CHEM 3311 (Richardson) First Hour Exam - September 25, 2012

Your Name Key

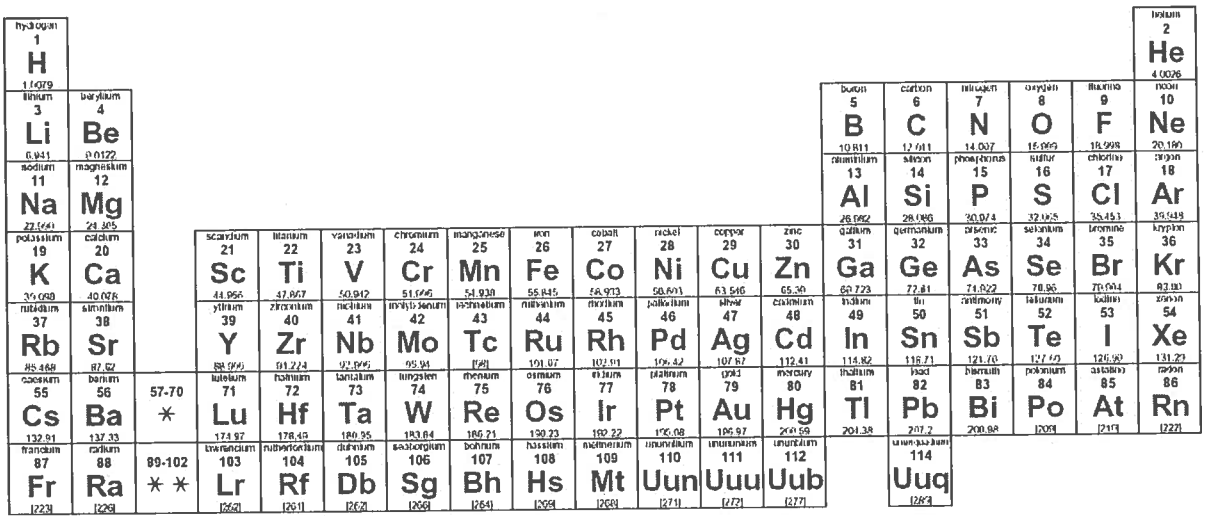
Student ID No. _____

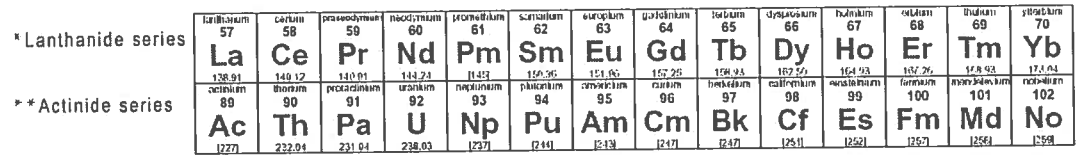
Recitation Day/Time _____

Recitation TA (circle one) Thomas Carey, Adam Csakai, Jake Greenberg, Maria Kolber, Tim Rochelle, Mike Springer

Question	Score	Out of
1		20
2		15
3		20
4		20
5		5
6		10
7		5
8		5
Total		100

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 ziplock bag. Use the backs of the pages for scratch work. Please put all your answers on the test in pen, not pencil.





pKa Values

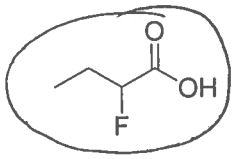
HI	-10.1	H_2O	15.7
HCl	-3.9	Alcohol (ROH)	16-18
H_3O^+	-1.7	HC≡CH	26
CH_3COOH	4.7	NH_3	36
NH_4^+	9.3	$H_2C=CH_2$	45
Phenol	10	CH_4	60

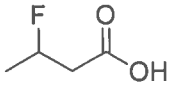
Average = 72.6
St Dev = 13.0
Max = 98.5
Min = 31.5

Name Key

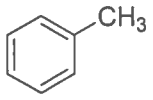
1) Acids and bases (20 pts)

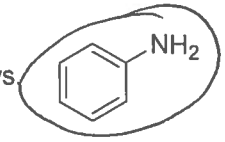
a. For each pair of compounds shown below, select the more acidic of the two compounds and explain your reasoning. (8 pts) (1 pt per circle, 1 pt per reason)



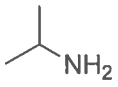
vs.


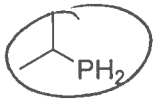
Reason: Stronger inductive effect stabilizes the ⊖ charge better, since the electron-withdrawing group is closer.



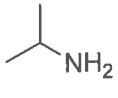
vs.


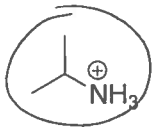
Reason: C & N are in same row of periodic table, so more electronegative atom (N) = more acidic.



vs.


Reason: N & P are in same column of periodic table, so larger atom (P) = more acidic.



vs.


Reason: $-\overset{\oplus}{N}H_3$ has a positive charge & can more easily lose an $H^{\oplus}$

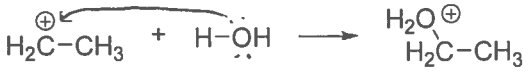
b. For each of the following reactions, does the equilibrium favor the reactants or products? (3 pts) (1 pt each)

$HI + H_2O \rightleftharpoons I^- + H_3O^+$ (pKa = −10.1; pKa = −1.7) **products**

$HC{\equiv}CH + NH_2^- \rightleftharpoons HC{\equiv}C^{\ominus} + NH_3$ (pKa = 26; pKa = 36) **products**

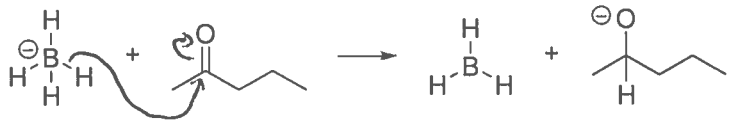
$CH_4 + CH_3O^- \rightleftharpoons CH_3^- + CH_3OH$ (pKa = 60; pKa = 16–18 (for ROH)) **reactants**

c. Complete each arrow-pushing mechanism and identify the HOMO and LUMO of each reaction. (9 pts) (1 pt for arrows, 1 for HOMO, 1 for LUMO)



HOMO: nb on O (lone pair)
LUMO: nb on C (empty p orbital)

HOMO: C–C π
LUMO: H–Br σ*

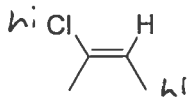


HOMO: B–H σ
LUMO: C–O π*

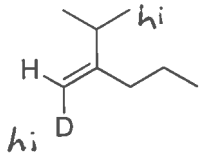
Name Key

2) Alkene naming and stereoisomers (15 pts)

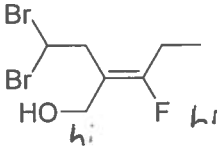
a. Assign an E or Z descriptor to the following molecules. D is deuterium, an atom with the same atomic ~~weight~~ number as hydrogen, but with an atomic weight of 2 instead of 1. (6 pts)



E (2 pts each)

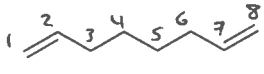


E

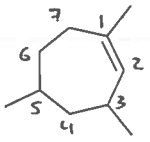


Z

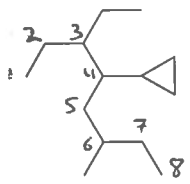
b. Name the following structures. Include E/Z descriptors where appropriate. (6 pts)



Name: 1,7-octadiene (2 pts each; -0.5 for E/Z, numbering, & alphabetizing wrong)



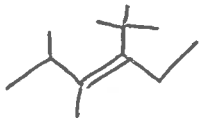
Name: (Z)-1,3,5-trimethyl-1-~~ene~~ cycloheptene

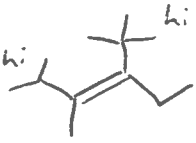


Name: 4-cyclopropyl-3-ethyl-6-methyloctane

c. Draw the structure of (Z)-4-*tert*-butyl-2,3-dimethyl-3-hexene. (3 pts)

Draw connectivity first, ignoring E/Z:



Now check E/Z: 

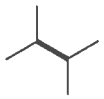
...it's Z. ok. (-1 pt for E isomer)

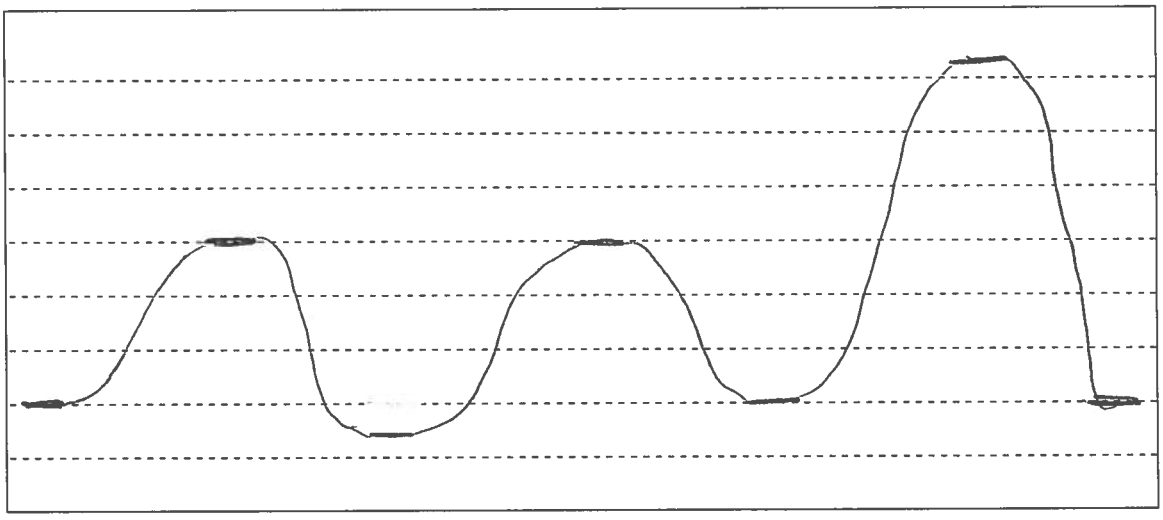
Name Key

3) The structure of 2,3-dimethylbutane is shown below. Sighting along the C2-C3 bond (shown in bold), show a Newman projection for the molecule for dihedral angles in increments of 60°. **Keep the front atom stationary and rotate the back atom clockwise**. For each conformation, plot these energy levels and create a conformational energy diagram. You do not need to calculate the exact energy for each level – a rough estimate is acceptable. (20 pts)

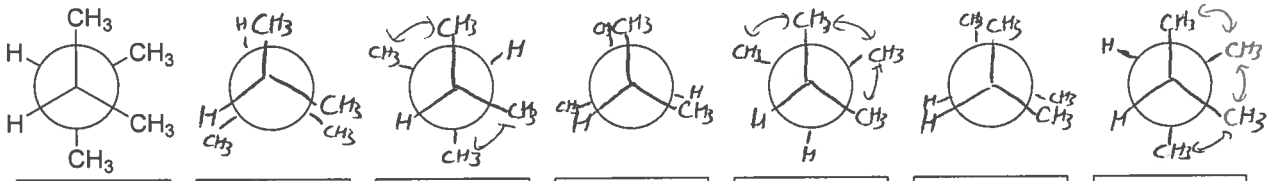
Interaction	Energy (kcal/mol)
H/H eclipsed	1
CH_3/H eclipsed	1.15
CH_3/ CH_3 eclipsed	3.6
CH_3/ CH_3 gauche	0.67

(-2 for ignoring bolded sentence)

2,3-dimethylbutane: 



(8 pts)



(1 pt each)

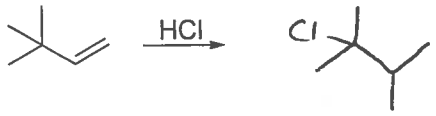
Interactions:	Interactions:	Interactions:	Interactions:	Interactions:	Interactions:	Interactions:
3 x CH_3/CH_3 gauche	2× CH_3/H eclipsed 1× CH_3/CH_3 eclipsed	2× CH_3/ CH_3 gauche	2× CH_3/H eclipsed 1× CH_3/CH_3 eclipsed	3× CH_3/CH_3 gauche	2× CH_3/CH_3 eclipsed 1× H/H eclipsed	3× CH_3/CH_3 gauche

(1 pt each)

Name Key

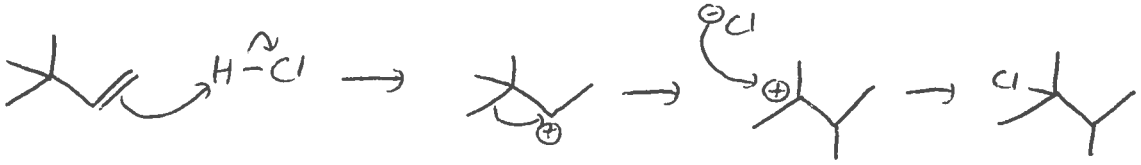
4) Additions to alkenes (20 pts)

a. Predict the major product of the reaction shown below. (4 pts)



(-2 pts for  ,
-4 pts for )

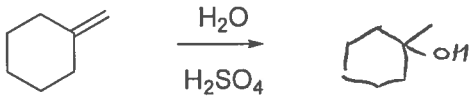
b. Write an arrow-pushing mechanism for this reaction. Show all intermediates including correct formal charges, but do not show transition states. (10 pts)

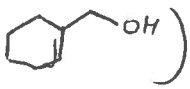


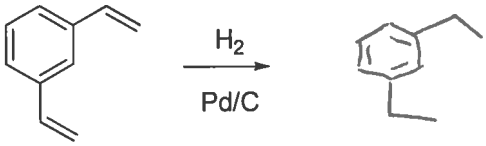
2° carbocation rearranges to 3° carbocation.

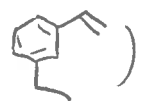
(-5 pts for no methyl shift; -1 pt for each missing/incorrect arrow)

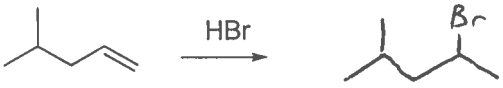
c. Predict the products of the following reactions. (6 pts) (2 pts each)



(-1 pt for )



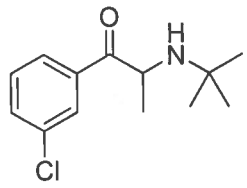
(-1 for )



(-2 pts for )

Name Key

5) Wellbutrin, shown below, is an antidepressant and smoking cessation aid. Which of the listed functional groups does Wellbutrin contain? Circle all that apply. (5 pts)

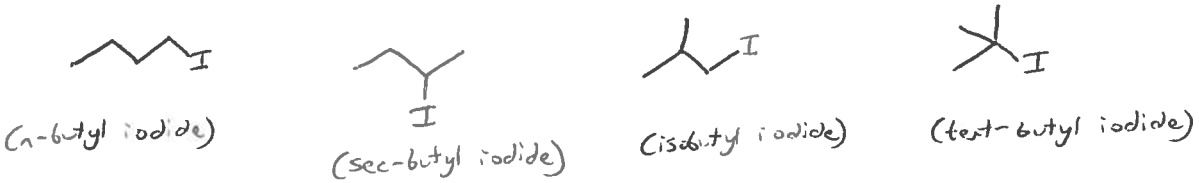


(-1 pt for each incorrect circle/ lack of circle)

Aldehyde | (Ketone) | Amide | (Amine) | (Aromatic Hydrocarbon)

Alkyne | Alcohol | Ester | Nitrile | Carboxylic Acid

6) Draw all the constitutional isomers with formula C_4H_9I, using bond-line structures. Be careful not to repeat any structures. (10 pts)



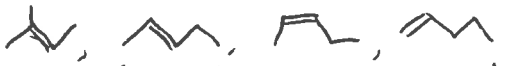
(n-butyl iodide) (sec-butyl iodide) (isobutyl iodide) (tert-butyl iodide)

(2.5 pts each)

7) Put the following alkenes in order of stability, from most stable to least stable.
2-methyl-2-butene, 1-pentene, (E)-2-pentene, (Z)-2-pentene (5 pts)

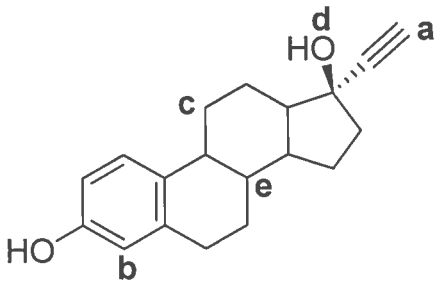
3 R groups | 1 R group | 2 R groups, trans | 2 R groups, cis

Most to least stable:



2-methyl-2-butene, (E)-2-pentene, (Z)-2-pentene, 1-pentene

8) The structure of ethynyl estradiol, an oral contraceptive, is shown below. For each of the labeled atoms, describe the hybridization as sp, sp^2, or sp^3. (5 pts)



a = sp
b = sp^2
c = sp^3
d = sp^3
e = sp^3

(1 pt each)