CH 223: Organic Chemistry (TTh)

September 19, 1989

NAME (Please print in full) _____
Last First Middle

College of Registration _____

S.S. No. _____

1. _____
2. _____
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Total _____

1. (15 pts) Rank the following by numbering 1, 2, 3:

1)	1	2	3	**3)**	2	1	3	**5)**	1	3	2
2)	3	2	1	**4)**	3	1	2				

a) According to the polarity of the covalent bond. (1 = most polar)

F - F C - O C - N

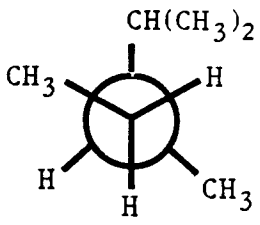
b) According to percent of s-character about the underlined c-atom. (1 = greatest)

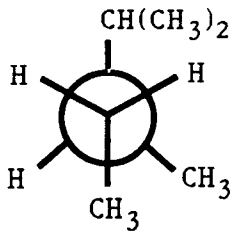
$CH_3\underline{C}N$ $CH_3\underline{C}HO$ $CH_3\underline{CH_2}OH$

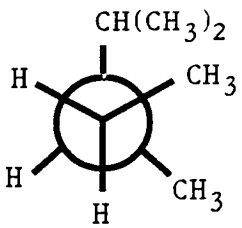
c) In order of increasing acidity. (1 = least acidic)

CH_4 CH_3OH CH_3NH_2

d) According to stability. (1 = most stable)





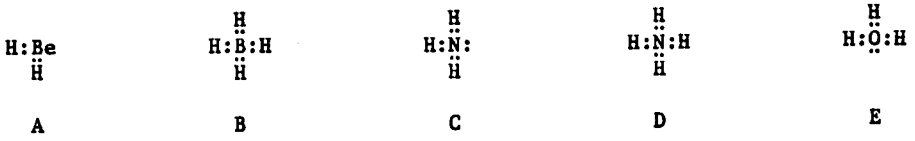


e) According to the common number of valencies. (1 = greatest number)

C O N

2. (20 pts) Circle the correct answer.

a) Listed below are electron dot formulas for several simple molecules and ions. All valence electrons are shown; however, electrical charges have been omitted deliberately.



A B C D E

Which of the structures actually bear a positive charge?

(1) A
(2) B
(3) C
(4) C and E
(5) D and E

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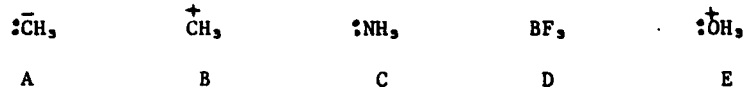
b) Which of the following would have a trigonal planar (or triangular) structure?



A B C D E

(1) A,B, and D
(2) B and D
(3) D only
(4) B,D, and E
(5) all of the above

---

c) Which principle(s) or rule must be used to determine the correct electronic configuration for carbon?

(1) Aufbau Principle
(2) Hund's Rule
(3) Pauli Exclusion Principle
(4) (1) and (2) only
(5) All three

---

d) In quantum mechanics a node (nodal surface or plane) is:

(1) a place where Ψ is negative.
(2) a place where Ψ is positive.
(3) a place where $\Psi = 0$.
(4) a place where Ψ^2 is large.
(5) a place where Ψ^2 is negative.

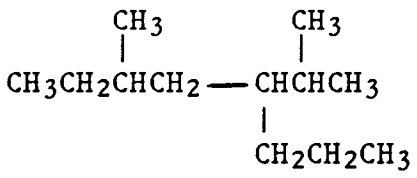
---

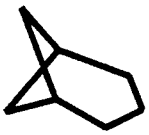
e) Which of the acids below would have the strongest conjugate base?

(1) CH_3CH_2OH $K_a = 10^{-18}$
(2) CH_3CO_2H $K_a = 1.76 \times 10^{-5}$
(3) $ClCH_2CO_2H$ $K_a = 155 \times 10^{-5}$
(4) Cl_2CHCO_2H $K_a = 5140 \times 10^{-5}$
(5) Cl_3CCO_2H $K_a = 90000 \times 10^{-5}$

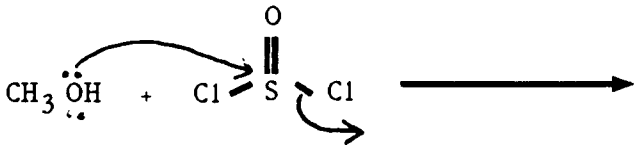
3. (55) Follow the directions for each part.

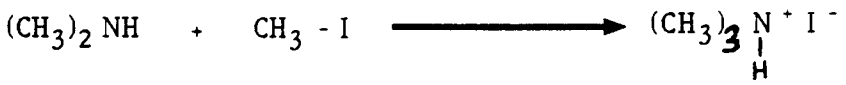
a) (6 pts) Provide IUPAC names for the following molecules





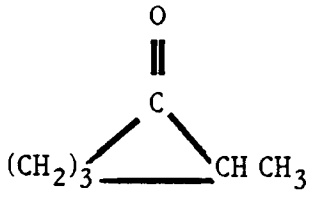
b) (6 pts) Draw products indicated by the arrows or arrows indicating how the products were formed as required.





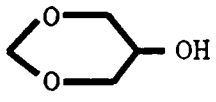
c) (6 pts) Convert to bond line notation:

$(CH_3)_3\ CO\ CH\ (CH_3)_2$



d) (4 pts) Provide a conformational drawing for the most stable conformation of trans-1,3-dimethylcyclobutane.

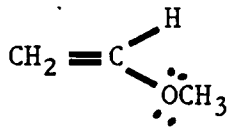
e) (6 pts) Draw the following molecule in its most stable conformation. Explain why the more stable conformation has an axial hydroxyl group.



f) (6 pts) What is the relationship between HOC≡N (A) and HN=C=O (B)? Will treatment of A or B with base afford the same or different conjugate base? Explain.

g) (4 pts) Draw pictorial representations of a σ bond and a π-bond.

h) (9 pts) Draw resonance structures for the following compounds:



i) (4 pts) Show how phase is involved in bonding by drawing pictures showing:

Bonding overlap between a 2Px orbital of carbon and a 2Px orbital of another carbon to form a σ bond.

j) (4 pts) Write an <u>algebraic expression</u> for the LCAO-MO representation of the following:

The antibonding orbital of C-C π-bond.

4. (10 pts) Draw the possible chain conformations of 1,1,2-trimethyl cyclohexane by completing the following structures. If a gauche butane interaction is worth 0.9 Kcal/mole, which conformation is more stable and by <u>how much</u>. Show all calculations.

CH 223: Organic Chemistry (TTh)

October 10, 1989

NAME (Please print in full) _____
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S.S. No. _____

1. _____
2. _____
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Total _____

(Please answer questions 1-2 on the scantron sheet (with soft pencil) and the remaining questions directly on the exam in(ink.)

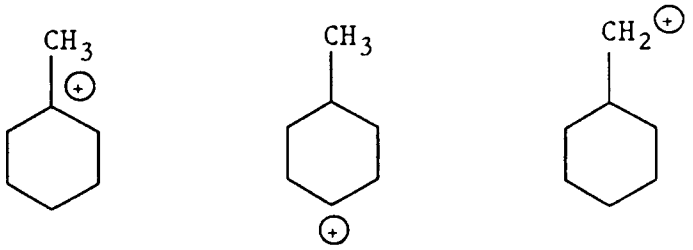
1. **(15 pts)** Rank the following by numbering 1, 2, 3:

1)	1	2	3	**3)**	2	1	3	**5)**	1	3	2
2)	3	2	1	**4)**	3	1	2				

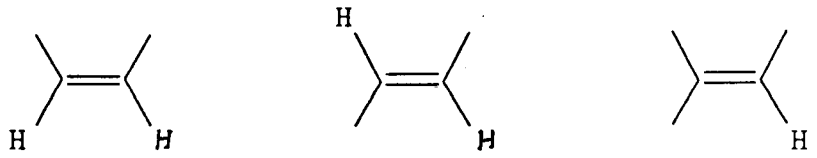
a) According to reactivity toward HX (1 = greatest)

$(CH_3)_3COH$ $CH_3CH_2CH_2OH$ $(CH_3)_2CHOH$

b) According to stability (1 = most stable)



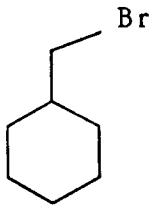
c) According to olefin stability (1 = most stable)

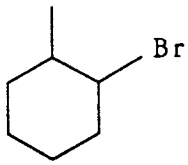


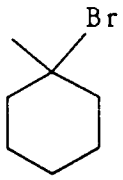
d) According to radical stability (1 = most stable)

$(CH_3)_2CH\ CH_2\ CH_2^{\bullet}$ $(CH_3)_2\overset{\bullet}{C}HCH_3$ $(CH_3)_2\overset{\bullet}{C}CH_2CH_3$

e) According to the rate in an E1 elimination (1 = fastest)







2. **(18 pts)** Circle the correct answer.

a) The t-butyl carbocation is stabilized by the delocalization of the positive charge through _____ orbitals.

(1) sp^2/p (4) p/sp^3

(2) sp^2/sp^3 (5) p/p

(3) sp^3/s

b) The p-orbital of a methyl cation, CH_3^+, contains how many electrons?

(1) one
(2) two
(3) three
(4) four
(5) none

c) 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

d) Which of the following compounds can exhibit cis-trans isomerism?

A. 1-pentene
B. 2-pentene
C. 2-methyl-2-pentene
D. 1,2-dibromoethene
E. 1,1-dichloroethene

(1) B,C,D

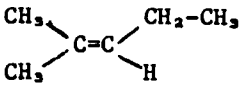
(2) A,C,E

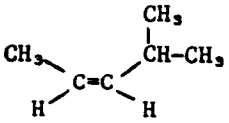
(3) B,D

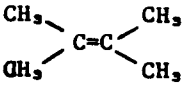
(4) B,C

(5) none of the above

e) Which reaction would you expect to liberate the least heat?

(1)  + $9O_2 \longrightarrow 6CO_2 + 6H_2O$

(2)  + $9O_2 \longrightarrow 6CO_2 + 6H_2O$

(3)  + $9O_2 \longrightarrow 6CO_2 + 6H_2O$

(4) $CH_2{=}CHCH_2CH_2CH_2CH_3 + 9O_2 \longrightarrow 6CO_2 + 6H_2O$

(5) $CH_2{=}CCH_2CH_2CH_3 + 9O_2 \longrightarrow 6CO_2 + 6H_2O$

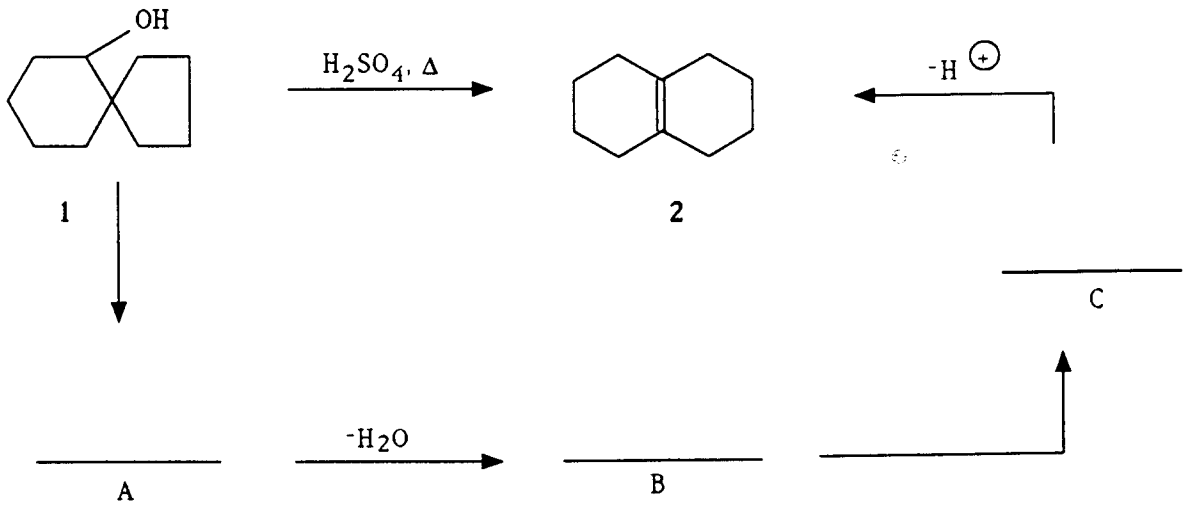
f) Which statement(s) is (are) true of acid-catalyzed alcohol dehydrations?

(1) Protonation of the alcohol is a fast step.
(2) Formation of a carbocation from the protonated alcohol is a slow step.
(3) Rearrangements of less stable carbocations to more stable carbocations are common.
(4) Loss of a proton by the carbocation is a fast step.
(5) all of the above

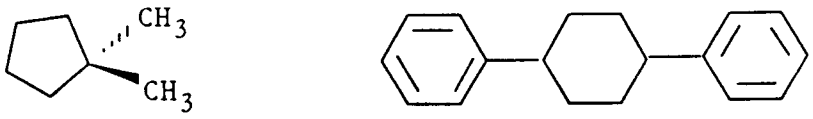
3. (33) Follow the directions for each part

a) **(5 pts)** Using a conformational sawhorse drawing, depict the <u>transition state</u> for the dehydrohalogenation reaction. Use as your system the dehydrohalognation of bromoethane with hydroxide ion as base. (p. 190)

b) **(6 pts)** Acid catalyzed dehydration of **1** led to alkene **2**. Write a palusible mechanism for this transformation by drawing structures for intermediates A, B, and C that may be present during the course of the reaction. (p. 6.20b)

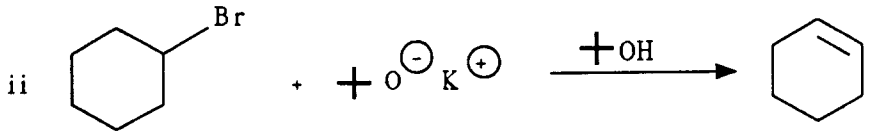


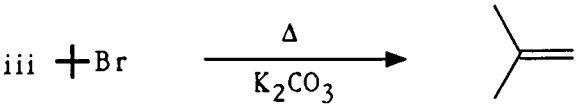
c) **(5 pts)** Indicate with arrows at the appropriate locations the number of <u>distinct</u> alkylbromides that can be formed upon <u>mono</u>bromination.

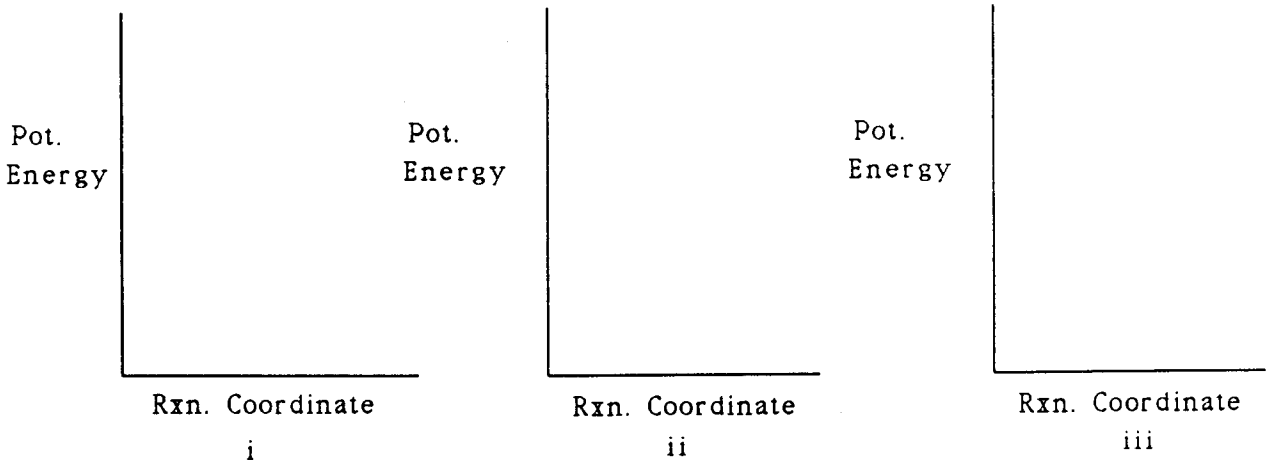


d) **(9 pts)** Draw a reasonable potential energy diagram for the following reactions.

i $CH_3CH_3 + I_2 \xrightarrow{h\upsilon} CH_3CH_2I$

ii 

iii 



e) **(9 pts)** Fill in the following table.

atom	O	N	C
valence electrons			
common valency			
valency for formal charge of +1			

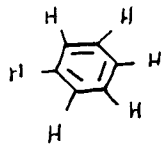
4. **(12 pts)** Hydrocarbons are chlorinated with t-Butylhypochlorite.

a) t-BuOCl + CH_3CH_3 $\xrightarrow{\text{Heat}}$ t-BuOH + CH_3CH_2Cl

Assuming a free radical chain mechanism, write the most likely initiation step (bond energies: CH_3CH_2 - H, 98; C - O, 85; O - Cl, 50, Kcal/mole.

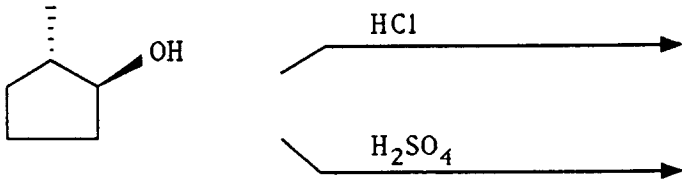
b) Consider the possible free readical chain chlorination of benzene. Given the following bond dissociation energies (a) write the chain propagating steps; (b) calculate ΔH° for each chain propagating step and (c) explain why this is not or is a good procedure for the preparation of chlorobenzene.

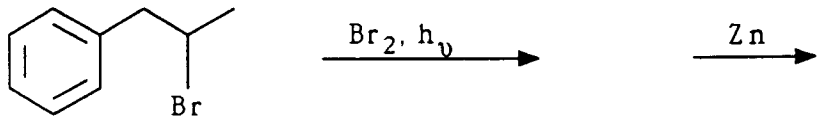
C_6H_5 - H	112 Kcal/mole	H - Cl	103
C_6H_5 - Cl	86	Cl - Cl	58
C_6H_5 - CH_3	93	CH_3 - H	104
		$(CH_3)_3CO-H$	102

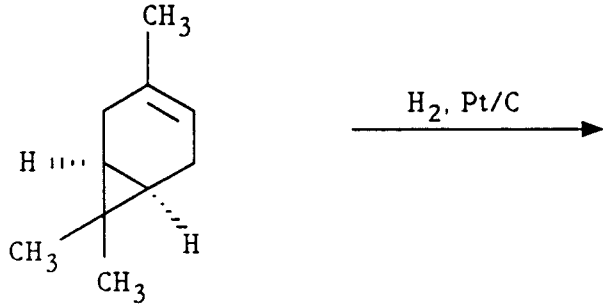


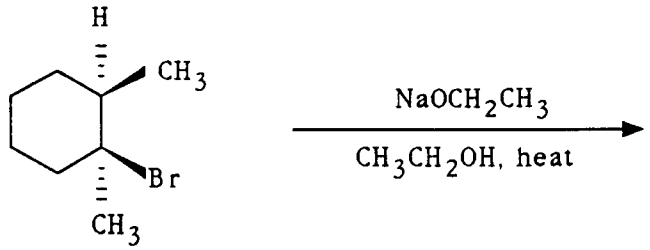
Benzene

5. **(24 pts)** Indicate all products that may be formed. Where appropriate indicate stereochemistry and/or regiochemistry for full credit. 49









CLEMSON UNIVERSITY

CH 223: Organic Chemistry (TTh)

November 14, 1989

NAME (Please print in full) _____
Last First Middle

College of Registration _____

S. S. No. _____

1. _____

2. _____

3. _____

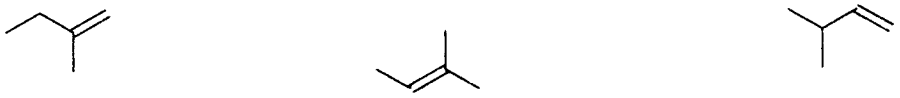
(Please answer question 1 on the scantron sheet (with soft pencil) and the remaining questions directly on the exam in ink.) Total _____

1. (15 pts) Rank the following by numbering 1, 2, 3:

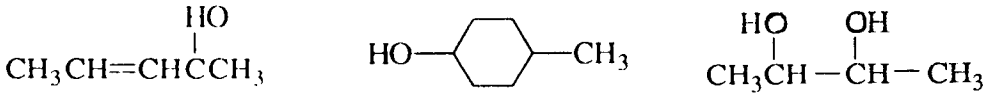
1)	1	2	3	**3)**	2	1	3	**5)**	1	3	2
2)	3	2	1	**4)**	3	1	2				

Part A (15 pts) Rank the following by numbering 1, 2, 3:

1. According to reactivity with Br_2 (1 = most reactive) p. 7, 11.



2. According to number of stereoisomers (1 = greatest no.) p. 275, 277,285.



3. According to reactivity with LiI in acetone (1 = most reactive) Table 9.2.

$(CH_3)_2CHBr$ CH_3Br CH_3CH_2Br

4. According to reactivity of the nucleophile (1 = most reactive) Table 9.4.

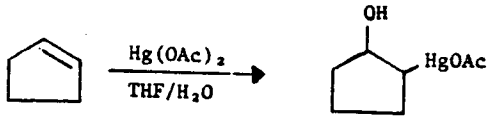
$I^{\ominus}$ H_2O $RCOO^{\ominus}$

5. According to reactivity in aqueous HCOOH (1 = most reactive) Table 9.5.

CH_3CH_2Br $(CH_2)_3CBr$ $(CH_3)_2CHBr$

Part B: Choose the correct answer

6. What is the electrophilic species involved in the initial step of the reaction below?



(1) ^{+}OH

(2) $^{+}HgOAc$

(3) H_3O^{+}

(4) THF

(5) the THF/H_2O complex

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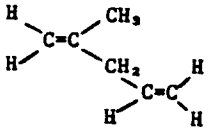
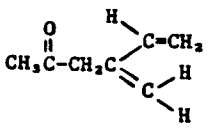
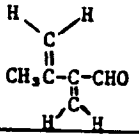
7. What is the structure of the compound that yields 2 moles of formaldehyde (HCH) and 1 mole of CH_3CCH_2CHO upon ozonolysis followed by treatment with zinc in water?

(1) 

(2) 

(3) 

(4) 

(5) 

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8. Cis-trans isomers are:

(1) diastereomers

(2) enantiomers

(3) stereoisomers

(4) structural isomers

(5) answers (1) and (3)

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9. Which of the following statements is (are) true of an S_N2 reaction of R-2-bromobutane with hydroxide ion?

(1) Doubling the hydroxide ion would double the rate of the reaction. (Assume that all other experimental conditions are unchanged.)

(2) The reaction would occur with inversion of configuration.

(3) Doubling the concentration of R-2-bromobutane would double the rate of the reaction. (Assume that all other experimental conditions are unchanged.)

(4) Answers (1) and (2) only are true.

(5) Answers (1), (2), and (3) are true.

10. Which of the following is <u>not</u> true of enantiomers?

(1) Have the same boiling point.

(2) Have the same melting point.

(3) Have the same specific rotation.

(4) Have the same density.

(5) Have the same chemical reactivity.

11. Which of the following statements 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 solvents.

(4) Answers (1) and (3) only are true.

(5) Answers (1), (2), and (3) are true.

2 (32 pts) Follow the Directions for each part

A (8 pts) Give the mechanistic symbols (S_n1, S_n2, E1, E2) that are most consistent with each of the following. p. 9.20.

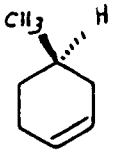
i These reaction mechanisms are concerted processes.

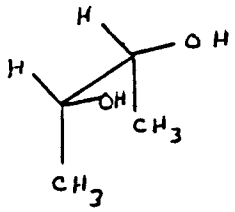
ii Reactions proceeding by these mechanisms are stereospecific

iii These reaction mechanisms are the ones most likely to have been involved when the products are found to have a different carbon skeleton than the substrate

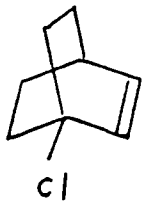
iv Alkyl iodides react faster than alkyl bromides in reactions that proceed by these mechanisms.

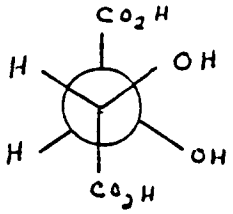
B (6 pts) Assign absolute configurations as R or S to the chiral centers in the following molecules. p. 266, 275

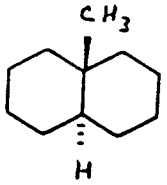


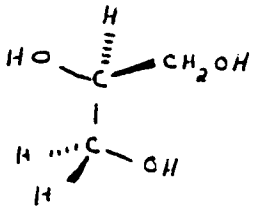


C (8 pts) Cirlce the following structures that are chiral p. 286, p . 8.19

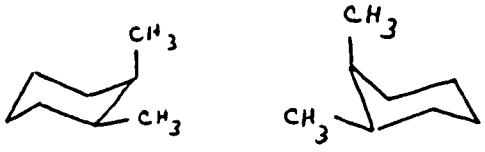




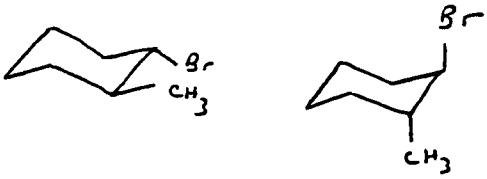




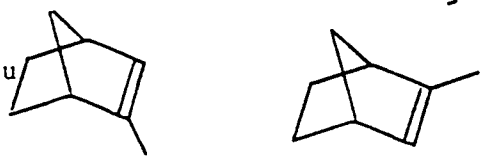
D (10 pts) Indicate the relationship between the following molecules as conformational enantiomers, conformational diastereomers, configurational enantiomers, configurational diastereomers or identical structures.



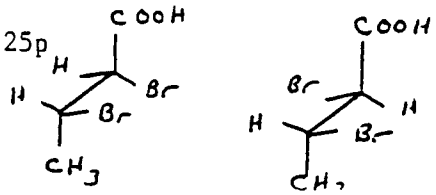
p. 8.25k



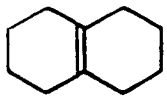
p. 8.25u



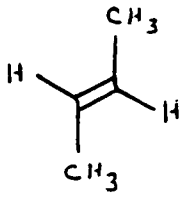
p. 8.25p



(36 pts)
Predict the major products for the following reactions. All important diastereomers must be drawn. Full credit requires indication of regiochemsitry and/or stereochemistry where appropriate.

p. 7.22k 

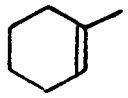
1. O_3, CH_2Cl_2
2. H_2O, Zn



Br_2, CCl_4
p. 279

$Hg(OAc)_2$, H_2O
p. 219

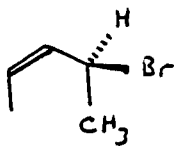
Cl_2, H_2O
p. 233



1. B_2H_6
2. $NaOH/H_2O_2$
p. 225

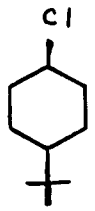
Br_2, peroxides
p. 7.4

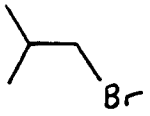
$KMnO_4$, warm!
p. 7.15



CH_3CO_3H/CH_2Cl_2
P. 8.36

$Na^{\oplus}\,{}^{\ominus}CN$
ethanol-water
p. 9.16d

p. 9.16k  + $PhS^{\ominus}\,{}^{\oplus}Na$ ⟶

p. 316 

NaOEt/EtOH
55°C ⟶