Exam #2
Chem 2310 - Organic I Chemistry
Dr. Davies
Tuesday October 18, 2005

Ch. 4 Study of Chemical Reactions
Ch. 5 Stereochemistry
Ch. 6 Alkyl halides: Substitution / Elimination Reactions

Name: Key

My signature indicates that I have neither given nor received any unauthorized assistance on this exam.

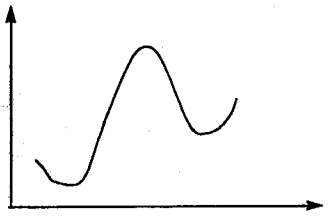
Signature: _____

Tips
Look over the whole exam first.
Check the page numbers to make sure you are not missing any pages. If you are missing a page, trade for another exam at the desk.
Read questions thoroughly.
Do the problems you know first.
Show all your work.
Relax, and just do the best you can.

I. Theory

1. Based upon the energy diagram shown below, circle all statements that must be true. (3 points)

a) The ΔS° for the reaction is positive.
b) The ΔG° for the reaction is negative.
c) The ΔS° for the reaction is negative.
d) The K_{eq} for the reaction is less than one.
e) The rate equation is first order.



2. Use the table of bond dissociation energies on the last page of the exam to calculate the overall enthalpy of the reaction below in kcal/mol. Then state whether the reaction is endothermic or exothermic. (5 points)

3°C-H 3°C-I

$(CH_3)_3CH + I_2 \rightarrow (CH_3)_3CI + HI$

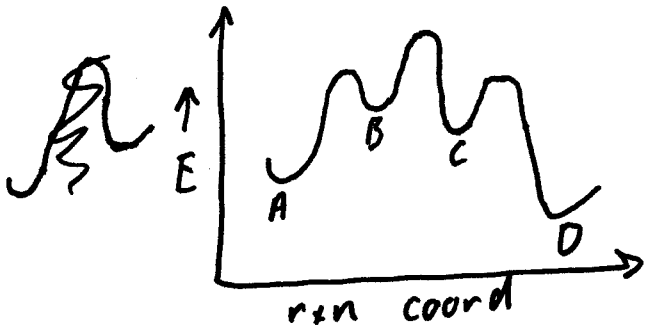
+91 kcal/mol +136 kcal/mol -50 kcal/mol -71 kcal/mol

+6 kcal/mol, endothermic

Use the following information to answer questions 3 and 4. Consider the three-step mechanism for the reaction of A through intermediates B and C to product D shown below:

$A \rightarrow B$ $E_a = +9$ kcal / mol, $\Delta H^\circ = +6$ kcal / mol
$B \rightarrow C$ $E_a = +5$ kcal / mol, $\Delta H^\circ = -2$ kcal / mol
$C \rightarrow D$ $E_a = +3$ kcal / mol, $\Delta H^\circ = -7$ kcal / mol

3. Draw an energy diagram for the reaction described above. (3 points)



4. Which step is the rate determining step? (2 points)

a) $A \rightarrow B$ (b) $B \rightarrow C$ c) $C \rightarrow D$ d) insufficient information

1pt

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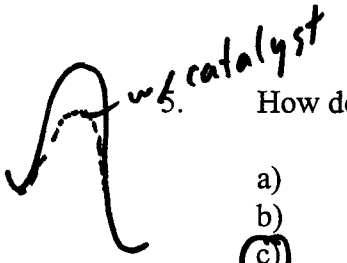


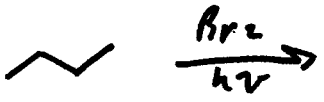
5. How does a catalyst accelerate a reaction? (2 points)

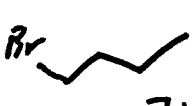
a) It stabilizes the reactant.
b) It destabilizes the reactant. 1pt
c) It stabilizes the transition state.
d) It destabilizes the transition state. 1pt.
e) It stabilizes the intermediate.
f) It destabilizes the intermediate.

6. Which of the following is a carbene? (2 points)

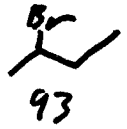
a) $CH_2{=}CHO^-$ b) $CH_3CH_2^{\cdot}$ c) $:CCl_2$ d) $CH_3CH_2^+$ e) NCO^-

7. If the ratio of 1-bromobutane to 2-bromobutane formed from free radical bromination of n-butane is 7:93, what is the relative reactivity of 2° vs 1° hydrogens in this system? Show all of your work for full credit. (5 points)





7:



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select: rxt × prob.

1° 7 = a × 6

a = 7/6 = 1.17

1.17/1.17 = 1

2° 93 = b × 4

93/4 = b

b = 23.3/1.17 = 20

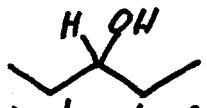
Rel. Rxt.

1° vs 2°

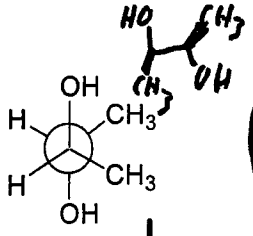
1 : 20

8. Identify the following structures as chiral or achiral. Circle any meso structures. (8 points)

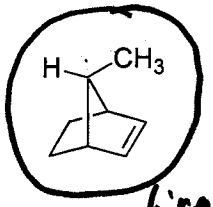
$CH_3CH_2CH(OH)CH_2CH_3$



achiral - plane of symm.



chiral



achiral

9. What are stereoisomers? (2 points) p.167 compounds w/ the same molec. formula & the same connectivity but different spatial arrangements

10. Circle all statements that are true of chloroform. (3 points)

a) Chloroform has a density less than 1.0 g/mL (H_2O) No
b) It is a suspected carcinogen.
c) Chloroform was once used as an anesthetic.
d) Its trade name is freon. No

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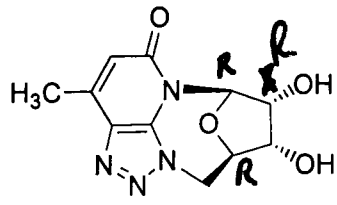
11. The following structure has been found to have moderate activity against hepatitis C, a disease that damages the liver (*J. Med. Chem.* **2005**, 6454). Label the configuration of each chiral center as R or S. (8 points)



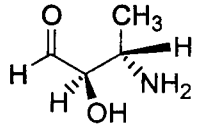
R (accept either)

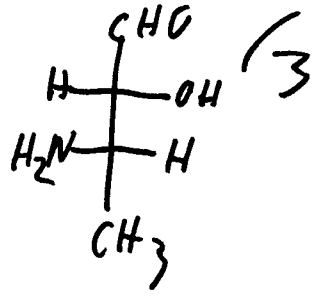
12. A new isolated natural product was found to be optically active. When 2.0 g of the pure substance was dissolved in 10 mL of ethanol and placed in a 50 cm sample tube an optical rotation of +2.57° was observed. What is the specific rotation of this natural product? Show all of your work for full credit! (4 points)

$$[\alpha] = \frac{\alpha}{c \cdot l} = \frac{2.57^\circ}{\left(\frac{2.0\,g}{10\,mL}\right)(5\,dm)} = \boxed{2.57^\circ}$$

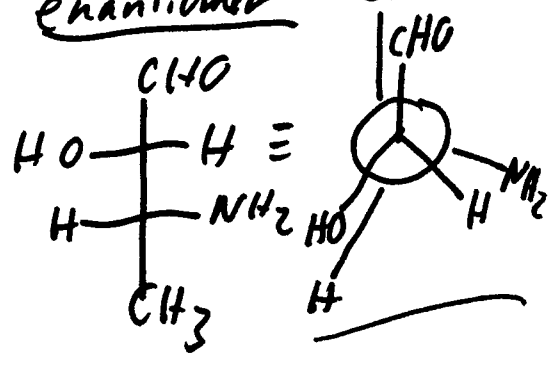
10cm = 1dm

13. Translate the following structure to a Fischer projection and then draw its enantiomer in a Newman projection siting down the C2-C3 bond. (6 points)



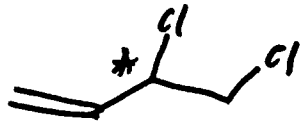


enantiomer



14. Compound **I** is an acyclic chiral compound, having a molecular formula of $C_4H_6Cl_2$. Neither of the chlorines are vinylic. Provide a structure for compound **I**. (3 points)

10 - 2 = 8
-6
2H
1° unsat



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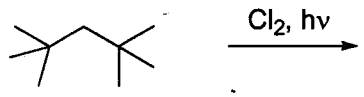
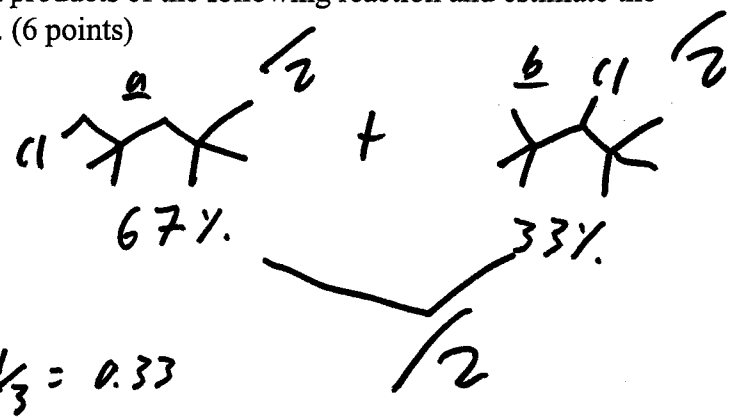
III. Reactions

1. Predict the monochlorination products of the following reaction and estimate the percent ratio of each product. (6 points)

sel = rxt + prob.





a sel = 1 × 18 = 18 ✓

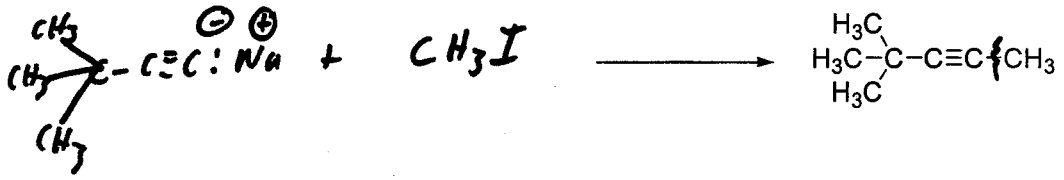
b sel = 2 × 4.5 = 9 ✓

a : b

2 : 1

2/3 = 0.67 1/3 = 0.33

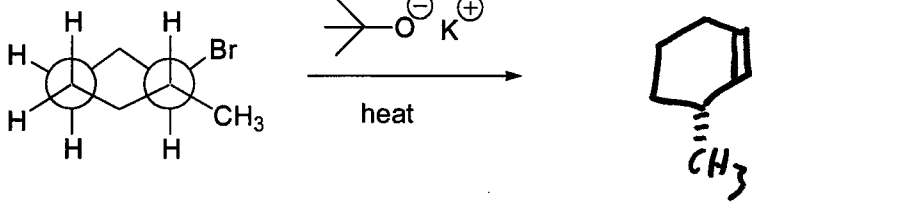
2. Show how the following product could be made using an S_N2 reaction. (4 points)



3. Draw the major product of the following reaction in a perspective structure or a chair structure. Include any relevant stereochemistry. (3 points)

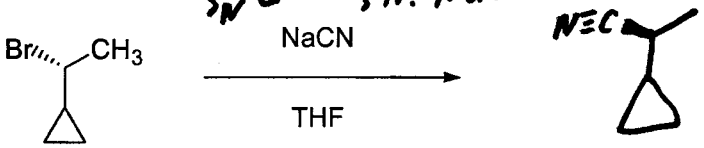
E2 (anti-copl.)

only product



4. Complete the following reaction by filling in the major product(s) of the following reaction. Include any relevant stereochemistry. (3 points)

S_N2 str. Nu:



No C+ = No RAR

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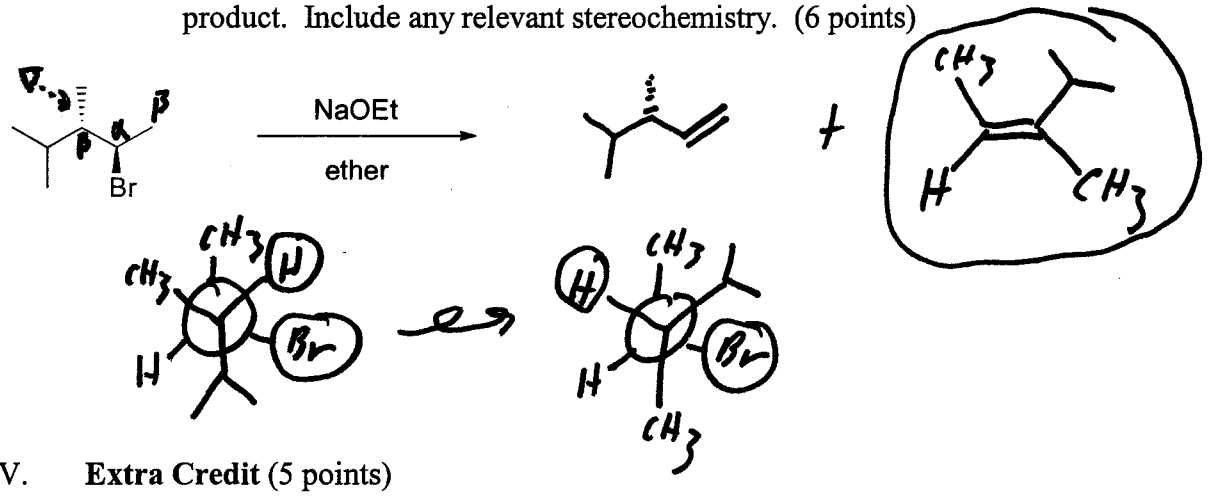
5. Predict all possible elimination products and circle the structure of the major product. Include any relevant stereochemistry. (6 points)



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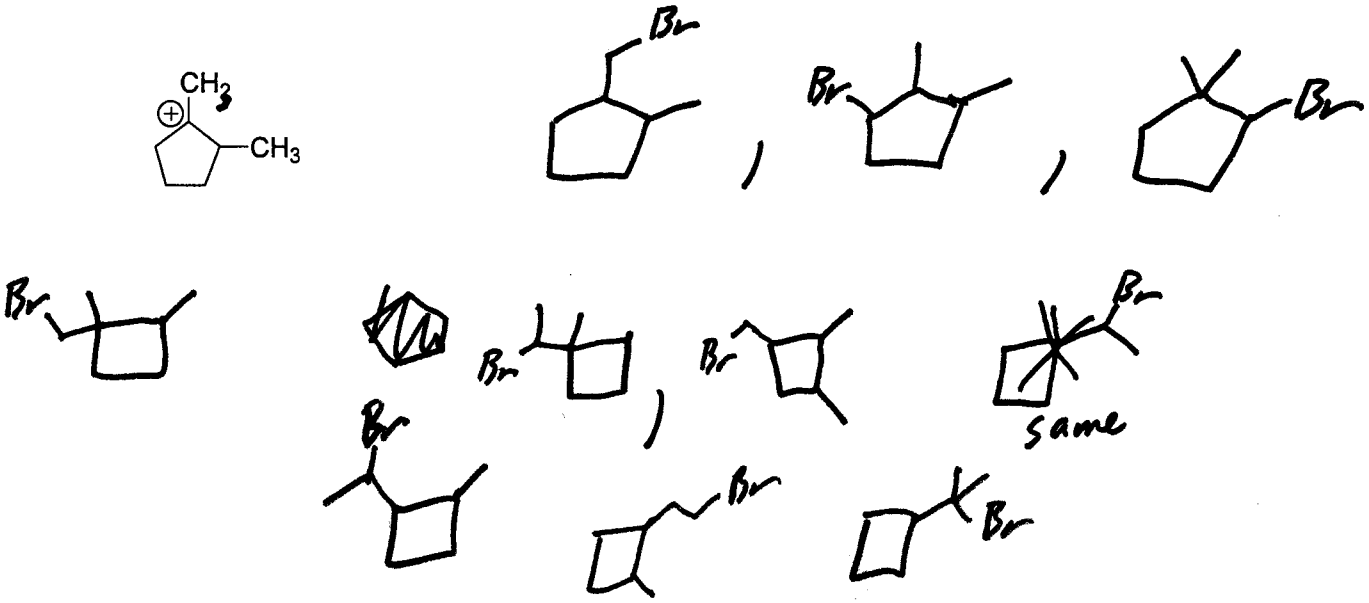
IV. **Extra Credit** (5 points)

1. Draw the structure of 5 isomers having a molecular formula of $C_7H_{13}Br$ that will rearrange to the carbocation shown below in a solvolysis reaction.



You received _____ points out of 100 points possible. To check your overall performance in lecture see http://vista.weber.edu/

TABLE 4-2 Bond-Dissociation Enthalpies for Homolytic Cleavages
A:B ⟶ A· + ·B

Bond	Bond-Dissociation Enthalpy kJ/mol	kcal/mol
H—X bonds and X—X bonds		
H—H	435	104
D—D	444	106
F—F	159	38
Cl—Cl	242	58
Br—Br	192	46
I—I	151	36
H—F	569	136
H—Cl	431	103
H—Br	368	88
H—I	297	71
HO—H	498	119
HO—OH	213	51
Methyl bonds		
CH_3—H	435	104
CH_3—F	456	109
CH_3—Cl	351	84
CH_3—Br	293	70
CH_3—I	234	56
CH_3—OH	381	91
Bonds to primary carbons		
CH_3CH_2—H	410	98
CH_3CH_2—F	448	107
CH_3CH_2—Cl	339	81
CH_3CH_2—Br	285	68
CH_3CH_2—I	222	53
CH_3CH_2—OH	381	91
$CH_3CH_2CH_2$—H	410	98
$CH_3CH_2CH_2$—F	448	107
$CH_3CH_2CH_2$—Cl	339	81
$CH_3CH_2CH_2$—Br	285	68
$CH_3CH_2CH_2$—I	222	53
$CH_3CH_2CH_2$—OH	381	91
Bonds to secondary carbons		
$(CH_3)_2CH$—H	397	95
$(CH_3)_2CH$—F	444	106
$(CH_3)_2CH$—Cl	335	80
$(CH_3)_2CH$—Br	285	68
$(CH_3)_2CH$—I	222	53
$(CH_3)_2CH$—OH	381	91
Bonds to tertiary carbons		
$(CH_3)_3C$—H	381	91
$(CH_3)_3C$—F	444	106
$(CH_3)_3C$—Cl	331	79
$(CH_3)_3C$—Br	272	65
$(CH_3)_3C$—I	209	50
$(CH_3)_3C$—OH	381	91
Other C—H bonds		
$PhCH_2$—H (benzylic)	356	85
CH_2=$CHCH_2$—H (allylic)	364	87
CH_2=CH—H (vinyl)	464	111
Ph—H (aromatic)	473	113
C—C bonds		
CH_3—CH_3	368	88
CH_3CH_2—CH_3	356	85
CH_3CH_2—CH_2CH_3	343	82
$(CH_3)_2CH$—CH_3	351	84
$(CH_3)_3C$—CH_3	339	81