# 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.

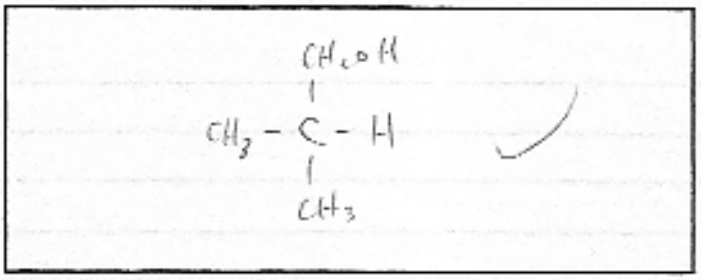
**<u>Note:</u>** This examination runs for a total of 180 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **<u>no credit</u>**.

**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

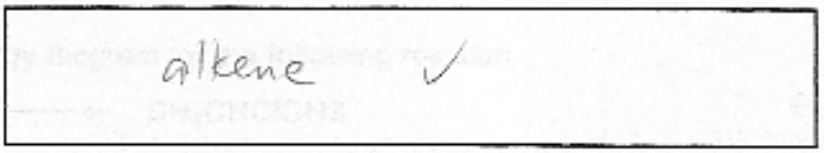


(b) A hydrocarbon has the formula $C_7H_{12}$, it exhibits the following spectroscopic properties: IR: peaks at 3072, 2900-3000, 1649 and 888 $cm^{-1}$; $^1H$ NMR spectrum δ = 1.3 (m, 2H); 1.7 (m, 4H); 2.2 (m, 4H) and 4.8ppm (quintet, 2H); $^{13}C$ NMR: δ = 26.8; 28.7; 35.7; 106.9 and 149.7ppm; hydrogenation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

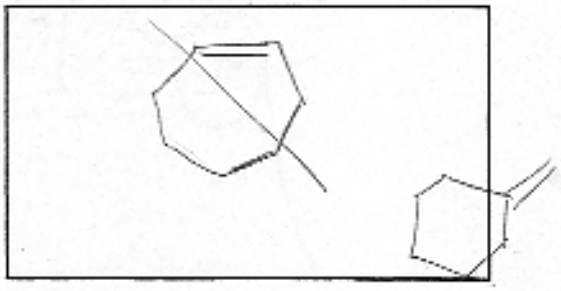
Answer: 2

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




(iii) What is the structure of the hydrocarbon?

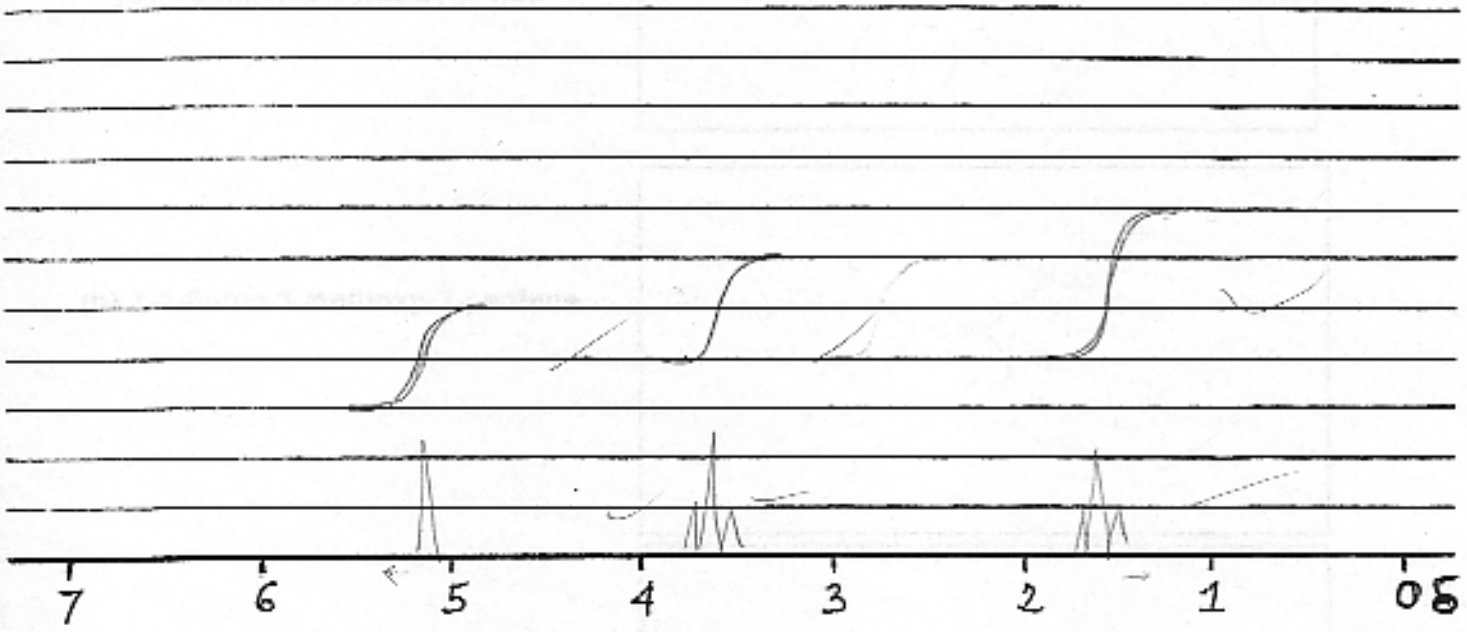
Answer:



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

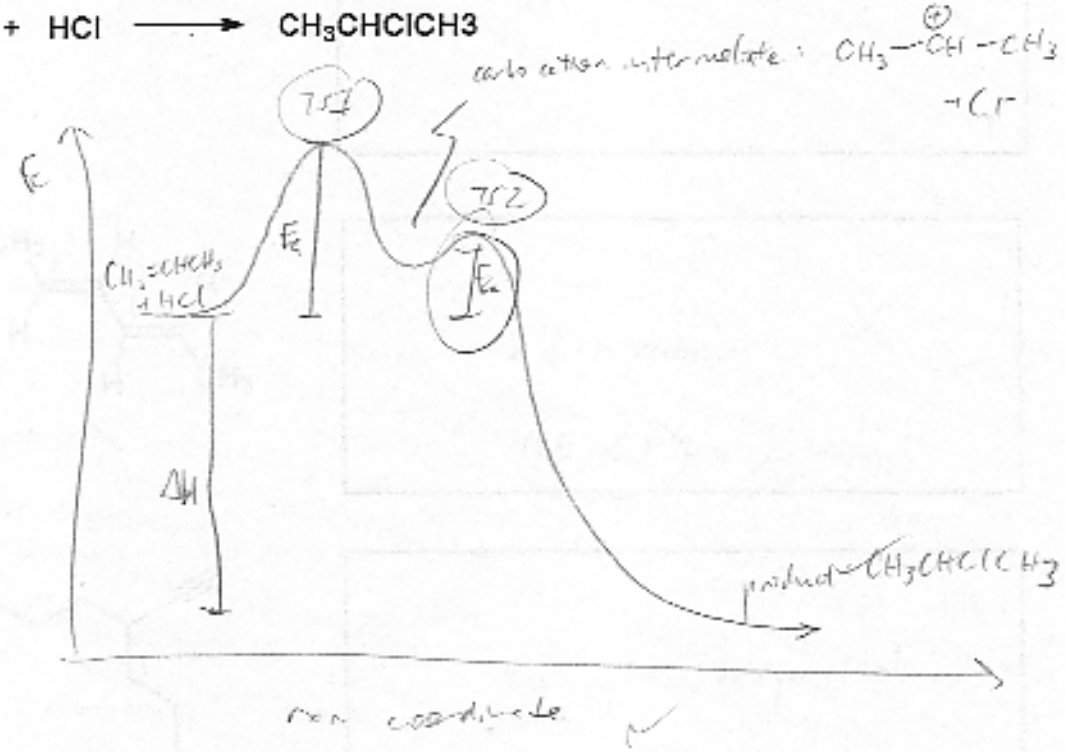
(Circle one) 3310 $cm^{-1}$ 2120 $cm^{-1}$ 1950 $cm^{-1}$ 1640 $cm^{-1}$ 1430 $cm^{-1}$ 888 $cm^{-1}$

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.



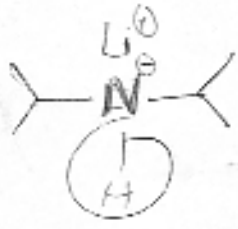

(b) Show a fully labeled energy diagram for the following reaction

$CH_2=CHCH_3 + HCl \longrightarrow CH_3CHClCH3$

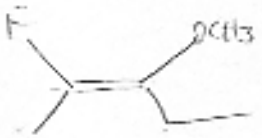


3. **[15 Points]** Name or draw as appropriate the following molecules. Show stereochemistry if relevant.

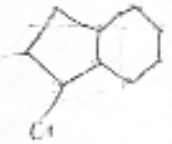
(a) Lithium diisopropylamide



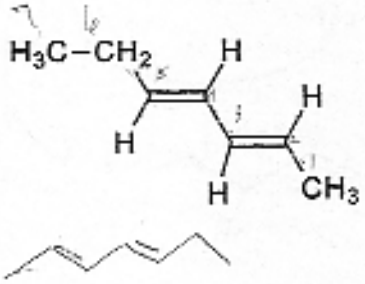
(b) Z-2-fluoro-3-methoxy-2-pentene



(c) 7-chlorobicyclo[4.3.0]nonane



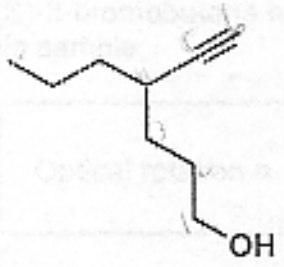
(d)



2,4-heptdiene

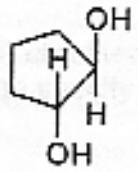
(2E,4E)-2,4-heptdiene

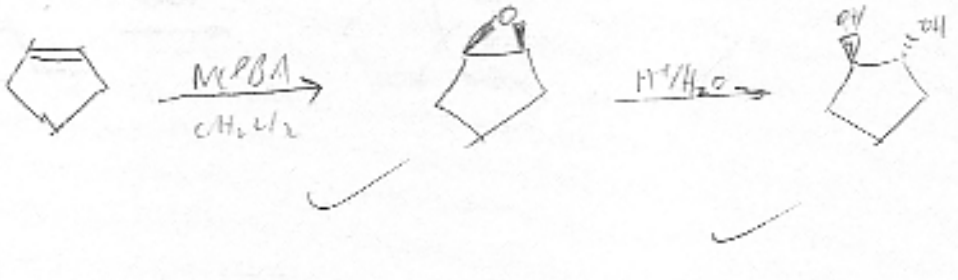
(e)



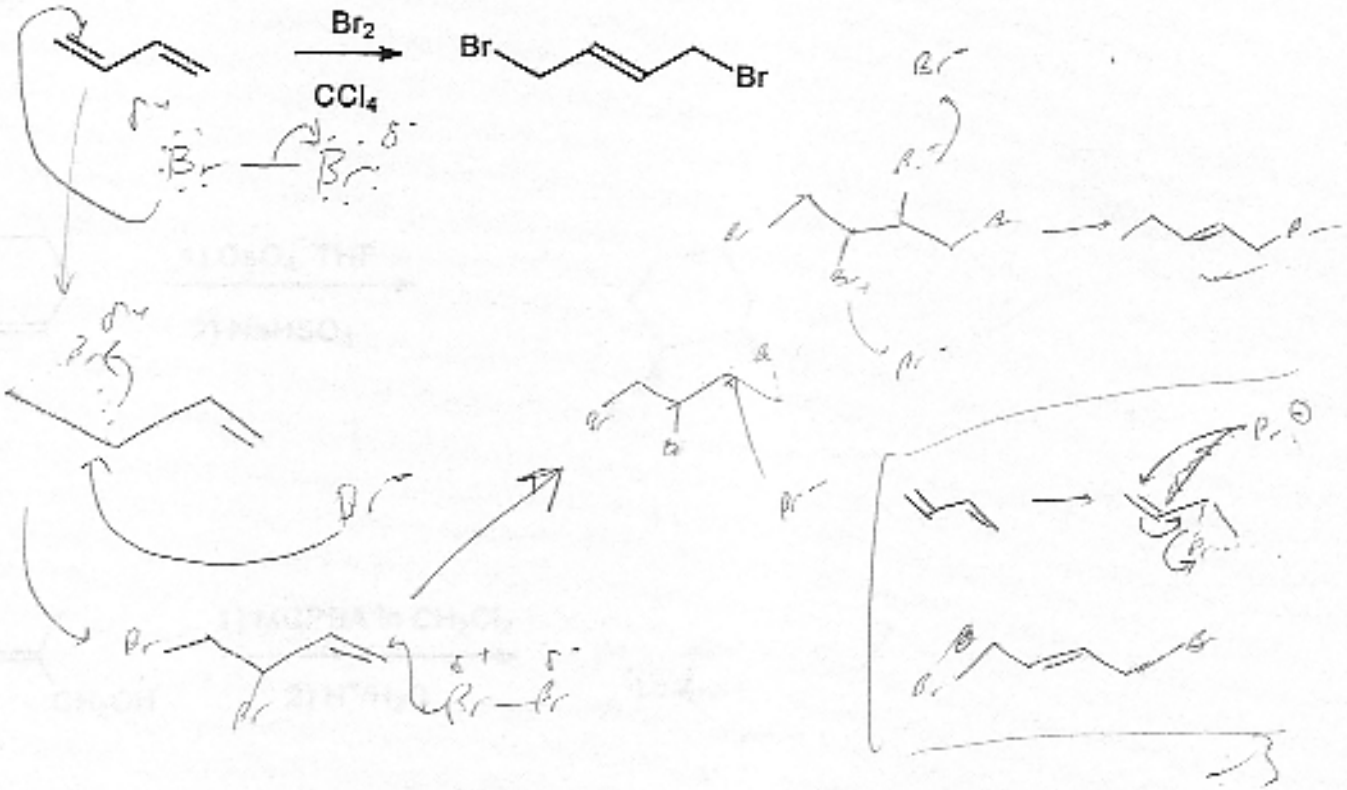
4-propyl-5-hexyn-1-ol

**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:

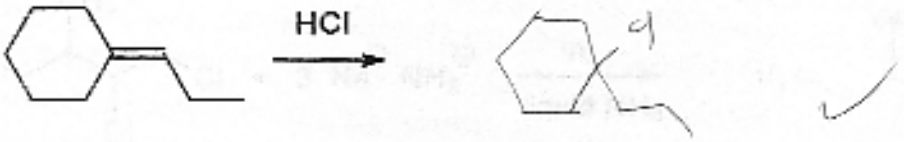


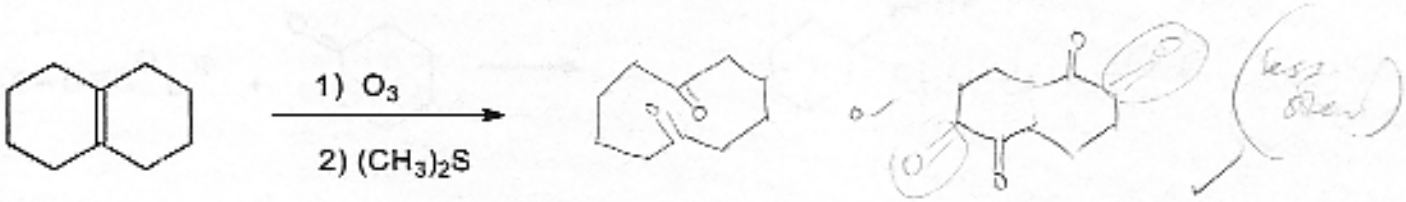

c) The optical purity of a sample of (R)-2-bromobutane is 80%. What is its optical rotation given that pure (S)-2-bromobutane has a specific rotation of +25°. Also calculate the percentage of S-isomer in this sample.

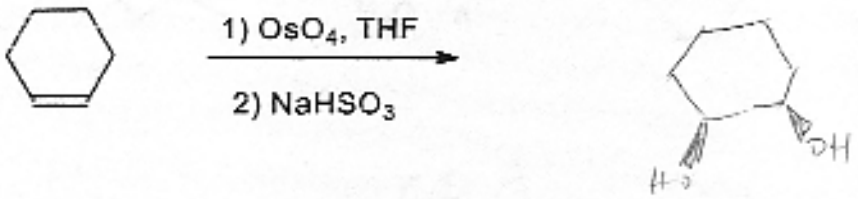
**Answers:**

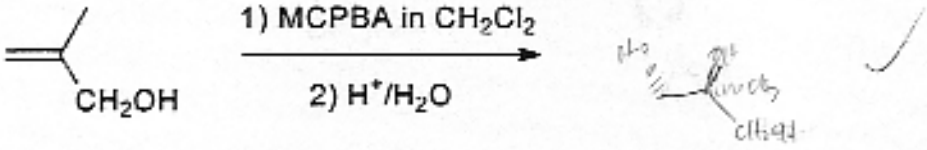
| Optical rotation = −20° | Percentage of S isomer in sample = 10% |
|---|---|

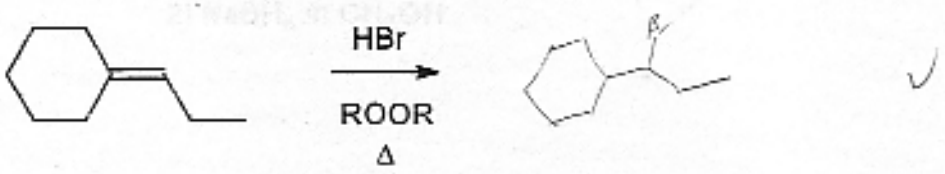
5. [**15 Points**] Show the major product(s) obtained in the reactions below. Do not include minor products or by-products. Be sure to specify stereochemistry where appropriate



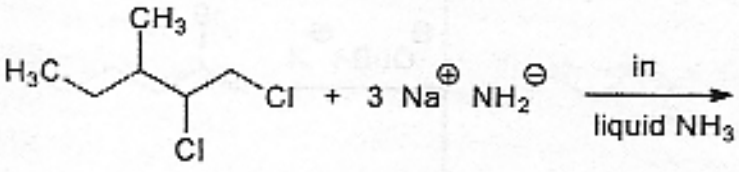



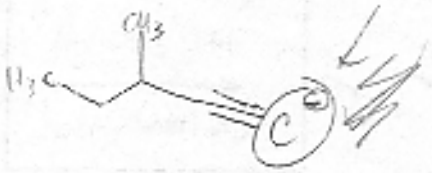



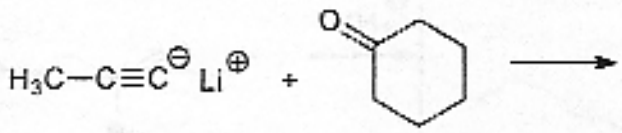



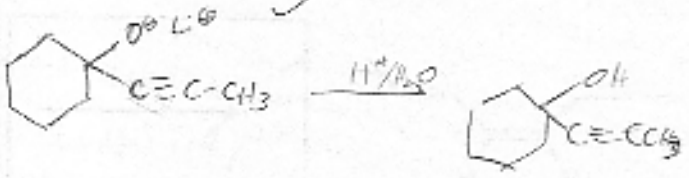



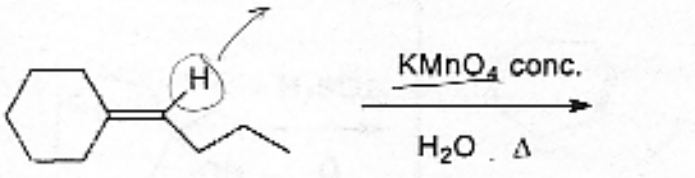
6. [**17 Points**]. Show the major product(s) obtained in the reactions below. Be sure to specify stereochemistry where appropriate

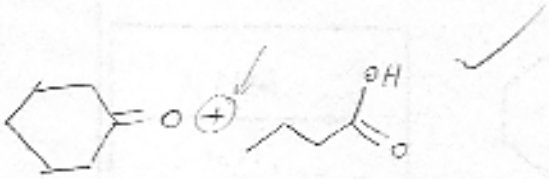


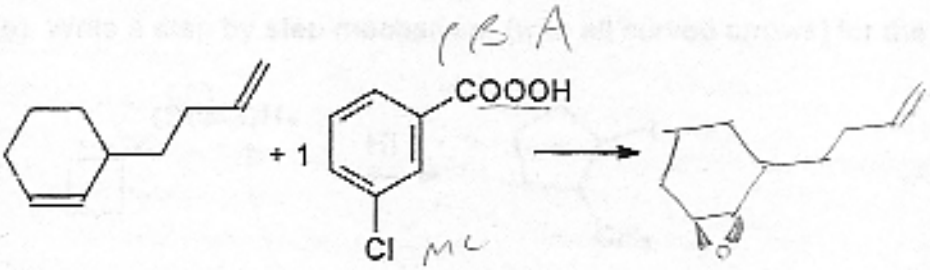



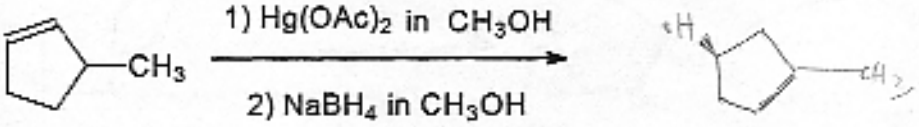


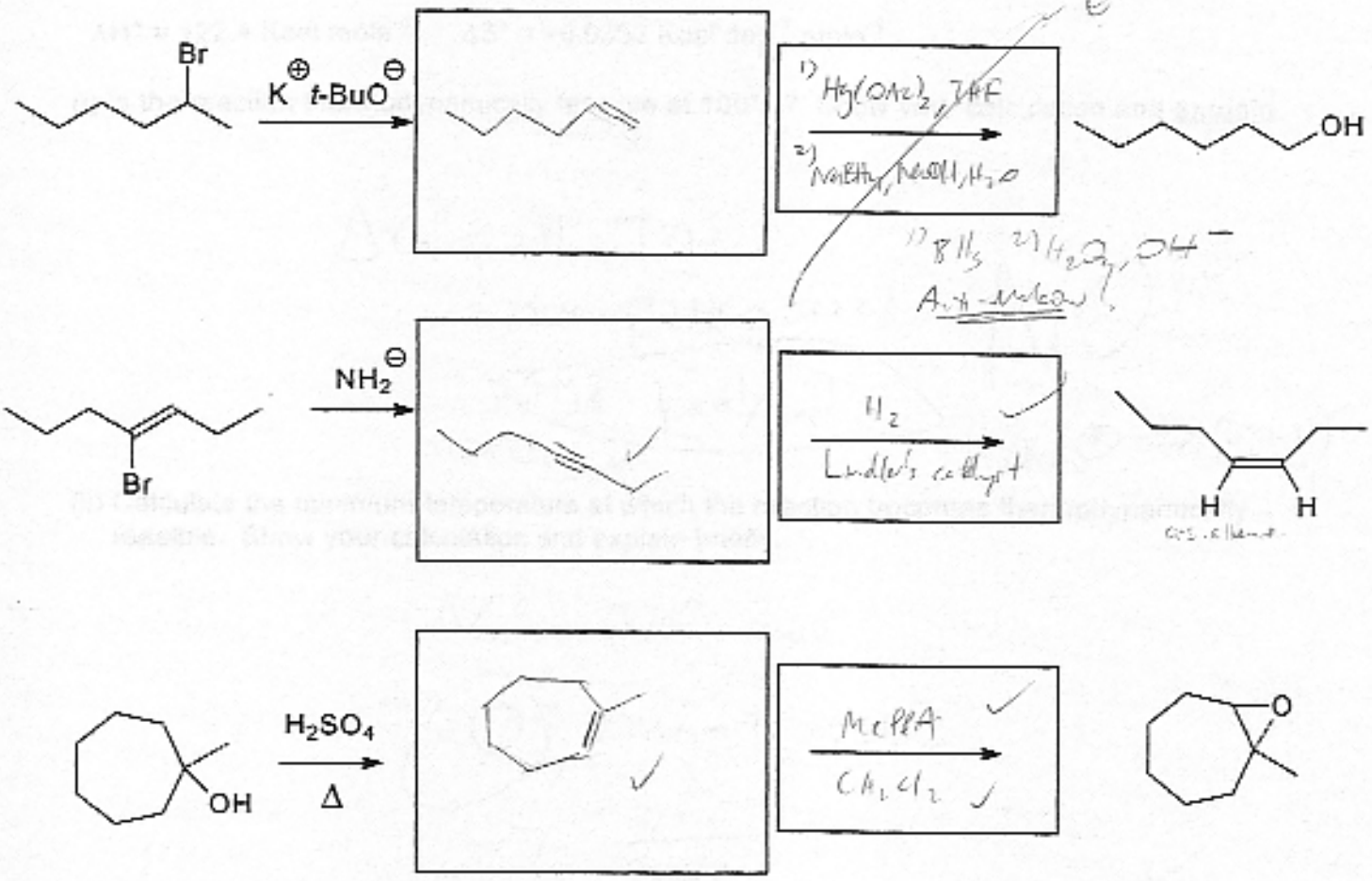



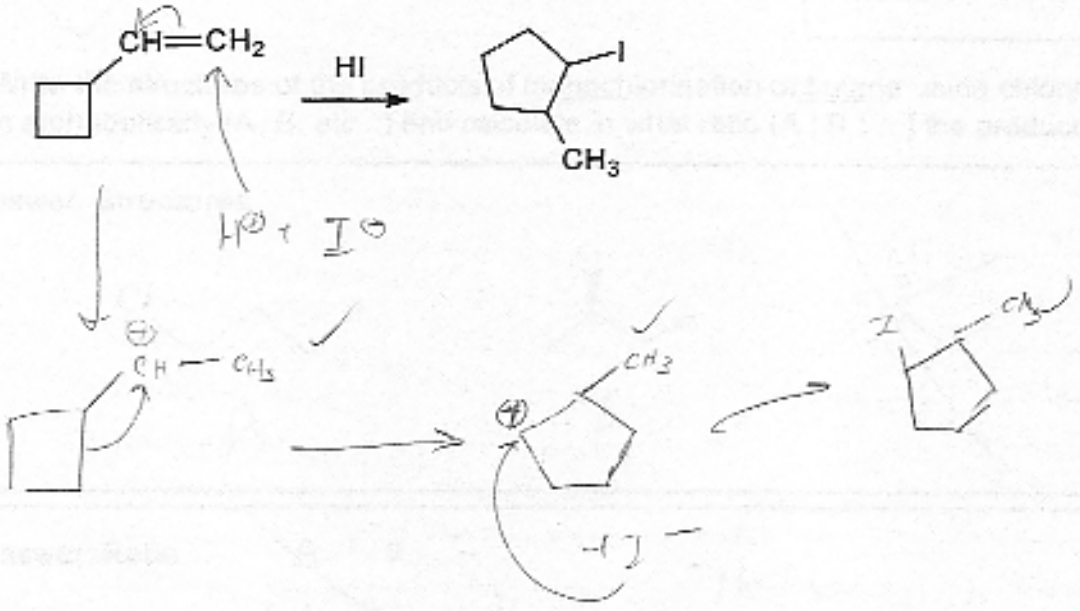


7. [**19 Points**] (a) For each of the reaction sequences below show a clear structure for the missing intermediate and the reagents used for the second step.




(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**.

$\Delta G_1° = \Delta H° - T\Delta S°$

$= 22.4 - (373)(0.0333)$

$= 9.98$ kcal/mol

NO. ✓

$\Delta G_1$ ⊕ ⇒ (uphill)

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

$\Delta G_1° = \Delta H° - T\Delta S°$

$0 = 22.4 - T(0.0333)$

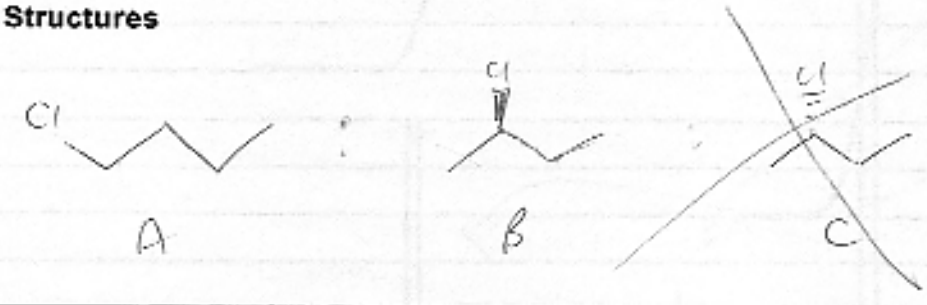
$T = \frac{22.4}{0.0333}$ ✓

$= 673$ K

**Answer:** $T > 673$ K

(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**

~~A : B : C~~

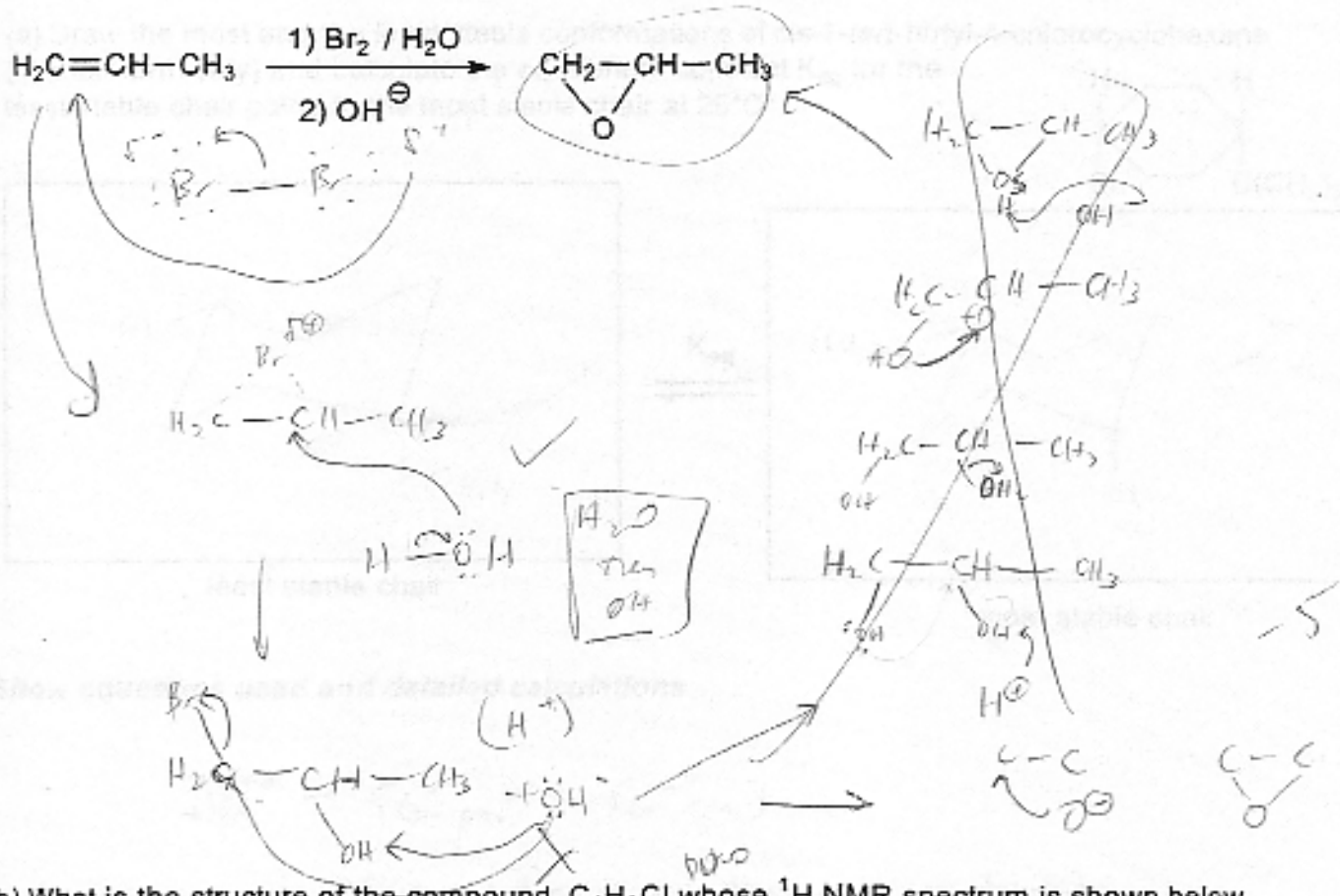
~~(1 : 4 : 4)~~

A : B

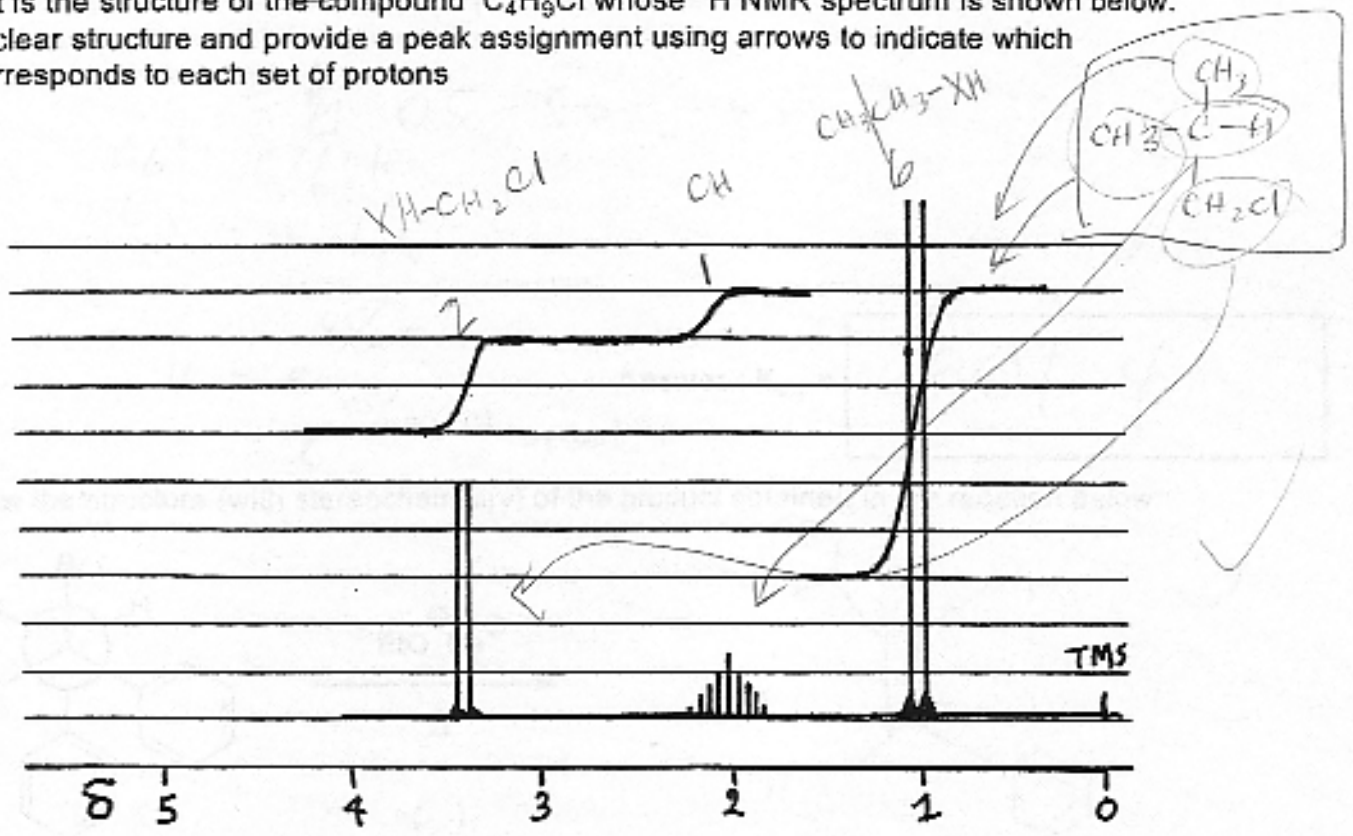
16 : 6

3

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

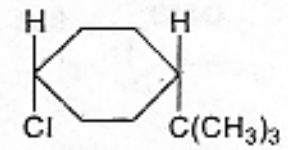


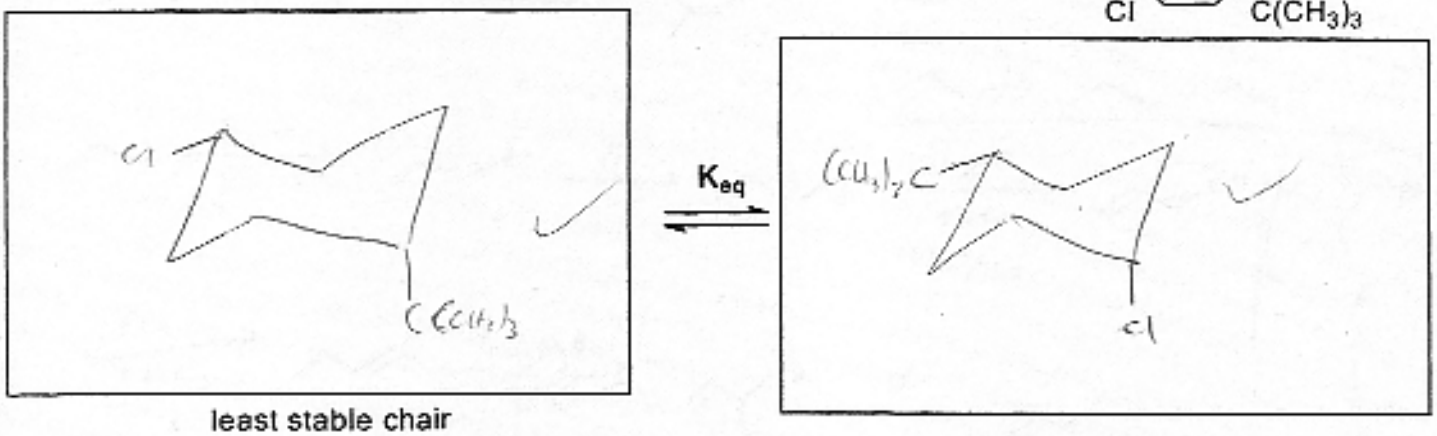

(b) What is the structure of the compound $C_4H_9Cl$ whose $^1H$ NMR spectrum is shown below. Write a clear structure and provide a peak assignment using arrows to indicate which peak corresponds to each set of protons



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***

$\Delta G^\circ = [G^\circ \text{ prod.}] - [G^\circ \text{ react.}]$

(not counting the rate ~~const~~ at because the H)

$= 0.5 - 5.0 = -4.5$

$\Delta G^\circ = -RT \ln K$

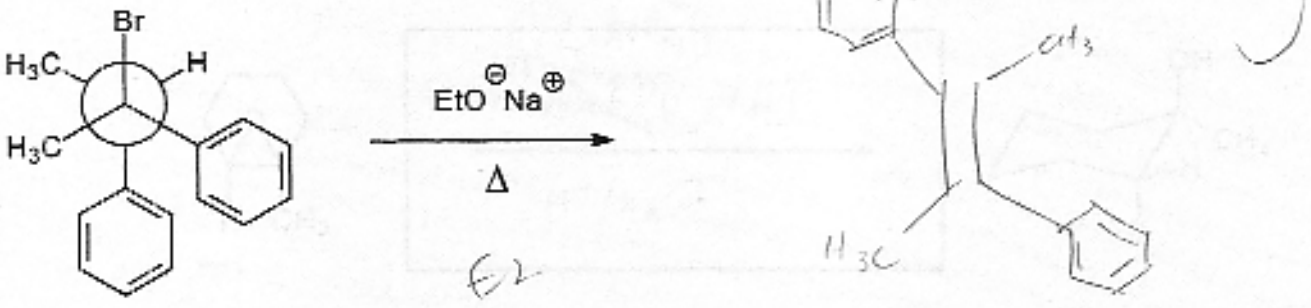
$-4.5 = -RT \ln K$

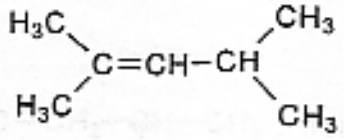
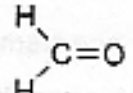
$K = e^{4.5/RT}$

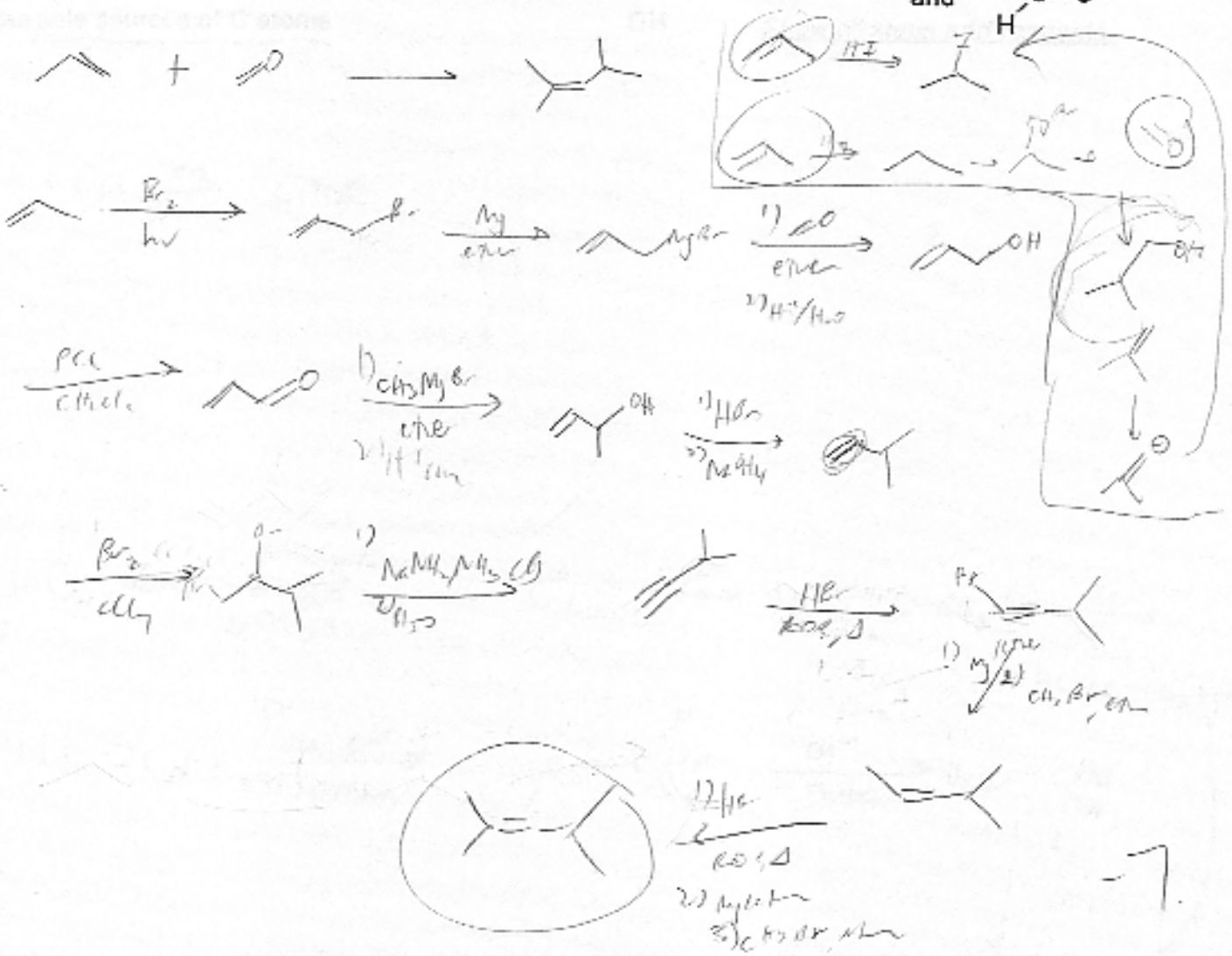
$= e^{4.5/0.002 \cdot 298} = 1901.4$

**Answer : $K_{eq}$ =** 1901.4

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

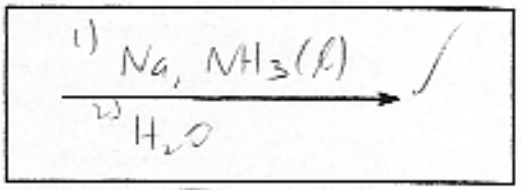


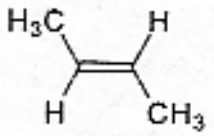
11. **[19 Points]** (a) propose a synthesis of  from $H_2C{=}CH{-}CH_3$ and 

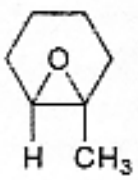


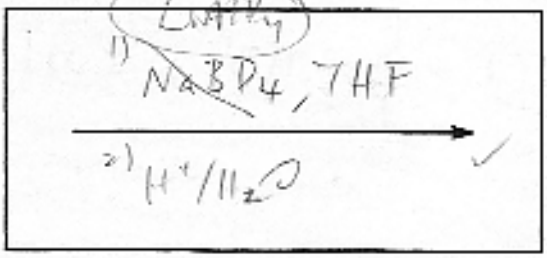
(b) Show the missing reagents required to effect the following transformations:

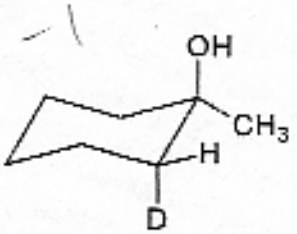
$H_3C{-}C{\equiv}C{-}CH_3$ → *trans alkene*



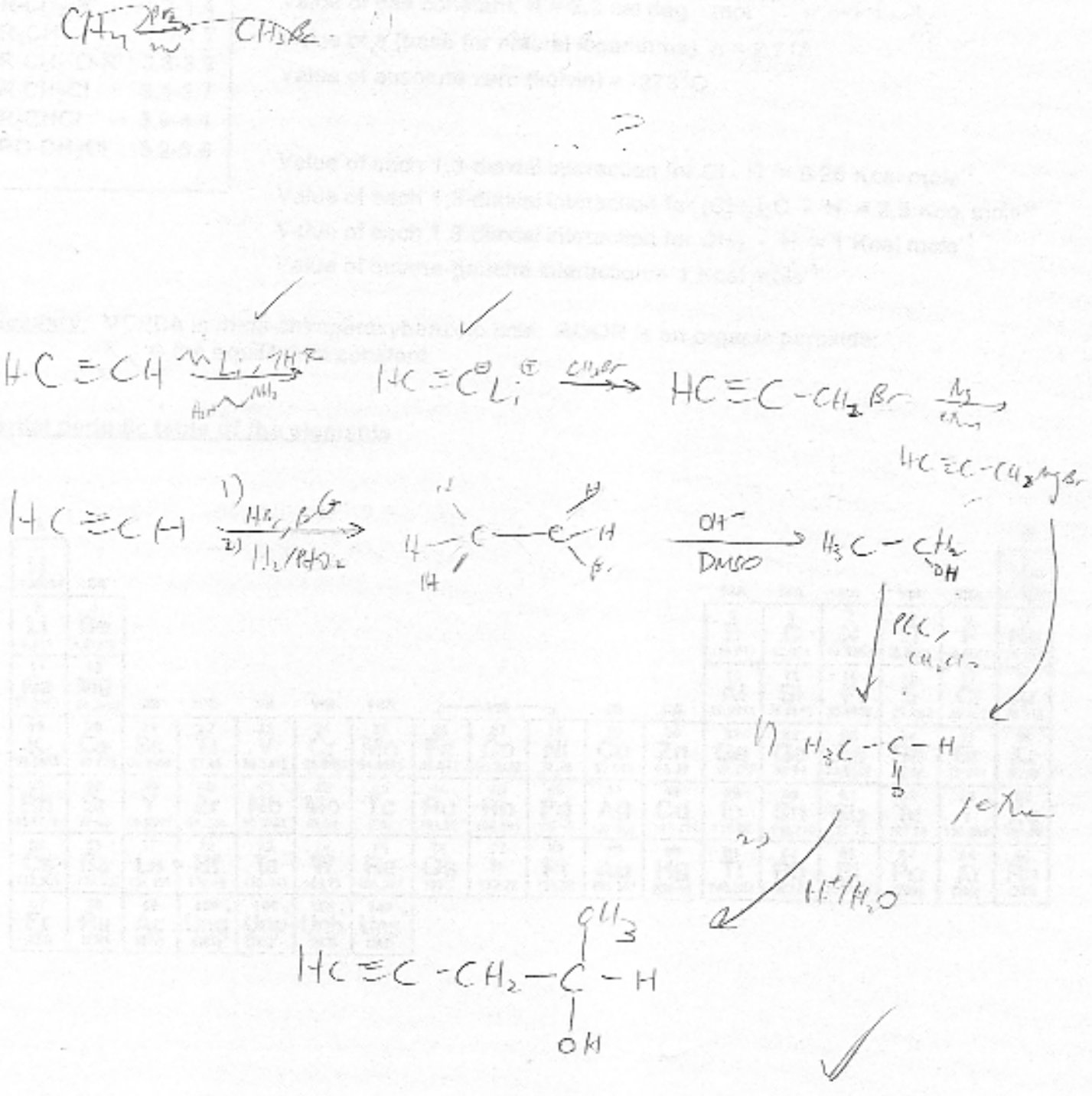




12. [ **15 Points**]

Propose a step by step synthesis of $HC\equiv C-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$ 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) | | | | | | | | | | | |