

EXAMINATION 1

Chemistry 3A
 Professor Carolyn Bertozzi
 Professor Peter Vollhardt
 October 1, 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.

161	Baryza, Jeremy	_____	311	Adronov, Alex	_____
111	Goon, Scarlett	_____	321	Mullins, Sarah	_____
121	Yeston, Jake	_____	331	Esker, Todd	_____
131	Gruneich, Jeffrey	_____	341	Shaffer, Wendy	_____
141	Richards, Steven	_____	351	Loftus, Christine	_____
151	Berglund, Timna	_____	411	Lemieux, George	_____
211	Thornton, Joel	_____	421	Essy, Blair	_____
221	Moore, Jennifer	_____	511	Staunton, Joanna	_____
361	Paisner, Sara	_____	521	Magliery, Thomas	_____
371	Tellers, David	_____	531	Marcordes, Belinda	_____

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 11 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!**

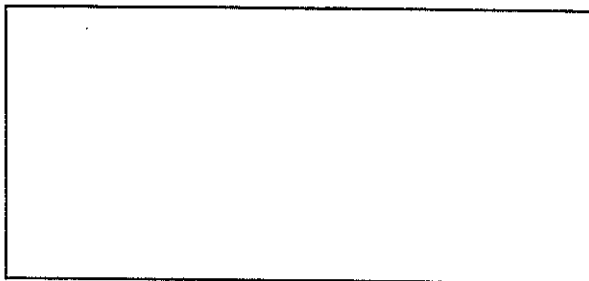
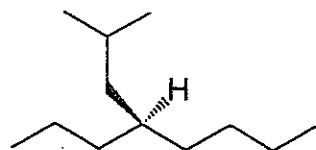
DO NOT WRITE IN THIS SPACE

I.	_____	(30)
II.	_____	(20)
III.	_____	(30)
IV.	_____	(20)
V.	_____	(15)
VI.	_____	(55)
VII.	_____	(15)
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*).

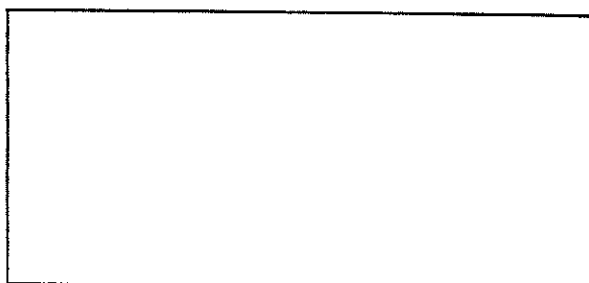
a.



b.

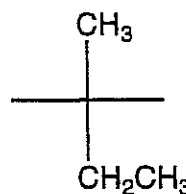


racemic

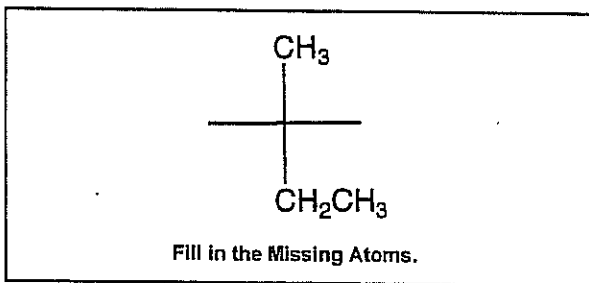


c.

(*R*)-2-bromobutane
(Fischer projection)

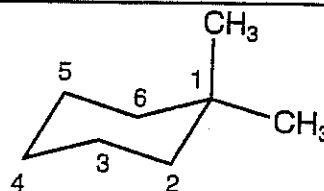


Fill in the Missing Atoms.

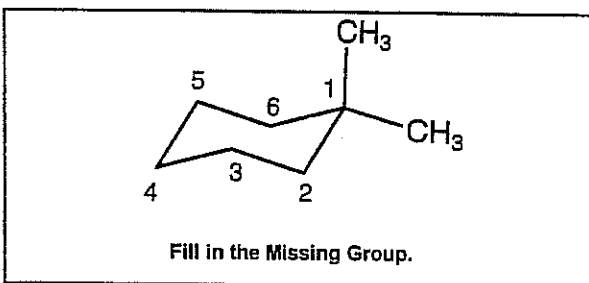


d.

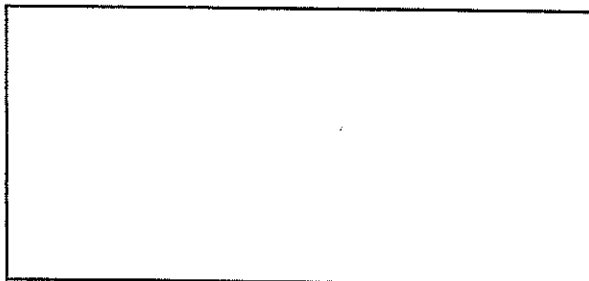
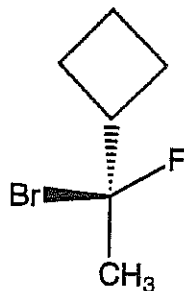
(*R*)-3-Fluoro-1,1-dimethylcyclohexane



Fill in the Missing Group.



e.



II. [20 Points]

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

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 ^{2,8,18,18,6}

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

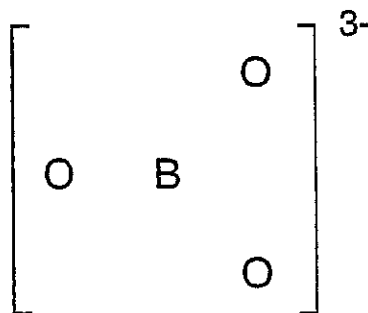
a.



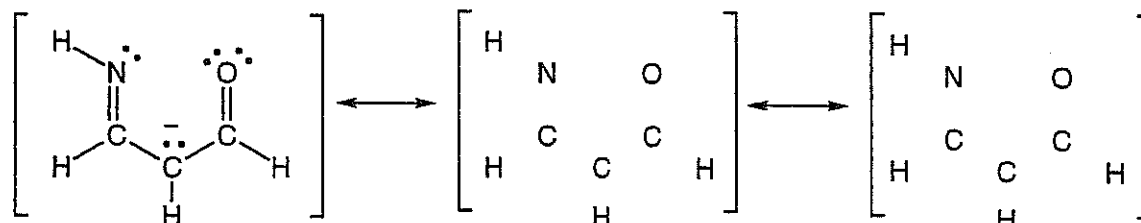
b.



c.



d.



Fill in the two additional octet resonance structures and circle the strongest contributor to the overall structure.

III. [30 Points]

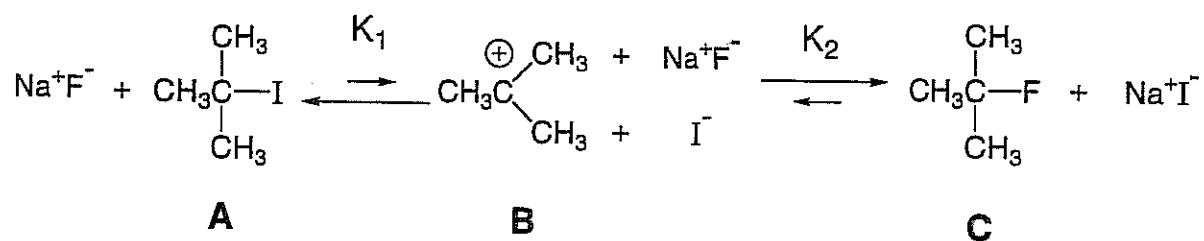
Trifluoroborane (boron trifluoride), BF_3 , reacts with F^- to form the tetrafluoroborate ion, BF_4^- .



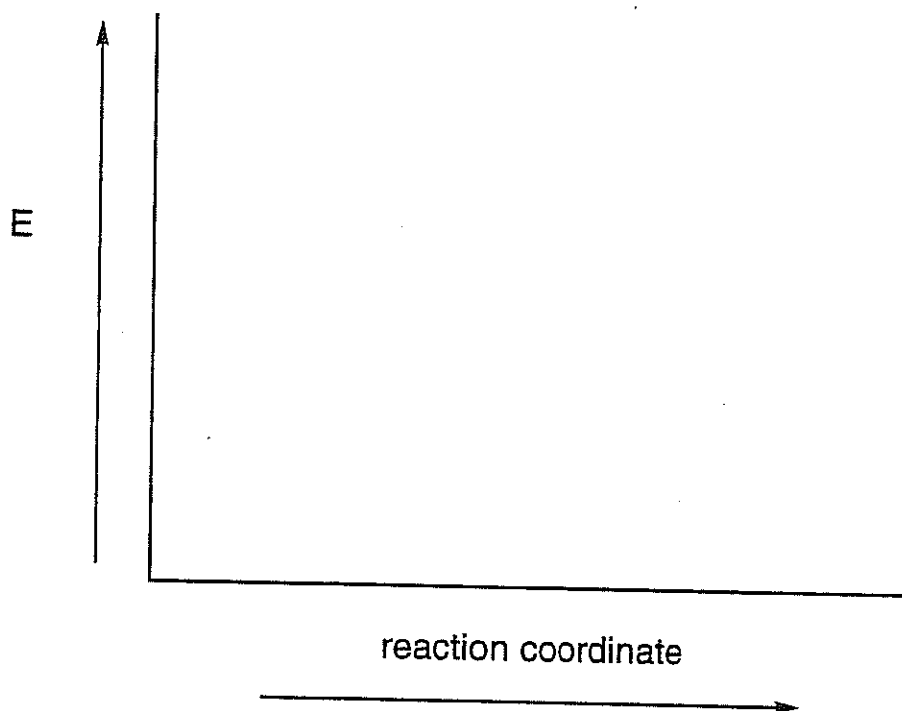
- a. Draw the orbital on BF_3 involved in this bond formation and show its overlap with the appropriate atomic orbital of F^- . Clearly label these orbitals (e.g. $1s$, $2s$, $2p$, $3s$, $3p$, sp , sp^2 , sp^3 , etc.).
- b. Draw the energy diagram for the formation of BF_4^- by the reaction of BF_3 with F^- . 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 (e.g. reaction with H^+) of the boron in BF_3 to furnish a stable bond? Explain.

IV. [20 Points]

Treatment of 2-iodo-2-methylpropane (**A**) with sodium fluoride (1 equivalent) led to the exclusive formation of 2-fluoro-2-methylpropane (**C**) via the intermediate 1,1-dimethylethyl (*t*-butyl) cation (**B**), according to the following scheme:



Independent generation of **B** revealed that it reacts faster with iodide than with fluoride ion. 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**.



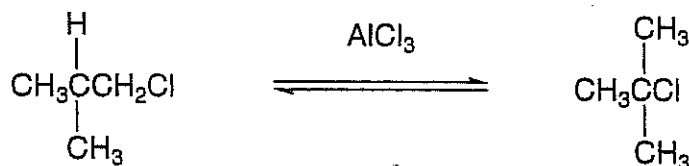
V. [15 Points]

Lewis acids, such as AlCl_3 , can cause isomerization of haloalkanes.

A in A-B	B in A-B						
	-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 ₃ CH ₂ CH ₂ —	98	107	81	68	53	91	78
(CH ₃) ₂ CH—	94.5	106	81	68	53	92	93
(CH ₃) ₃ C—	93	110	81	67	52	93	93

Note: These numbers are being revised continually because of improved methods for their measurement. Some of the values given here may be in (small) error.

- a. Using the table above to estimate the relevant bond dissociation energies, calculate the ΔH° of the following reaction. Show your work.



$\Delta H^\circ =$

- b. Circle one.

The two chlorides above are:

constitutional isomers

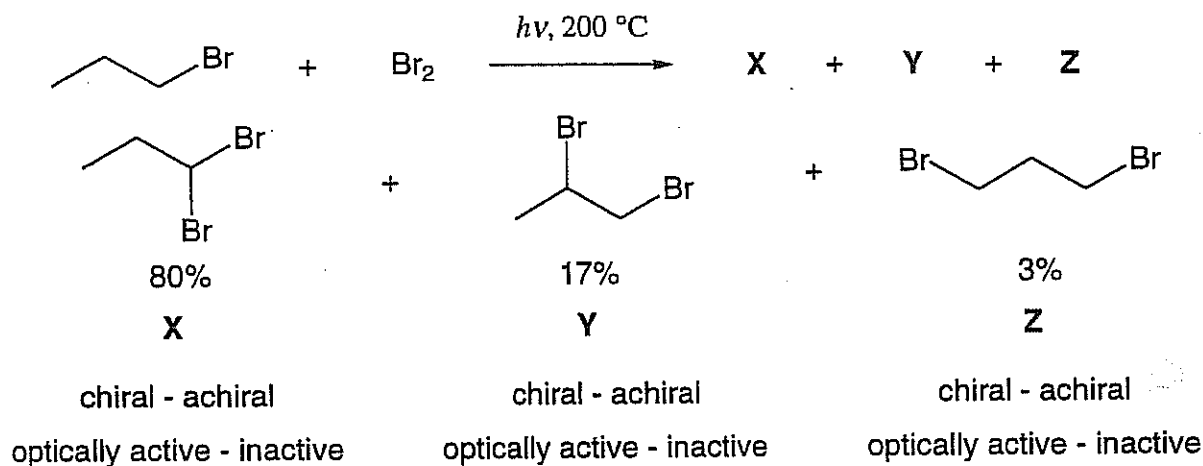
stereoisomers

- c. Do you expect the ΔS° for this reaction to be large and positive, large and negative, or negligible? Explain your answer.

Answer:

VI. [55 Points]

The free radical bromination of 1-bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, at 200°C results in a mixture of dibromides, as shown below, from which 1,2-dibromopropane, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{Br}$, can be separated by careful distillation.

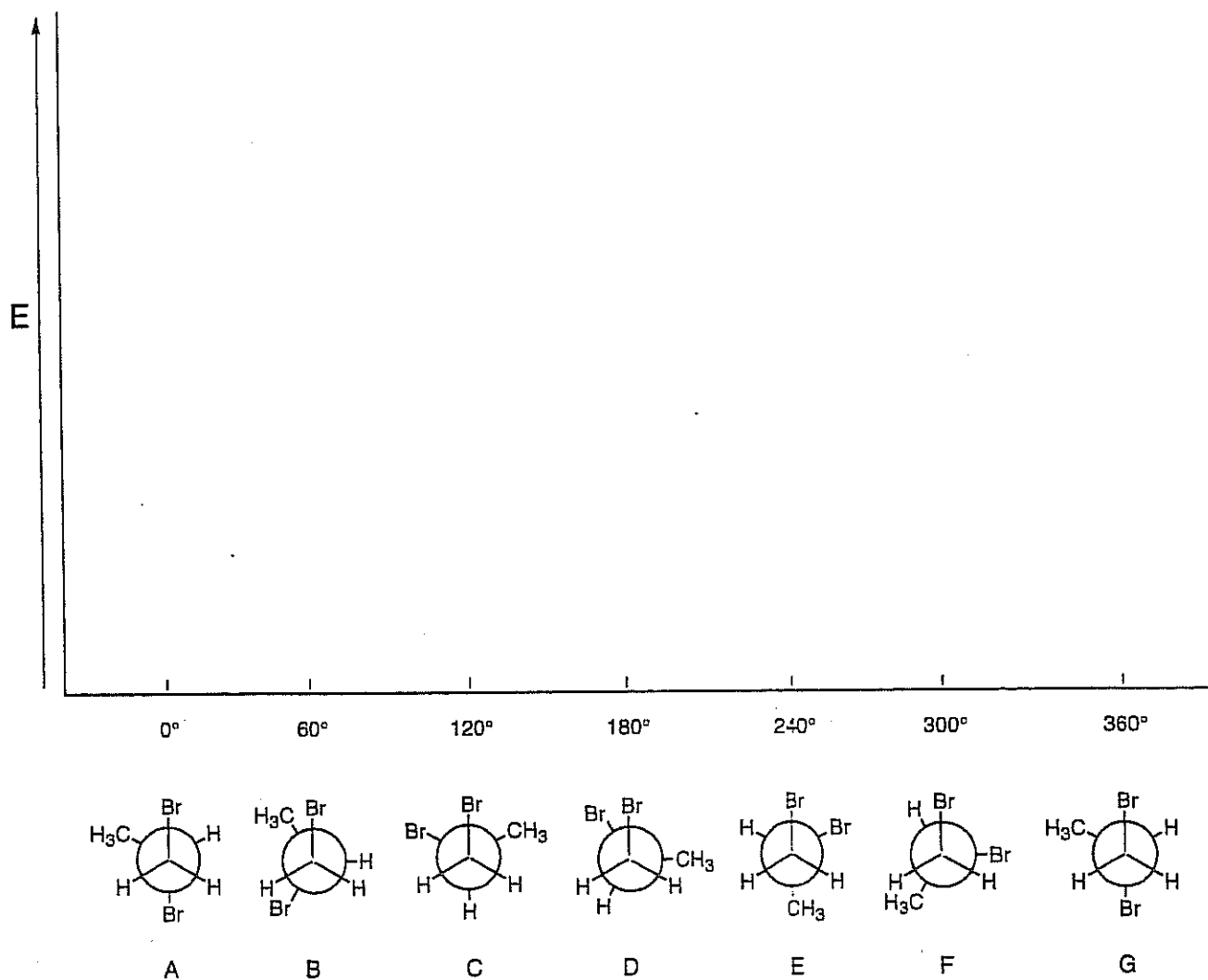


- Circle the appropriate labels to indicate whether the respective product is chiral or achiral, and optically active or inactive.
- From the % yield data, calculate the approximate relative reactivity of the hydrogens at C1, C2, and C3 in the starting material during this transformation.

Answer: Relative reactivity of H1 : H2 : H3 =

- Formulate the propagation steps in the mechanism of that part of the reaction that leads to 1,2-dibromopropane.

- d. Complete the following diagram by adding a qualitative potential energy curve for the rotation about the C1 - C2 bond of 1,2-dibromopropane, starting with the conformation shown at 0° and turning C2 (the back carbon in the Newman projection) by 60° increments. Indicate qualitatively (but clearly) the positions (i.e. relative energies) of the maxima and minima of the curve. Hint: CH_3 is larger than Br.

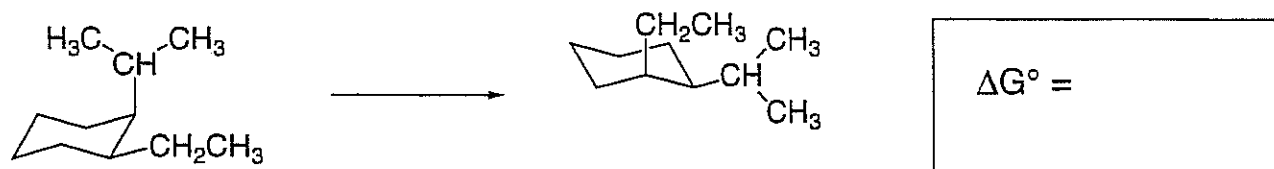
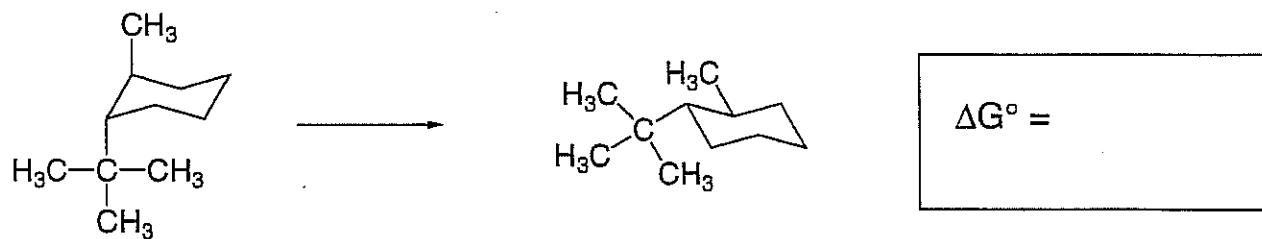


VII. [15 Points]

The following values represent ΔG° for the conversion of the equatorial to the axial conformer of the corresponding substituted cyclohexane,

	ΔG° (kcal / mol)
—H	0
—CH ₃	1.7
—CH ₂ CH ₃	1.8
—CH(CH ₃) ₂	2.2
—C(CH ₃) ₃	5.0

calculate ΔG° for the following conversion.



VIII. (15 points)

Place an 'X' mark in the box designating the most accurate statement.

a. The ΔH° of an organic reaction:

- reflects entropy changes.
- is highly negative for fast transformations.
- can be estimated by subtracting the sum of the DH° values of the bonds formed from those broken.
- is the symbol for the rate in the Arrhenius equation.

b. Covalent bonding is strongest when:

- lone electron pairs are involved.
- the atoms are large.
- bonding and antibonding molecular orbitals cancel each other.
- it is the result of overlap between atomic or hybrid orbitals of similar size and energy.

c. The compounds *cis*- and *trans*-1,3-dimethylcyclohexane are:

- identical.
- stereoisomers.
- interconverted by ring flip.
- rotamers.

d. The heat of formation, ΔH_f° , of diamond (a form of carbon) equals $+0.45 \text{ kcal mol}^{-1}$ relative to carbon in its standard state: graphite. This observation means that:

- the diamond form of carbon is more stable than that of graphite.
- the combustion (burning) of diamond produces more heat than that of an equal amount of graphite.
- diamond is harder than graphite.
- diamond is rapidly converted to graphite.

e. The rate of the free radical halogenation of alkanes can be increased by:

- choosing more selective reagents.
- increasing the temperature.
- diluting the starting materials in an inert solvent.
- cooling the reaction medium to retard the termination process.