EXAMINATION 1

Chemistry 3A
Kim Lavoie
Peter Vollhardt
February 27, 2003

Name: Key
[Print first name before second! Use capital letters!]

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

110	Olga Fedin	270	Staffan Westerberg
120	Sean Wiedemann	310	Cindy Chang
130	Kristie Koske	320	Raja Sivamani
140	Stephanie Chan	360	Ravi Chandrasekaran
160	Zack Fresco	370	Douglas Mitchell
170	Andrew Chi	410	Amish Patel
180	Hany Eitouni	420	Matt Banghart
190	Jenn Barbarow	460	Nicholas Ohler
210	Nicholas Agard	470	Greg Watkins
220	Jimmy Blair	510	Ben Huang
230	Scott Laughlin	520	Tanya Leavy
240	Carl Mieczkowski	560	Josh Goldberger
260	Jessica Defreese	570	Josh Gilmore

Making up an I Grade _____

(If you are, please indicate the semester during which you took previous Chem 3A _____________).

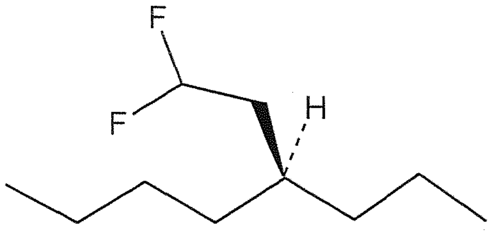
Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have 15 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure 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.	_____	(20)
II.	_____	(20)
III.	_____	(40)
IV.	_____	(30)
V.	_____	(40)
VI.	_____	(30)
VII.	_____	(20)
Total:	_____	(200)

I. [20 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis, trans, R, S,* or *meso*). Indicate with a circle whether the molecule is chiral or achiral.

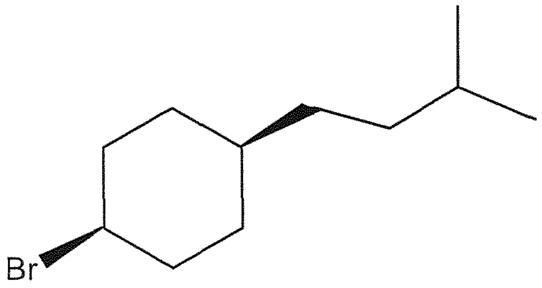
a.



4S-(2,2-Difluoroethyl)-octane

[✓ chiral] achiral

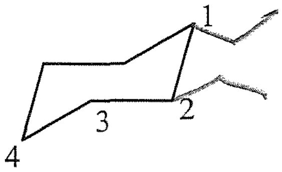
b.



Cis-1-Bromo-4-(3-methyl-butyl)cyclohexane

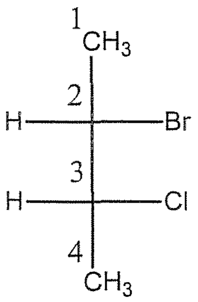
chiral [✓ achiral]

c. *trans*-1,2-Diethylcyclohexane



[✓ chiral] achiral

d.

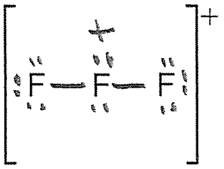


(2S,3R)-2-Bromo-3-chloro-butane

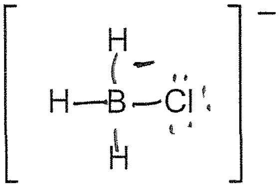
[✓ chiral] achiral

II. [20 Points] Write the best Lewis resonance structure for each of the following molecules. Remember to assign charges!

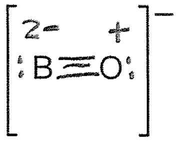
a.



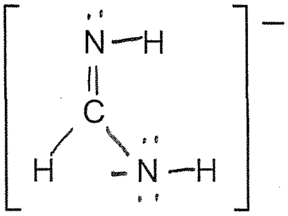
b.



c.



d.



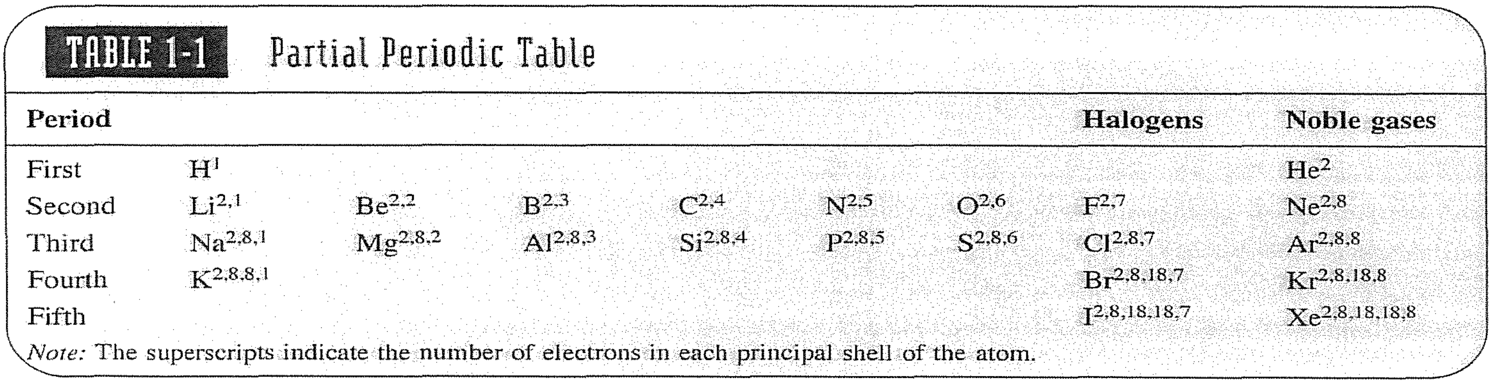


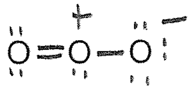
TABLE 1-1 Partial Periodic Table

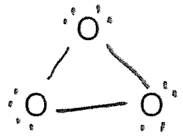
Period							Halogens	Noble gases
First	H^{1}							He^{2}
Second	$Li^{2,1}$	$Be^{2,2}$	$B^{2,3}$	$C^{2,4}$	$N^{2,5}$	$O^{2,6}$	$F^{2,7}$	$Ne^{2,8}$
Third	$Na^{2,8,1}$	$Mg^{2,8,2}$	$Al^{2,8,3}$	$Si^{2,8,4}$	$P^{2,8,5}$	$S^{2,8,6}$	$Cl^{2,8,7}$	$Ar^{2,8,8}$
Fourth	$K^{2,8,8,1}$						$Br^{2,8,18,7}$	$Kr^{2,8,18,8}$
Fifth							$I^{2,8,18,18,7}$	$Xe^{2,8,18,18,8}$

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

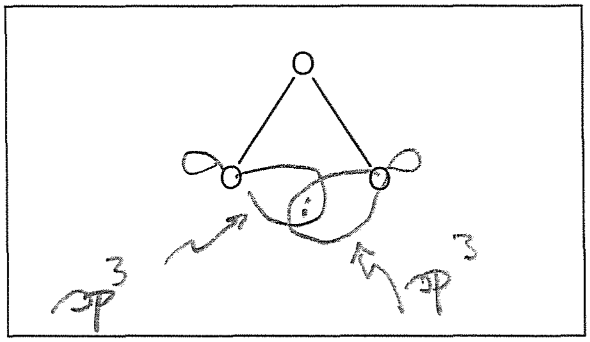
III. [40 Points] Ozone, O_3, exists in the acyclic form, but has a cyclic isomer.

a. Draw both in their best Lewis octet versions.

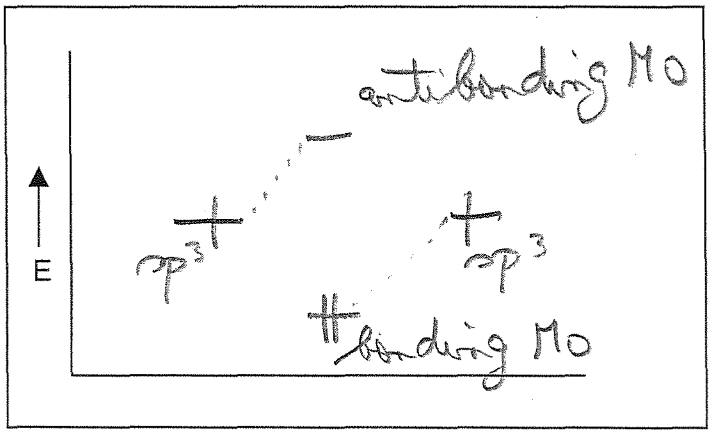




b. Show the orbital overlap picture for one of the O–O bonds in cyclic ozone.
Label clearly the overlapping orbitals (e.g. *s*, *p*, sp^3, etc.). **Hint**: Recall cyclopropane!



c. Show the orbital splitting associated with the O–O σ bond above in an energy level diagram.
Label each level clearly [e.g. *s*, *p*, sp^3, bonding molecular orbital (MO), etc.].



d. Place an "X" in the box for the two most plausible reasons why ozone is acyclic, but cyclopropane is not. Note: only two marks are allowed!

☐ oxygen is more electronegative than carbon

☒ the O–O bond is much weaker than the C–C bond

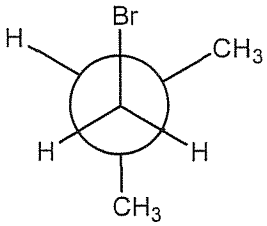
☒ acyclic O_3 is stabilized by resonance

☐ the entropy for ring opening in cyclic O_3 is much more positive than in cyclopropane

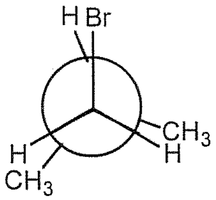
☐ cyclic O_3 has no eclipsing hydrogens

☐ the barrier to ring closure of ozone is too high

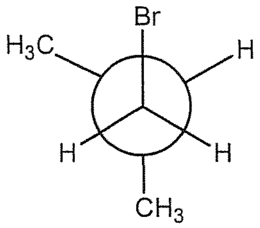
IV. [30 Points] Consider the rotation about the C1-C2 bond in 1-bromo-2-methylpropane, illustrated by the series of Newman projections A-F generated by the sequential clockwise motion of the back-carbon (C2) in increments of 60°.



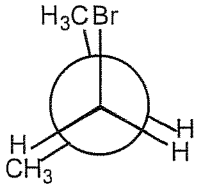
A



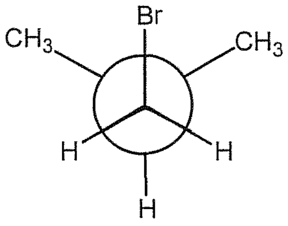
B



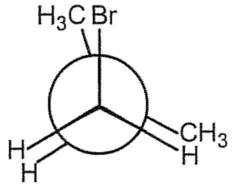
C



D



E



F

a. Indicate by circling the appropriate letter the rotamers that contain substituents which are (with respect to each other) anti or gauche, or rotamers that are eclipsed or staggered:

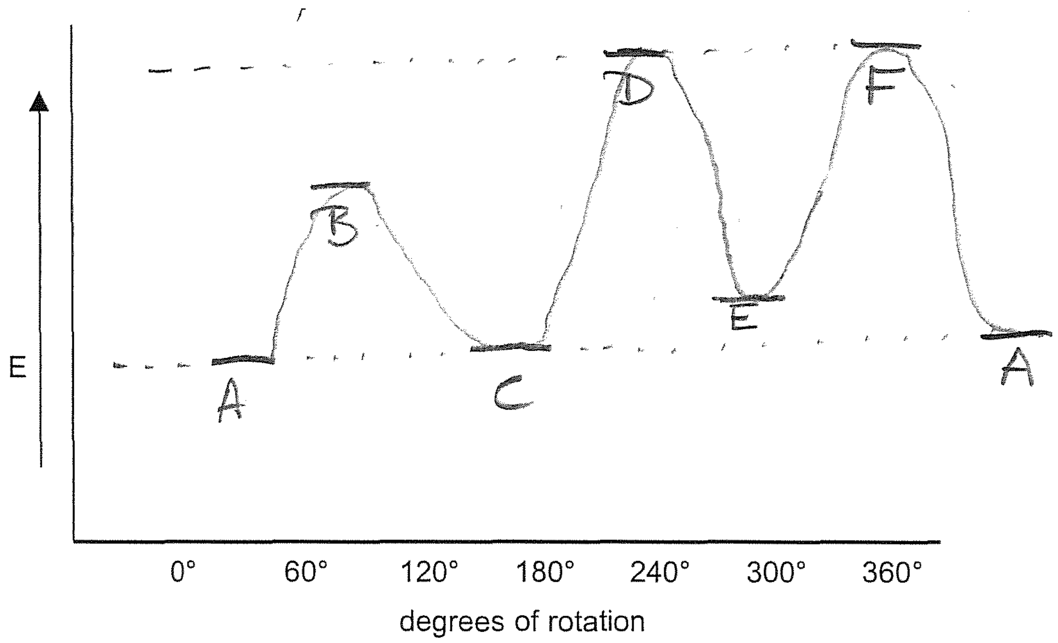
anti: [✓ A] B [✓ C] D E F

gauche: [✓ A] B [✓ C] D [✓ E] F

eclipsed: A [✓ B] C [✓ D] E [✓ F]

staggered: [✓ A] B [✓ C] D [✓ E] F

b. Draw a potential energy diagram for this movement. Start by assigning a relative energy to each rotamer on the diagram before drawing the interconnecting curve.



A **B** **C** **D** **E** **F** **A**

c. Two of the staggered rotamers have the same energy. Show which ones by placing the appropriate letters in the box.

A, C

d. Two of the eclipsed rotamers have the same energy. Show which ones by placing the appropriate letters in the box.

D, F

V. [40 Points] We have learned that ethane undergoes radical bromination to bromoethane, by attack of Br$^{\cdot}$ on a methyl hydrogen.

$$\underset{101}{CH_3{-}CH_3} + \underset{46}{Br_2} \xrightarrow{h\nu} CH_3{-}\underset{70}{CH_2{-}Br} + \underset{87}{HBr} \qquad (1)$$

In principle, however, the reaction could have taken a different path, namely attack on carbon to give bromomethane.

$$\underset{90}{CH_3{-}CH_3} + \underset{46}{Br_2} \xrightarrow{h\nu} 2\ \underset{2x\ 70}{CH_3{-}Br} \qquad (2)$$

a. Using the Tables provided on p. 9, calculate the ΔH° values for reactions (1) and (2).

ΔH° (1) : $= (101 + 46) - (70 + 87)$

$= 147 - 157 = -10$ kcal mol^{-1}

ΔH° (2) : $= (90 + 46) - (2x\ 70) = 136 - 140 = -4$ kcal mol^{-1}

b. Is the reaction (2) thermodynamically feasible? Circle the right answer.

Answer: [✓ Yes] No

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

	B in A–B						
A in A–B	–H	–F	–Cl	–Br	–I	–OH	–NH_2
H—	104	136	103	87	71	119	108
CH_3—	105	110	85	70	57	93	84
CH_3CH_2—	101	111	84	70	56	94	85
$CH_3CH_2CH_2$—	101	110	85	70	56	92	84
$(CH_3)_2CH$—	98.5	111	84	71	56	96	86
$(CH_3)_3C$—	96.5	110	85	71	55	96	85

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.

TABLE 3-2 Bond-Dissociation Energies for Some Alkanes

Compound	DH° (kcal mol^{-1})	Compound	DH° (kcal mol^{-1})
$CH_3{+}H$	105	$CH_3{+}CH_3$	90
$C_2H_5{+}H$	101	$C_2H_5{+}CH_3$	89
$C_3H_7{+}H$	101	$C_2H_5{+}C_2H_5$	88
$(CH_3)_2CHCH_2{+}H$	101	$(CH_3)_2CH{+}CH_3$	88
$(CH_3)_2CH{+}H$	98.5	$(CH_3)_3C{+}CH_3$	87
$(CH_3)_3C{+}H$	96.5	$(CH_3)_2CH{+}CH(CH_3)_2$	85.5
		$(CH_3)_3C{+}C(CH_3)_3$	78.5

Note: See footnote for Table 3-1.

TABLE 3-4 DH° Values for the Elemental Halogens

Halogen	**DH° (kcal mol^{-1})**
F_2	38
Cl_2	58
Br_2	46
I_2	**36**

c. Formulate the first propagation step for reactions (1) and (2).

Reaction (1) — 1st Propagation Step :

$$CH_3CH_2\underset{101}{-H} + Br^{\cdot} \longrightarrow CH_3CH_2^{\cdot} + \underset{87}{HBr}$$

Reaction (2) — 1st Propagation Step :

$$\underset{90}{CH_3-CH_3} + Br^{\cdot} \longrightarrow {}^{\cdot}CH_3 + \underset{70}{CH_3Br}$$

d. Calculate the ΔH° values for the two reactions in c.

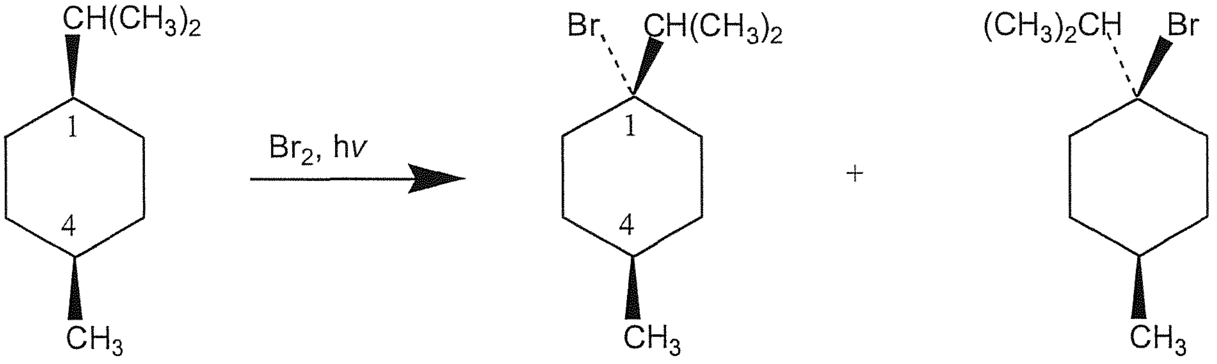
(1) ΔH° (1st propagation step) : $101 - 87 = +14$ kcal mol^{-1}

(2) ΔH° (1st propagation step) : $90 - 70 = +20$ kcal mol^{-1}

e. Considering the results of d., can you think of a reason why ethane reacts with bromine to give bromoethane and not bromomethane?

The 1st propagation step is more endothermic for making bromomethane when compared to that for making bromoethane.

VI. [30 Points] Compound **A** undergoes radical bromination to give **B** and **C**, among other products.



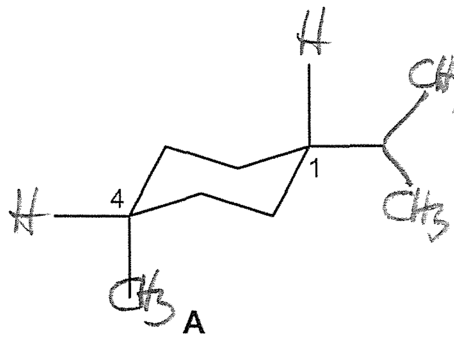
A **B** **C**

TABLE 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial

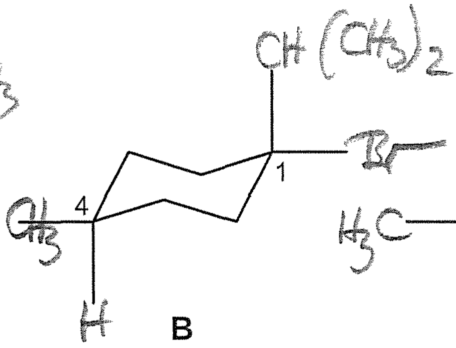
Substituent	ΔG° (kcal mol^{-1})	Substituent	ΔG° (kcal mol^{-1})
H	0	F	0.25
CH_3	1.70	Cl	0.52
CH_3CH_2	1.75	Br	0.55
$(CH_3)_2CH$	2.20	I	0.46
$(CH_3)_3C$	≈ 5	HO	0.94
$HO-\overset{O}{\overset{\|}{C}}$	1.41	CH_3O	0.75
$CH_3O-\overset{O}{\overset{\|}{C}}$	1.29	H_2N	1.4

Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

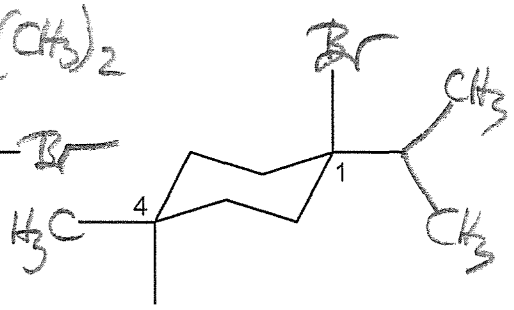
a. Given the values in the Table and using the cyclohexane stencils provided, show the structures of the most stable conformers of A, B, and C. For each, calculate the free energy of "ring flip" to the less stable conformer.



A



B



C

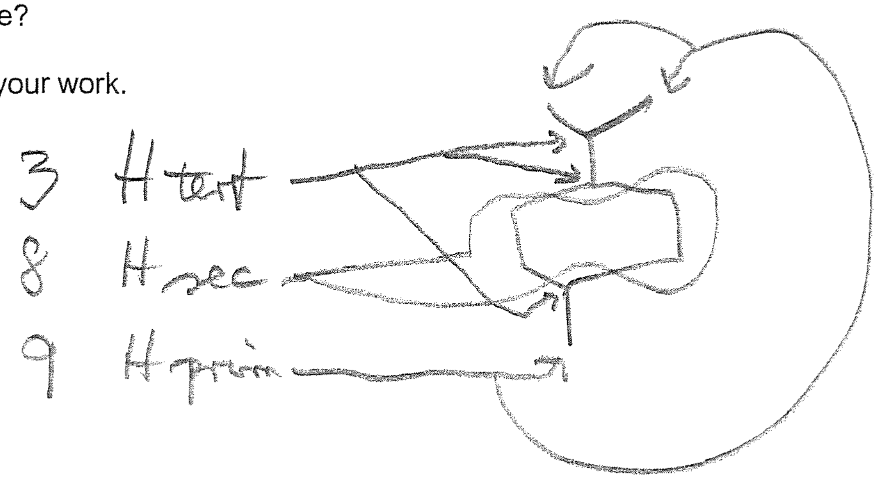
$\Delta G°$ to less stable conformer	+0.5	+0.05	+3.35

b. The molecule **A** has primary, secondary, and tertiary hydrogens. Considering the relative reactivity in brominations of C–H :

primary : secondary : tertiary = 1 : 80 : 1700,

what would you expect the ratio of all primary to all secondary to all tertiary substitution products to be?

Show your work.



$(9 \times 1) : (8 \times 80) : (3 \times 1700) = 9 : 640 : 5100$

VII. [20 Points] Place an X mark in the box designating the most accurate statement.

a. The ΔH° of an organic reaction:

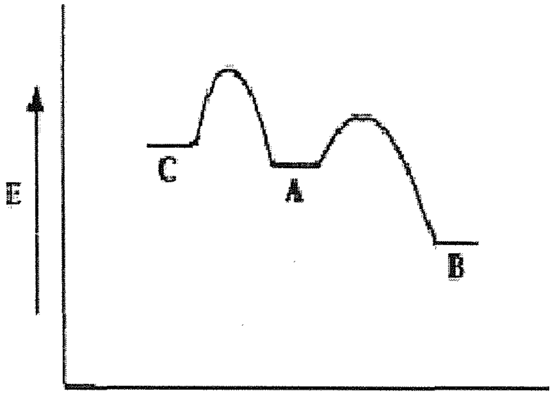
☐ reflects entropy changes

☐ 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. When considering the following potential energy diagram:



☒ compound **A** will convert to **B** faster than it will to **C**.

☐ **C** is the thermodynamically most stable component of the mixture and will form at the greatest rate from **A** or **B**.

☐ **B** will convert to **C** faster than **A** will.

☐ none of the above

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

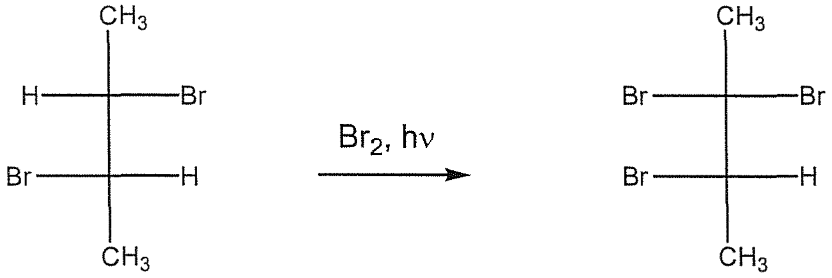
☐ identical

☒ stereoisomers

☐ interconverted by ring flip

☐ rotamers

d. The bromination of 2*S*,3*S*-dibromobutane **A** gives 2,2,3-tribromobutane **B**:

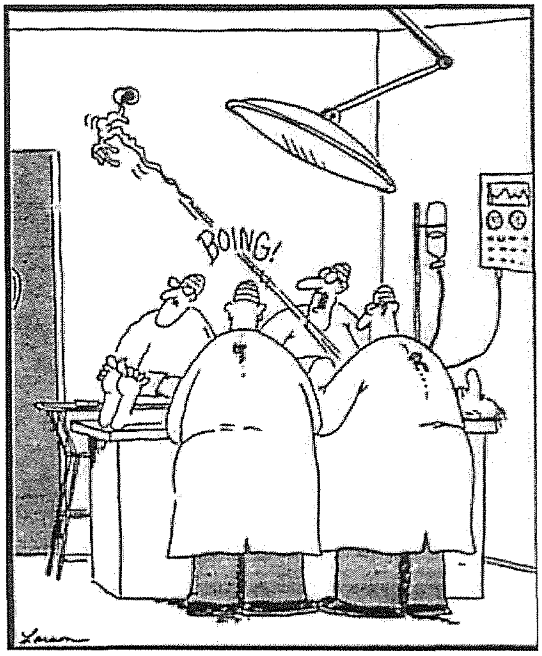


☒ in optically active form

☐ as a racemate

☐ as a meso compound

☐ as an achiral molecule



THEY FLUNKED 3A LAB

* The End *