THE UNIVERSITY OF BRITISH COLUMBIA

CHEMISTRY 123 FINAL EXAMINATION

16 April 2007

This examination consists of **14** numbered pages.

TIME LIMIT: 2.5 HOURS

PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER

GIVEN NAME(S): Answer Key (IN INK)

SURNAME: _____ (CAPITALS) (IN INK)

STUDENT NUMBER: _____ (IN INK)

SIGNATURE: _____ (IN INK)

NO CALCULATORS ALLOWED PREPROGRAMMED WITH ANY CHEMISTRY OR PHYSICS FORMULAE OR TEXTUAL MATERIAL. MOLECULAR MODELS ARE ALLOWED.

Lecture Section (check √ your section)

___ 201 (MWF 1:00) Drs. Wang/Ruddick
___ 202 (MWF 2:00) Drs. Wang/Ruddick
___ 209 (MWF 9:00) Drs. Patey/Sherman
___ 210 (MWF 10:00) Drs. Patey/Sherman
___ 211 (MWF 11:00) Dr. Liu
___ 299 (T,Th 9:30) Drs. Patey/Sherman
___ 222 (T,Th 2:00) Drs. Patey/Sherman

Question	Maximum	Obtained	Initials
1	7		
2	10		
3	5		
4	8		
5	4		
6	4		
7	6		
8	4		
9	3		
10	9		
11	5		
TOTAL	65		

REGULATIONS FOR EXAMINATIONS

1. Each candidate must be prepared to produce upon request, a Library/AMS card for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidates shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates guilty of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:

(a) Having at the place of writing any books, papers or memoranda, calculators, audio or visual cassette players or other memory aid devices, other than those authorized by the examiners.
(b) Speaking or communicating with other candidates.
(c) Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.

5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.

***** ANSWER ALL QUESTIONS *****

***** ADDITIONAL DATA *****

ATTACHED ARE AN EQUATIONS SHEET AND A PERIODIC TABLE.

1. [7 points] When metallic copper is shaken with a solution of a copper salt, the following redox reaction occurs:

$$Cu(s) + Cu^{2+}(aq) \leftrightarrows 2\ Cu^{+}(aq)$$

The equilibrium constant of this reaction at 25 °C is 5.0×10^{-5}. Suppose that you attempt to use the above reaction to make an electrochemical cell at 25 °C.

(a) For this cell the net reaction is as written above, and Cu(*s*) takes part in the half-reaction at each electrode. Write out the reactions occurring at the electrodes.

Anode: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Cathode: $Cu^{+}(aq) + e^- \longrightarrow Cu(s)$

(b) Evaluate the standard potential $\Delta\varepsilon^0$. $\Delta\varepsilon^0 =$ -0.13 V

$$\Delta\varepsilon^\circ = \frac{RT}{nF}\ln K = \frac{(8.314)(298.15)}{2\times96500}\times\ln(5.0\times10^{-5}) = -0.13\text{V}$$

(c) If $[Cu^{2+}] = 1.0$ M, at what concentration of $Cu^{+}(aq)$ would the cell become spontaneous?

$$K = \frac{[Cu^{+}]^2}{[Cu^{2+}]} = [Cu^{+}]^2 = 5.0\times10^{-5}$$

$[Cu^{+}] =$ 7.07×10^{-3} M

$[Cu^{+}] = 7.07\times10^{-3}$ M at equil.

To be spontaneous, $Q < K$, $[Cu^{+}] < 7.07\times10^{-3}$ M

(d) Given the standard half-reaction potential of the Cu^{2+}/Cu electrode,

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s), \qquad \varepsilon^0(Cu^{2+}/Cu) = 0.33\text{ V},$$

calculate the standard half-reaction potential of the Cu^{+}/Cu electrode:

$$Cu^{+}(aq) + e^- \rightarrow Cu(s), \qquad \varepsilon^0(Cu^{+}/Cu) =$$ 0.46 V

$$\Delta\varepsilon^\circ = \varepsilon^\circ(Cu^{2+}/Cu) - \varepsilon^\circ(Cu^{+}/Cu)$$

$$-0.13 = 0.33 - \varepsilon^\circ(Cu^{+}/Cu)$$

$$\varepsilon^\circ(Cu^{+}/Cu) = 0.46\text{ V}$$

2. [10 points] 0.500 moles of anilinium acetate, $[C_6H_5NH_3^+][CH_3COO^-]$, are dissolved in water to give 500 mL of solution at 25 °C. The following equilibrium is established in solution:

$$C_6H_5NH_3^+ + CH_3COO^- \leftrightarrows C_6H_5NH_2 + CH_3COOH$$

At 25 °C, the dissociation constants of acetic acid (CH_3COOH), aniline ($C_6H_5NH_2$), and water are $K_a(CH_3COOH) = 1.80\times10^{-5}$, $K_b(C_6H_5NH_2) = 4.50\times10^{-10}$, and $K_w = 1.00\times10^{-14}$, respectively.

(a) Write out an expression for the equilibrium constant, K, of the reaction written above.

$$K = \frac{[C_6H_5NH_2][CH_3COOH]}{[C_6H_5NH_3^+][CH_3COO^-]}$$

(b) Show that the equilibrium constant K can be written as:

$$K = K_w/[K_a(CH_3COOH) \times K_b(C_6H_5NH_2)].$$

$$\frac{[C_6H_5NH_2]}{[C_6H_5NH_3^+]} = \frac{[HO^-]}{K_b} \quad , \quad \frac{[CH_3COOH]}{[CH_3COO^-]} = \frac{[H_3O^+]}{K_a}$$

$$K_w = [H_3O^+][HO^-]$$

$$K = \frac{[C_6H_5NH_2][CH_3COOH]}{[C_6H_5NH_3^+][CH_3COO^-]} = \frac{[OH^-]}{K_b} \times \frac{[H_3O^+]}{K_a} = \frac{K_w}{K_aK_b}$$

(c) Calculate the equilibrium constant K. K = 1.23

$$K = \frac{K_w}{K_aK_b} = \frac{1.00\times10^{-14}}{(1.80\times10^{-5})(4.50\times10^{-10})} = 1.23$$

2. (Continued)

(d) Calculate the concentration of aniline at equilibrium. $[C_6H_5NH_2]$ = 0.526M

$C_6H_5NH_3^+ + CH_3CO_2^- \rightleftharpoons C_6H_5NH_2 + CH_3CO_2H$

initial	0.5/0.5 M	1M	0	0
equil.	1−x	1−x	x	x

$$K = \frac{x^2}{(1-x)^2} = 1.23 \; ; \quad \frac{x}{1-x} = (1.23)^{1/2} = 1.11$$

$$1.11 - 1.11x = x \; ; \quad 1.11 = 2.11x$$

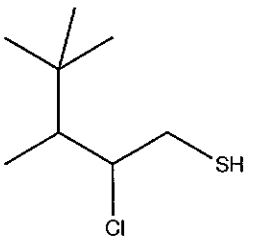
$$\frac{1.11}{2.11} = x = 0.526\,M$$

(e) Calculate the pH of the solution at equilibrium. pH = 4.70

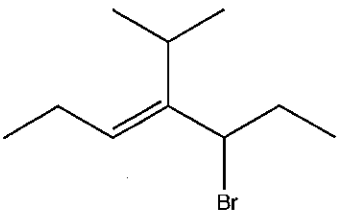
$$[H_3O^+] = K_a \frac{[CH_3CO_2H]}{[CH_3CO_2^-]} = K_a \frac{x}{1-x} = 1.11 \times 1.80\times10^{-5} = 2.00\times10^{-5}$$

$$pH = -\log[2.00\times10^{-5}] = 4.70$$

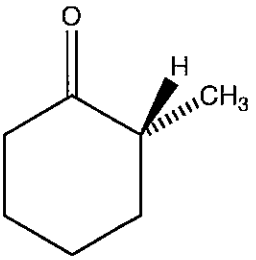
3. [5 points] Name the following compounds. Be sure to indicate stereochemistry where appropriate.

(a) 

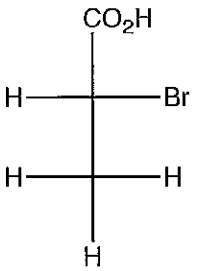
2-chloro-3,4,4-trimethyl pentane thiol

(b) 

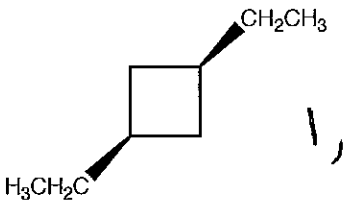
(E)-5-bromo-4-isopropyl-3-heptene

(c) 

(R)-2-methylcyclohexanone

(d) 

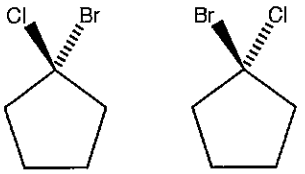
(R)-2-bromopropanoic acid

(e) 

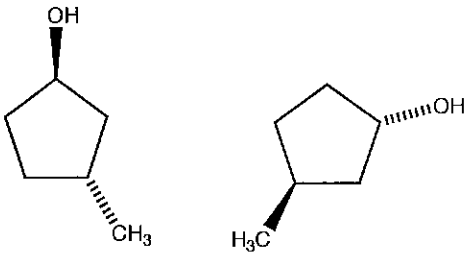
1,3-cis-diethylcyclobutane

4. [8 points] Below are eight pairs of structural formulas. In the box to the right of each pair, place the number (from the six terms listed below) that BEST describes the relationship between the two structures. NOTE: Each term may be used more than once and not all terms need be used. **Also, Circle all the meso compounds.**

1. Identical
2. Diastereomers
3. Conformers
4. Constitutional isomers
5. Enantiomers
6. None of the above relationships

(a) 

1

(b) 

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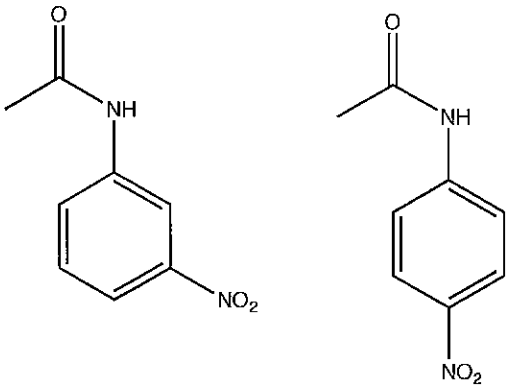
(c) 

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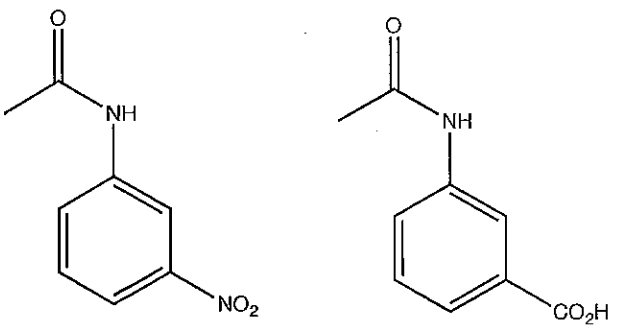
(d) 

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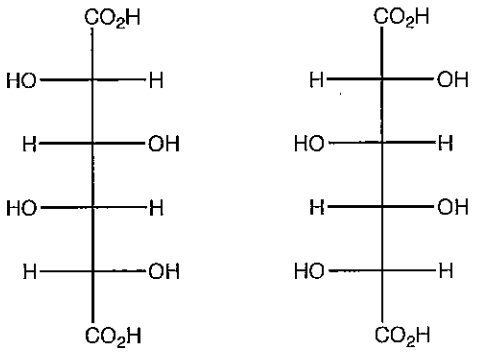
4. (Continued)

(e)



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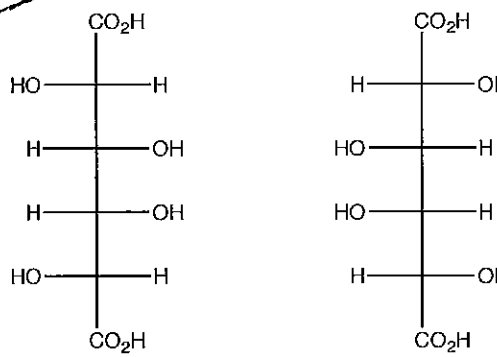
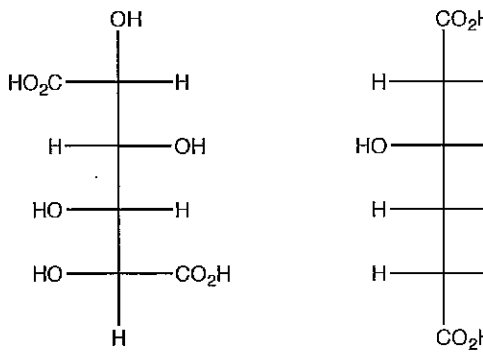
(f)



1

(g)



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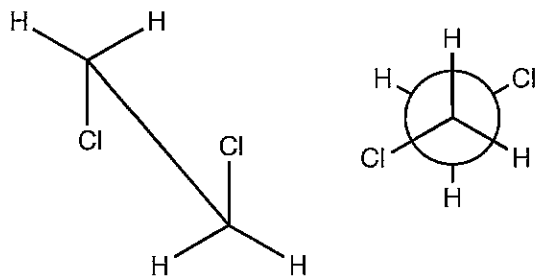
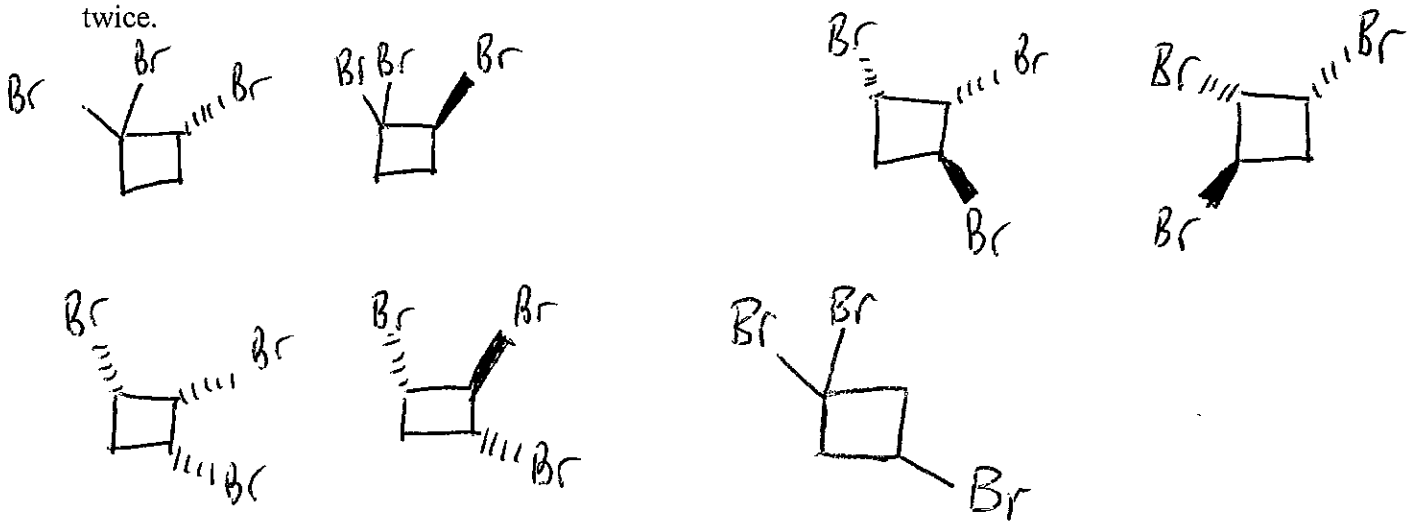
(h)



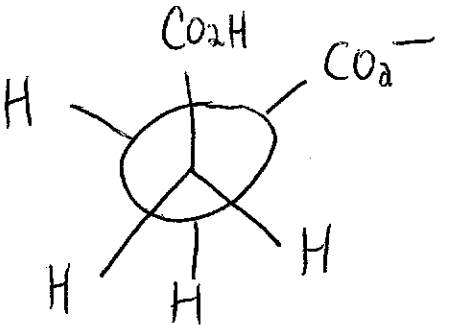
1

5. [4 points] Draw all of the constitutional isomers and stereoisomers of compounds named tribromocyclobutane (all structures must contain a cyclobutane ring). Do not draw any isomer twice.



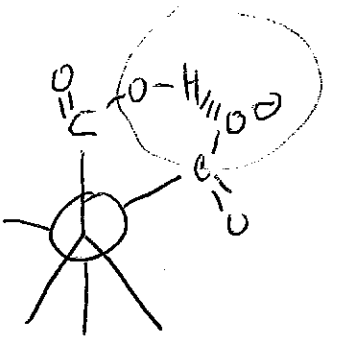
6. [4 points] Butanedioate monoanion, $HO_2C–CH_2–CH_2–CO_2^-$, is found to exist 100% in the gauche conformation in the solvent tetrahydrofuran (THF, a polar aprotic solvent). In water, the monoanion is found to equally populate the anti and gauche conformations.

(a) Draw a Newman Projection of butanedioate monoanion in its most stable conformation when it is dissolved in THF.



(b) Explain the conformational preference found in THF.

There is a (charged) hydrogen bond between the CO_2^- and the CO_2H.

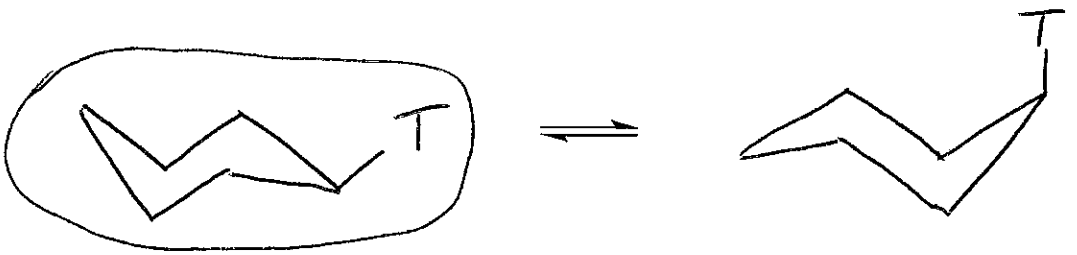


(c) Rationalize how water nullifies the conformational preference.

H_2O hydrogen bonds to RCO_2H and $R'CO_2^-$ (different waters to each) and breaks up the intramolecular H-bond.

7. [6 points] Tritium (T), an isotope of hydrogen, is more stable in the equatorial position of cyclohexane by $\Delta G° = -0.0460$ kJ/mol (-0.0110 kcal/mol) at 298 K.

(a) Draw mono-tritiated cyclohexane in its **two** most stable conformations. **Circle** the most stable.



(b) Calculate the mole ratio of the two conformations at 298 K and enter the ratio in the boxes below in the form 1.00:something.

Ratio [1.02] : [1.00]

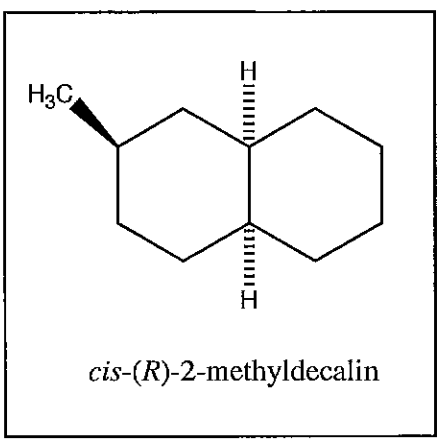
$\Delta G° = -RT\ln K$; $K = e^{-\Delta G°/RT} = e^{(0.0460 \times 10^3 \frac{J}{K})/(8.314)(298)}$

$K = e^{0.0186} = 1.019 = 1.02$

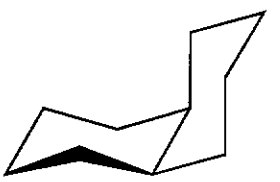
(c) What mole% of mono-tritiated cyclohexane will exist in its most stable conformation?

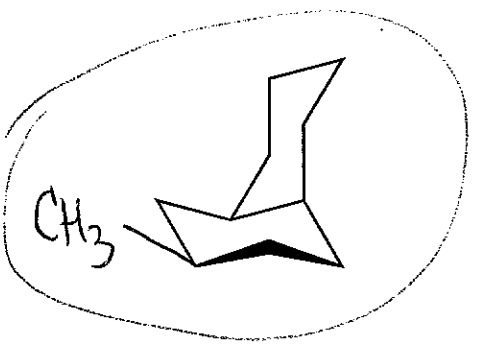
$\frac{1.02}{1.00 + 1.02} = 50.5\%$

8. [4 points] (a) Using one of the templates below, draw *cis*-(*R*)-2-methyldecalin in its most stable conformation.



cis-(*R*)-2-methyldecalin



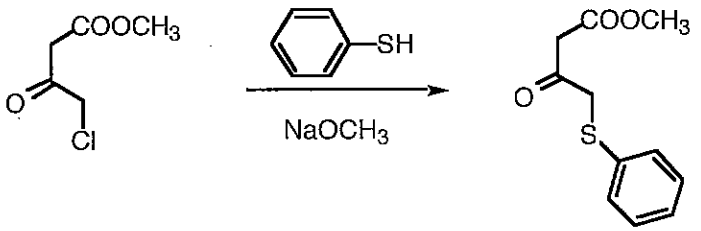


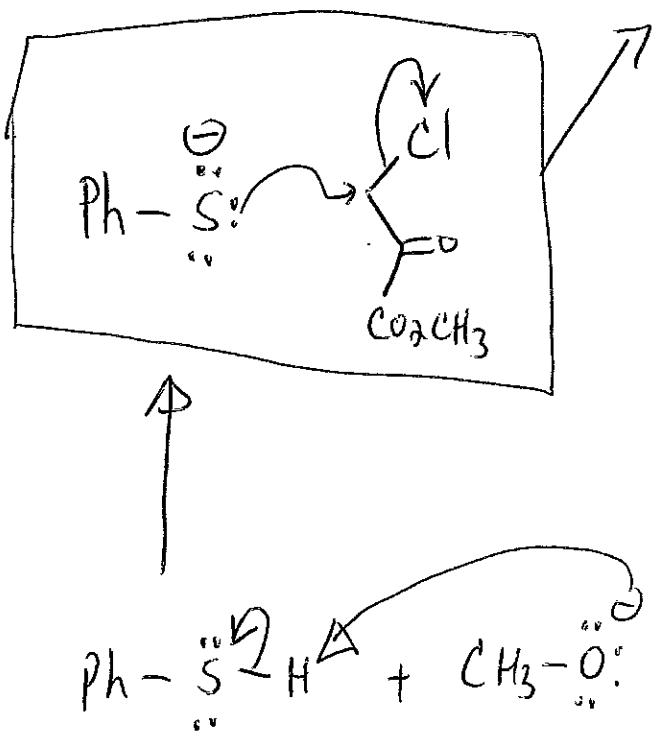
8. (Continued)

(b) *Cis*-decalin can ring-flip. *Trans*-decalin cannot ring-flip, as it is kinetically locked in one conformation. Assuming *cis*-decalin and *trans*-decalin can be set in equilibrium with each other, briefly explain which isomer would be entropically favored.

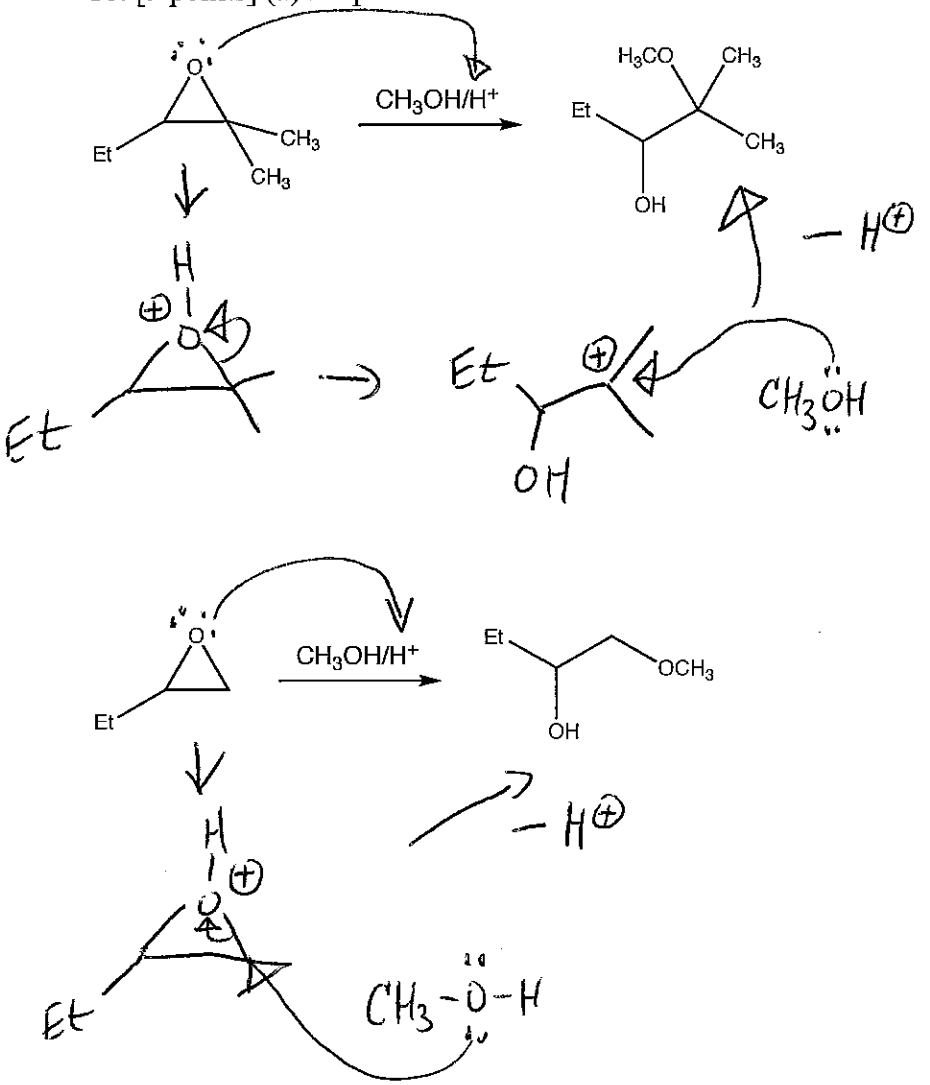
(cis.) Having 2 possible conformations versus 1 for trans, cis is more disordered.

9. [3 points] Propose a mechanism for the reaction below:





10. [9 points] (a) Propose a mechanism for each reaction below.



(b) Which center reacts the slowest under the above conditions (assume the products shown are the major products)?:

(1) Primary (2) Secondary (3) Tertiary

(c) Explain how you arrived at your answer to part (b).

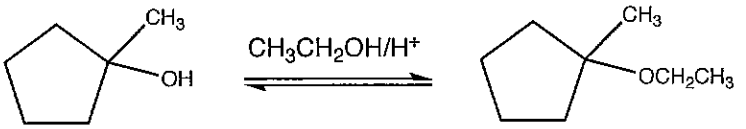
Top reaction: 3° reacted over 2°

Bottom reaction: 1° " "

or: 1° faster than 2° at SN2

3° " " at SN1

11. [5 points] Answer the following questions with respect to the reaction below.



(a) When the concentration of the methylcyclopentanol is doubled, the equilibrium constant will:

(1) Double
(2) Half
(3) Increase, but not double
(4) Remain the same
(5) Cannot predict from the given information

(b) When the concentration of the methylcyclopentanol is doubled, the reaction rate will:

(1) Double
(2) Half
(3) Increase, but not double
(4) Remain the same
(5) Cannot predict from the given information

(c) Assuming the reaction is reversible, if a dehydrating agent is added to the reaction mixture, the reaction will:

(1) Shift to the right
(2) Shift to the left
(3) Shift both ways
(4) Remain the same
(5) Cannot predict from the given information

(d) If the temperature is increased, the equilibrium constant will:

(1) Increase
(2) Decrease
(3) Remain the same
(4) Likely change, but can't predict which direction based on the given information

(e) The optical activity does not change as this reaction proceeds because:

(1) The product is racemic
(2) The product and starting material are achiral
(3) The configuration is inverted
(4) The reaction is S_N2