FINAL EXAMINATION

Organic Chemistry, Chem 220
9 A.M.; Saturday, December 11, 2010

NAME (print): ____

TA:____________________ Section Day:____________ Section Time:_____________

Take a few moments to look over the exam. Do problems first with which you are most comfortable. Important points and unknowns are in **bold** type. Do all **preliminary** work on the worksheets. The worksheets will **not** be graded. The exam is the length of two hour exams with an additional one hour for review. **STOP** writing when you are asked to do so. Put your name on the **cover sheet and subsequent pages** (except for Work Sheets) where indicated. **No calculators or electronic devices.** A Periodic Table and Bond Dissociation Energy table are on page 15. Isotope abundance and A-values tables are on page 16.

.**REMEMBER:** Neatness is to your advantage.

Have a GREAT winter break!

1. Spectroscopy/Structure (25 pts) _________
2. Reactions I (32 pts; 4 of 5) _________
3. Potpourri (40 pts; 8 of 10) _________
4. Synthesis (25 pts.) _________
5. Thermochemistry (25 pts.) _________
6. Reactions II (30 pts., 6 of 8) _________
7. Kinetics/
Thermodynamics (20 pts.) __________
8. Mechanisms (25 pts.) __________

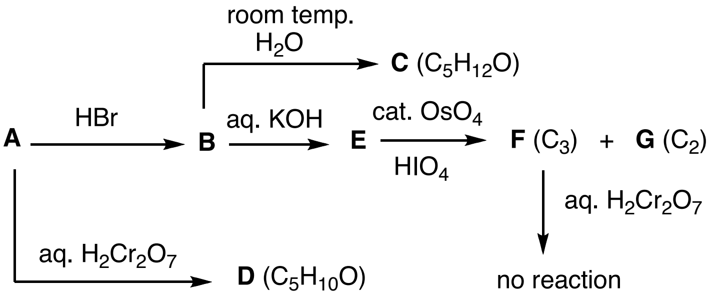
Total (222 pts)

Note: The final exam is worth 160 points toward the final grade. The grade shown above will be multiplied by 0.72 to obtain the adjusted score (222 x 0.72 = 160).

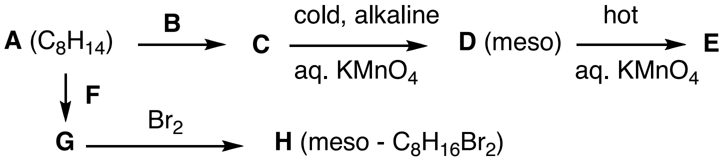
1. **Spectroscopy/Structure :** (25 pts.) Achiral compound **A** ($M^+ = 112$; Degrees of Unsaturation = 2) is inert to aqueous chromic acid and its infrared spectrum displays a strong absorption at 1717 cm^{-1}. Compound **A** reacts with **one equivalent** of Grignard reagent **B** (RMgBr) to form a mixture of achiral diastereomers **C** and **C'**, each of whose mass spectrum displays a molecular ion at $M^+ = 128$. Compound **C** is more stable than compound **C'**. Compounds **C** and **C'**, together or separately, react **readily** with catalytic H_2SO_4 by an E1 mechanism to give two isomers [(±)-**D** (major) and achiral **E** (minor)]. Ozonolysis and dimethyl sulfide reduction of compound (±)-**D** provides **F**, which upon reduction with $LiAlH_4$ gives **G**, **3-methylheptan-1,6-diol**. Exposure of **E** to excess hot aqueous $KMnO_4$ gives rise to compounds **A** and **H**. What are the structures of **A – H**? **Show your reasoning.** [**Hint:** Work backwards from **G**.]

2. **Reactions I:** (4 x 8 pts. = 32 pts.) **Do 4 of 5.** Provide structures for the unknown compounds. Be explicit about stereochemistry, optical activity, racemates, etc. No mechanisms required! **If you do more than four problems, cross out (with a large X through the solution) the one that you do not want graded**.

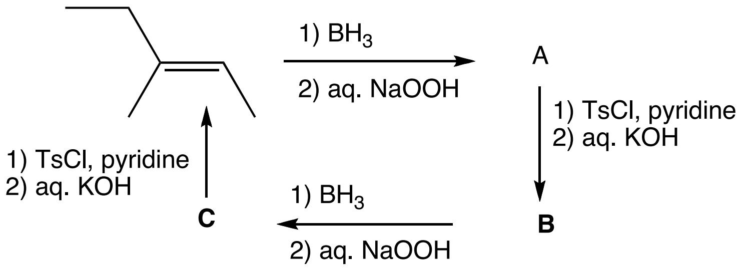
a)



b)

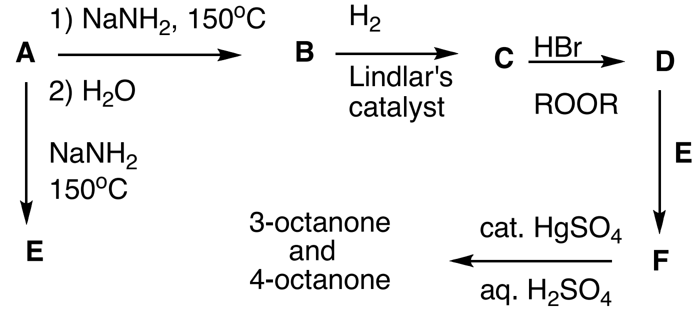


c)

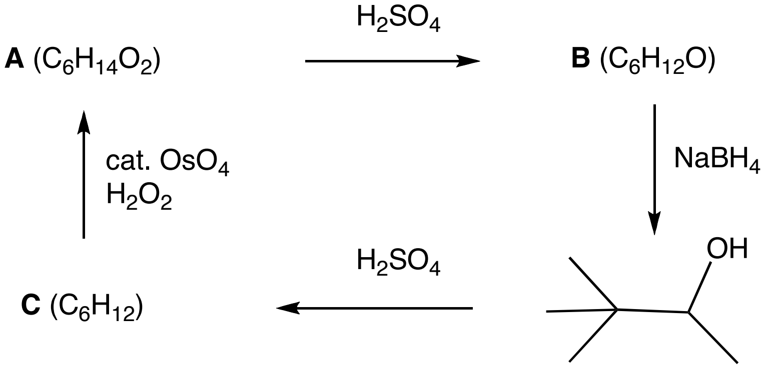


…continued

d)

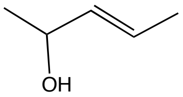

A
1) $NaNH_2$, 150°C
2) H_2O
B
H_2
Lindlar's catalyst
C
HBr
ROOR
D
E
$NaNH_2$
150°C
E
F
cat. $HgSO_4$
aq. H_2SO_4
3-octanone and 4-octanone

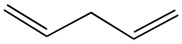
e)

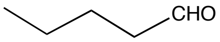

A ($C_6H_{14}O_2$)
H_2SO_4
B ($C_6H_{12}O$)
$NaBH_4$
OH
H_2SO_4
C (C_6H_{12})
cat. OsO_4
H_2O_2

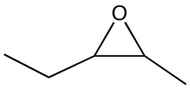
3. **Potpourri:** (8 x 5 pts. = 40 pts.) Do **8 of 10** problems**. If you do more than eight problems, cross out (with a large X through the solution) the ones that you do not want graded**.

i) a) **Circle** the greatest number of compound(s) that are at the same oxidation level. b) Place a **square** around those functional groups that have sp^2 hybridization.

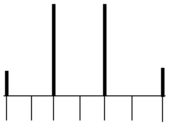


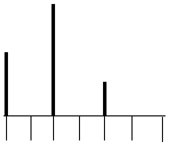


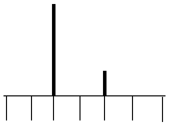


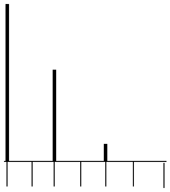


ii) **Circle** the mass spectral pattern that is typical of the ion $CHCl_2^+$? **Explain briefly** and provide relative intensities.









iii) Testosterone $C_{19}H_?O_2$ contains four rings, one secondary alcohol, one ketone and one double bond. What is the molecular formula of this steroid? **Show work**.

iv) The specific rotation of (*S,S*)-tartaric acid is [α] = -12°. What is the percentage of each enantiomer in a mixture of the two enantiomers that has [α] = +2°. **Show work**.

…continued

v) **Circle** the terms that apply to E2 eliminations.

orbital overlap

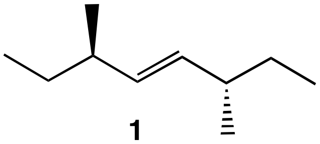
rehybridization

isotope effect

intermediate

kinetically controlled

vi) (*E*)-(3*R*,6*S*)-3,6-dimethyl-4-octene (**1**) is a meso compound yet it does not have a plane of symmetry. What makes it meso? [**Hint:** Think of one of the two reasons why meso-tartaric acid is actually meso.]

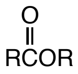


1

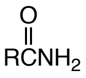
vii) Provide a **diagram and an equation** that relates bond dissociation energy and heat of formation for a generic alkane, R-H.

…continued

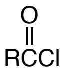
viii) The bonds (shown as line bonds) in each of the following functional groups absorb energy in the infrared region. **Number** the structures on the lines in order of increasing vibrational frequency (1 = lowest; 5 = highest).


$\overset{\overset{O}{\|}}{RCOR}$ _____

R-Br _____


$R\overset{\overset{O}{\|}}{C}NH_2$ _____

RO-H _____

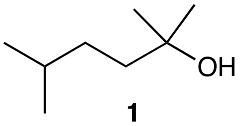

$R\overset{\overset{O}{\|}}{C}Cl$ _____

ix) In the free radical chlorination of (*S*)-1-chloro-2-methylbutane to form dichloropentanes, **draw** the dichloride(s) that is no longer optically active. Give a **ONE WORD** explanation why it is no longer optically active.

x) **Circle** the bases that are protonated by 1-butyne.

KNH_2 RMgCl CH_3ONa NH_3 LiOH

4. **Synthesis:** (25 pts.) Design a synthesis of of 2,5-dimethylhexan-2-ol (**1**) using 2-methyl-2-bromopropane (C_4H_9Br) as your **only** source of carbon. All other reagents are available to you. No mechanisms are required.



1

5. **Thermochemistry:** (25 pts.) Determine the heat of formation of chlorocyclooctane prepared by the free radical chlorination of cyclooctane. Provide the two propagation steps and the overall reaction for this process**. Place the reactants and products in the appropriate boxes.** Compute the heats of each reaction using the data in the BDE Table (pg. 15) and the following data: ΔH_f° (HCl) = -22.1 kcal/mol; ΔH_f° (cyclooctane) = -29.7 kcal/mol.
Show work.

Propagation step 1

☐ + ☐ → ☐ + ☐ ________ kcal/mol

________ ________ ________ ________

Propagation step 2

☐ + ☐ → ☐ + ☐ ________ kcal/mol

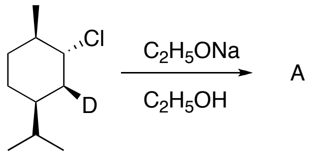
________ ________ ________ ________

Overall reaction

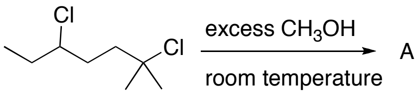
☐ + ☐ → ☐ + ☐ ________ kcal/mol

6. **Reactions II:** (30 pts.) **Do 6 of 8.** Provide structures for the unknown compounds or provide reagents. Be explicit about stereochemistry, optical activity, racemates, etc. No mechanisms required! **If you do more than 6 problems, cross out (with a large X through the solution) the one(s) that you do not want graded**.

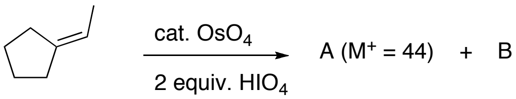
a)



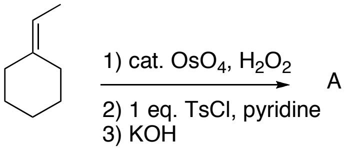
b) (R) -



c)

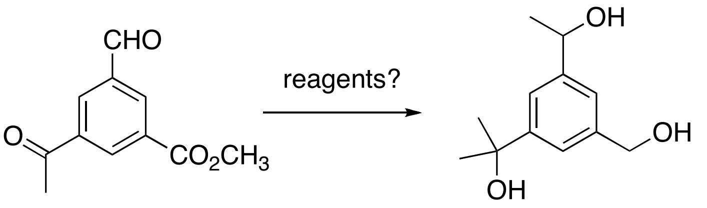


d)

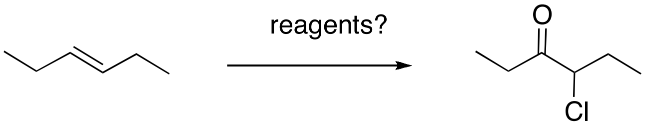


…continued

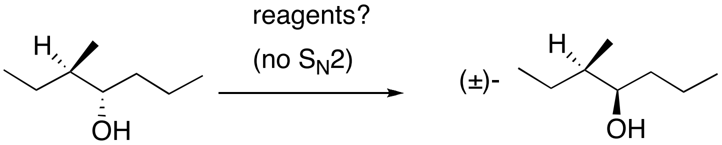
e)



f)



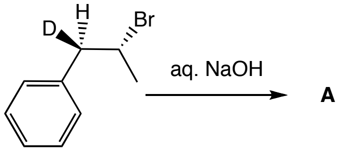
g) (±)-



h) $(S)\text{-}CH_3CH_2CH_2CHDBr \xrightarrow[\text{1 equiv. thiophenol}]{\text{1 equiv. aq. KOH}} A$

7. **Kinetics/Thermodynamics:** (20 pts.) Do **2 of 4**. Keep your answer short and to the point! **If you do more than two problems, cross out (with a large X through the solution) the one(s) that you do not want graded**.

a) What is the structure of **A** and why? Is the reaction kinetically or thermodynamically-controlled? Why? **Be concise.**



b) The E2 reaction of 2-bromobutane with strong base (kinetically-controlled) **does not** give the same distribution of butenes (there are three of them) that is obtained by acid-catalyzed dehydration of 2-butanol (thermodynamically-controlled). **Explain briefly.**

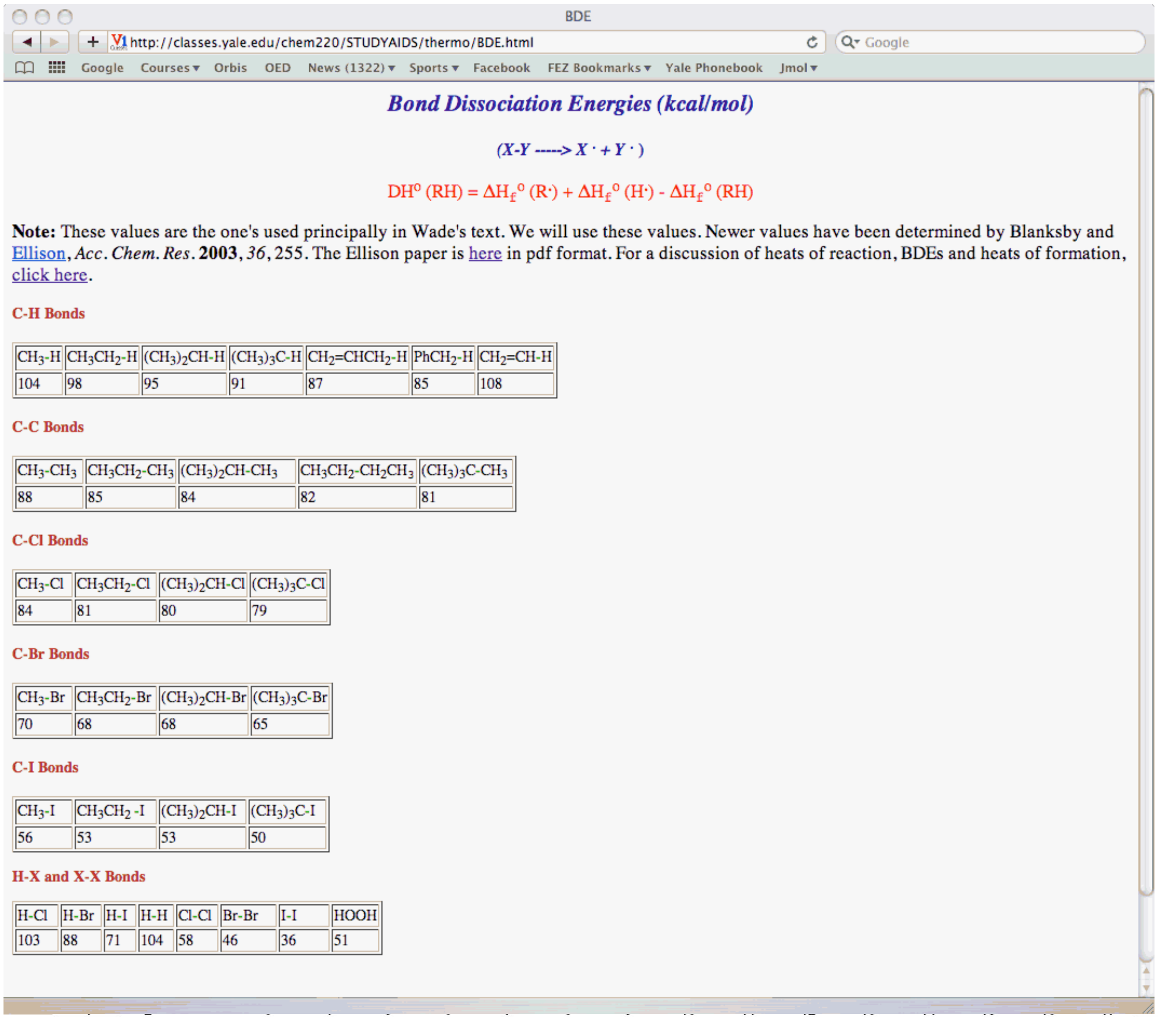
…continued

c) The formation of cyclohexene from 1,7-octadiene in the presence of Grubbs' catalyst (Ru=CHPh) and Fischer esterification illustrate two different techniques for shifting unfavorable, equilibria. **Explain briefly**.

d) In acyclic compounds and flexible ring compounds, why is anti-periplanar (180° dihedral angle) favored over syn-periplanar (0° dihedral angle) in E2 elimination?

8. **Mechanisms:** (25 pts) Provide a mechanism using the curved arrow formalism for **one** of the following reactions. **If you do more than one problem, cross out (with a large X through the solution(s) of the one(s) that you do not want graded**.

a) Swern oxidation of 2-deuterio-2-butanol
b) The conversion of 3-hexyne to (*E*)-3-hexene
c) The conversion of 3-hexyne to 3-hexanone in the presence f $HgSO_4$
d) ozonolysis of cyclohexene



Bond Dissociation Energies (kcal/mol)

($X\text{-}Y \longrightarrow X\cdot + Y\cdot$)

$DH^o (RH) = \Delta H_f^o (R\cdot) + \Delta H_f^o (H\cdot) - \Delta H_f^o (RH)$

Note: These values are the one's used principally in Wade's text. We will use these values. Newer values have been determined by Blanksby and Ellison, *Acc. Chem. Res.* **2003**, *36*, 255. The Ellison paper is here in pdf format. For a discussion of heats of reaction, BDEs and heats of formation, click here.

C-H Bonds

CH_3-H	CH_3CH_2-H	$(CH_3)_2CH$-H	$(CH_3)_3C$-H	CH_2=$CHCH_2$-H	$PhCH_2$-H	CH_2=CH-H
104	98	95	91	87	85	108

C-C Bonds

CH_3-CH_3	CH_3CH_2-CH_3	$(CH_3)_2CH$-CH_3	CH_3CH_2-CH_2CH_3	$(CH_3)_3C$-CH_3
88	85	84	82	81

C-Cl Bonds

CH_3-Cl	CH_3CH_2-Cl	$(CH_3)_2CH$-Cl	$(CH_3)_3C$-Cl
84	81	80	79

C-Br Bonds

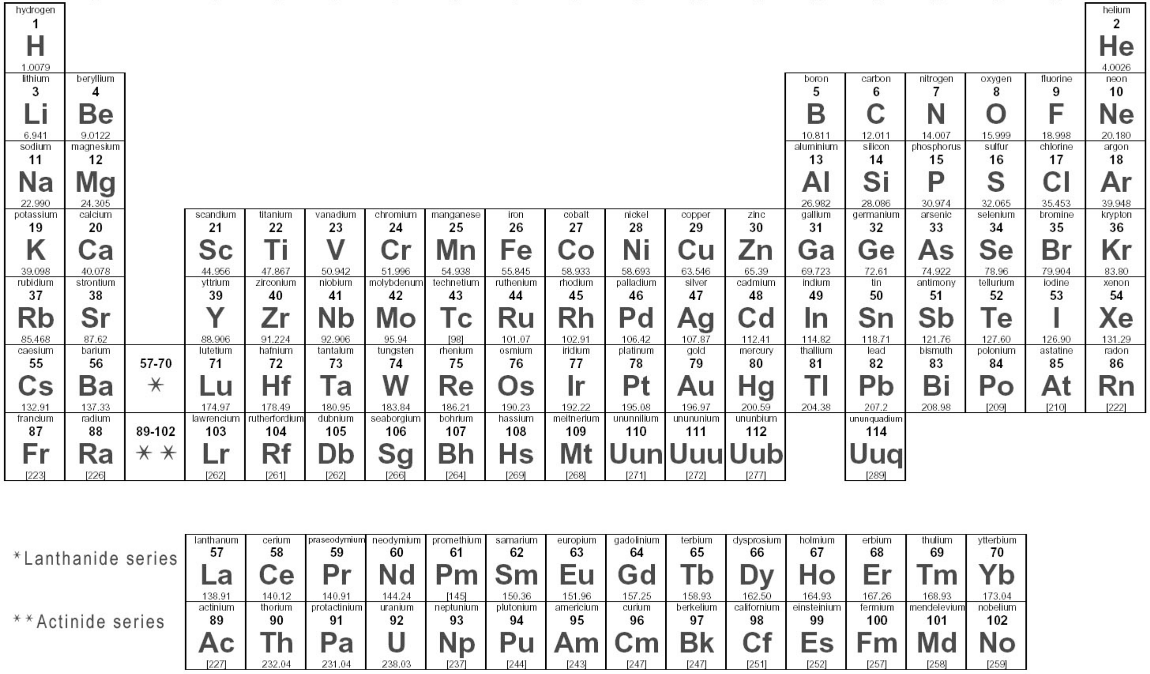
CH_3-Br	CH_3CH_2-Br	$(CH_3)_2CH$-Br	$(CH_3)_3C$-Br
70	68	68	65

C-I Bonds

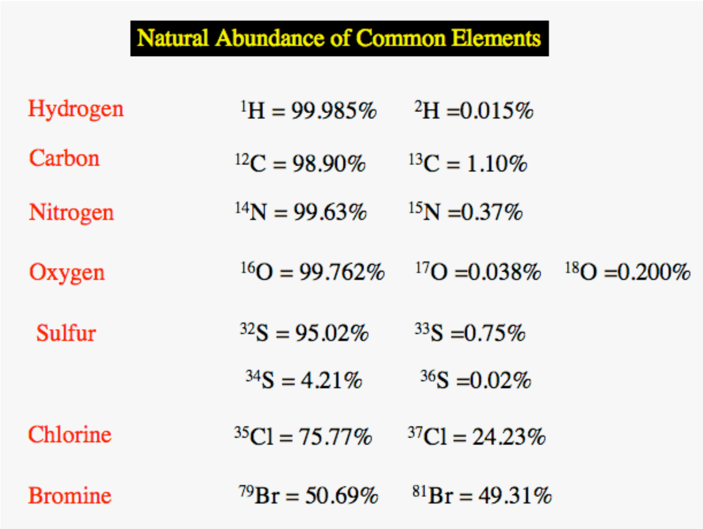
CH_3-I	CH_3CH_2 -I	$(CH_3)_2CH$-I	$(CH_3)_3C$-I
56	53	53	50

H-X and X-X Bonds

H-Cl	H-Br	H-I	H-H	Cl-Cl	Br-Br	I-I	HOOH
103	88	71	104	58	46	36	51

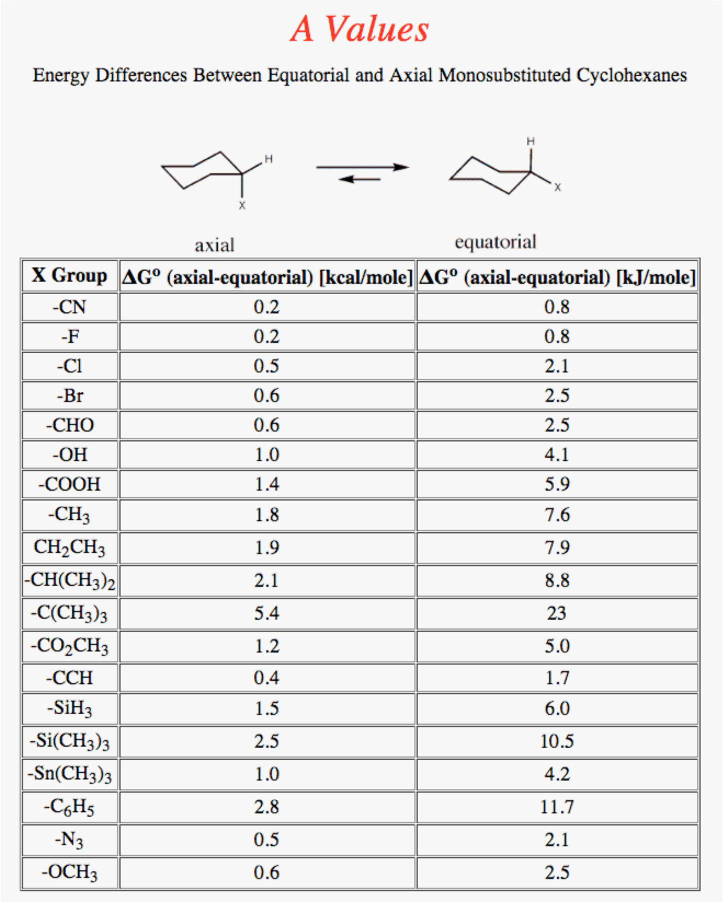


hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				
*Lanthanide series			lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04		
* *Actinide series			actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]		



Natural Abundance of Common Elements

Hydrogen	^{1}H = 99.985%	^{2}H =0.015%	
Carbon	^{12}C = 98.90%	^{13}C = 1.10%	
Nitrogen	^{14}N = 99.63%	^{15}N =0.37%	
Oxygen	^{16}O = 99.762%	^{17}O =0.038%	^{18}O =0.200%
Sulfur	^{32}S = 95.02%	^{33}S =0.75%	
	^{34}S = 4.21%	^{36}S =0.02%	
Chlorine	^{35}Cl = 75.77%	^{37}Cl = 24.23%	
Bromine	^{79}Br = 50.69%	^{81}Br = 49.31%	



A Values

Energy Differences Between Equatorial and Axial Monosubstituted Cyclohexanes

X Group	ΔG° (axial-equatorial) [kcal/mole]	ΔG° (axial-equatorial) [kJ/mole]
-CN	0.2	0.8
-F	0.2	0.8
-Cl	0.5	2.1
-Br	0.6	2.5
-CHO	0.6	2.5
-OH	1.0	4.1
-COOH	1.4	5.9
$-CH_3$	1.8	7.6
CH_2CH_3	1.9	7.9
$-CH(CH_3)_2$	2.1	8.8
$-C(CH_3)_3$	5.4	23
$-CO_2CH_3$	1.2	5.0
-CCH	0.4	1.7
$-SiH_3$	1.5	6.0
$-Si(CH_3)_3$	2.5	10.5
$-Sn(CH_3)_3$	1.0	4.2
$-C_6H_5$	2.8	11.7
$-N_3$	0.5	2.1
$-OCH_3$	0.6	2.5