EXAMINATION 1

Chemistry 3A
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Arlyn Myers
Peter Vollhardt
February 23, 1999

Name:____________________________
[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.

111	Joe Riggenberg	_____	361	Ryan Smith	_____
121	Polly Berseth	_____	371	Kristina Haman	_____
131	Jun Yin	_____	381	Jocelyn Grunwell	_____
141	David Nauman	_____	391	Kathy Winans	_____
151	Jeff Janes	_____	411	David Gray	_____
211	Jennifer Tripp	_____	421	Sara Paisner	_____
221	David Tully	_____	431	Scarlett Goon	_____
311	Jason Robinson	_____	511	Andy Martin	_____
321	Alex Adronov	_____	521	Fabian Fischer	_____
331	Matt Purdy	_____	531	Tony Tang	_____
341	Greg Watkins	_____	541	Marcus Strawn	_____
351	Lily Huang	_____	551	Lei Wang	_____

Making up an I Grade _____

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

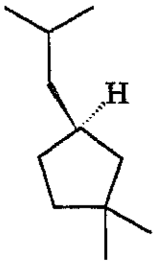
Please write the answer you wish to be graded in the spaces provided. Do scratch work on the back of the pages. This test should have 13 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure that 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

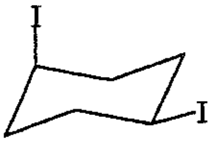
I.	_____	(30)
II.	_____	(20)
III.	_____	(30)
IV.	_____	(10)
V.	_____	(50)
VI.	_____	(40)
VII.	_____	(20)
Total:	_____	(200)

I. [30 Points]
Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, *S*, *or meso*).

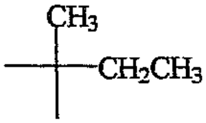
a.



b.



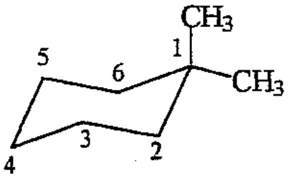
c.
(*R*)-2-Bromobutane
(Fischer projection)



Fill in the Missing Atoms.

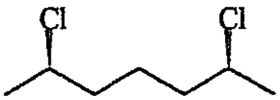
d.

(*R*)-2-Ethyl-1,1-dimethylcyclohexane



Fill in the Missing Group.

e.



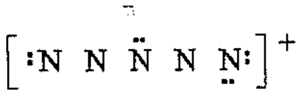
II. [20 Points]
The molecules depicted below have made recent chemical headlines. (You are encouraged to look up the literature reference). Write the most favorable Lewis *octet* structure for each. Don't forget formal charges; some of the details, such as some lone pairs or some bonds, are given).

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							$I^{2,8,18,18,7}$	$Xe^{2,8,18,18,8}$

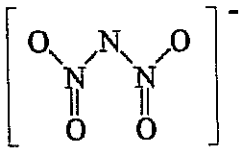
Note: The superscripts indicate the number of electrons in each principal shell of the atom.

a. *Chem. Eng. News*, 1.25.1999, p. 7. Explosive! After N_2 and N_3^- (azide), only the third all nitrogen species ever to be isolated.

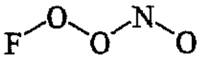


$$[:N\ N\ \ddot{N}\ N\ \underset{\cdot\cdot}{N}:]^+$$

b. *J. Am. Chem. Soc.* **1997**, *119*, 9405: dinitramide ion, potential rocket propellant.



c. *J. Am. Chem. Soc.* **1997**, *119*, 2894: fluorine nitrate, a stratospheric intermediate in ozone depleting cycles.



d. *J. Am. Chem. Soc.* **1997**, *119*, 2819: nitrilimines; organic building blocks.

$$\left[\ H\ C\ N\ N\ H \longleftrightarrow H\ C\ N\ N\ H\ \right]$$

Draw the two octet resonance forms and <u>circle</u> the stronger contributor.

III. [30 Points]
Ethynyl anion, HC_2^-, is a strong base that is protonated by H^+ (e.g. from water) to give ethyne (acetylene), C_2H_2.

$$\text{H}-\text{C}\equiv\text{C}\!:^- \; + \; \text{H}^+ \;\longrightarrow\; \text{H}-\text{C}\equiv\text{C}-\text{H}$$

Ethynyl anion Ethyne; p*K*a = 25

a. Draw the orbital on HC_2^- involved in this bond formation and show its overlap with the appropriate atomic orbital of H^+. 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 orbital energy splitting diagram for the formation of C_2H_2 by the reaction of HC_2^- with H^+. 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.

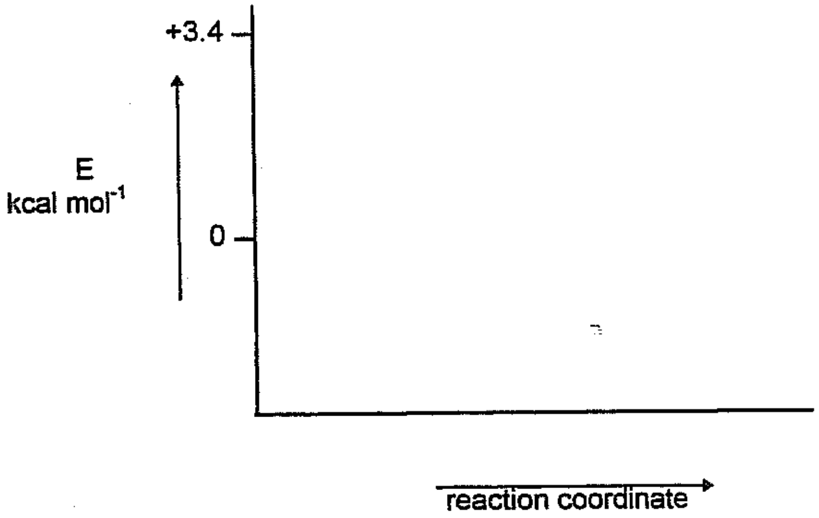
c. In view of the above, would you consider the hydride addition (e.g. reaction with H^-) of the negatively charged carbon in HC_2^- to furnish a stable bond? Explain (one sentence).

IV. [10 Points]

The eclipsed rotamer of propane is a transition state in the rotation around the C-C bond which has an E_a = 3.4 kcal mol^{-1}. Draw a potential energy diagram for the process:

Propane (eclipsed) $\longrightarrow$ Propane (staggered)

A **B**



Note: This is a rotation from A (propane eclipsed) to B (propane staggered) only; *do not* draw the energy diagram for the *full* rotation in propane!

V. [50 Points]
Methane reacts with BrCl to give mainly CH_3Cl + HBr.

$$CH_4 + BrCl \xrightarrow{h\nu} CH_3Cl + HBr$$

a. Using the Table below and the $\Delta H°$ (Br—Cl) = 52, calculate the $\Delta H°$ of this process in the box below. (Show your work).

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	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

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.

$\Delta H°$ =

b. The alternative products of this reaction would be CH_3Br + HCl.

Calculate the $\Delta H°$ for that process.

$\Delta H°$ =

c. Given the observed products of this reaction, the results from a. and b. seem surprising, requiring an analysis of the mechanism. The initiation step results in $Br^{\bullet}$ and $Cl^{\bullet}$, both of which will react with CH_4 to generate $CH_3^{\bullet}$. To help you with the solution to this problem, it is best to start your propagation cycle with $CH_3^{\bullet}$.

Formulate the propagation steps for both processes (starting with $^{\bullet}CH_3$), and calculate the $\Delta H°$ of the two possible outcomes of the attack of $^{\bullet}CH_3$ on Br—Cl.

Propagation steps to give CH_3Cl + HBr :

$\Delta H°$ (1st step) =

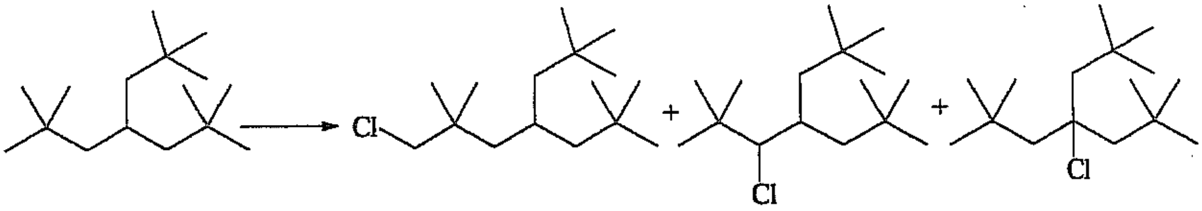
Propagation steps to give CH_3Br + HCl

(ΔH° (1st step) =

d. How do the results of c. allow you to explain that CH_3Cl and HBr are the main products (one sentence)?

e. The selectivity for H abstraction of Br—Cl in its chlorinations of hydrocarbons is similar to that observed using Br_2 ($H_{tert} : H_{sec} : H_{prim}$ = 1600 : 50 : 1). Why?

f. Reaction of Br—Cl with the hydrocarbon A gives three monochlorination products B, C, and D.

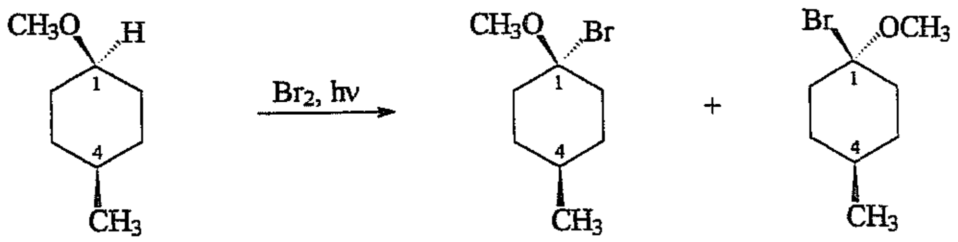


A **B** **C** **D**

Calculate the *ratio* (%ages are *not* needed) of B : C : D. Show your work.

VI. [40 Points]

Compound A undergoes free radical bromination to B and C (among other products).



A **B** **C**

a. Circle any of the letters A, B, C above to indicate a chiral compound.

b. Explain in one sentence how this halogenation can give both B and C and not just B.

c. B and C (circle one) are

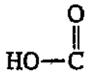
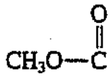
constitutional isomers

enantiomers

diastereomers

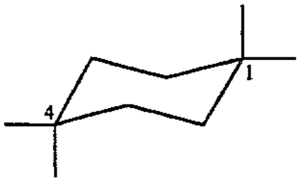
d. Using the values in the Table below and the cyclohexane stencils provided, show the structures of the most stable conformers of A, B, and C. For each calculate the free energy of "ring flip" to the less stable conformer.

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**

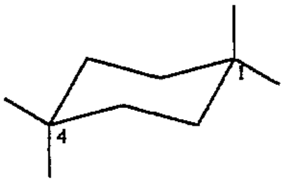
Substituent	ΔG° (kcal mol^{-1})	Substituent	ΔG° (kcal mol^{-1})
H	0	F	0.25
CH_3	1.70	Cl	0.52
CH_3CH_2	1.75	Br	0.55
$(CH_3)_2CH$	2.20	I	0.46
$(CH_3)_3C$	≈ 5	HO	0.94
 $HO{-}\overset{\overset{O}{\|}}{C}$	1.41	CH_3O	0.75
 $CH_3O{-}\overset{\overset{O}{\|}}{C}$	1.29	H_2N	1.4

Note: In all examples, the equatorial form is more stable.

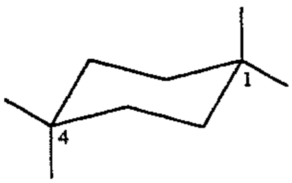
Answer:



A



B

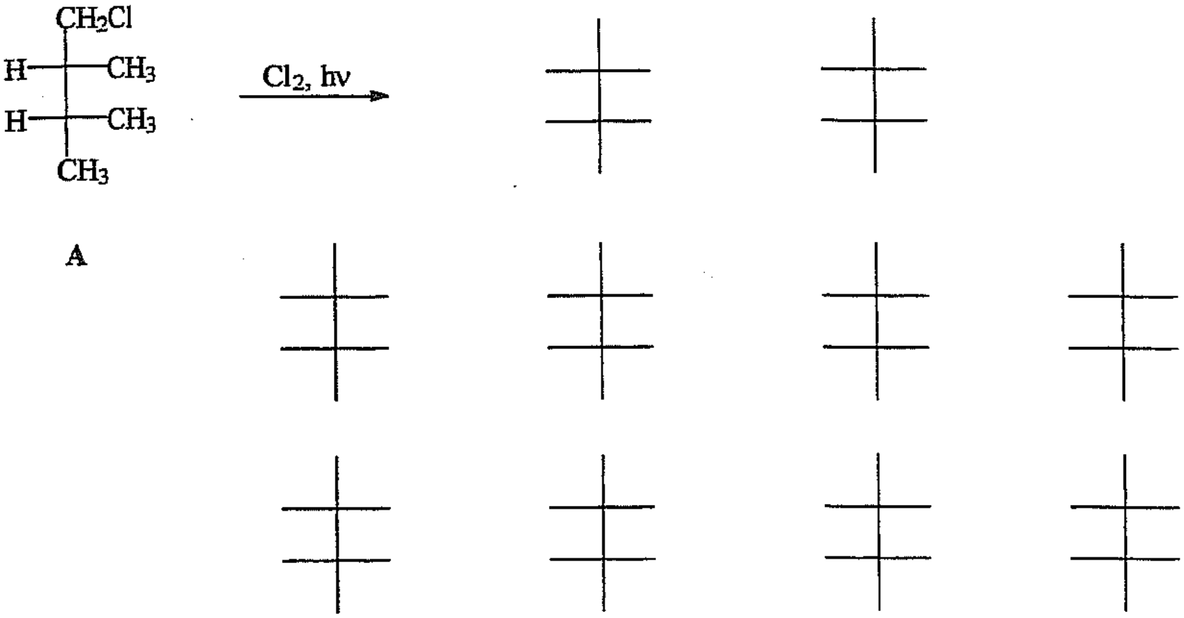


C

ΔG° to less
stable conformer

VII. [20 Points]

a. Draw all the products of the monochlorination of the enantiomer A. Use the Fischer projections provided (more than you need), starting at carbon 1.



A

b. Circle the compounds that are formed which would be optically active (i.e. chiral and only one of both enantiomers).