Easily Legible Printed Name:
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CHEM 3351 (100), Fall 2015 Professor Walba First Hour Exam September 22, 2015

- 1) 20
- 2) 20
- 3) 20
- 4) 20
- 5) 20

100

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Signature: Key

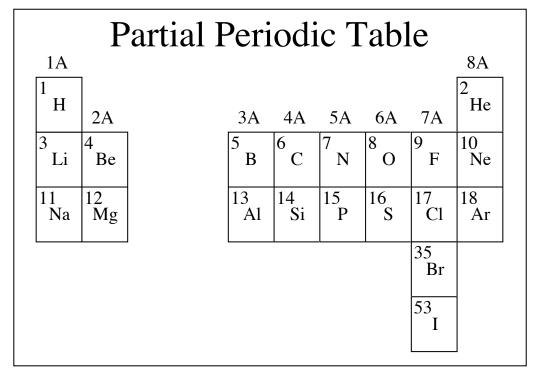
Recitation TA Name:

Recitation day and time:

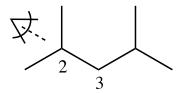
This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear Ziploc bag. Please put all your answers on the test in the appropriate place. Use the backs of the pages for scratch (there are two additional blank scratch sheets after the last page of the exam). DO NOT PUT ANSWERS ON THE SCRATCH SHEETS.

## PLEASE read the questions very carefully!

## PLEASE legibly print your name on each page of the exam.

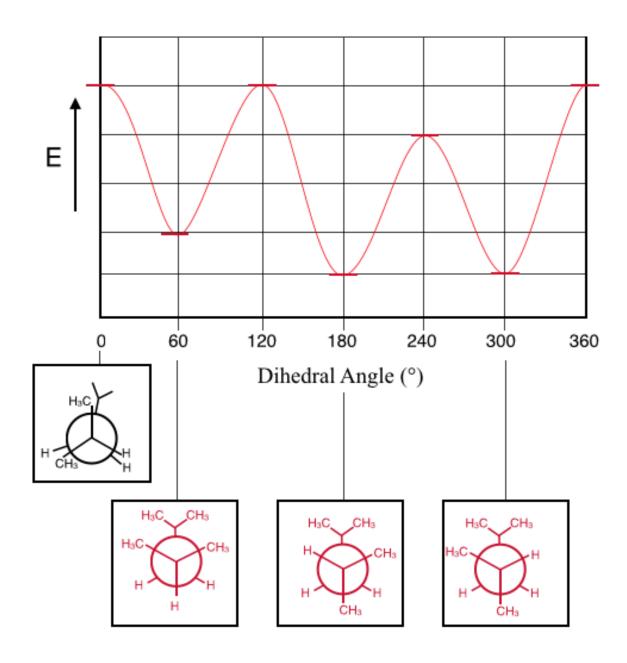


1 (20 pts) a) For 2,4-dimethylpentane (structure shown at right), let the eclipsed conformation shown in the Newman projection on the energy diagram below be defined as the 0° dihedral angle.



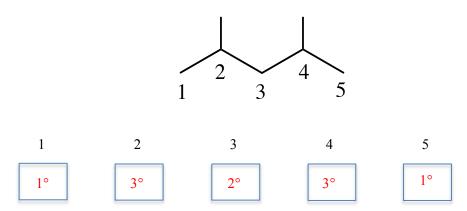
Draw Newman projections of the three **staggered** conformations of 2,4-dimethylpentane sighting down the C2-C3 bond, in the boxes. Please **rotate the front carbon clockwise** moving from 0° to 60°, 180°, and 300°.

Complete the energy diagram by indicating the relative energy of **all** the conformations (eclipsed, staggered, and everything in between) in the rotation from  $0^{\circ}$  to  $360^{\circ} = 0^{\circ}$  using a smooth curve.

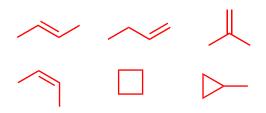


1- continued

b) Give the degree of substitution  $(1^{\circ}, 2^{\circ}, 3^{\circ}, \text{ or } 4^{\circ})$  for carbons 1 - 5 (the main chain) of 2,4-dimethylpentane.



c) Draw skeletal structures (molecular graphs NOT showing the hydrogens) of all possible isomers (constitutional isomers and stereoisomers) for hydrocarbons with the molecular formula  $C_4H_8$ . Draw each isomer only once. Points will be deducted for missing structures, and for drawing the same structure more than once.

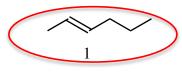


2) (20 pts) Draw skeletal structures of the following compounds carefully showing stereochemistry where appropriate.

- a) 2-Chlorobutane
- b) (E)-2-Bromo-3,4-dimethyl-2-pentene
- c) (Z)-2-Chloro-2-butene

- d) (E)-4-Isopropyl-4-octene
- e) 3-Bromo-5-chloro-2-methylheptane
- f) Isobutylcyclohexane

2f) For the pair of isomers indicated below, circle the molecular structure of the isomer with the highest standard heat of formation ( $\Delta H_F$ ).





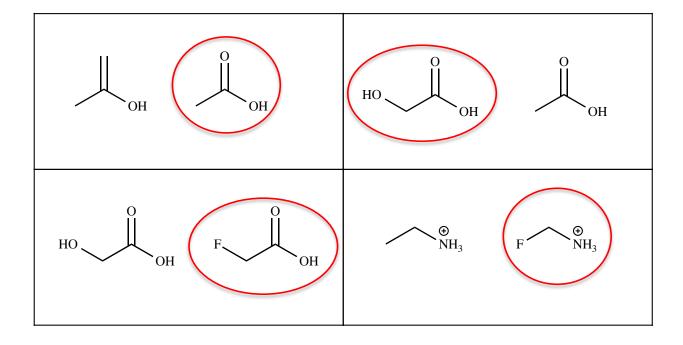
- g) Which isomer in part 2f) is more stable, 1 or 2?
- 2

h) Give a very brief explanation (it has to fit in the box below) for **why** your choice in part 2g) is more stable.

Isomer 2 is more stable than isomer 1 because it has more  $sp^2-sp^3$  bonds (stronger bonds), and fewer  $sp^3-sp^3$  bonds (weaker bonds). The  $sp^2-sp^3$  bonds are stronger because the  $sp^2$  orbitals are smaller (more s character), and make shorter bonds. Shorter bonds are stronger.

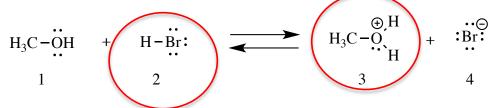
3) (20 pts) a) For each of the following structures, indicate the correct formal charge on each atom (following normal convention, don't indicate "0" on an atom if it has no formal charge). Assume **all** valence electrons are shown.

b) For each of the following pairs of compounds, circle the stronger Brønsted acid.



4) (20 pts) a) With regard to the following equilibrium

equation:



- i. Circle the molecules acting as Brønsted acids.
- ii. Which acid is stronger? (Use the compound number in the equation to indicate your choice).

2

iii. Does the equilibrium favor the starting materials or the products?

**Products** 

iv. Give the **major** reason why the stronger acid is stronger (e.g. "compound x is the stronger acid because...).

Compound 2 (HBr) is a stronger acid than  $H_3O^+$  due to the weak H-Br bond, which dominates the charge effect that makes  $H_3O^+$  a stronger acid than  $H_2O$ .

b) With regard to the following equilibrium equation:

- i. Circle the molecules acting as Brønsted acids.
- ii. Which acid is stronger? (Use the compound number in the equation to indicate your choice).

3

iii. Does the equilibrium favor the starting materials or the products?

Starting materials

iv. Give the **major** reason why the stronger acid is stronger (e.g. "compound x is the stronger acid because...).

Compound 3 ( $H_3O^+$ ) is a stronger acid than  $NH_4^+$  because oxygen is more electronegative than nitrogen, making the  $H_3O^+$  less stable than the  $NH_4^+$ .

5) (20 pts) a) Give the structure of the major product obtained in the following reaction.

b) Propose an arrow-pushing mechanism for the reaction in part 5a) above.

Each of the following reactions proceeds in one step, with no reactive intermediates involved. Propose an arrow-pushing mechanism for each reaction.

c) 
$$-C \equiv C$$
: +  $\stackrel{\cdots}{\longrightarrow}$   $\stackrel{\cdots}{\longrightarrow}$  + :Br:  $\stackrel{\cdots}{\longrightarrow}$ 

$$-C \equiv C: \qquad \qquad + : Br: \qquad \qquad + :$$

## 5 – continued

d) 
$$O: H + O: H$$