of protonated methoxide (methanol,  $\text{CH}_3\text{OH}$ ) is 15.5.



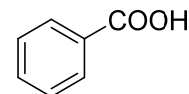
$\text{p}K_a = 16.5$

(a)



$\text{p}K_a = 10.0$

(b)



$\text{p}K_a = 4.2$

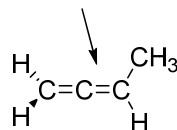
(c)

none of the above

(d)

The point of this problem is to emphasize that acid–base reactions are governed by  $\text{p}K_a$  values that describe equilibria. Just because only 1 out of 10 or 100 or 1,000 or 10,000 molecules will be deprotonated doesn't necessarily mean this deprotonation is insignificant. In the cases above—with OH groups—you will reach equilibrium quickly. If you were trying to deprotonate a very, very weak acid, e.g. an alkane with  $\text{p}K_a = 50$ , there will probably be a massive kinetic barrier to deprotonation so you essentially don't see any of it (and don't reach equilibrium quickly).

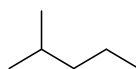
- (2)     D     What types of orbitals are involved in the indicated connection between the second and third carbon atoms of 1,2-butadiene (**A**)?

**A**

- (a) only  $sp$ -hybridized orbitals  
 (b) only  $sp^2$ -hybridized orbitals  
 (c)  $sp$ -hybridized and  $sp^2$ -hybridized orbitals  
 (d)  $sp$ -hybridized,  $sp^2$ -hybridized, and unhybridized  $p$  orbitals  
 (e)  $sp$ -hybridized,  $sp^2$ -hybridized, and  $sp^3$ -hybridized orbitals  
 (f)  $sp$ -hybridized,  $sp^2$ -hybridized,  $sp^3$ -hybridized, and unhybridized  $p$  orbitals

The indicated double bond is between an  $sp$ -hybridized carbon atom and an  $sp^2$ -hybridized carbon atom. Thus, the  $\sigma$  bond is created by the overlap of an  $sp$  orbital with an  $sp^2$  orbital. The  $\pi$  bond is formed by the overlap of an unhybridized  $p$  orbital on each atom.

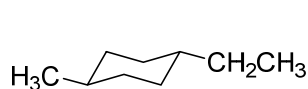
- (3)     D     What statement is not true of compound **B**?

**B**

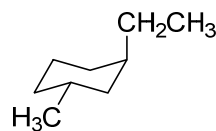
- (a) **B** is a saturated hydrocarbon  
 (b) **B** is named 2-methylpentane  
 (c) **B** can serve as a Brønsted–Lowry acid  
 (d) **B** has at least one isomer that contains a cycloalkane ring  
 (e) **B** is polar (has a non-zero net dipole moment)

Compound **B** is saturated because it has no  $\pi$  bonds. It can serve as a Brønsted–Lowry acid because it has hydrogen atoms—although it is an extraordinarily weak acid. **B** is polar—albeit, again, very weakly polar—because it is not perfectly symmetrical. **B** ( $C_6H_{14}$ ) does not have an isomer that is a cycloalkane, because it would have two fewer H atoms per ring, meaning the molecular formula would be different from  $C_6H_{14}$ .

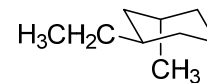
- (4)     C     Which of the following structures represents the most stable conformation of *trans*-1-ethyl-3-methylcyclohexane?



(a)



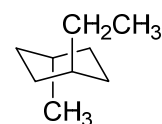
(b)



(c)



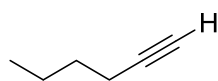
(d)



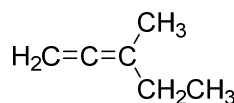
(e)

Structure (d) is not a *trans* compound (having the two substituents on opposite sides of the ring). Structures (a) and (e) are 1,4-substituted, not 1,3-substituted. Structures (b) and (c) both represent *trans*-1-ethyl-3-methylcyclohexane, but (c) is more stable because the larger substituent (ethyl) occupies an equatorial rather than axial position. This configuration minimizes unfavorable steric interactions between the substituent and atoms in the ring.

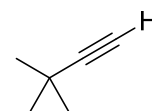
- (5)     E     Which structure drawn below represents the most acidic hydrocarbon of molecular formula  $C_6H_{10}$  that also has a single tertiary carbon atom?



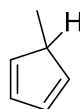
(a)



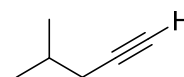
(b)



(c)



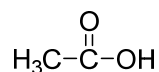
(d)



(e)

Structure (d) is not an isomer of  $C_6H_{10}$ . The hydrogens bonded to  $sp$ -hybridized carbons will be the most acidic protons among these compounds, with  $pK_a \approx 25$ . Of these, only compound (e) has a  $3^\circ$  carbon—a carbon bonded to three other carbons.

(6)     C     What statement is not true of acetic acid (**C**,  $H_3CCOOH$ )

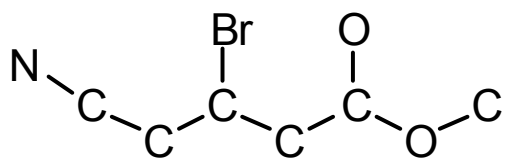
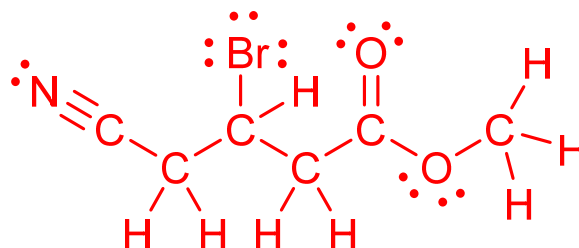


**C**

- (a) **C** has an  $sp^3$ -hybridized carbon atom
- (b) the conjugate base of **C** is stabilized by a resonance effect
- (c) trichloroacetic acid ( $Cl_3CCOOH$ ) acid has a higher  $pK_a$  than **C** due to an inductive effect
- (d) the bond angles around the carbon bonded to oxygen are close to  $120^\circ$
- (e) molecules of **C** are capable of hydrogen bonding

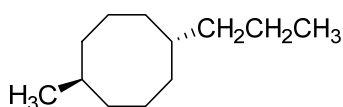
The methyl carbon in **C** is  $sp^3$ -hybridized. The conjugate base of **C**, acetate, has two major resonance forms in which the extra negative charge density is placed on either oxygen atom. The bond angles around the carbonyl carbon atom are close to  $120^\circ$  because it is  $sp^2$ -hybridized. The presence of an H atom bonded to an atom of relatively high electronegativity means that molecules of **C** are capable of both donating and accepting hydrogen bonds. Trichloroacetic acid is more acidic than **C** because the presence of the electronegative chlorine atoms helps stabilize the extra negative charge density in the conjugate base by an inductive effect. Thus, trichloroacetic acid will have a lower  $pK_a$  than acetic acid.

**Problem II.** Lewis Structure (18 points). Complete the Lewis structure for the ester methyl 3-bromo-4-cyanobutanoate (**D**) that has been started on your answer sheet. The compound has the molecular formula  $C_6H_8BrNO_2$  and no atoms in the structure bear a formal charge. There are no C–C  $\pi$  bonds in the structure. All atoms in the structure (aside from hydrogen) have a full octet. Explicitly include—i.e., draw out—all hydrogens, bonding pairs, lone pairs, and non-zero formal charges on your Lewis structure.

**D****D**

**Problem III.** Short Answers (18 points). Write your answers in the appropriate boxes on your answer sheet.

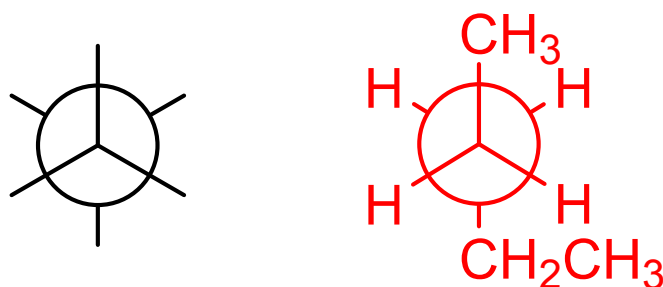
(1) (9 points) Provide the systematic name for compound **E**.

**E**

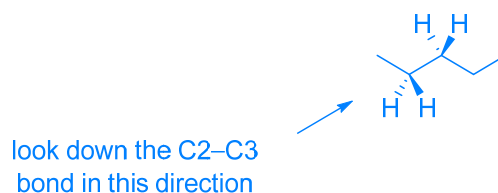
*trans*-1-methyl-5-propylcyclooctane

Note that regardless of whether you begin numbering at the methyl or the propyl carbon on the ring, one substituent will have a locant of 1 and the other will have a locant of 5. The tie-breaker that gives the methyl group the 1 is that 'methyl' comes earlier alphabetically than 'propyl'.

(2) (9 points) Draw a Newman projection of the most stable conformation of pentane ( $C_5H_{12}$ ) while “looking down” the C2–C3 bond (the bond between the second and third carbon atoms of the chain). The drawing has been started for you on your answer sheet.



This is pentane:



Note that you want to place the relatively large methyl and ethyl substituents *anti* to each other to minimize their unfavorable steric interaction.

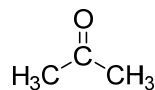
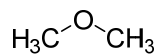
**Problem IV.** Explanations (34 points). For each question below, provide a brief explanation of no more than four sentences. For questions 1 and 2, also write the letter of your selection in the box on the answer sheet. You should draw out any relevant resonance forms, if the concept factors into your explanation.

(1) (9 points) Of compounds **F** and **G**, which has the higher solubility in water?

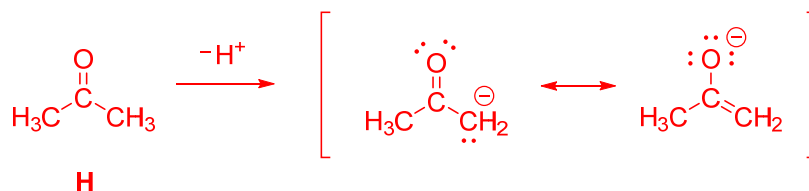


Water molecules are quite polar, and correspondingly, water will serve as a good solvent for polar and ionic compounds. While both **F** and **G** are alkyl amines, the N–H bonds in **F** allow it to both donate and accept hydrogen bonds with water, whereas the nitrogen in **G** can only accept hydrogen bonds. The two extra (hydrophobic) ethyl groups in **G** also require more energetically unfavorable solvation by water. Compound **F**, ethylamine, will have the higher solubility.

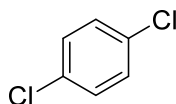
(2) (9 points) Of compounds **H** and **J**, which is the stronger acid?

**H****J**

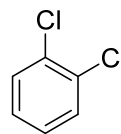
To compare the relative acidity of the compounds, we should compare the relative stability of their conjugate bases (the species you get following deprotonation). The conjugate base of compound **J** has a formal charge on the terminal carbon atom that is partially stabilized by the adjacent electronegative oxygen atom via an inductive effect. In the case of **H**, the extra negative charge on the conjugate base can be delocalized onto the oxygen atom via a resonance effect. This delocalization, especially onto a relatively electronegative oxygen atom that can better stabilize negative charge than carbon, explains why **H** is a stronger acid.

**H**

(3) (8 points) Provide an explanation for why 1,2-dichlorobenzene (**M**) has a higher boiling point but a lower melting point than 1,4-dichlorobenzene (**K**).



b.p. = 173 °C  
m.p. = 52 °C

**K**

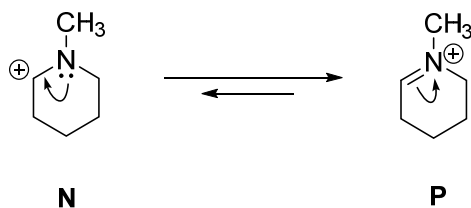
b.p. = 178 °C  
m.p. = -18 °C

**M**

The higher boiling point of **M** suggests stronger intermolecular forces for **M** than **K**. These can be attributed to the net dipole moment present in **M** and absent in **K**. While melting points also depend on the strength of intermolecular forces, they also depend on how well the molecules pack into a crystalline lattice. While the intermolecular forces are similar for both molecules, **K** packs better into lattices because it is more symmetrical than **M**.



(4) (8 points) Explain what is wrong with the following figure.



The cations **N** and **P** are not different compounds; they are resonance structures used to describe the electronic structure of the same species. As such, it makes no sense to view these structures as if they were in equilibrium. The use of the double arrows is inappropriate; they should be replaced by a single double-headed arrow ( $\leftrightarrow$ ).

Note that there is nothing wrong with:

- this use of curved arrows to “push electrons”
- the bond angles of the nitrogen in structure **N**. The point of resonance structures is that the atoms do not move—just the distribution of electrons.
- Structure **P**. This structure is favorable—even though nitrogen bears the positive formal charge—because every atom is given a full octet.