

Rogers

CHEM 221 - ORGANIC CHEMISTRY I MIDTERM EXAMINATION

INSTRUCTIONS: PLEASE READ THIS PAGE WHILE WAITING TO START YOUR EXAM.

This test paper includes 3 pages (both sides) plus a periodic table including electronegativity data; **note that a table of pK_a values is provided** on the back of the periodic table. Check that your paper is complete. You can remove the last page if you wish. Model kits and calculators are permitted; cell phones and electronic dictionaries are not allowed. You have the whole class (75 minutes) to complete the test. Read through the whole test quickly before starting. **GOOD LUCK!**

LAST NAME: marking scheme FIRST NAME: _____

STUDENT NUMBER: _____

Mark breakdown:

Average grades:

Page 2.	8.4 / 12	70%
Page 3.	12.0 / 17	70%
Page 4.	7.3 / 10	73%
Page 5.	6.0 / 12	50%

TOTAL: 33.7 / 50 (maximum grade ⁵¹/50)

PERCENT: 67.3 %

EARNED toward
FINAL GRADE: 10.1 / 15

I was very pleased with these...
← ...but quite disappointed here. Please work on explaining why phenomena are observed, rather than just summarizing what is observed.

1. (7 marks) TRUE or FALSE? Circle T or F to describe the following statements.

- T / F The C-Br bond in bromoethane can be described as involving $2sp^3-3sp^3$ orbital overlap.
 \uparrow
 no ($n=4$ for Br)
- T / F In Kekulé structures, H atoms bonded to heteroatoms are included but lone pairs are not included.
 \rightarrow like Lewis but without lone pairs
- T / F Resonance delocalization can occur if two π -bonds are separated by an sp^3 -hybridized C atom.
 no p orbital
- T / F Any molecule or atom described as a Brønsted base can also be described as a Lewis base.
- T / F When assigning E/Z configuration, a $-C\equiv CH$ group has higher priority than a $-CH(CH_3)_2$ group.
 $\begin{array}{c} \text{---} \\ \text{C} \\ \text{---} \\ \text{---} \end{array} \quad \begin{array}{c} \text{---} \\ \text{C} \\ \text{---} \\ \text{H} \end{array}$
- T / F At room temperature, an alkene is able to rotate about its π -bond but it cannot isomerize.
 no
- T / F The most acidic H in any molecule is the H that is held to the molecule by the weakest bond.
 \rightarrow leads to formation of most stable conjugate base. no.

2. (1 mark) Which of the following species are examples of tertiary amines? Circle your choice(s).

- a) $(CH_3)_3CNH_2$
 b) $(CH_3)_3N$
 c) $(CH_3)_2N(CH_2CH_3)$
 d) $(CH_3)_3NHCl$
- b 0.5
 c 0.5
 d 0.5

3. (1 mark) M.O. theory states that when two atomic orbitals overlap, two new orbitals form. They are:

- a) a lower energy bonding orbital & a higher energy nonbonding orbital no
 b) a lower energy bonding orbital & a higher energy antibonding orbital
 c) a lower energy σ orbital & a higher energy π orbital no
 d) a lower energy σ^* orbital & a higher energy σ orbital
 no

4. (1 mark) The larger the number of closed-shell resonance contributors that can be drawn for a species, the more _____ the species is. Choose the correct word to complete this statement.

- a) hybrid
 b) unstable
 c) reactive
 d) stable
- d

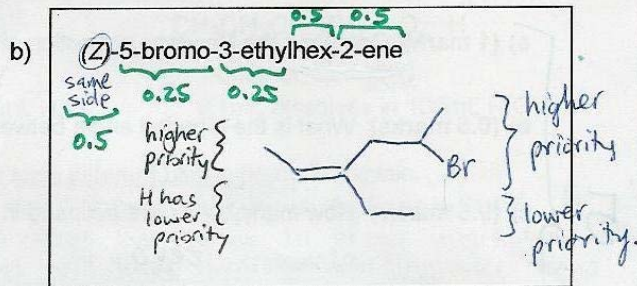
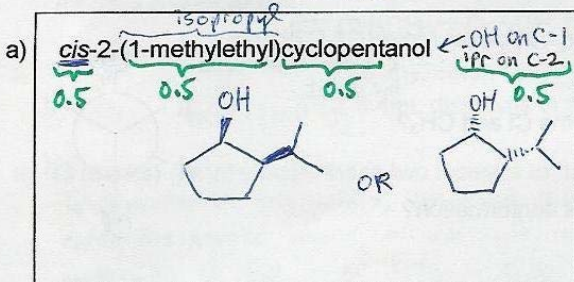
5. (2 marks) Which of the following bases would be strong enough to deprotonate $CH_3-C\equiv CH$?

- a) $(CH_3)_3CO^-$ $(CH_3)_3COH$ 19
 b) CH_3COO^- CH_3COOH 4.7
 c) $(CH_3)_2CHNH^-$ CH_3NH_2 similar 40
 d) HCO_3^- H_2CO_3 6.4

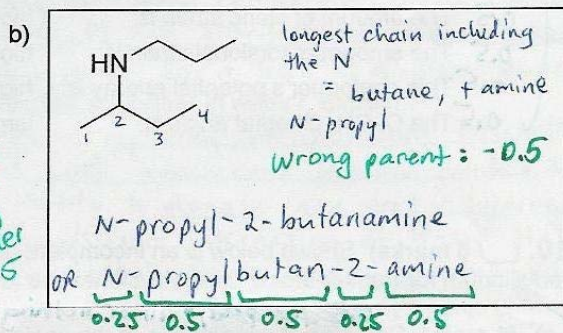
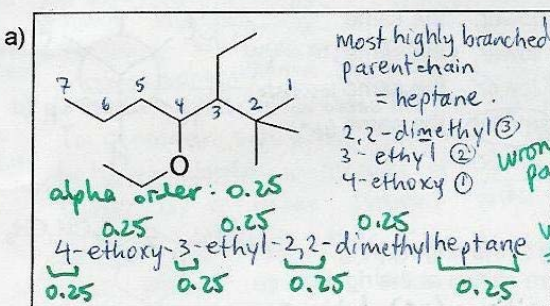
$pK_a \sim 25$
 similar to $HC\equiv CH$

pK_a of conjugate acid must be higher than pK_a of H you want to remove.

6. (4 Marks) Draw a line (skeletal) structure for each of the following compounds:



7. (4 Marks) Provide a systematic IUPAC name for each of the following compounds:



8. (9 marks) There are six isomers with the formula C_4H_8 .

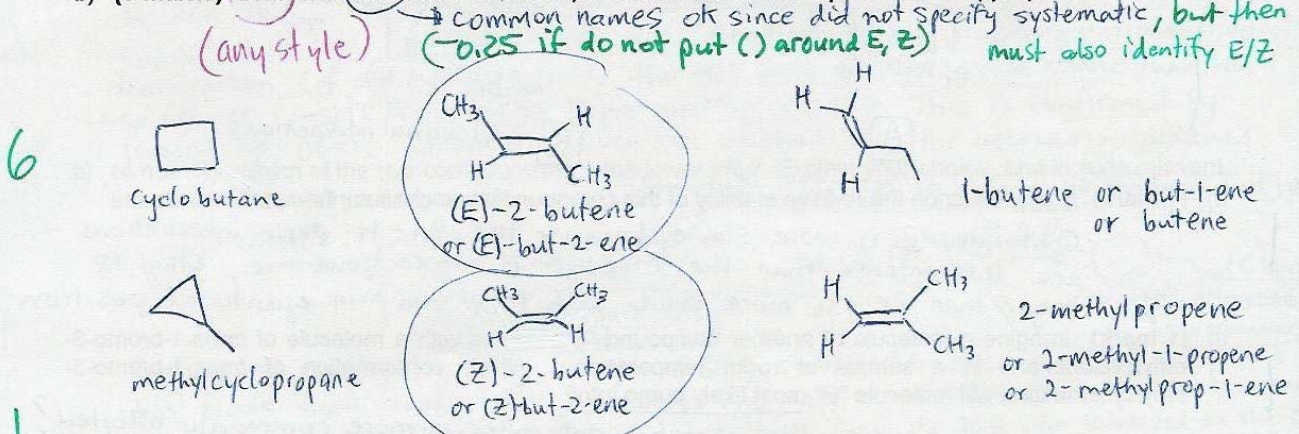
a) (2 marks) Calculate the number of elements (degrees) of unsaturation present in these isomers. What does this mean?

2

$$\text{degree of unsaturation} = \frac{2C + 2 - H}{2} = \frac{2(4) + 2 - 8}{2} = 1$$

Means: Every isomer has either 1 ring or 1 π -bond in it (it is "missing" 2H's compared to an alkane)

b) (6 marks) Draw and name all six isomers, and include E/Z descriptors where appropriate.



c) (1 mark) Two of the compounds in part (b) are geometric isomers of each other. Circle this pair.

1

17

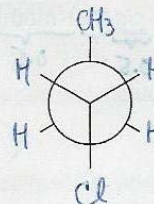
↳ cis/trans isomers of alkenes...
the E isomer above is trans-2-butene
the Z isomer above is cis-2-butene



9. (5 marks) Think about the conformation of 1-chloropropane in which the Cl and CH₃ groups are anti.

a) (1 mark) Complete the Newman projection of this conformer (down C1-C2 bond):

C-1 should be in the front.



b) (0.5 marks) What is the dihedral angle between the Cl and CH₃?

180°

c) (0.5 marks) How many bonds are eclipsed in this conformation?

zero

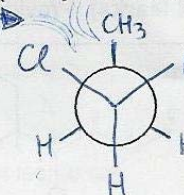
d) (3 marks) Imagine the molecule rotates 120° about its C1-C2 bond. Draw the new conformation's Newman projection (use the circle below) and complete the following statements (circle your choices):

0.5 The amount of steric strain is: higher, lower, the same

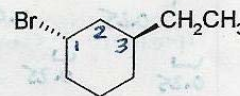
0.5 The amount of torsional strain is: higher, lower, the same (no eclipsed bonds)

0.5 This conformer's potential energy is: higher, lower, the same

0.5 The Cl-CH₃ dihedral angle is: larger, smaller, the same 60°



10. (5 marks) Shown below is an incomplete drawing of the ring-flipping equilibrium for *trans*-1-bromo-3-ethylcyclohexane (structure shown at the right).

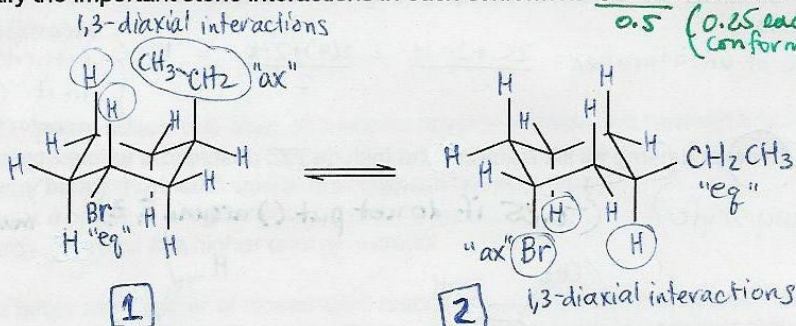


a) (1 mark) Complete the structures of the conformers by adding the hydrogens and substituents. Br and CH₂CH₃

b) (1 mark) Label the substituents as axial ("ax") or equatorial ("eq") in each conformer.

c) (1 mark) Identify the important steric interactions in each conformer. Circle the substituents involved.

name
0.5



d) (1 mark) Briefly describe the relative stability of this compound's two chair conformers.

Conformer **2** is more stable because the Br-H steric interactions are less intense than the CH₂CH₃-H interactions i.e., ethyl is larger than Br, so more stable with ethyl group in equatorial position.

e) (1 mark) Imagine a molecule of another compound "B" collides with a molecule of *trans*-1-bromo-3-ethylcyclohexane in a sample at room temperature. Which conformation of *trans*-1-bromo-3-ethylcyclohexane will molecule "B" most likely bump into?

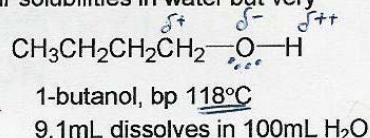
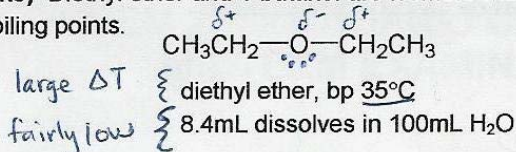
i.e.: which conformer is more commonly adopted?

Ans: the more stable conformer, with ethyl group equatorial, is the conformation that most molecules will be found in ∴ most likely for another molecule (B) to collide with.

10

X = 0.5 marks

11. (6 marks) Diethyl ether and 1-butanol are isomers with similar solubilities in water but very different boiling points.



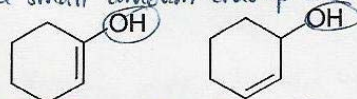
a) (3 marks) What causes these two isomers to have such different boiling points? Explain.

3
 To consider boiling points, we must think about a pure sample of each compound. To enter the vapour phase, a molecule must break away from all of its interactions with molecules of the same kind. 1-butanol will have hydrogen bonding interactions as its strongest ~~force~~ intermolecular force, whereas diethyl ether will have dipole-dipole interactions as its strongest intermolecular force; both molecules have similar van der Waals forces since their alkyl chains are similar (total # C is same, with no branching). Because H-bonds are stronger than d-d interactions, more energy is required for butanol to vaporize, so it boils at a higher temperature.

b) (3 marks) What causes these two isomers to have similar solubilities in water? Explain.

3
 To consider solubility, we must think about replacing intermolecular interactions between ~~similar~~ molecules of same kind with interactions between solute + solvent. Water is a polar solvent with the ability to donate and accept hydrogen bonds. Diethyl ether can accept H-bonds via interaction of H_2O 's $\text{H}^{\delta+}$ atom with ether's oxygen's lone pairs, but the alkyl chains have only weak vdw forces by which they can interact with water; overall, ether is only slightly soluble in water. Butanol is also only slightly soluble, even though it can both donate + accept H-bonds; the 4C chain requires so many H_2O molecules to interact via vdw forces rather than $\text{H}_2\text{O}-\text{H}_2\text{O}$ H-bonds that only a small amount ends up dissolving.

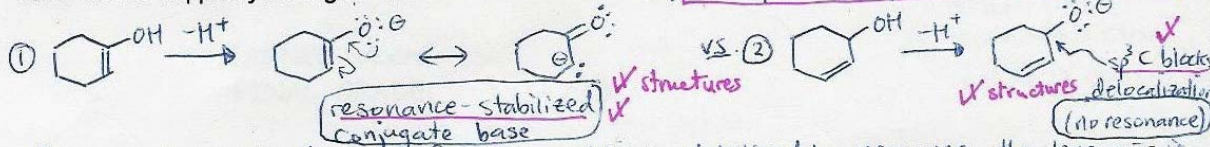
12. (6 marks) Two isomeric cyclohexenyl alcohols are shown here:



a) (2 marks) Which is the most acidic H in each molecule? Why?

2
 For both molecules, the hydroxyl H is the most acidic H. All other H's are bonded to C. The H that leads to the most stable conjugate base is the easiest H to lose (ie: most acidic H). Because oxygen is more electronegative than carbon (of any hybridization), the $-\text{O}^-$ anion would be more stable than the $-\text{sp}^3\text{C}^-$ or $-\text{sp}^2\text{C}^-$ formed by deprotonating at a C-H. This is confirmed by looking up pK_a s, which are lower for alcohols than for alkenes or alkanes.

b) (4 marks) Which of the two compounds has the lower pK_a ? Explain your choice, and include relevant structures to support your arguments.



12
 Because the conjugate base of compound 1 is stabilized by resonance, the lone pair is less reactive than usual (it is delocalized over many atoms rather than localized on the one oxygen atom). Compound 2's conjugate base has its lone pair localized on the O because of the sp^3C atom that separates the π system from the oxygen atom, which prevents delocalization. Thus, 2's conjugate base has a more reactive lone pair than 1's conjugate base, so 2's anion is a stronger base. This means it is better at carrying protons than 1's anion, so 2 is a weaker acid. Thus: 1 is more acidic \therefore has lower pK_a .