Chemistry 3A - Spring 2000
Final

Professor Jean Fréchet

May 15, 2000

Your full signature_____

Print your full name_____
(Last name, First name, Middle)

Your SID_____

Please check the section number and name of your GSI/TA.

___161 Verdugo,Dawn
___171 Klopp,John
___181 Borths,Christopher
___191 Fujdala,Kyle
___111 Watkins,Gregory
___121 Blackwell,Bethany
___131 Fox,Daniel
___141 Werkema,Evan
___261 Peterka,Darcy
___271 Lee,Charles
___211 Tripp,Jennifer
___221 Padilla,Omayra
___361 Haman,Kristina
___371 Hecht,Stefan
___311 Saxon,Eliana
___321 Cook,Brian
___461 Purdy,Matthew
___471 Evans,John
___411 Holland,Andrew
___421 Duncan,Andrew
___431 Trimble,Alexander
___511 Marcaurelle,Lisa
___521 Jen,Wendy
___531 Ling,Frank

If you are making up an I-grade, indicate the semester you took 3A_____ and the Professor_____.

This exam has **14** pages; **make sure that you have them all.**

Please be sure to use the <u>very</u> useful data given on page 14.

We will only grade answers that are in the designated spaces. Please do your scratch work on the backs of the exam pages. Write only **<u>one</u>** answer to each problem; multiple answers will receive **<u>no</u>** credit, even if one of them is correct.

<u>Note:</u> This examination runs for a total of 180 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **<u>no credit</u>**.

Do Not Write in this Box.

1.	(16)
2.	(19)
3.	(15)
4.	(16)
5.	(15)
6.	(17)
7.	(19)
8.	(17)
9.	(16)
10.	(16)
11.	(19)
12.	(15)
Total	(200)

1. **[16 Points]** (a) propose a structure for an alcohol $C_4H_{10}O$ that has the following ^{13}C NMR data: "normal" (proton decoupled) spectrum: peaks at δ = 19.0, 31.6, and 69.5 ppm; DEPT-90: δ = 31.6ppm; DEPT-135: positive peaks at δ = 19.0 and 31.6; negative peak at δ = 69.5 ppm

Your answer should show a clear structure

(b) A hydrocarbon has the formula C_7H_{12}, it exhibits the following spectroscopic properties: IR: peaks at 3072, 2900-3000, 1649 and 888 cm^{-1}; ^1H NMR spectrum δ = 1.3 (m, 2H); 1.7 (m, 4H); 2.2 (m, 4H) and 4.8ppm (quintet, 2H); ^{13}C NMR: δ = 26.8; 28.7; 35.7; 106.9 and 149.7ppm; hydrogenation affords a product with the formula C_7H_{14}. (*Note:* m *means "multiplet"*)

(i) What is what is its degree of unsaturation of the hydrocarbon C_7H_{12}?

Answer:

(ii) What characteristic functional group is responsible for the IR band at 1649 cm^{-1}?

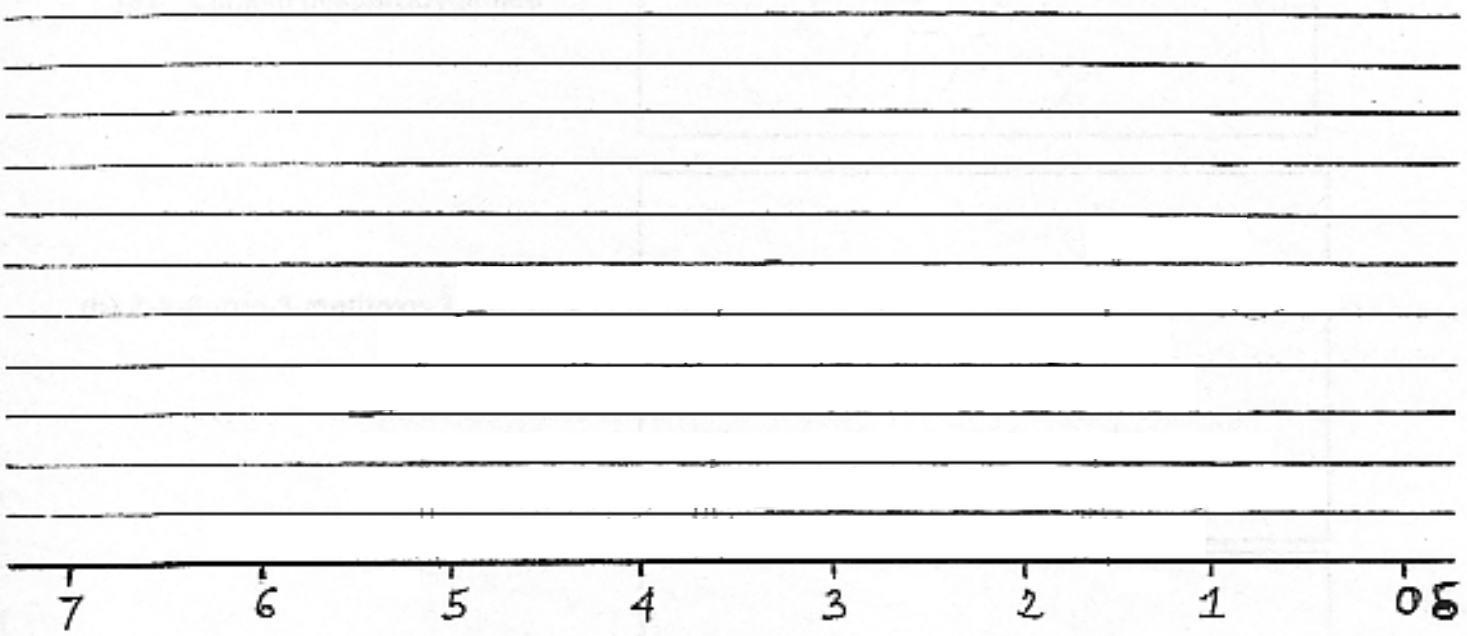
(iii) What is the structure of the hydrocarbon?

Answer:

(c) The characteristic IR stretching frequency for the carbon-carbon triple bonds of alkynes is:

(Circle one) 3310 cm^{-1} 2120 cm^{-1} 1950 cm^{-1} 1640 cm^{-1} 1430 cm^{-1} 888 cm^{-1}

2. [**19 Points**] (a) Draw the ^{1}H NMR spectrum for $ClCH_2OCH_2CH_3$ assuming perfect splitting of peaks. Make sure the location of the peaks is appropriate and label each peak. Also draw a realistic step integration.



(b) Show a fully labeled energy diagram for the following reaction

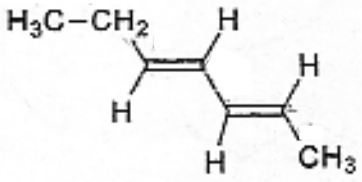
CH_2=$CHCH_3$ + HCl ⟶ $CH_3CHClCH3$

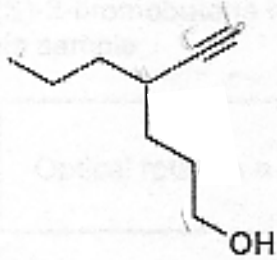
3. **[15 Points]** Name or draw as appropriate the following molecules. Show stereochemistry if relevant.

(a) Lithium diisopropylamide

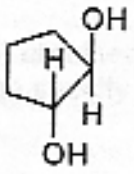
(b) Z-2-fluoro-3-methoxy-2-pentene

(c) 7-chlorobicyclo[4.3.0]nonane

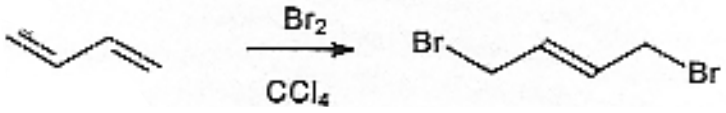
(d) 

(e) 

4. [**16 Points**]

(a) Show a step-by-step synthesis of  from cyclopentene  (no mechanism)

(b) Show a step-by-step mechanism (including curved arrows) for the following reaction:

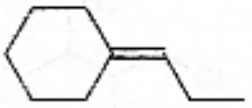


c) The optical purity of a sample of (R)-2-bromobutane is 80%. What is its optical rotation given that pure (S)-2-bromobutane has a specific rotation of +25°. Also calculate the percentage of S-isomer in this sample.

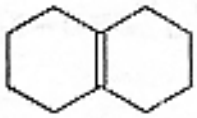
Answers:

Optical rotation =	Percentage of S isomer in sample =

5. [**15 Points**] Show the major product(s) obtained in the reactions below. Do not include minor products or by-products. Be sure to specify stereochemistry where appropriate



HCl

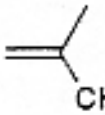


1) O_3

2) $(CH_3)_2S$

1) OsO_4, THF

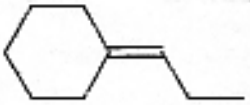
2) $NaHSO_3$



CH_2OH

1) MCPBA in CH_2Cl_2

2) H^+/H_2O

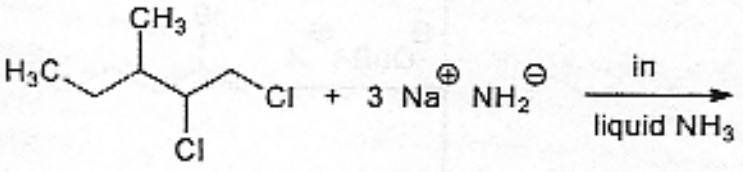


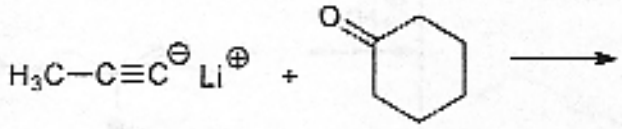
HBr

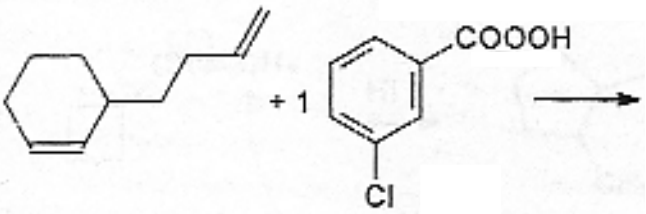
ROOR

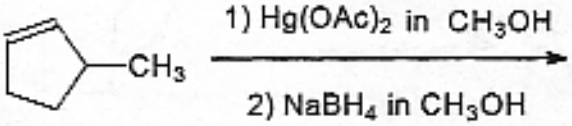
Δ

6. [**17 Points**]. Show the major product(s) obtained in the reactions below. Be sure to specify stereochemistry where appropriate

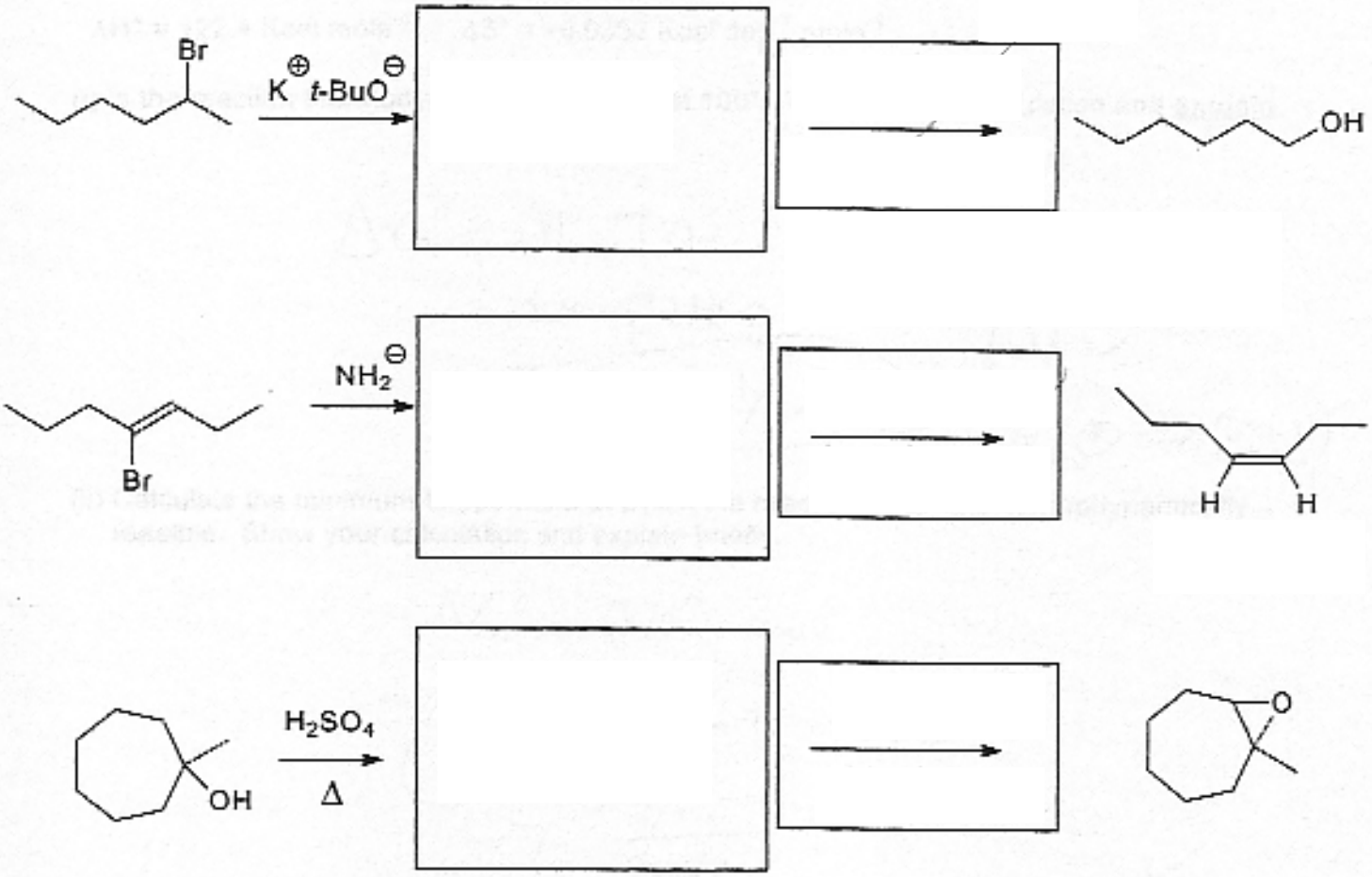




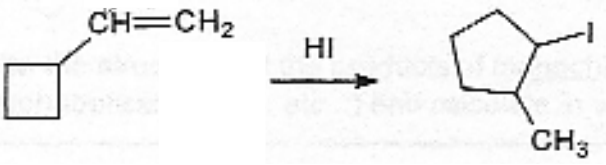




7. [**19 Points**] (a) For each of the reaction sequences below show a clear structure for the missing intermediate and the reagents used for the second step.



(b) Write a step by step mechanism (with all curved arrows) for the following reaction:



8. **[17 Points]**

(a) Consider the following reaction: $CH_3CH_2CH_2CH=CH_2 \longrightarrow CH_2=CH_2 + CH_3CH=CH_2$

$\Delta H° = +22.4$ Kcal mole^{-1} $\Delta S° = +0.0333$ Kcal deg^{-1} mole^{-1}

(i) Is the reaction thermodynamically feasible at 100°C? Show your calculation and **explain**.

(ii) Calculate the minimum temperature at which the reaction becomes thermodynamically feasible. Show your calculation and explain briefly.

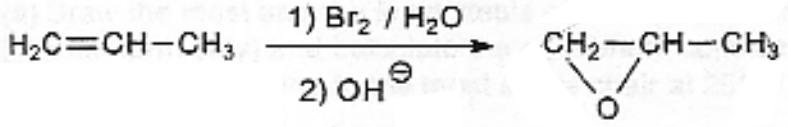
Answer:

(b) Write the structures of the products of monochlorination of butane using chlorine and light, label them alphabetically (A, B, etc...) and calculate in what ratio (A : B : ...) the products will be formed.

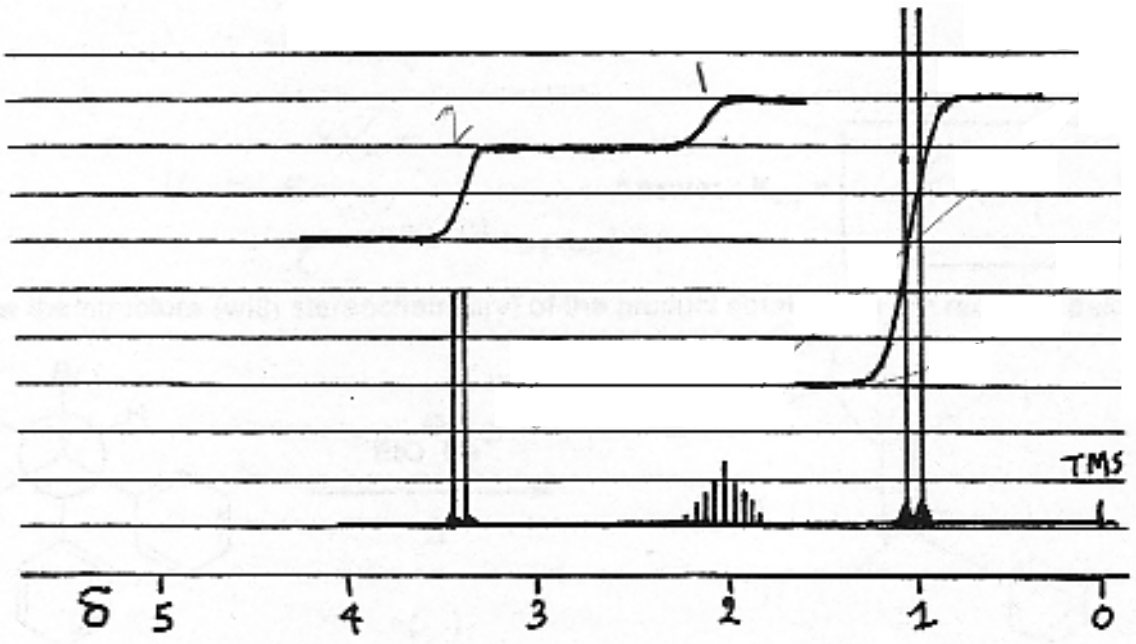
Answer: **Structures**

Answer: **Ratio**

9. [16 Points] (a) Show a step by step mechanism (with curved arrows) for the reaction:

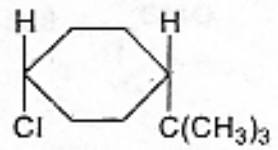


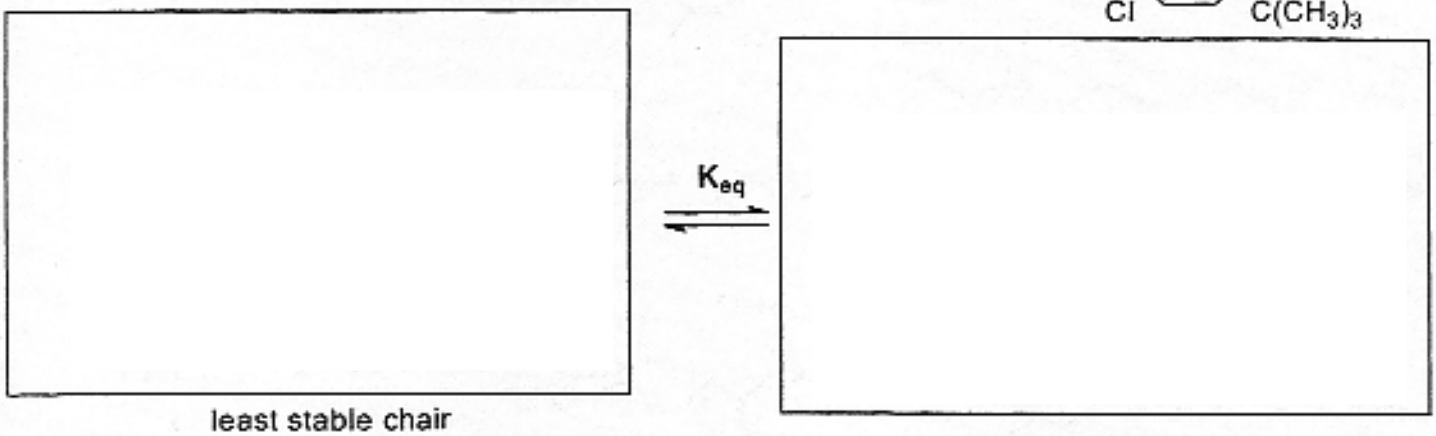
(b) What is the structure of the compound C_4H_9Cl whose ^1H NMR spectrum is shown below. Write a clear structure and provide a peak assignment using arrows to indicate which peak corresponds to each set of protons



10. **[16Points]**

(a) Draw the most and the least stable conformations of cis-1-*tert*-butyl-4-chlorocyclohexane (in chair form only) and calculate the equilibrium constant K_{eq} for the least stable chair going to the most stable chair at 25°C





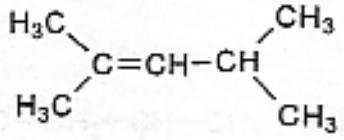
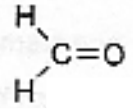
least stable chair

most stable chair

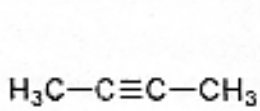
Show equations used and detailed calculations

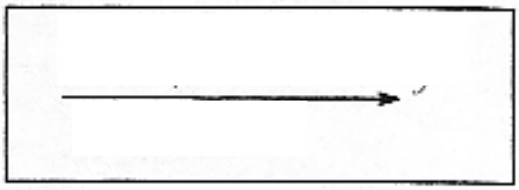
Answer : K_{eq} =

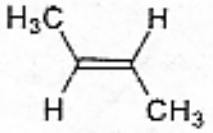
(b) Show the structure (with stereochemistry) of the product obtained in the reaction below:

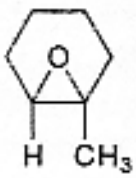
11. **[19 Points]** (a) propose a synthesis of  from $H_2C{=}CH{-}CH_3$ and 

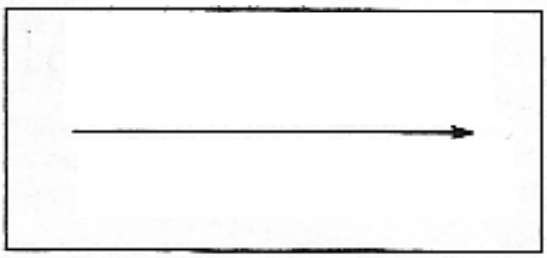
(b) Show the missing reagents required to effect the following transformations:

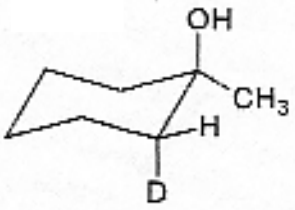




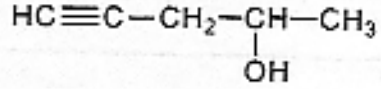








12. [**15 Points**]

Propose a step by step synthesis of  from ethyne and methane as the sole sources of C atoms

Show all steps and reagents.

Note: **There are no questions to be answered on this page.**
Not all of the data provided may be needed

Typical ^{1}H NMR chemical shifts

$R\text{-}CH_3$	0.8-1.1
$R\text{-}CH_2\text{-}R'$	1.2-1.4
R_3CH	1.4-1.7
$R\text{-}CH_2\text{-}O\text{-}R'$	3.3-3.9
$R\text{-}CH_2Cl$	3.4-3.7
R_2CHCl	3.9-4.4
$RO\text{-}CH_2Cl$	5.2-5.6

Relative reactivity of CH bonds in radical chlorination
Tertiary : Secondary : Primary = 5 : 4 : 1

Value of gas constant: R = 2.0 cal deg^{-1} mol^{-1} = 0.002 kcal/K·mol

Value of e (base for natural logarithms) e = 2.718

Value of absolute zero (kelvin) = -273°C

Value of each 1,3-diaxial interaction for Cl - H = 0.25 Kcal mole^{-1}

Value of each 1,3-diaxial interaction for $(CH_3)_3C$ - H = 2.5 Kcal mole^{-1}

Value of each 1,3-diaxial interaction for CH_3 - H = 1 Kcal mole^{-1}

Value of butane-gauche interaction = 1 Kcal mole^{-1}

Glossary: MCPBA is *meta*-chloroperoxybenzoic acid; ROOR is an organic peroxide; K_{eq} is the equilibrium constant.

Partial periodic table of the elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 La • 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac ▲ (227)	104 • Unq (261)	105 • Unp (262)	106 • Unh (263)	107 • Uns (262)											