

CHEM 3311-200 Fall 2006

Exam 1

Professor R. Hoenigman

Average = 69

High = 92

Low = 34

I pledge to uphold the CU Honor Code:

Signature _____

Name (printed) _____

Last four digits of your student ID number _____

Recitation TA _____

Recitation number, day, and time _____

You have 1 hour and 30 minutes to complete this exam.

No model kits or calculators allowed.

Periodic table and scratch paper are attached.

PUT YOUR NAME ON ALL PAGES OF THE EXAM.

DO NOT TURN THIS PAGE UNTIL INSTRUCTED TO DO SO.

Recitation Sections:

#	Day	Time	TA
211	Monday	8 am	Noel
251	Monday	2 pm	Carolynn
291	Monday	5 pm	Heather
252	Tuesday	12 pm	Sam
293	Tuesday	5 pm	Carolynn
212	Wednesday	8 am	Noel
253	Wednesday	1 pm	Tom
292	Wednesday	5 pm	Heather
213	Friday	8 am	Heather

Score:

Page 1 _____/10 Page 5 _____/10

Page 2 _____/10 Page 6 _____/15

Page 3 _____/15 Page 7 _____/18

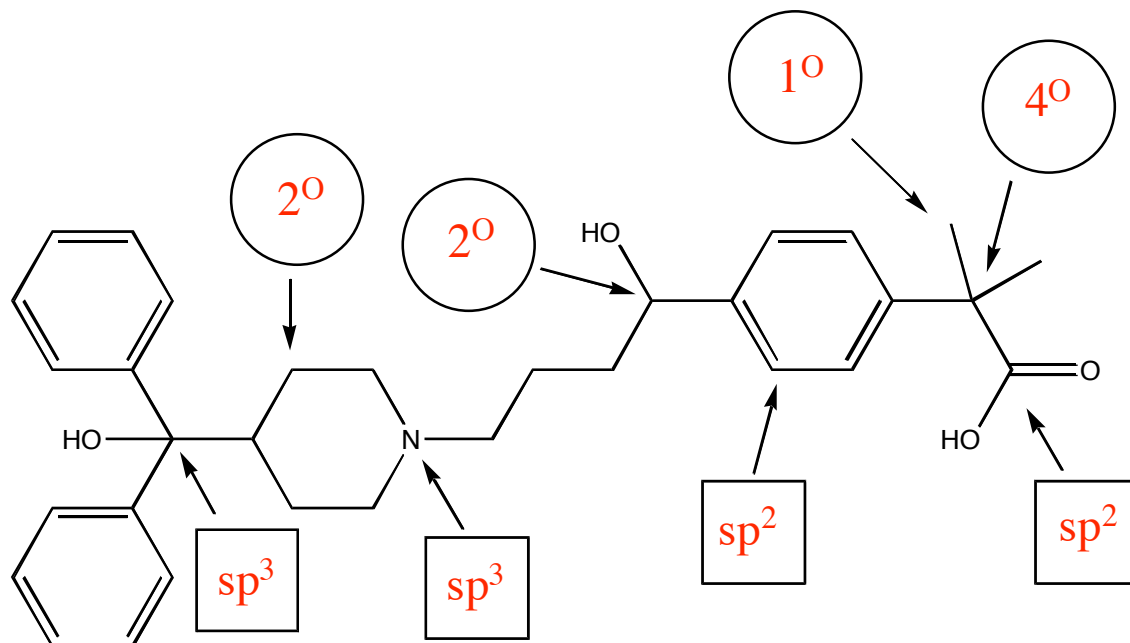
Page 4 _____/12 Page 8 _____/10

TOTAL _____/100

1. (8 pts) Allegra®, shown below, is a common antihistamine.

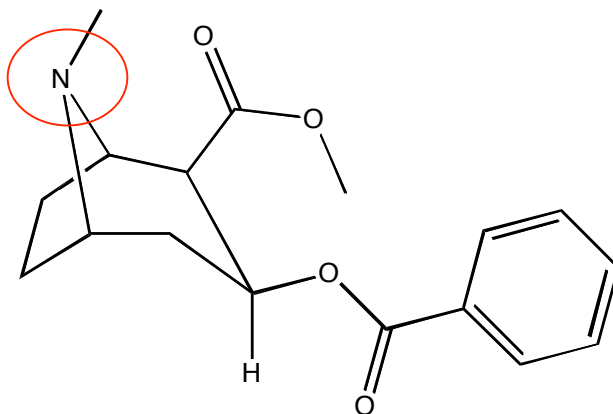
(1 point each)

- A. Label each atom indicated by a box as sp^3 , sp^2 , sp , or none of these.
B. Label each atom indicated by a circle as 1° , 2° , 3° , or 4° .



2. (2 pts) Cocaine is commonly available as a hydrogen chloride salt (known as “blow”). Blow can be reacted with a base to produce the freebase form of cocaine (known as “crack”, shown below). Which atom in freebase cocaine is the most basic atom? Clearly circle your choice.

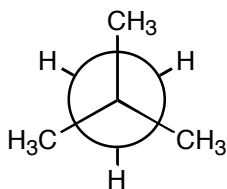
(2 points)



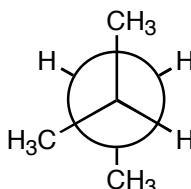
3. (10 pts) State whether the following pairs of compounds are constitutional isomers, stereoisomers, conformers, resonance structures, the same structure, or have no relation. Place your answer in the box.

(2 points each)

A.



and



Constitutional Isomers
Book Problem 3.24a

B.

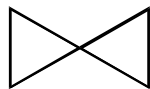
2,4-dimethylpentane

and

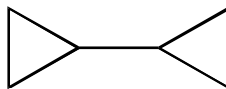


Same Structure
Book Problem 3.16b

C.

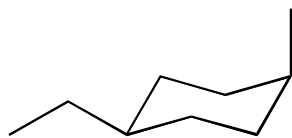


and

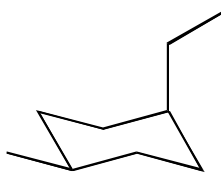


No Relation
Similar to Book Problem 3.26c

D.



and



Conformers
Book Problem 3.24e

E.

4-isobutyl-1,1-dimethylcyclohexane
(Book Problem 2.28c)

or

1,1-dimethyl-4-(1-methylpropyl)cyclohexane

Constitutional Isomers

4. (10 pts) The heat of combustion of cyclohexane is approximately 945 kcal/mol (~3950 kJ/mol) and the heat of combustion of cyclopropane is approximately 500 kcal/mol (~2090 kJ/mol).

(2 points each)

- A. Why does cyclohexane liberate nearly twice as much energy as cyclopropane upon reaction with oxygen?

Cyclohexane has twice as many carbons and hydrogens as cyclopropane.

- B. In the late 1800's Baeyer suggested that all cycloalkanes were planer and cyclopentane would be the most stable cycloalkane. How do chemists know that Baeyer was wrong, and that cyclohexane is the most stable cycloalkane and, in fact, has no ring strain? (*i.e.* What experimental evidence supports this statement?)

The heat of combustion per CH₂ group of cyclohexane is the same as that of an unstrained reference alkane.

- C. Use the fact that cyclohexane is unstrained to calculate the strain energy of cyclopropane.

$$\Delta H_{\text{comb}}(\text{unstrained cyclopropane}) = 945/2 = 472 \text{ kcal/mol}$$

$$\begin{aligned} \text{Strain Energy} &= 500 \text{ kcal/mol} - 472 \text{ kcal/mol} = 28 \text{ kcal/mol} \\ &= 115 \text{ kJ/mol} \end{aligned}$$

- D. What two structural factors contribute to the strain energy of cyclopropane?

torsional strain and angle strain

- E. Why are these two factors absent in chair cyclohexane?

Cyclohexane exists mainly in the chair conformation where the bond angles are 109.5° and there are no eclipsing interactions.

5. (5 pts) How many C₈H₁₆ constitutional isomers can be named as cyclopentanes according to IUPAC nomenclature? Give a numeric answer between 1 and 10 in the box below. To solve this problem use the scratch paper to draw the substituted cyclopentane isomers.

(freebie – everyone gets full credit)

9 (see page 9 for structures)

6. (12 pts) Petroleum, a major source of alkanes, is processed in a refinery, such as the Colorado Mining Company in Commerce City.

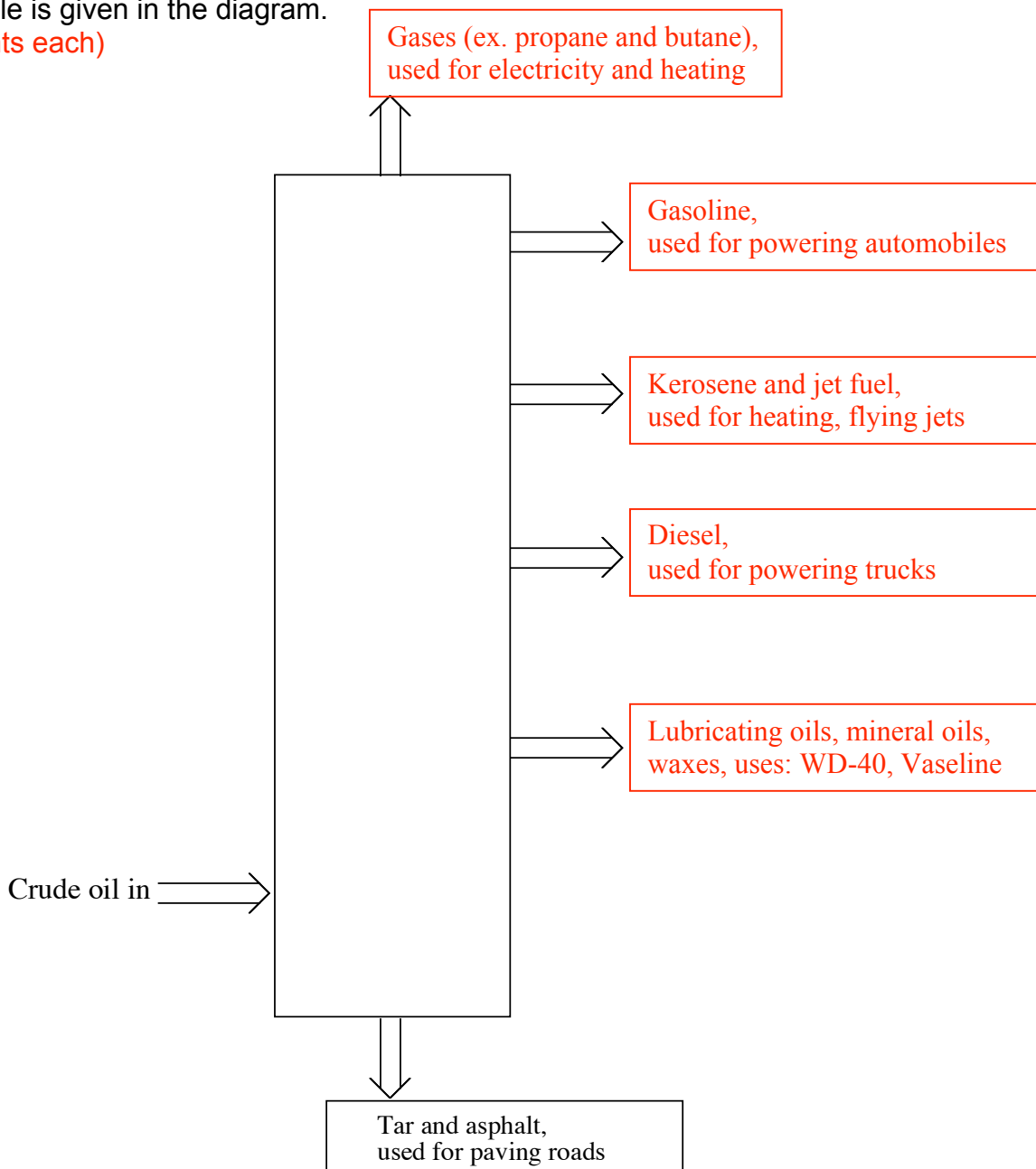
A. List the three steps of refining petroleum.

(1 point each)

1. Fractional Distillation
2. Cracking
3. Reforming

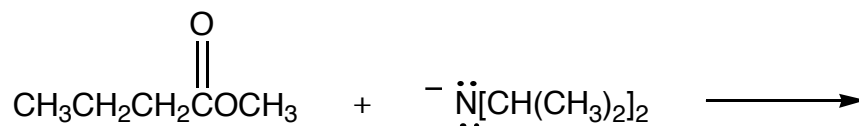
B. On the diagram below, label 3 out of 5 products from the distillation of crude oil and give one use for each of the 3 products you label. One example is given in the diagram.

(3 points each)

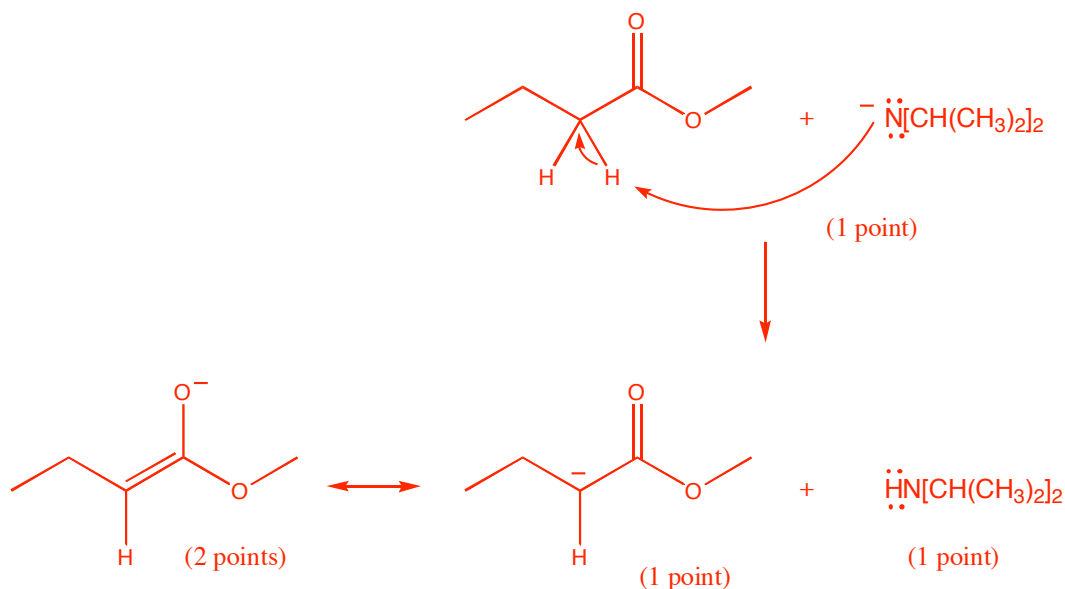


7. (10 pts) This problem is a two-part question.

- A. For the following acid-base reaction, use curved arrows to show the formation of products. Show all major resonance structure(s) of the conjugate base. Be sure to include all non-zero formal charges.



(Book Problem 1.71e)



- B. Predict whether the equilibrium lies to the left or right. Explain your reasoning.

(5 points)

The equilibrium will lie to the right. The conjugate base of the ester is resonance stabilized (2 resonance structures) and is less basic than the $[(\text{CH}_3)_2\text{CH}]_2\text{N}^-$ ion (1 resonance structure). Thus, the ester is a stronger acid than the amine, and the equilibrium will lie to the side with the weaker acid.

8. (15 pts) For each of the following pairs, circle the compound that has the *lower* heat of combustion. In the box, give a brief reason for your choice.

(1 point for correct circle, 2 points for explanation)

A.

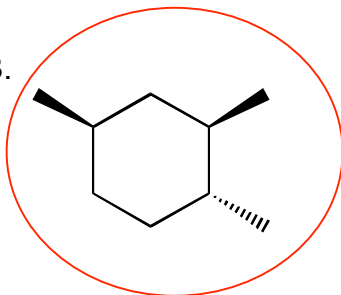
cis-1-isopropyl-3-methylcyclobutane

or

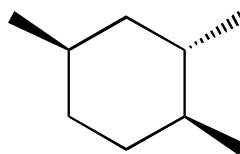
trans-1-isopropyl-3-methylcyclobutane

Less steric strain.

B.



or



All the substituents are equatorial, less 1,3-diaxial interactions.

Book Problem 3.28d

C.

cis-1-ethyl-2-*sec*-butylcyclopropane

or

trans-1-ethyl-2-isopropylcyclobutane

Less torsional strain and less ring strain.

D.

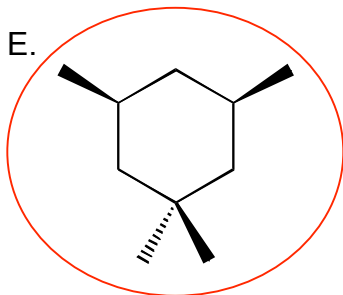
cis-1-*tert*-butyl-4-(1,1-dimethylpropyl)cyclohexane

or

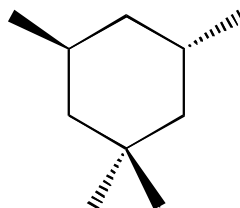
trans-1-*tert*-butyl-4-(1,1-dimethylpropyl)cyclohexane

Both substituents are equatorial, less 1,3-diaxial interactions.

E.



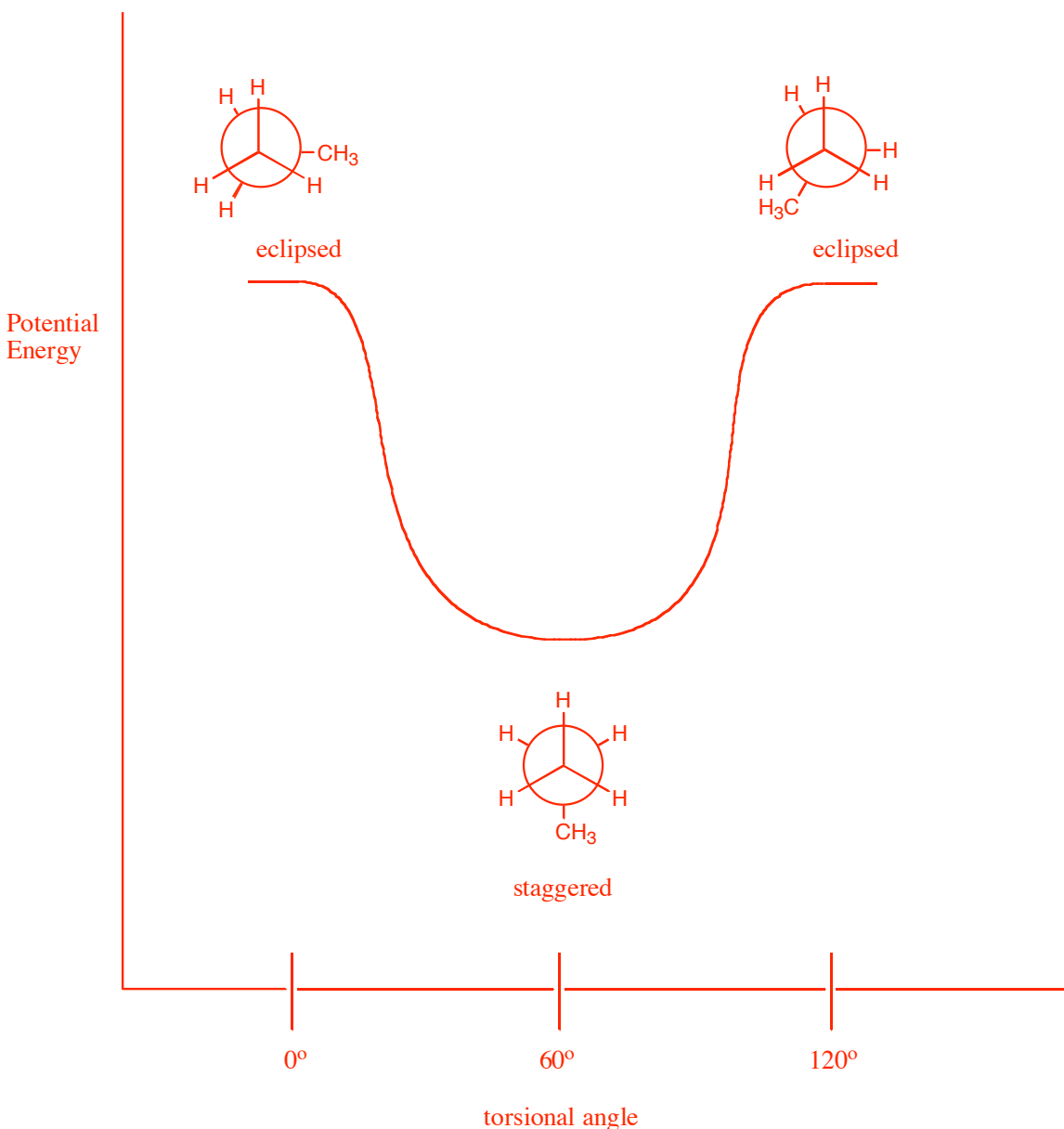
or



The methyls on carbons 3 and 5 are both equatorial, less 1,3-diaxial interactions.

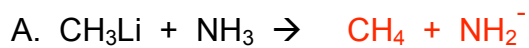
Book Problem 3.29

9. (18 pts) Draw a Newman projection for the most stable conformation of propane, as viewed down the C1-C2 bond. Draw a potential energy diagram illustrating how the energy changes qualitatively as a function of the torsional angle between a hydrogen atom and the methyl group. Draw Newman projections for each maximum and minimum conformation. Clearly label your axes and show the relative energy of each conformation. Label the conformations as gauche, anti, staggered, and/or eclipsed. You need only show rotation from $\theta = 0^\circ$ to $\theta = 120^\circ$.



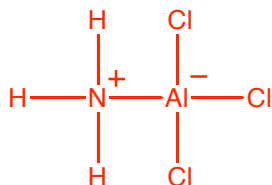
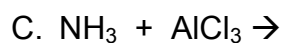
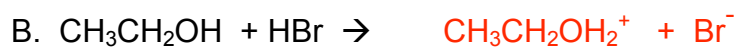
10. (10 pts) Complete the following acid-base reactions. Show all non-zero formal charges. If no reaction occurs write NR.

(2 points each)



pKa: 36 60

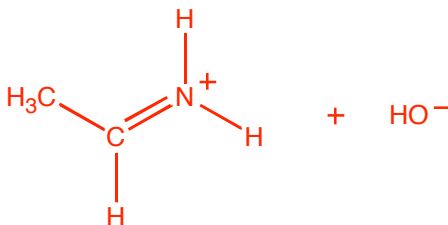
CH_3Li is an ionic compound: $\text{CH}_3^- \text{Li}^+$



This is a Lewis acid-base reaction.



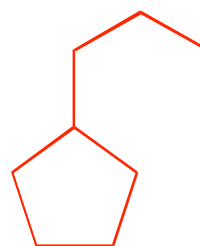
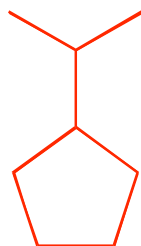
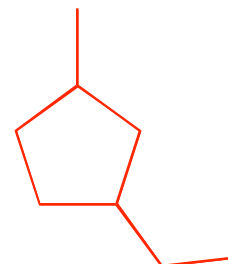
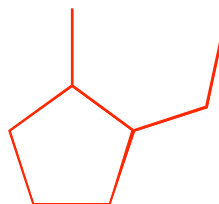
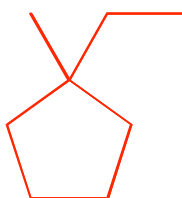
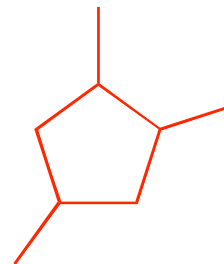
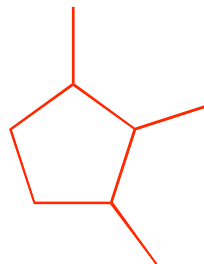
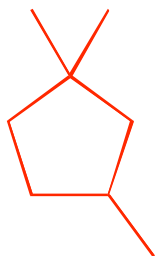
$\text{CH}_3\text{CH}_2\text{SH}$ is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$.



Book Problem 1.69c

Scratch Page

Isomers for problem 5:



Name: _____

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Scratch Page