CHEM 3311
Dr. Minger

Hour Exam #2
June 21, 2022

Name Key
PRINT CLEARLY

Put a check by your recitation section:

___ 111 Charlie

___ 112 Joy

___ 113 Alan

___ 114 Claire

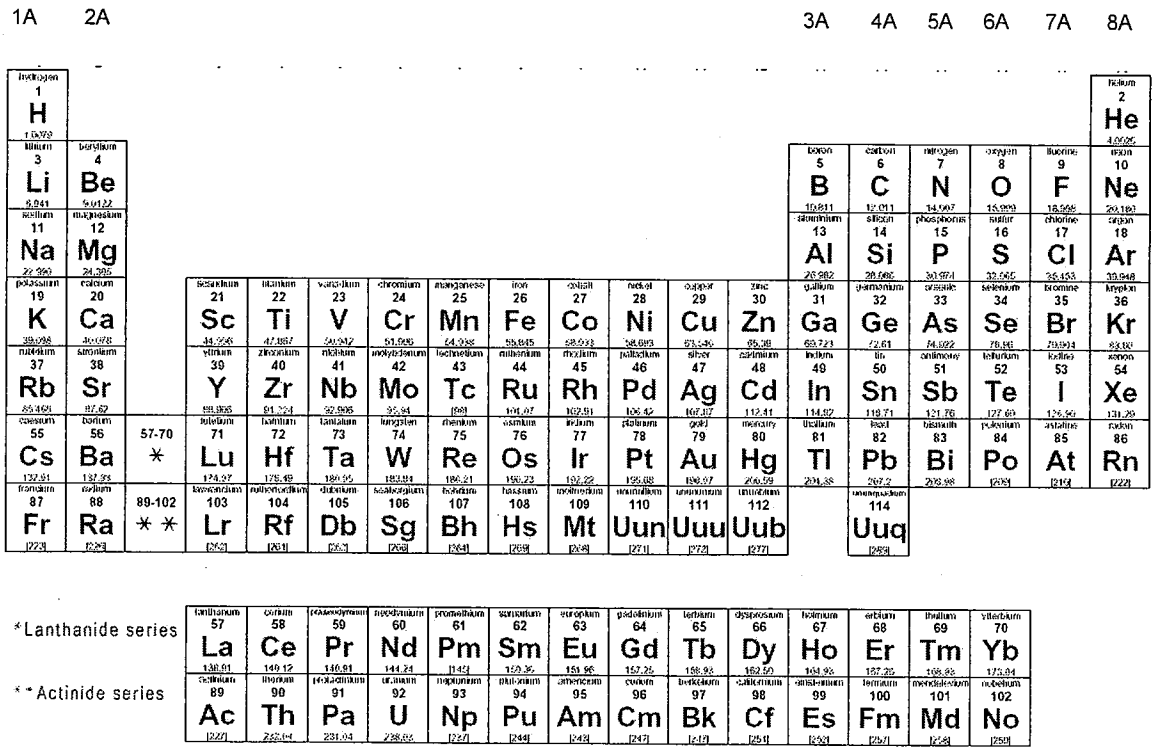
___ 115 Garrett

Sign the Honor Code pledge:

I pledge that on my honor, as a University of Colorado at Boulder student, I have neither given nor received unauthorized assistance on this exam.

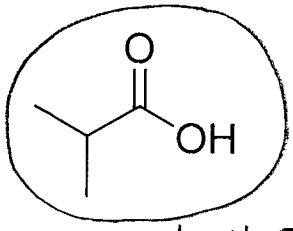
_____
Signature

Instructions and a periodic table are on the other side of this page.
Please read the instructions carefully!

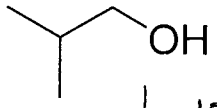


General Instructions: There are 10 questions plus one extra credit question for a total of 11 questions (some have multiple parts). Be sure you have them all. Read each question carefully so that you know exactly what is being asked and what you need to write or draw. DO NOT USE COLORED INK. (You can use highlighters.) Your work on scratch pages will not be graded, so be sure everything you want graded is written on the exam itself and in the spaces provided for answers.

1. Circle the stronger acid. (Lone pairs are omitted; all atoms are neutral.) (5 pts)

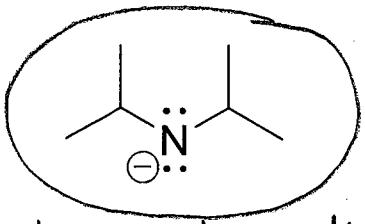


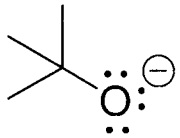
pka 4-5



pka 15-18

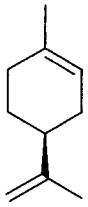
2. Circle the stronger base. (Lone pairs and charges are shown; counter ions have been omitted for clarity.) (5 pts)



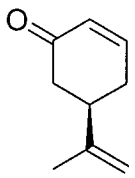


N is less electronegative than O – its e^- are more available for bonding

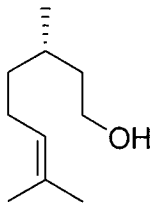
3. Determine the absolute configuration of the asymmetric carbon in each molecule. Write your answer in the box below each structure. (9 pts)



S

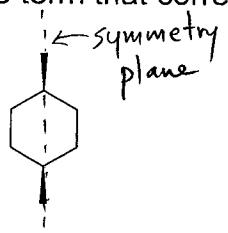


R



S

4. Circle the term that correctly describes each structure. (18 pts)

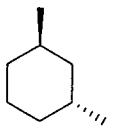


Chiral

(Achiral)

Achiral & meso

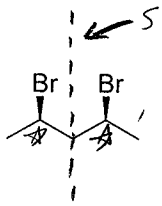
(no asymmetric C's)



(Chiral)

Achiral

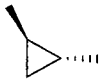
Achiral & meso



Chiral

Achiral

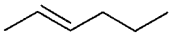
(Achiral & meso)



(Chiral)

Achiral

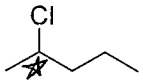
Achiral & meso



Chiral

(Achiral)

Achiral & meso



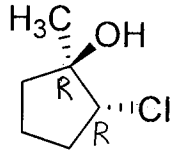
(Chiral)

Achiral

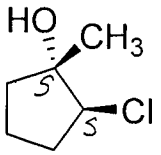
Achiral & meso

Has one asymmetric C; thus this constitution represents a chiral molecule (or racemic mixture)

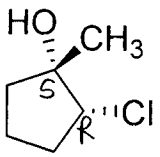
5. Circle the term that correctly describes the relationship between each pair of structures. (9 pts)



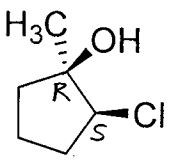
A



B



C



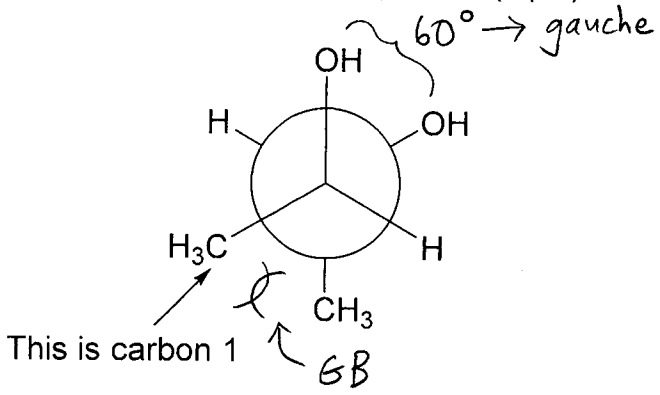
D

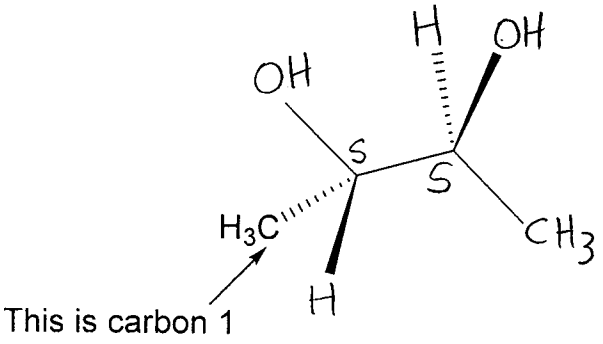
A and B	**enantiomers**	**diastereomers**	**identical**
B and C	**enantiomers**	**diastereomers**	**identical**
C and D	**enantiomers**	**diastereomers**	**identical**

6. In structure A, what is the relationship (torsion angle) between the OH and the Cl? Circle your response. (3 pts)

Eclipsed **Gauche** **Anti**

7a. On the left is a Newman projection of one of the staggered conformations of 2,3-butanediol. Convert the Newman projection on the left to a wedge-and-dash ("perspective") drawing by writing the correct atom or group labels (e.g. H, CH_3, OH) at the end of each bond. (5 pts)





7b. Circle the term that correctly describes this molecule (2 pts):

Chiral **Achiral** **Achiral & meso**

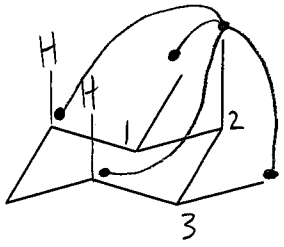
7c. Circle the term that correctly describes the torsion angle between the two OH groups in this conformation (2 pts):

Anti **Eclipsed** **Gauche**

7d. How many gauche butane interactions are present in this conformation? Write the number here (2 pts): 1

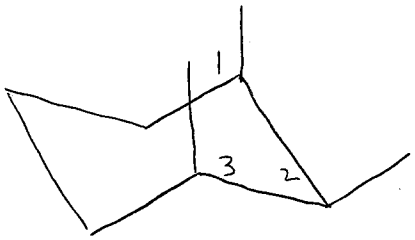
8. (10 pts for the following two questions)

8a. How many gauche butane interactions exist in this chair? Circle your answer.

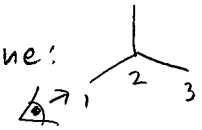


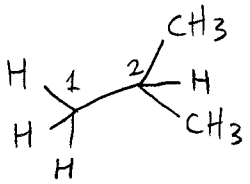
circle one: **0** **1** **2** **3** **(4)** **5**

8b. Draw the ring flip (the other chair conformation) of the molecule in 8a. Don't draw the hydrogens attached to the ring, just draw the three methyl groups. Be sure your chair is drawn properly according to the instructions given in class.

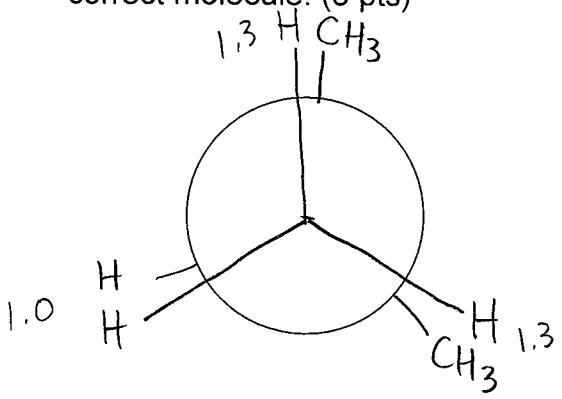


2-methylpropane:



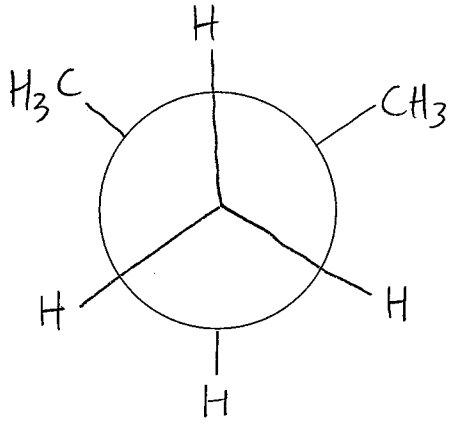


9a. Draw the least stable and most stable conformations of 2-methylpropane looking down the C1-C2 bond. Use the templates provided. Be sure you are drawing the correct molecule! (8 pts)



LEAST STABLE

total strain E = 3.6 kcal/mol



MOST STABLE

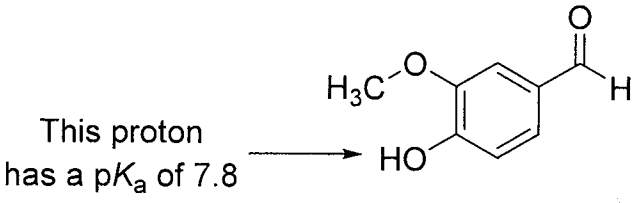
no strain → ∅ kcal/mol

9b. Calculate the barrier to rotation, in kcal/mol, around the C1-C2 bond in 2-methylpropane (see #9a!). A table of strain energies is provided for you. (Me = Methyl) (3 pts)

Interaction	Energy (kcal/mol)	Barrier to rotation =
Me-Me gauche ("gauche butane interaction")	0.8	3.6 − 0 = 3.6 kcal/mol
H-H eclipse	1.0	
Me-H eclipse	1.3	
Me-Me eclipse	4.0	

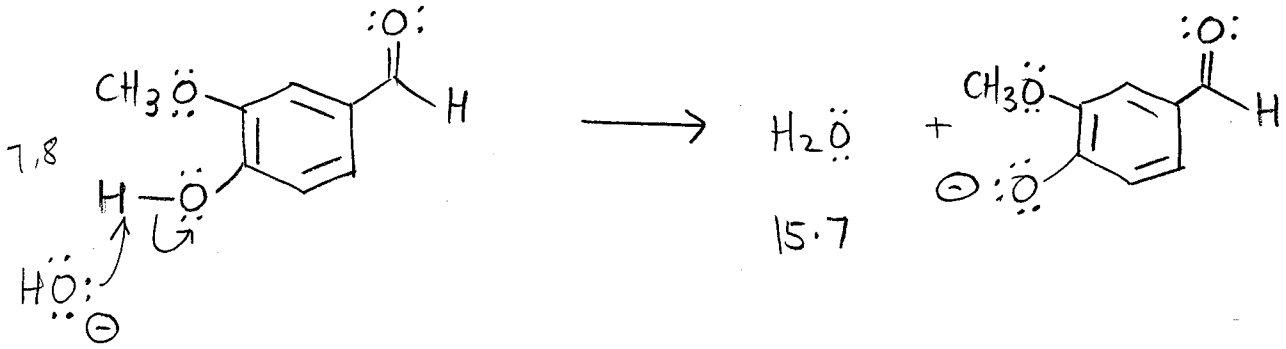
10. A compound called vanillin is one of the major components of the extract of vanilla beans:

Vanillin



In the structure above, all atoms are neutral but lone pairs are not explicitly drawn.

a. Using hydroxide ion as the Bronsted base, draw a mechanism to show the deprotonation of the OH group in vanillin. Include all necessary curved arrows, lone pair electrons and nonzero formal charges. Draw the products of the proton transfer reaction. You will need to redraw the structure of vanillin. (10 pts)



b. Identify the orbital that is the LUMO in this reaction (3 pts):

O-H σ* (in vanillin)

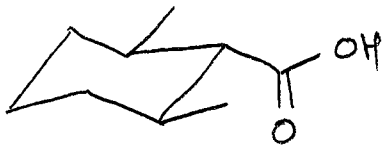
c. Estimate the equilibrium constant for the proton transfer you drew in part "a" (3 pts):

$K \cong 10^{(15.7-7.8)} \cong 10^{(16-8)} \cong 10^{8}$

c. Vanillin is an example of a phenolic compound. ("Phenol" is a term that describes a benzene ring with an OH group attached.) Which of the six factors that we discussed in class is responsible for the stabilization of the conjugate base of vanillin? (One or two words only; no explanation needed) (3 pts)

Resonance

- No GB interactions
- Has a pka ≈ 4



- Achiral & meso

11. **Extra credit.** World-famous pigeon chemist Professor Burblecoo, working with his research group, has been studying the properties of a mysterious Bronsted acid called "breadcrumb acid", which is a solid at room temperature.

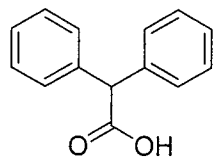
Unfortunately, the pigeon chemists in Prof. Burblecoo's research lab confuse "breadcrumb acid" with actual bread crumbs, and so supplies of this acid are generally gobbled up by the researchers before any experiments can happen. Fortunately, a different research group (one that does not have pigeon chemists) has determined the following information about breadcrumb acid:

Professor Burblecoo (seated on assistant professor's head) with several research associates, discussing the properties of "breadcrumb acid"

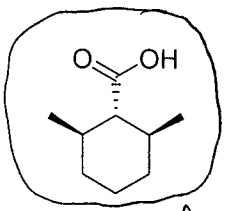
- When breadcrumb acid is deprotonated by hydroxide ion, the equilibrium constant for the proton transfer is about 10^{12}.
  Allows us to estimate its pka (see below)
- The most stable conformation of breadcrumb acid is a chair conformation.
  Structure must contain cyclohexane
- The LUMO of breadcrumb acid is an O-H σ* orbital. Could be an alcohol or carboxylic acid
- A pure sample of breadcrumb acid does not rotate plane polarized light.
  → So it's achiral or achiral and meso
- The most stable conformation of breadcrumb acid does not have any gauche butane interactions, though steric strain is present.

Based on these statements, circle the structure that is **most likely** to be breadcrumb acid. (5 pts)

X

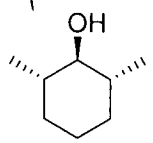


lacks ⬡, so no chairs

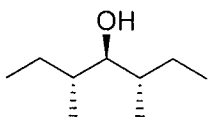


See top of page

pka ~15-18

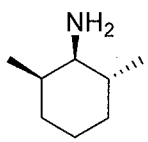


X



not ⬡ so no chair

X



chiral

$HA + OH^{\ominus} \xrightarrow{K \approx 10^{12}} A^{\ominus} + H_2O$

HA: Breadcrumb acid; $A^{\ominus}$: Conj. base of breadcrumb acid; H_2O: 15.7

$K \approx 10^{12} = 10^{(15.7-x)}$ → means $x \cong$ 4-ish (i.e. carboxylic acid)