EXAMINATION 1

Chemistry 3A
Professor K. Peter C. Vollhardt
February 20, 1996

Name: _____
(PRINT First name first, then Last name. Use capital letters!)

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

111	Yang, J.	_____	351	Holmes, D.	_____
121	Losser, J.	_____	361	Chan. E.	_____
131	Larson, D.	_____	371	Lee,T.	_____
141	Choong, I.	_____	381	Chang, H.	_____
151	Goodwin, M.	_____	411	Fuller, J.	_____
161	Chan, E.	_____	421	Baxter, B.	_____
211	Paikoff, S.	_____	431	Chin, J.	_____
221	Staunton, J.	_____	441	Schultz, M.	_____
311	Yang, J.	_____	511	Carroll, D.	_____
321	Esker, T.	_____	521	Gray, D.	_____
331	Sell, J.	_____	531	Staunton, J.	_____
341	Gountchev, T.	_____	541	Losser, J.	_____
			551	Kumaraswamy, S.	_____

Making-up an I grade _____
(If you are, please indicate the semester during which you took Chem 3A previously_____.)

Please write the answers you want graded in the spaces provided. Do scratch work on the backs of the pages. This test should have 15 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions at least twice; make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy! Good Luck!**

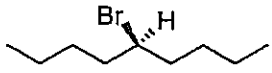
DO NOT WRITE IN THIS SPACE

I.	_____	(30)
II.	_____	(20)
III.	_____	(30)
IV.	_____	(20)
V.	_____	(15)
VI.	_____	(40)
VII.	_____	(30)
VIII.	_____	(15)
Total	_____	(200)

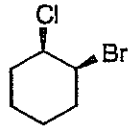
I. [30 Points]

Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary *(cis, trans, or R, S, meso).*

a.



b.



racemic

c.

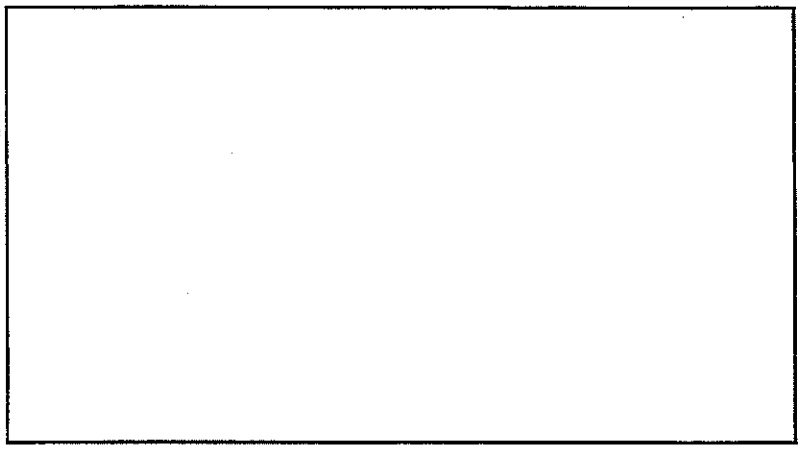
(2*R*, 3*S*)-2-Bromo-3-chlorobutane

(Fischer projection)

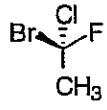
(fill in the missing atoms)

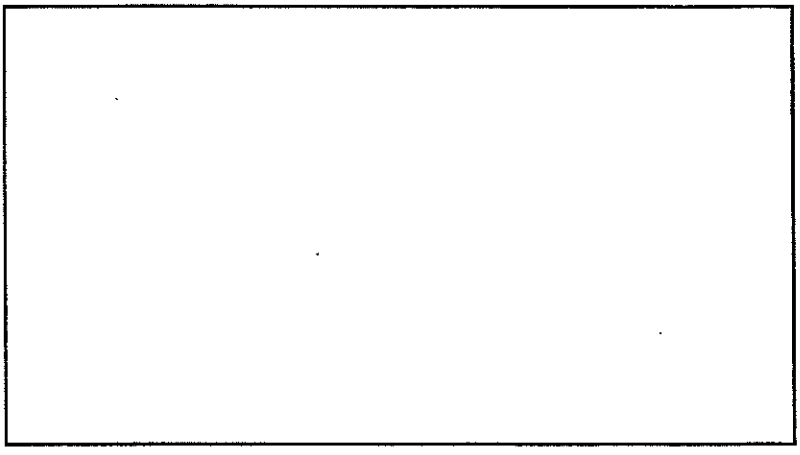
d.

cis-1-Cyclohexyl-4-methylcyclohexane



e.





II. [20 Points]

Write the most favorable Lewis *octet* structure for each of the molecules depicted below (don't forget formal charges).

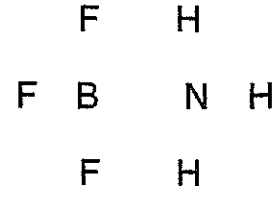
TABLE 1-1
Partial periodic table

Period							Halogens	Noble gases
First	H^{1}							He^{2}
Second	$Li^{2.1}$	$Be^{2.2}$	$B^{2.3}$	$C^{2.4}$	$N^{2.5}$	$O^{2.6}$	$F^{2.7}$	$Ne^{2.8}$
Third	$Na^{2.8.1}$	$Mg^{2.8.2}$	$Al^{2.8.3}$	$Si^{2.8.4}$	$P^{2.8.5}$	$S^{2.8.6}$	$Cl^{2.8.7}$	$Ar^{2.8.8}$
Fourth	$K^{2.8.8.1}$						$Br^{2.8.18.7}$	$Kr^{2.8.18.8}$
Fifth							$I^{2.8.18.18.7}$	$Xe^{2.8.18.18.8}$

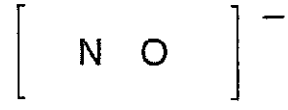
Note: The superscripts indicate the number of electrons in each energy level of the atom.

a.

b.

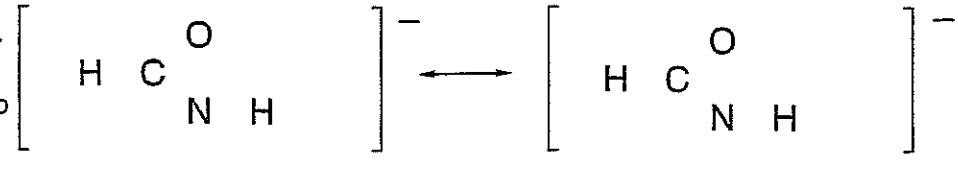


c.



d.

There are two octet resonance structures. Which one is a stronger contributor to the overall structure? (Circle)



III. [30 Points]

Trihydrogen cation H_3^+ is an ion observable in the gas phase by protonation of H_2 and represents the most simple cyclic triatomic molecule in the shape of an equilateral triangle.

$$H_2 + H^+ \longrightarrow H_3^+$$

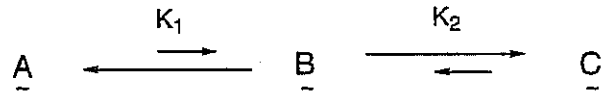
a. To derive a molecular orbital description of this protonation, first depict an energy diagram of the interaction of two hydrogen atoms giving H_2. Clearly label the energy levels as the appropriate atomic or molecular orbitals, draw an approximate picture of the bonding and antibonding molecular orbitals, and place the electrons into the correct levels.

b. Draw the energy diagram for the formation of H_3^+ by the reaction of H^+ with H_2. Clearly depict the energy levels of the orbitals entering into overlap and label them, and show the resulting bonding and antibonding molecular orbital levels. Place the relevant electrons into the various levels.

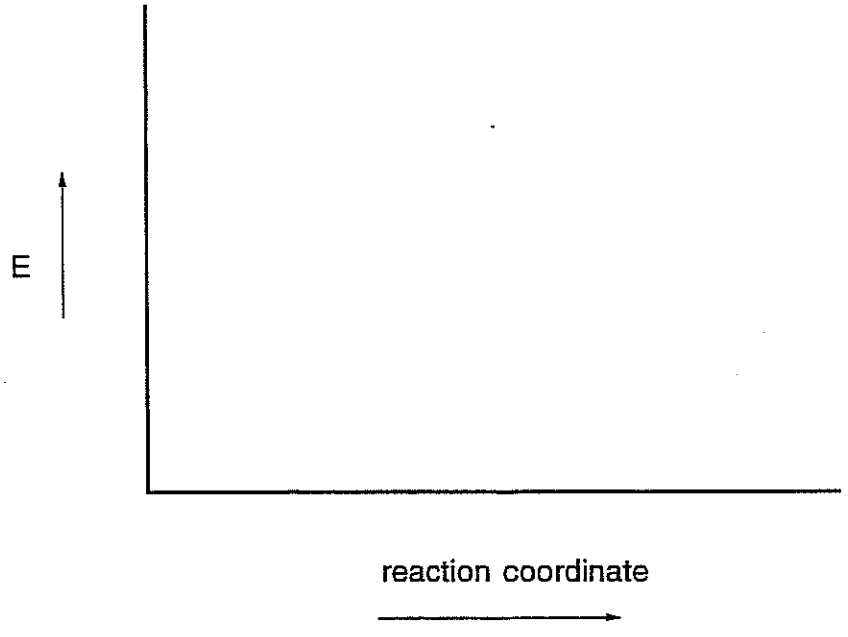
c. In view of the above, would you consider the protonation of helium to furnish a stable bond? Explain.

IV. [20 Points]

Heating a compound A to 100°C led to the exclusive formation of C. Mechanistic work showed that this reaction proceeds through an intermediate B, according to the following scheme:



Independent synthesis of B revealed that it is converted to A at room temperature, none of C being formed under these conditions. Draw a potential energy diagram describing the progress of the reaction from A to B to C. Clearly label the positions of A, B and C, and the transition states (TS) interconnecting the three reaction components. Circle the rate-determining TS for the conversion of A to C.



V. [15 Points]

We shall learn later in the course that alcohols may react with hydrogen halides to generate haloalkanes:

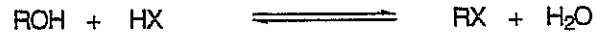
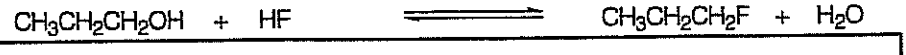


TABLE 3-1

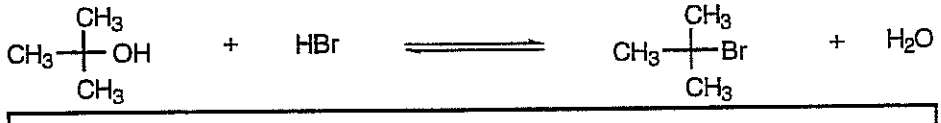
Bond-dissociation energies of some A–B bonds (DH° in kcal $mole^{-1}$)

	B						
A	H	F	Cl	Br	I	OH	NH_2
H	104	135	103	87	71	119	107
CH_3	105	110	85	71	57	93	80
CH_3CH_2	98	107	80	68	53	92	77
$CH_3CH_2CH_2$	98	107	81	68	53	91	78
$(CH_3)_2CH$	94.5	106	81	68	53	92	93
$(CH_3)_3C$	93	110	81	67	52	93	93

a. Using the table above, calculate the ΔH° of the following reactions. Show your work.



$\Delta H^\circ =$



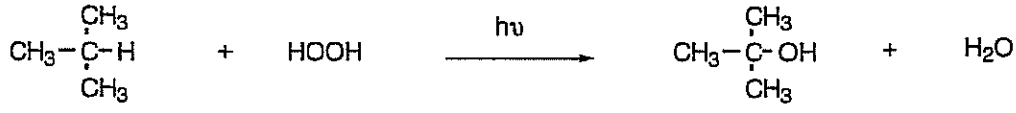
$\Delta H^\circ =$

b. Do you expect the ΔS^{o} for these reactions to be large and positive, large and negative, or negligible? Explain.

Answer:

VI. [40 Points]

Hydrogen peroxide, HOOH, converts alkanes to alcohols under free radical conditions with HO· as a chain carrier. For example:



a. Write a mechanism for this reaction including initiation, propagation, and (one) termination step.

Initiation:

Propagation:

Termination:

b. The O-O bond dissociation energy in H_2O_2 is 51 kcal mol^{-1} and other relevant DH° values are found in the table depicted in problem V.

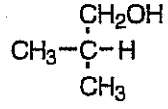
Calculate the enthalpies (ΔH°) of the overall transformation and of the propagation steps. Show your work.

ΔH° of overall reaction:

ΔH° of propagation steps:

c. The selectivity of HO• in attacking C-H bonds is: prim: sec: tert = 1: 65: 3500.

In the oxidation of 2-methylpropane what is the expected ratio of the observed product, $(CH_3)_3COH$, to the other possible product, $(CH_3)_2CH\,CH_2OH$?

Ratio $(CH_3)_3COH$:  =

d. The experimental heats of formation of the components of the oxidation in **a.** are given below.

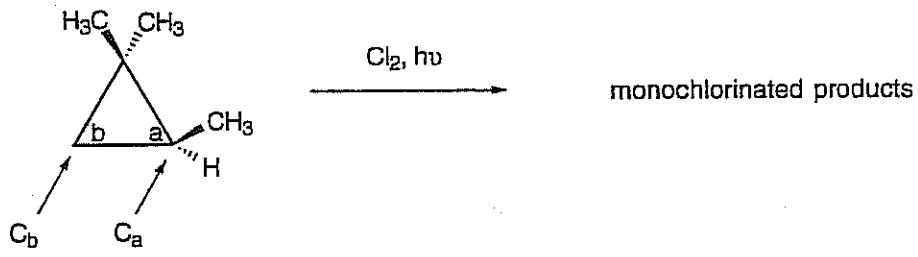
ΔH°_f (gas): $(CH_3)_3CH$ -32.4 H_2O_2 -32.6 $(CH_3)_3COH$ -74.8 H_2O -57.8 kcal mol^{-1}

Calculate again the ΔH° of the reaction. Show your work.

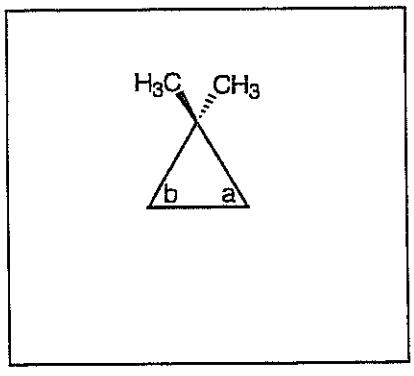
ΔH° =

VII. [30 Points]

Free radical chlorination of (2S)-1,1,2- trimethylcyclopropane is sluggish, but does furnish products of <u>monochlorination</u> at C_a and C_b.

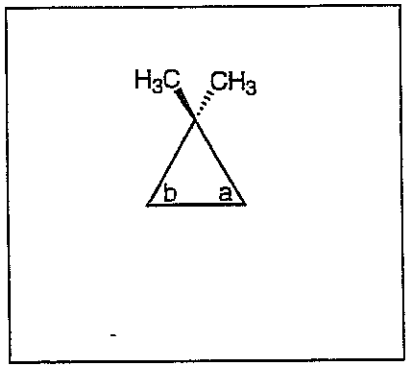


a. Draw all of them. Circle the appropriate descriptor for each product as chiral or achiral. Note: the five boxes may be in excess of what you need.



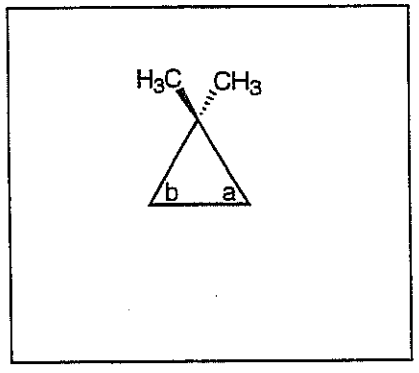
chiral

achiral



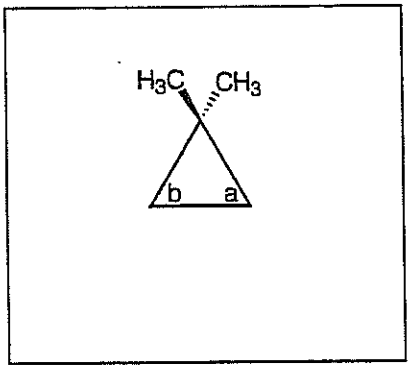
chiral

achiral



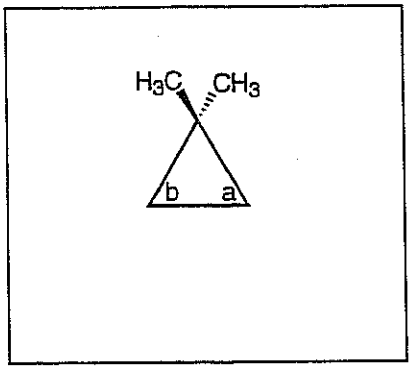
chiral

achiral



chiral

achiral



chiral

achiral

b. Do you expect chlorination at C_a to furnish optically active products? Explain.

c. Do you expect chlorination at C_b to furnish optically active products? Explain.

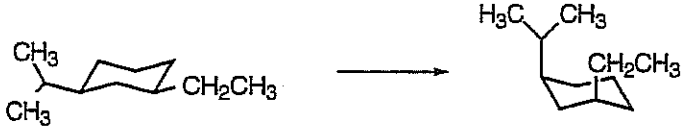
VIII. [15 Points]

Given the following values for the ΔG° of the ring flip for cyclohexane,

	ΔG° (kcal / mole)
-H	0
$-CH_3$	1.7
$-CH_2CH_3$	1.8
$-CH(CH_3)_2$	2.2
$-C(CH_3)_3$	5.0

Calculate ΔG° for the following conversions.

$\Delta G^\circ =$



$\Delta G^\circ =$