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!**

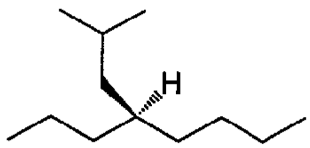
DO NOT WRITE IN THIS SPACE

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.

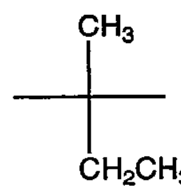


b.

racemic

c.

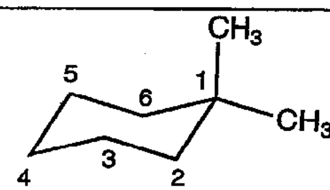
(*R*)-2-bromobutane
(Fischer projection)



Fill in the Missing Atoms.

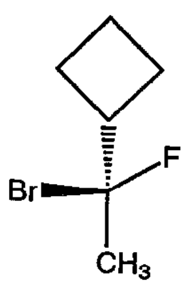
d.

(*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).

TABLE I-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 principal shell of the atom.

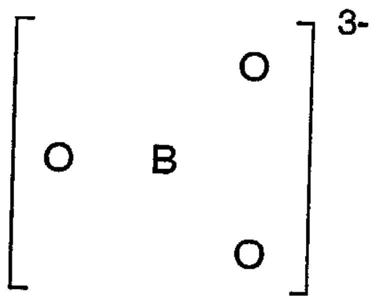
a.

S O S

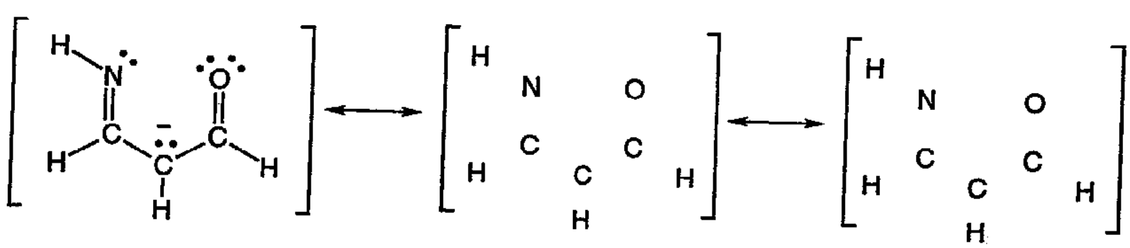
b.

N S F

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^-.

$$BF_3 + F^- \longrightarrow BF_4^-$$

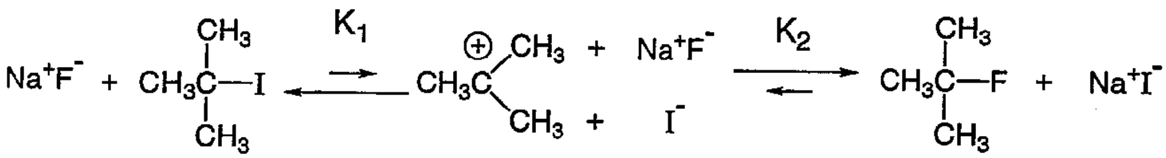
a. **Draw the orbital on BF_3 involved in this bond formation and show its overlap with the appropriate atomic orbital of F^-. Clearly label these orbitals (e.g. 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, *sp*, sp^2, sp^3, etc.).**

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.**

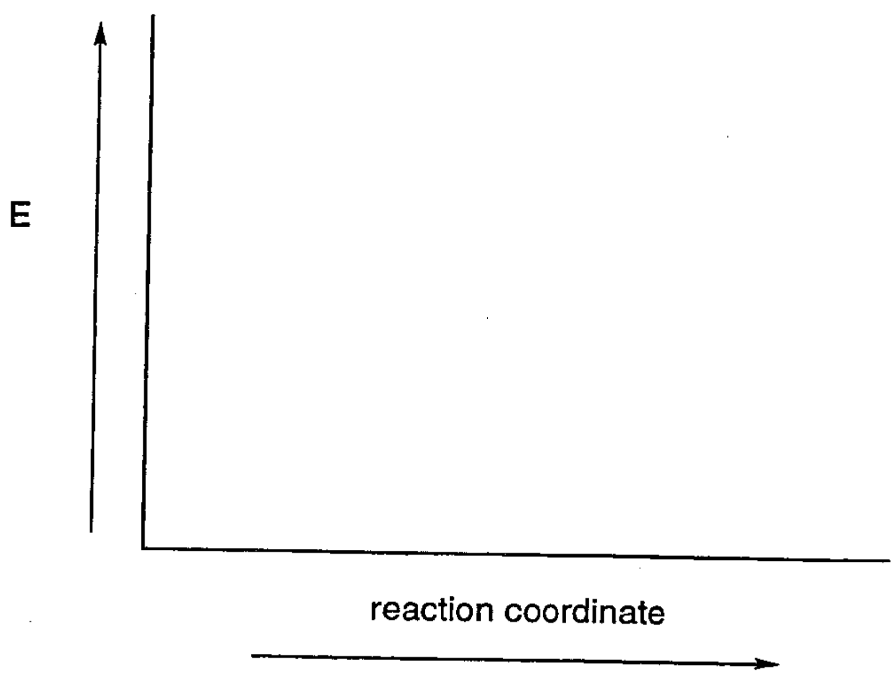
IV. [20 Points]

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:



A **B** **C**

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]

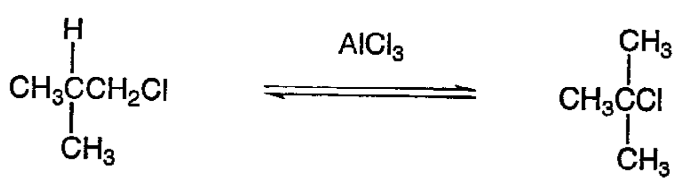
Lewis acids, such as $AlCl_3$, can cause isomerization of haloalkanes.

TABLE 3-1 Bond-Dissociation Energies of Various A–B Bonds ($DH°$ in kcal mol^{-1})

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
$CH_3CH_2CH_2$—	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

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.



ΔH°=

b. Circle one.
The two chlorides above are: constitutional isomers

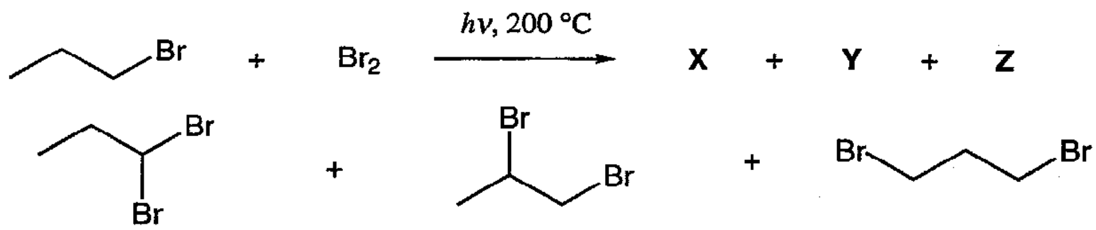
stereoisomers

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, $CH_3CH_2CH_2Br$, at 200°C results in a mixture of dibromides, as shown below, from which 1,2-dibromopropane, $CH_3CH(Br)CH_2Br$, can be separated by careful distillation.



80%	17%	3%
X	**Y**	**Z**
chiral - achiral	chiral - achiral	chiral - achiral
optically active - inactive	optically active - inactive	optically active - inactive

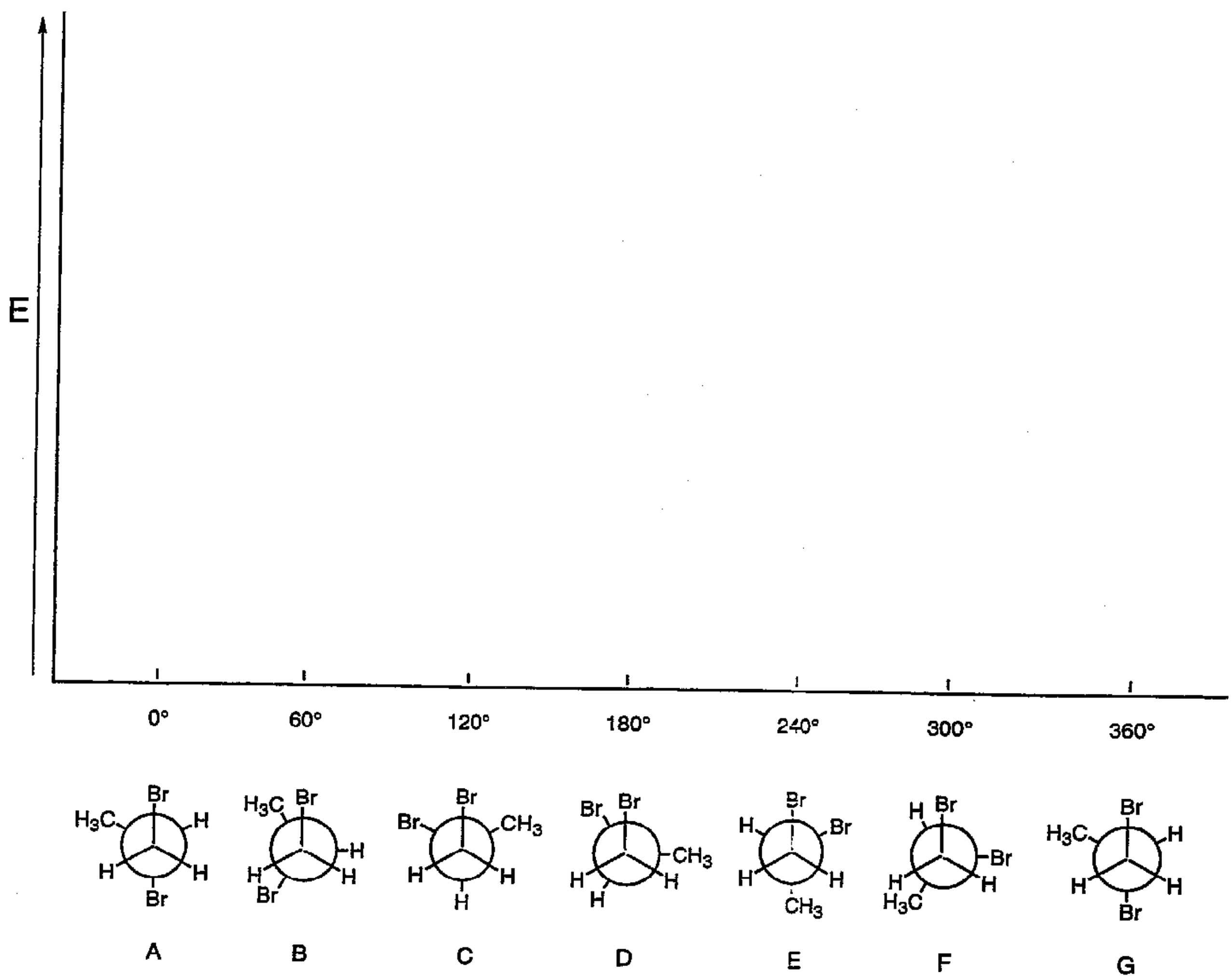
a. **Circle the appropriate labels to indicate whether the respective product is chiral or achiral, and optically active or inactive.**

b. **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 =

c. **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.**

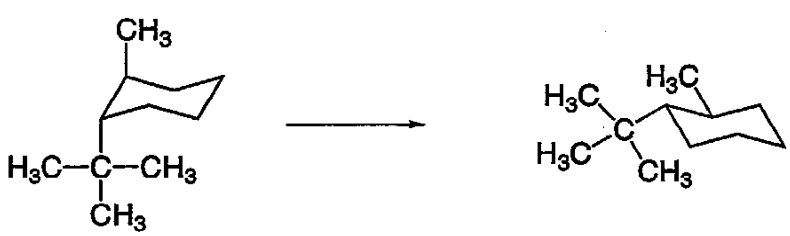


VII. [15 Points]

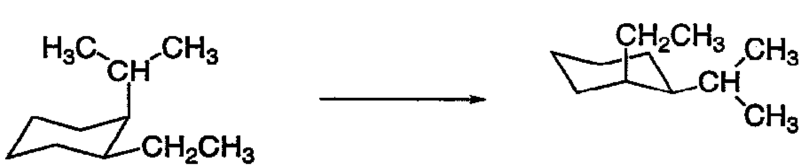
The following values represent $\Delta G°$ for the conversion of the equatorial to the axial conformer of the corresponding substituted cyclohexane,

	$\Delta G°$ (kcal / mol)
$-H$	0
$-CH_3$	1.7
$-CH_2CH_3$	1.8
$-CH(CH_3)-CH_3$	2.2
$-C(CH_3)_2-CH_3$	5.0

calculate $\Delta G°$ for the following conversion.



$\Delta G° =$



$\Delta G° =$

VIII. (15 points)

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

a. The $\Delta H°$ 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.

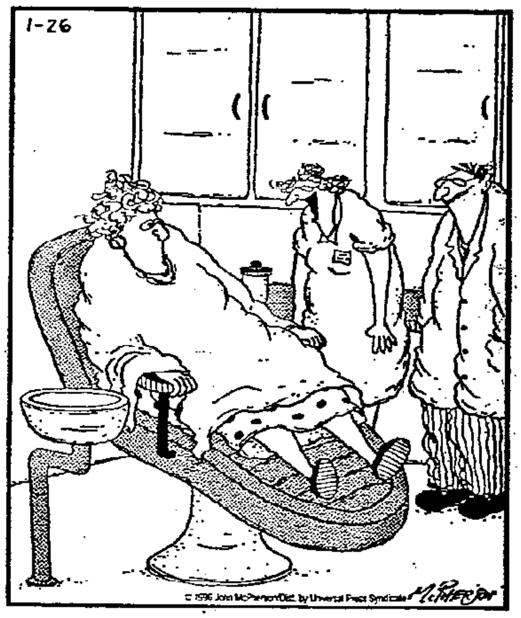
d. The heat of formation, $\Delta H_f°$, of diamond (a form of carbon) equals +0.45 kcal mol^{-1} relative to carbon in its standard state: graphite. This observation means that:

- ☐ 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.

Close to Home/John McPherson



"Dr. Vernley prides himself on his commitment to 100 percent organic dentistry. Today he'll be using bamboo drill bits, a yucca extract painkiller and adobe fillings."

THE END