CH 253 FALL 2000 EXAM #3

1. (20 points) Multiple choice. Circle the <u>one</u> best answer for each problem below.

A. Which of the following is true about <u>any</u> (R) enantiomer?

1. it is dextrorotatory
2. it is levorotatory
3. it is an equal mixture of + and -
4. it is the mirror image of the (S) enantiomer
5. (R) indicates a racemic mixture.

B. How many chiral stereoisomers can be drawn for $CH_3\overset{*}{C}HBr\overset{*}{C}HClCH_3$?

1. 1 2. 2 3. 3 4. 4 5. 8

C. Which object below is achiral?

1. a spiral wire 2. a screw 3. a baseball glove 4. an ear 5. sunglasses

D. A pentacoordinate carbon is a transition state in the _____ mechanism.

1. S_N1 2. S_N2 3. E1 4. E2 5. no mechanism

E. Which is a meso compound?

1. (2R,3R)-2,3-dibromobutane 2. (2R,3S)-2,3-dibromopentane
3. (2R,4R)-2,4-dibromopentane 4. (2R,4S)-2,4-dibromopentane
5. none of these

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F. Which of the following statement(s) is (are) true of S_N1 reactions of alkyl halides in general?

1. the rate of an S_N1 reaction depends on the concentration of the alkyl halide
2. the rate of an S_N1 reaction depends on the concentration of the nucleophile
3. S_N1 reactions of alkyl halides are favored by polar protic solvents
4. answers 1 and 3 only are true
5. answers 1, 2, and 3 are true

G. Which S_N2 reaction will occur most rapidly in aqueous acetone solution?

1. $NaOH + CH_3F \rightarrow CH_3OH + NaF$
2. $NaOH + CH_3Cl \rightarrow CH_3OH + NaCl$
3. $NaOH + CH_3Br \rightarrow CH_3OH + NaBr$
4. $NaOH + CH_3I \rightarrow CH_3OH + NaI$
5. They will all occur at the same rate

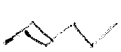
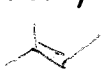
H. The relative nucleophilicities of species do not necessarily parallel the relative basicities of the same species because:

1. not all nucleophiles are bases, and vice versa
2. experimental measurements of sufficient accuracy are not available to make the comparisons
3. nucleophilicity is a thermodynamic matter; basicity is a matter of kinetics
4. basicity is a thermodynamic matter; nucleophilicity is a matter of kinetics
5. actually, the relative values do parallel one another

I. Rearrangements are likely to occur in which of the following reaction types?

1. S_N1 reactions 2. S_N2 reactions 3. E1 reactions
4. E2 reactions 5. both S_N1 and E1 reactions

J. For which of the following is E/Z isomerism impossible?

1. 2-hexene  2. 3-methyl-2-pentene 3. 3-hexene
4. 2-methyl-2-butene  5. 2-pentene

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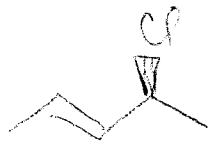
2. (15 points) Nomenclature. Draw the correct structure for each name provided below.

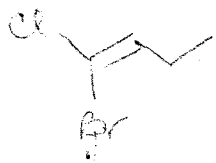
A) (E, 4S)-4-chloro-2-pentene



B) (R)-4-fluoro-2-pentyne

C) (S)-2-bromobutane

D) (Z)-1-bromo-1-chloro-1-butene



E) 5,6-dibromocyclohexene

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3. (8 points) Calculations...

A) An aqueous solution of pure stereoisomer X of concentration 0.10 g/mL had an observed rotation of -30° in a 1.0 dm tube at 25°C. What do you calculate its $[\alpha]_D$ to be at this temperature? (Show your work.)

3 $$[\alpha]_D = \frac{-30}{(0.1)(1)} = -300$$

B) Under identical conditions, but with a concentration of 0.050 g/mL, a solution of X had an observed rotation of +165°. Rationalize how this could be, and recalculate $[\alpha]_D$ for stereoisomer X.

3 $$[\alpha]_D = \frac{+165}{(0.05)(1)} = +3300$$

If the first rotation (part A) was

2 really +330° rather than -30°

then $[\alpha]_D = \frac{+330}{(0.1)(1)} = +3300$ - same number

Text:
5.42

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4. (5 points) Which reagent in each pair would be the more reactive nucleophile in a protic solvent?

A) CH_3NH^- or CH_3NH_2

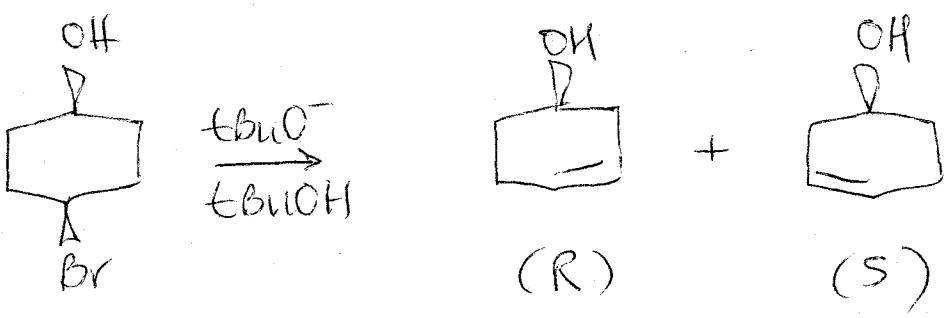
B) H_2O or H_3O^+

C) CH_3SH or CH_3OH

D) CH_3O^- or $CH_3CO_2^-$

E) Cl^- or I^-

5. (4 points) cis 4-bromocyclohexanol, when treated with *t*-BuO$^-$ in *t*-BuOH, gives compound C ($C_{10}H_{10}O$) as a racemic mixture. Compound C has an IR absorption in the 1620-1680 cm^{-1} region and in the 3400-3600 cm^{-1} region. Draw and label the (R) and (S) enantiomers of product C.



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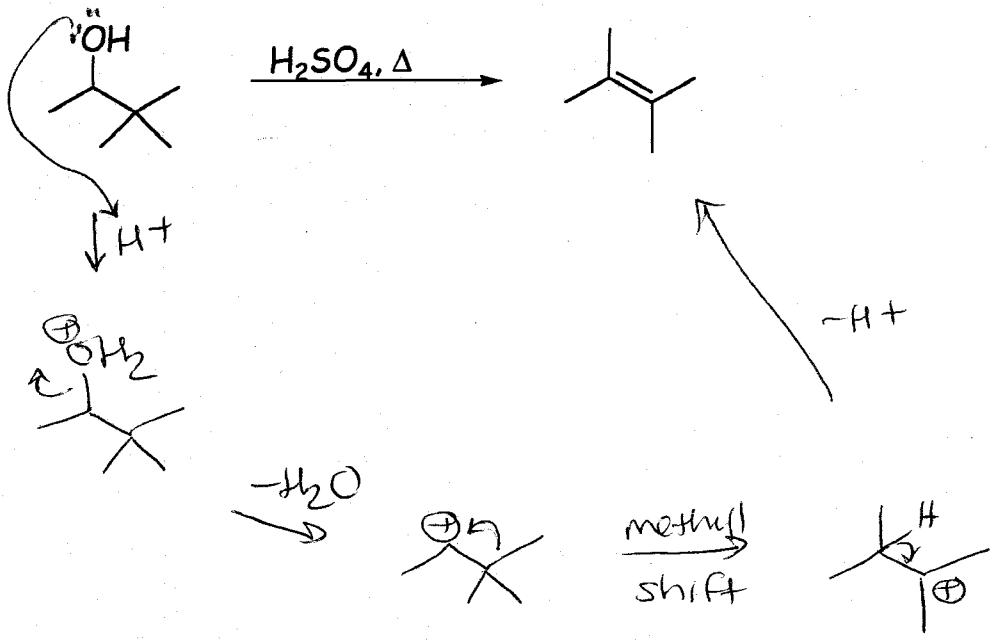
6. (6 points) Propose a mechanism for the following transformation, using proper electron-pushing formalisms.



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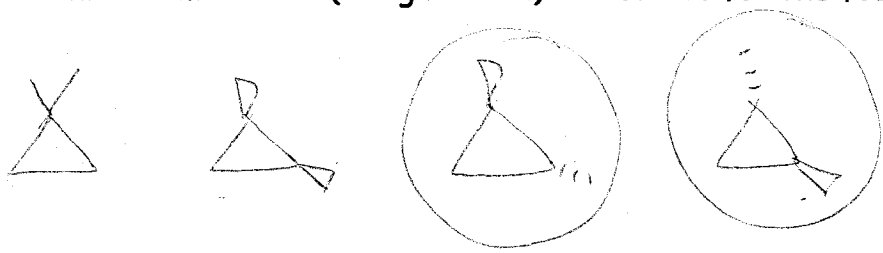
7. (14 points) There are four dimethylcyclopropane isomers.

A) Write three-dimensional (wedge-hatch) structures for the four isomers.



B) Which of these isomers are chiral? (Circle them in your answer above.)

C) If a mixture consisting of one mole of each of these isomers was subjected to simple gas chromatography, how many fractions would be obtained, and which compounds would each fraction contain?

three fractions

1. (achiral)

2. (meso)

3 and

(enantiomers)

racemic

D) How many of the fractions obtained in part C would be optically active?

None of them.

Text

5.37

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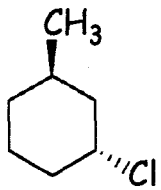
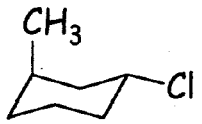
8. (8 points) What is the relationship between each pair of molecules shown below? (Possible answers include: identical, enantiomers, diastereomers, constitutional isomers)

a) 



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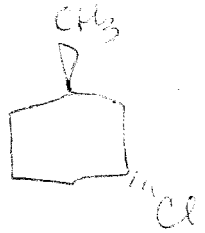
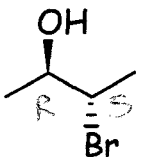
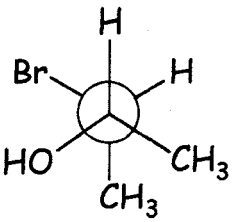


identical

b) 



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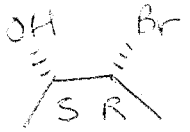
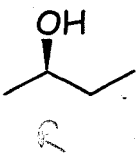
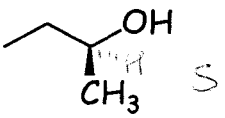
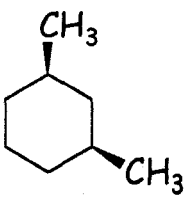


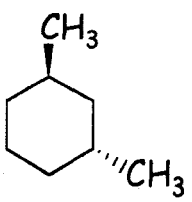
enantiomers

c) 



enantiomers

d) 



diastereomers

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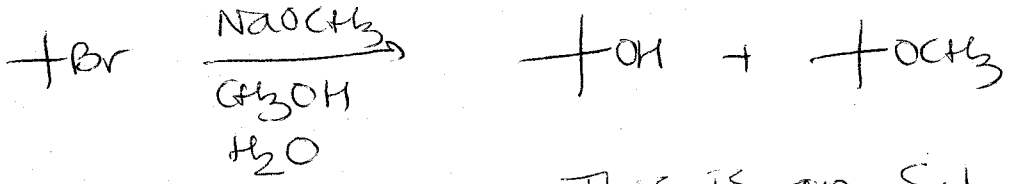
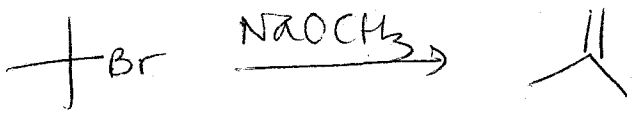
9. (5 points) Explain the following observations: When *tert*-butyl bromide is treated with sodium methoxide in a mixture of methanol and water, the rate of formation of *t*BuOH and *t*BuOCH$_3$ does not change appreciably as the concentration of NaOCH$_3$ is increased. However, increasing the concentration of NaOCH$_3$ causes a marked increase in the rate at which the *tert*-butyl bromide disappears from the mixture.



This is an S_N1 process which only depends on [tBr], not on [NaOCH$_3$]

Competing rxn:



This is an E2 process, so it depends both on [tBr] and on [NaOCH$_3$], and it contributes to the loss of tBr.

Text 6.28

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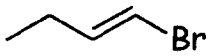
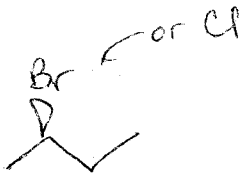
10. (21 points) Each of the following transformations is missing either reactant(s), reagent(s), or product(s). Fill in the missing information so as to successfully complete the reaction. Remember that "NRX" is always a possible ***PRODUCT***. Your best 7 of the 8 reactions given will be counted. Indicate stereochemistry where appropriate.

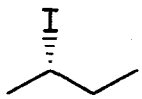
a) 

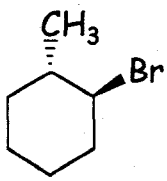
NaCN, DMSO →

NRXn

b) 

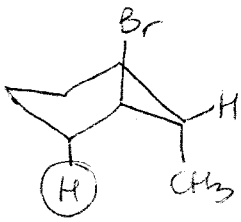
NaI, acetone →



c) 

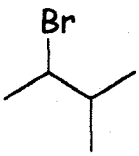
NaOH, EtOH, Δ →

⇌

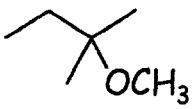


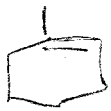
not anti

only

d) 

CH_3OH →





not possible

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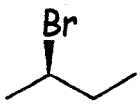
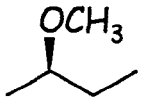
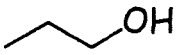
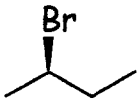
e) 

1) NaI, acetone
2) $NaOCH_3$, CH_3OH



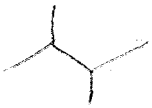
f) 

1) NaH
2) CH_3Br

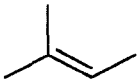
g) 

CH_3OH

racemic

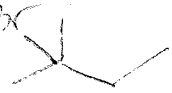
h) 

$NaOCH_3$, CH_3OH, Δ



Br ← or other L.G.

or

or other L.G. → Br 

Extra Credit: What are the top two international destinations for United States travelers? Canada and Mexico.

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