Chemistry 3A – Spring 2002
Final Exam

Professor Jean Fréchet

May 20, 2002

Your full signature__

Print your full name_

Your SID__

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

_____ 161 Margot Paulick
_____ 171 Danielle Dube
_____ 181 Matt Pratt
_____ 191 Laurie Schenkel
_____ 111 Cathleen Yung
_____ 121 Priya Sonik
_____ 131 Paul Furuta
_____ 141 Zach Fresco
_____ 261 Aaron Stutz
_____ 271 Vanessa Sun
_____ 211 Jamey Kain
_____ 221 Laura Anderson
_____ 361 Reema Thalji
_____ 371 Warren Wood
_____ 311 David Barry
_____ 321 Christina Brown
_____ 461 Aaron Stutz

_____ 471 Alex Kollias
_____ 411 Andrew Chi
_____ 421 Shahed Ghoghawala
_____ 431 Mike Slater
_____ 561 Jean Han
_____ 571 Ognjen Miljanic
_____ 511 Joe Kwon
_____ 521 Catherine Chan
_____ 531 Olga Fedin
_____ 541 Jason Serin

If you are making up an I-grade, indicate the semester you took 3A _____ and the Professor _____

This exam has **15** pages; **make sure that you have them all.**

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 **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

Note: 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 **no credit**.

Do not write in this box.

1.	18	(18)
2.	15	(15)
3.	12	(15)
4.	11	(11)
5.	14	(15)
6.	14	(14)
7.	12	(18)
8.	7	(12)
9.	7	(18)
10.	7	(15)
11.	13	(18)
12.	14	(14)
13.	14	(17)
TOTAL	158	(200)

Note: **There are no questions to be answered on this page,**
Note that some of the data provided may not be needed

Typical ^{1}H NMR chemical shifts δ

$R\text{-}CH_3$	0.7-1.3
$R\text{-}CH_2\text{-}R'$	1.2-1.6
R_3CH	1.4-1.8
$R\text{-}CH_2\text{-}O\text{-}R'$	3.3-4.0
$R\text{-}CH_2Cl$	3.4-3.7
R_2CHCl	3.9-4.4
$RO\text{-}CH_2Cl$	5.2-5.6
$RR'C{=}CH_2$	4.6-5.0
$RCH{=}CHR'$	5.2-5.7
$RC{\equiv}CH$	1.7-3.1
$CH_3\text{—}\overset{\overset{O}{\|\|}}{C}\text{—}R$	2.0-2.4
$\overset{\|}{C}{=}\overset{\|}{C}\text{—}CH_2\text{—}$	1.7-2.2

Typical ^{13}C NMR chemical shifts δ

$R\text{-}CH_3$	5-25
$R\text{-}CH_2\text{-}R'$	25-35
R_3CH	35-55
R_4C	30-45
$R\text{-}CH_2\text{-}O\text{-}R'$	50-90
$R\text{-}CH_2Cl$	25-50
$R\text{-}COOH$	170-180
$R\text{-}CH{=}CH\text{-}R'$	100-150
$R_2C{=}CR'_2$	100-150
$RC{\equiv}CR$	65-95
$CH_3\text{—}\overset{\overset{O}{\|\|}}{C}\text{—}R$	170-220

Infrared stretching in cm^{-1}

O-H (alcohol) 3200-3650
C-H (alkane) 2840-3000
C-H (alkene) 3050-3150
>C-H (alkyne) 3260-3330
C=O (aldehyde, ketone) 1690-1750
C=C (alkene) 1620-1680
C≡C (alkyne) 2100-2260
$R\text{—}\overset{\overset{O}{\|\|}}{C}\text{—}OR'$ (ester) 1735-1750

D is the symbol used to denote deuterium the isotope ^{2}H of hydrogen

Bond dissociation energies (in Kcal mole^{-1}): $H_2C{=}CH\text{—}H$ 108 ✓ $H_2C{=}CH\text{—}Cl$ 88 ✓

$H_2C{\equiv}CH_2$ { both sigma and pi bonds: 153 ; pi bond only: 65. ✓

$RO\text{—}CH_2$ 92 ✓ $RCH_2\text{—}Cl$ 80 ✓

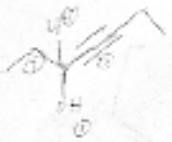
$RO\text{—}H$ 104 ✓ $RO\text{—}Cl$ 53 ✓

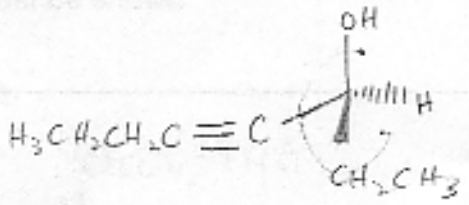
Partial periodic table of the elements

PERIOD							
1	1 H 1.008						2 He 4.003
2	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95

1. (18 Points). Name or draw the following molecules as appropriate (show stereochemistry)

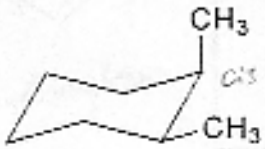
(a) (S)-4-heptyn-3-ol





3

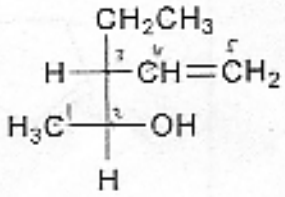
(b)



cis-1,2-dimethylcyclohexane

3

(c)



(2S,3R)-3-ethyl-4-pentyn-2-ol

3

(2S,3R)-3-ethyl

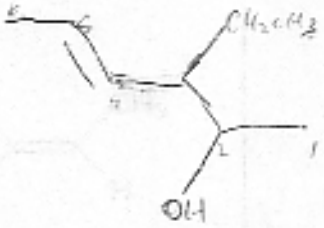
(d) $H-\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{C}H_3$

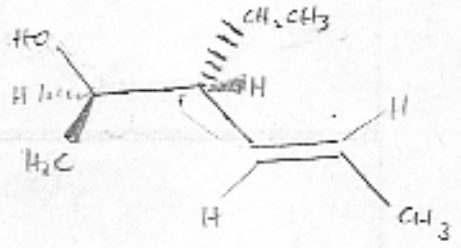
1,3-pentdiyne

3

(e)

(E)-(2R,3R)-3-ethyl-4-hexen-2-ol

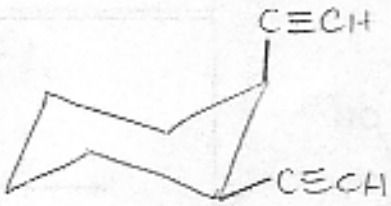




3

(f)

Cis-1,2-diethynylcyclohexane



3

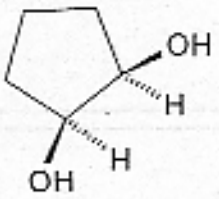
18

2. (15 Points) Complete the following reactions showing the reagents used to effect the desired transformation. In some cases more than one step is required, in such cases, all reagents and the order in which they are used must be shown

syn dihydroxylation

1) OsO_4, THF
2) H_2S

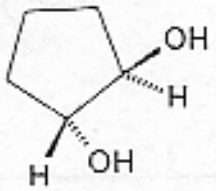
3

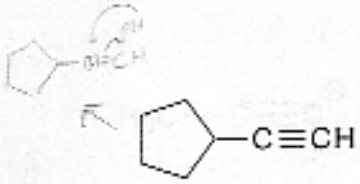


anti dihydroxylation

1) MCPBA, CH_2Cl_2
2) H^+/H_2O

3

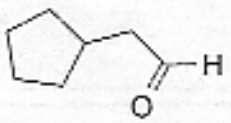


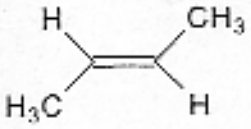


hydroboration-oxidation → tautomerization aldehyde

1) $(C_6H_{11})_2BH$, THF
2) H_2O_2, NaOH, H_2O

3

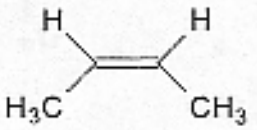




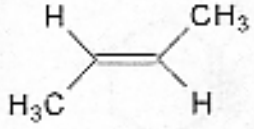
(1)-(3) → $H_3C-C\equiv C-CH_3$

1) Br_2, CCl_4
2) $NaNH_2$, $NH_3(\ell)$
3) H_2O
4) H_2, Ludlark catalyst

3



(pure cis isomer)

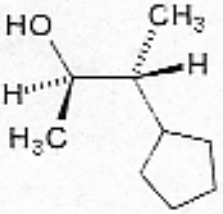


1) Br_2, hv
2) Mg, ether

1) MCPBA, CH_2Cl_2
2) 

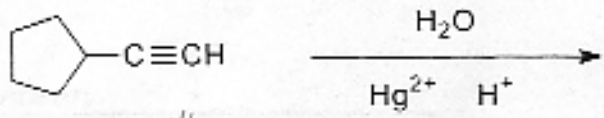
3) H^+/H_2O

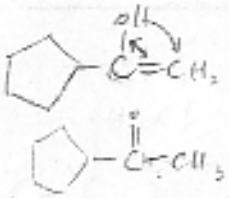
3

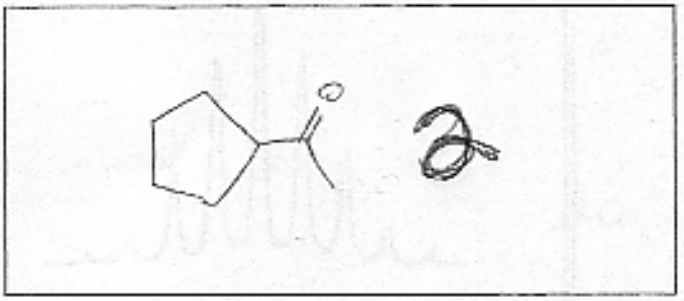


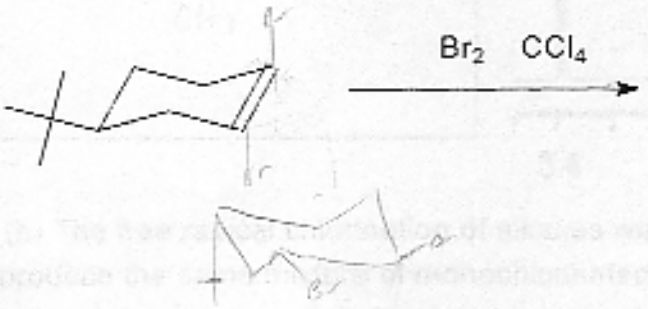
15

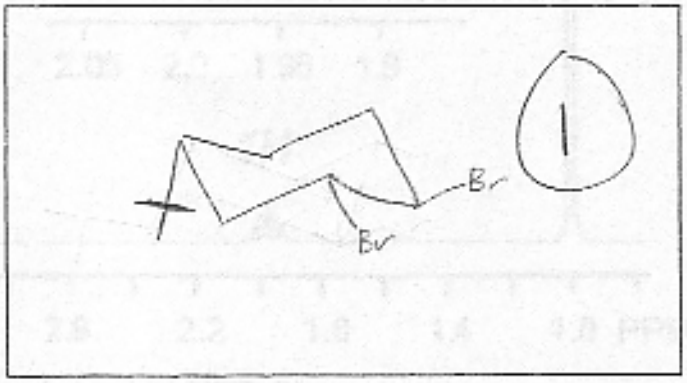
3. (15 Points). Complete the following reactions showing the major reaction product(s). show stereochemistry when relevant. Write NR if no reaction takes place.



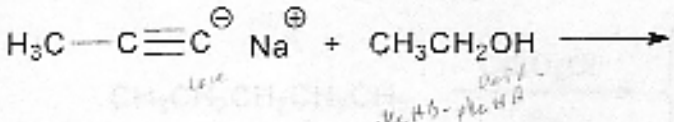


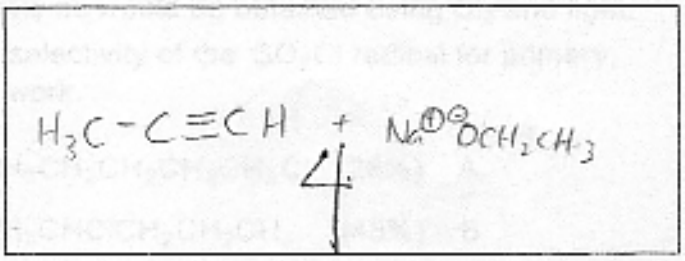


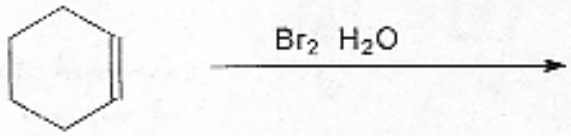


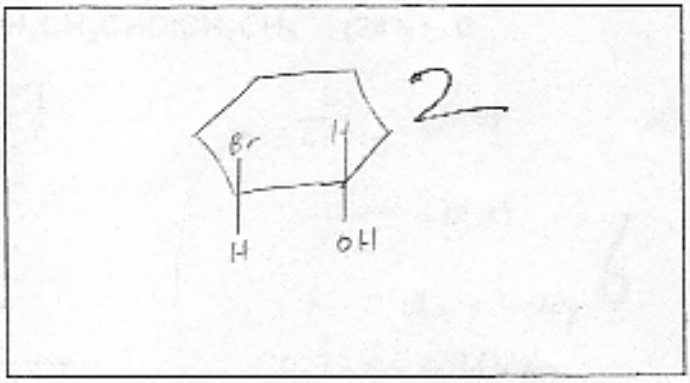


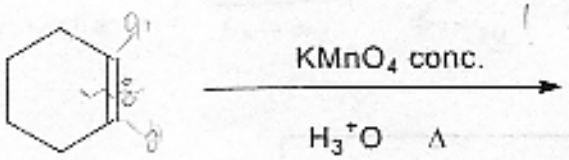
show most stable chair conformation of product!

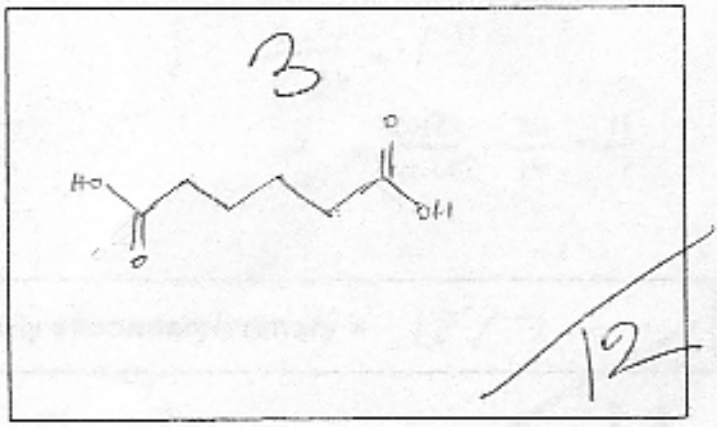






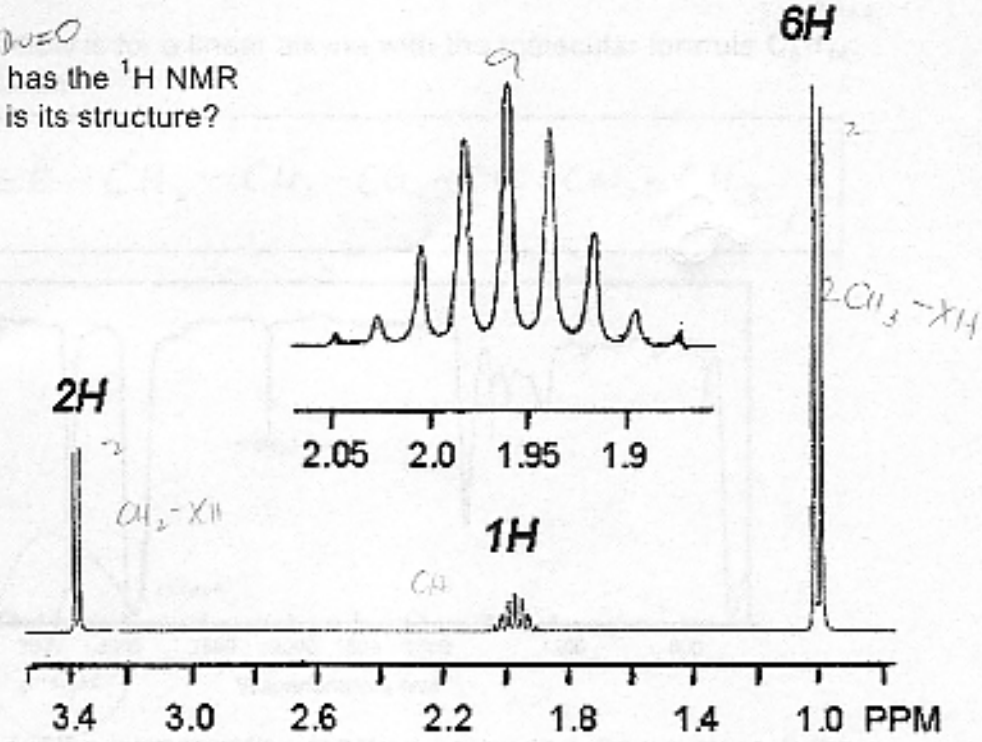




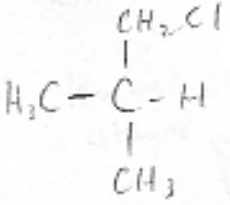


4. (11 Points)

(a) An unknown compound C_4H_9Cl has the ^1H NMR spectrum shown to the right. What is its structure?



Answer:



(b) The free radical chlorination of alkanes with sulfuryl chloride $ClSO_2Cl$ does not produce the same mixture of monochlorinated products as would be obtained using Cl_2 and light. Using the product compositions below, calculate the selectivity of the $\cdot SO_2Cl$ radical for primary, and secondary hydrogens. Show the details of your work.

$CH_3CH_2CH_2CH_2CH_3 \xrightarrow[h\nu]{ClSO_2Cl}$

- $CH_3CH_2CH_2CH_2CH_2Cl$ (28%) A
- $CH_3CHClCH_2CH_2CH_3$ (48%) B
- $CH_3CH_2CHClCH_2CH_3$ (24%) C

	1°	2°	2°
	A	B	C
# hydrogens available for more Chlorination	6	4	2
rel. reactivity	X	Y	Y
rel. yield	6x	4y	2y
% yield	$\frac{6y}{6x+6y}$	$\frac{4y}{6x+6y}$	$\frac{2y}{6x+6y}$

$\frac{6x}{6x+6y} = 0.28$

$\frac{x}{x+y} = 0.28$

$x = 0.28x + 0.28y$

$0.72x = 0.28y$

$\frac{0.28y}{0.72x} = 1$

$\frac{y}{x} = \frac{0.72}{0.28} = \frac{36}{14} = \frac{18}{7}$

Answer. Relative reactivity **secondary/primary =** 18/7

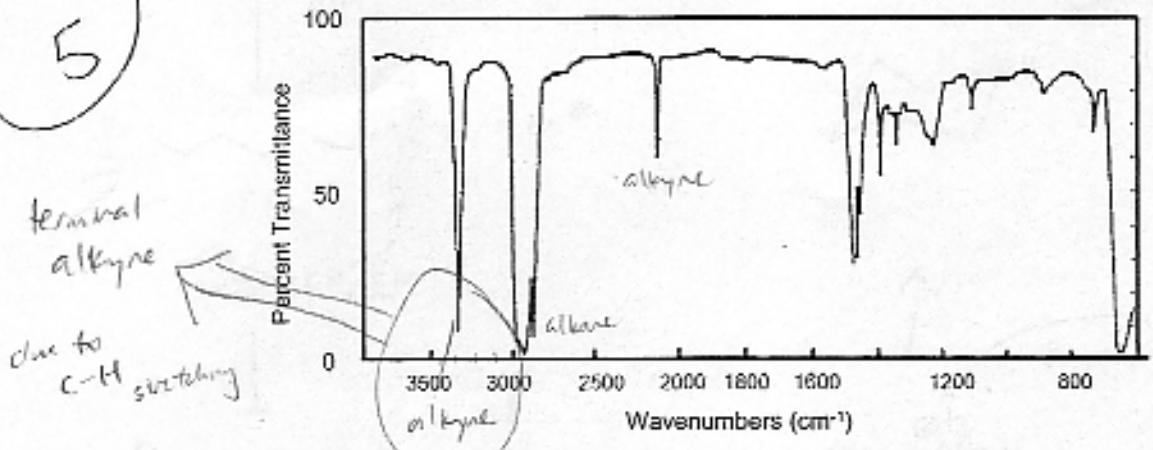
6

11

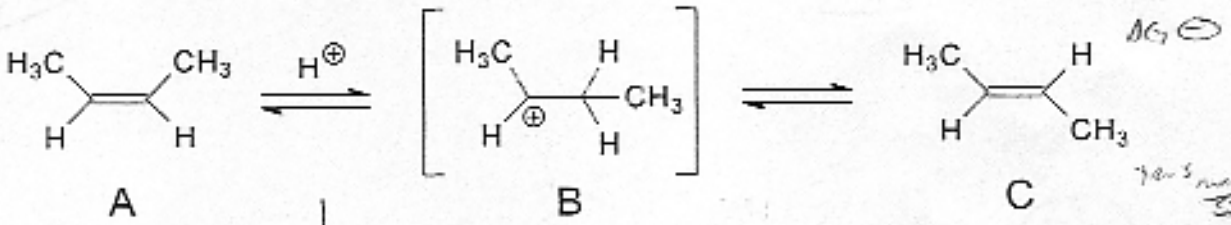
5. (15 Points) (a) The IR spectrum below is for a linear alkyne with the molecular formula C_8H_{14}. Write a clear structure for this hydrocarbon.

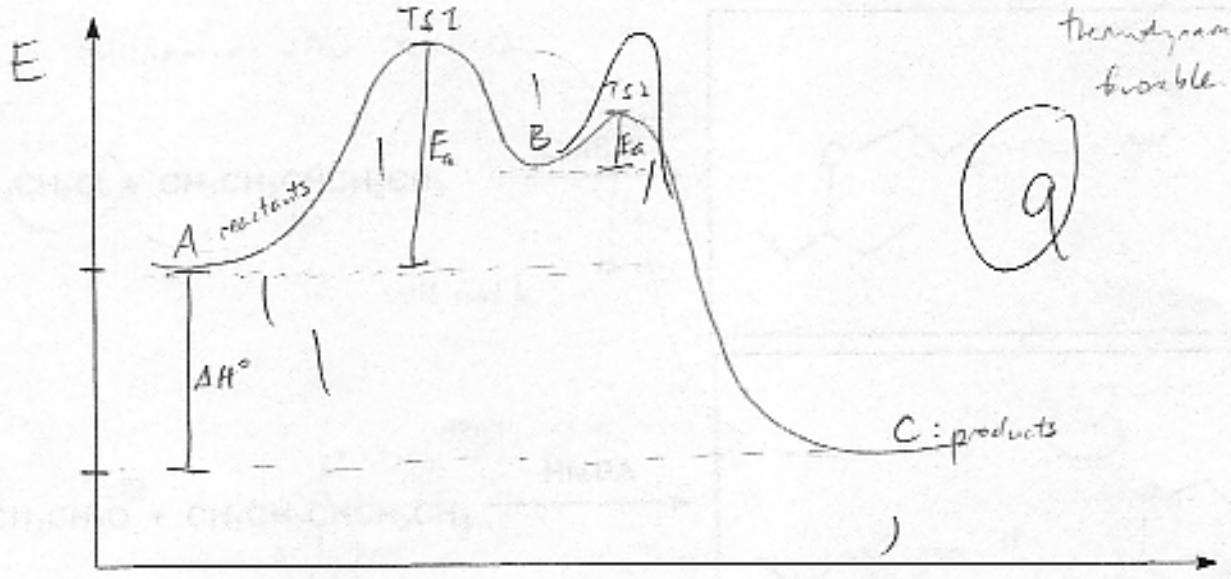
Answer: $HC\equiv C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

5



(b) Consider the mechanism shown for the isomerization reaction below and draw a clear, **fully labeled** potential energy diagram showing clearly the relative location of the key species A, B, C, and of any transition states.



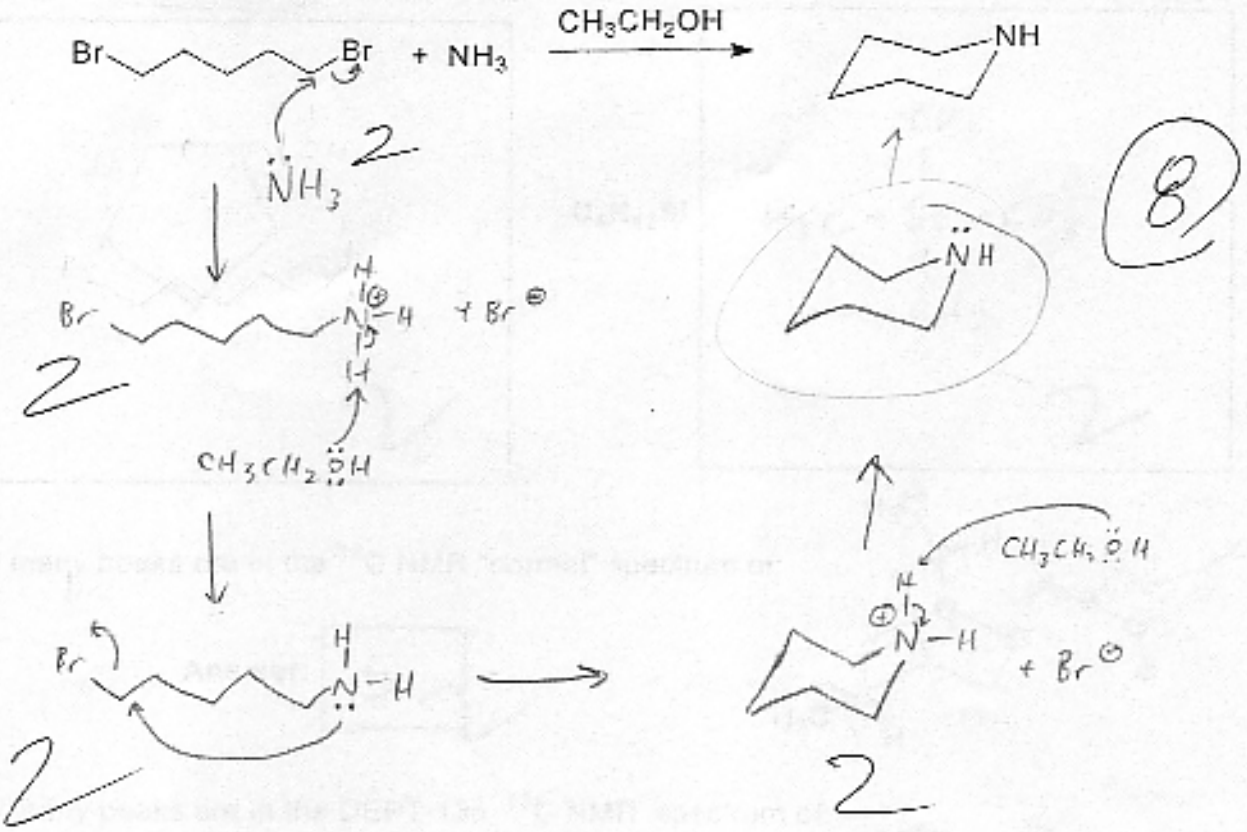


thermodynamically favorable

9

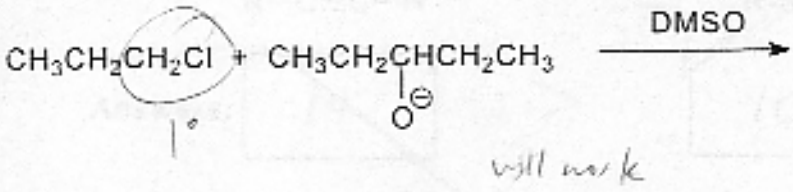
/14

6. (14 Points). (a) Show a detailed step by step mechanism (with curved arrows) explaining the the outcome of the following reaction:

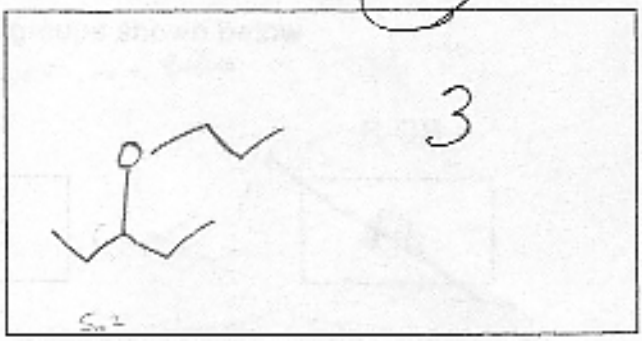


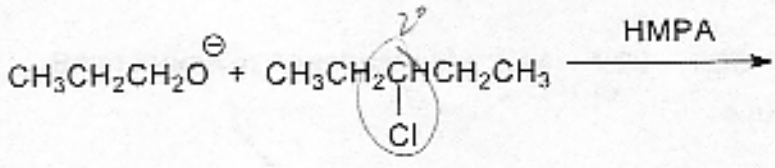
(b) Write the expected major product(s) of the following attempted ether syntheses 6

Williamson ether synthesis

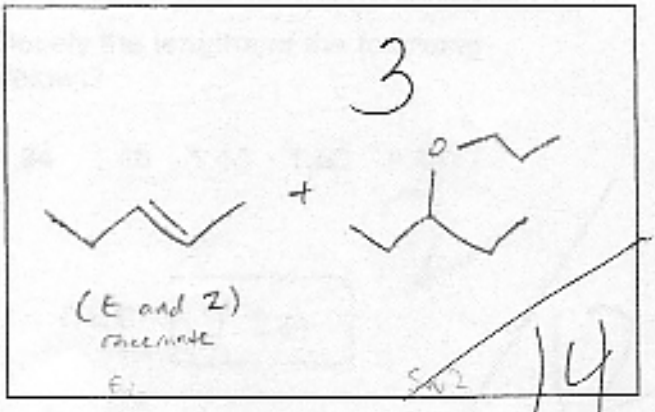


will work





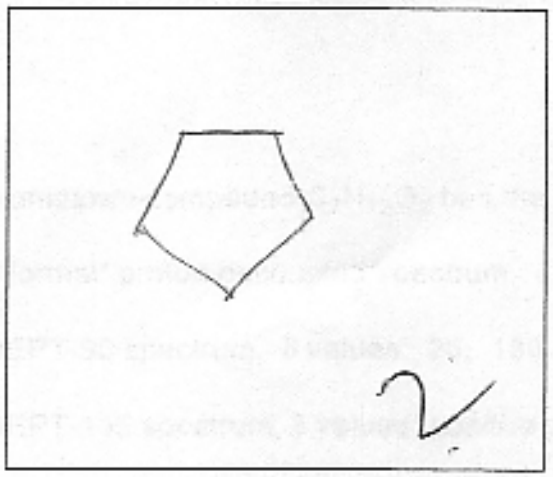
will have E2



14

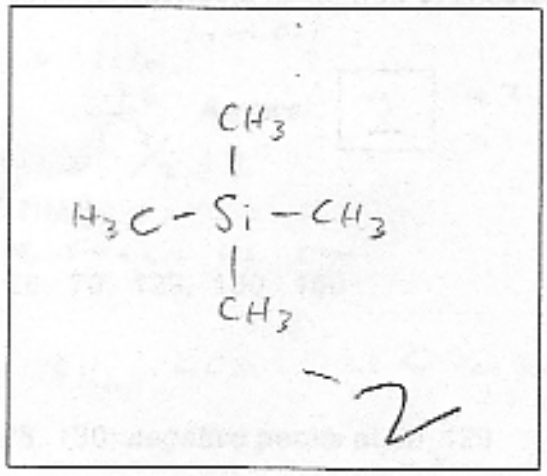
7. (18 Points). (a) Propose a reasonable structure for the organic compounds below that show only one peak in their ^{13}C NMR spectra.

C_5H_{10}



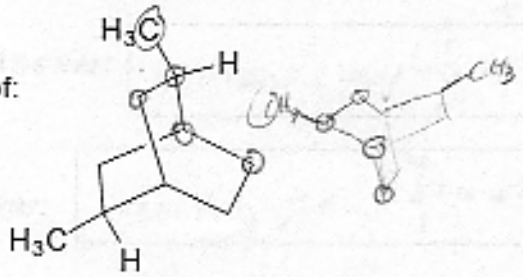
2

$C_4H_{12}Si$



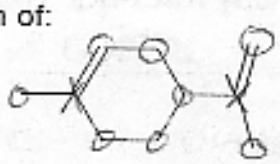
2

(b) How many peaks are in the ^{13}C NMR "normal" spectrum of:



Answer: 5 2

(c) How many peaks are in the DEPT-135 ^{13}C NMR spectrum of:



non-quat. C

Answer: 8 2

(d) Give the approximate pKa values for the functional groups shown below

C≡C-H ~25

less EN, more diffuse

R—C≡C—H R-SH R-OH

Answers: 14 > 10 < 12

(e) Which of the following bond lengths match most closely the lengths of the following carbon-carbon bonds (write *one* answer in each box below)?

Bond length in Angstroms (Å): 1.14 1.20 1.30 1.34 1.40 1.44 1.50 1.54

alkene

C—C 1.40 > C≡C 1.20

Argh, can't decide!

2

12

8. (12 Points) (a) A compound has the molecular formula $C_7H_{12}O_2$. What is its degree of unsaturation?

$7\times2 = 14+2 = 16$ (7 more O_2)
-12
$4/2 = 2$

Answer: 2 +2

(b) An unknown compound $C_7H_{12}O_2$ has the following ^{13}C NMR.

"Normal" proton decoupled spectrum, δ values: 19, 28, 70, 129, 130, 166 (CH_3 CH_2 C-O-C C=C C=C C=O)

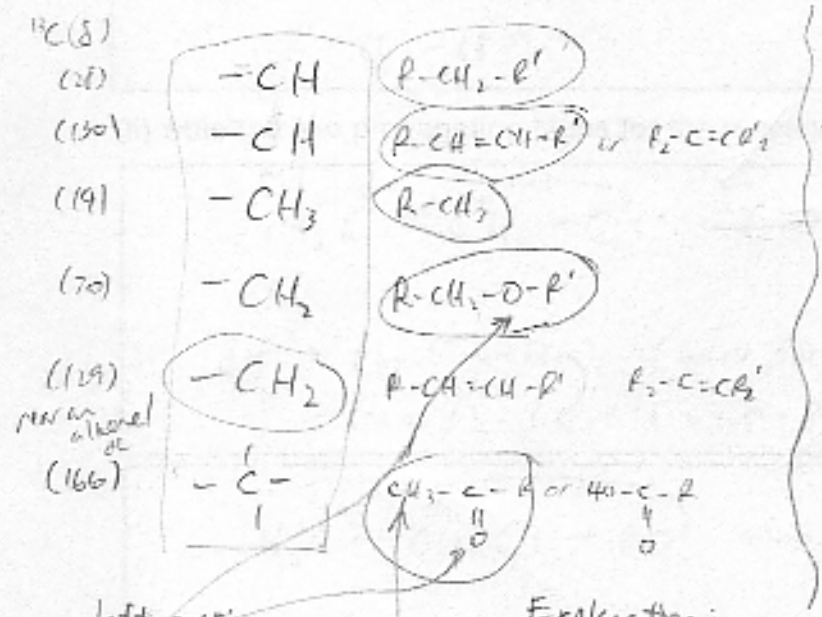
DEPT-90 spectrum, δ values: 28, 130 2 CH's 1 CH_3 2 CH_2's one C are upset

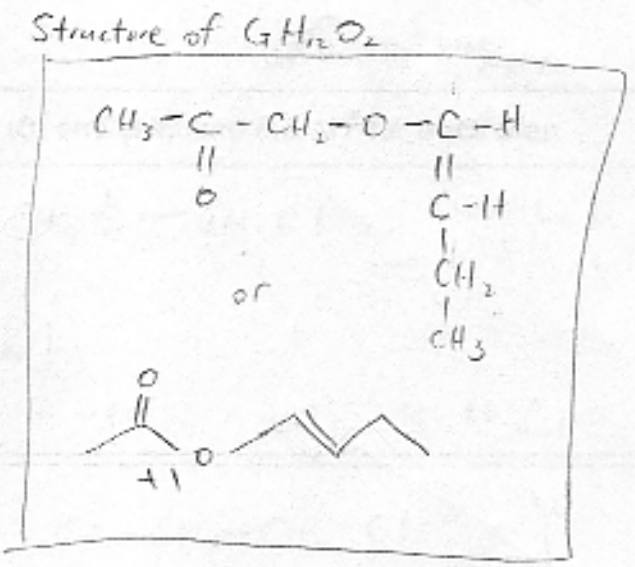
DEPT-135 spectrum, δ values: *positive* peaks at 19, 28, 130; *negative* peaks at 70, 129

(i) What type(s) of protons are observed by DEPT-90? **Answer:** tertiary, i.e. R'-C(H)-R'' +2

(ii) What type(s) of protons give rise to negative peaks in DEPT-135? **Answer:** secondary, i.e. -C(H)-H +2

(iii) What is the structure of the unknown compound $C_7H_{12}O_2$? **EXPLAIN** your reasoning.





Explanation:

The ^{13}C NMR spectra showed us that there were 2 CH's, 1 CH_3, 2 CH_2's, 1 quat. C, an internal alkene, a carbonyl group, and an ether oxygen. It was then just a matter of putting the pieces together.

7

9. (18 Points) Consider the two reactions of ethene shown below:

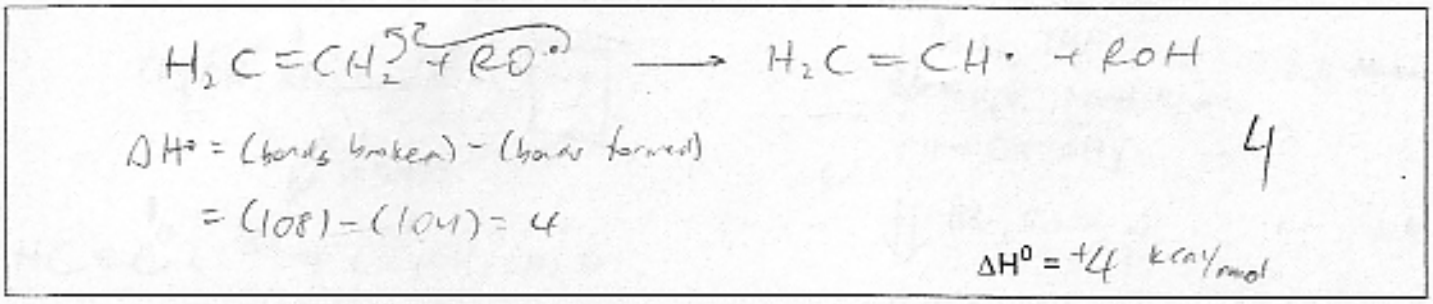
(a) $H_2C{=}CH_2 + RO{-}Cl \xrightarrow{h\nu} H_2C{=}CHCl + RO{-}H$

(b) $H_2C{=}CH_2 + RO{-}Cl \xrightarrow{h\nu} RO{-}CH_2{-}CH_2{-}Cl$

each involving the initiation step: $RO{-}Cl \xrightarrow{h\nu} RO\bullet + Cl\bullet$ [$\Delta H^0 = +53$ Kcal mole^{-1}]

Note that for each reaction, the initiation step is followed by reaction of RO• with ethene

(i) write the two propagation steps for the reaction (a) and calculate the ΔH^0 for each step



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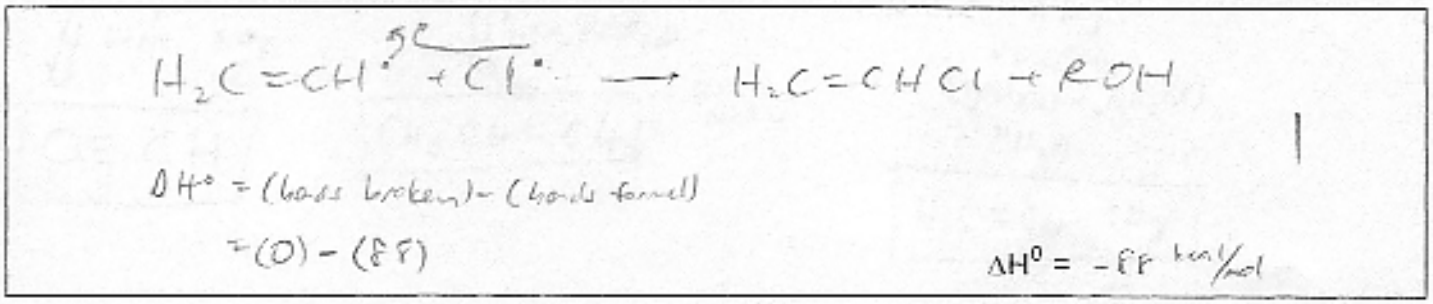

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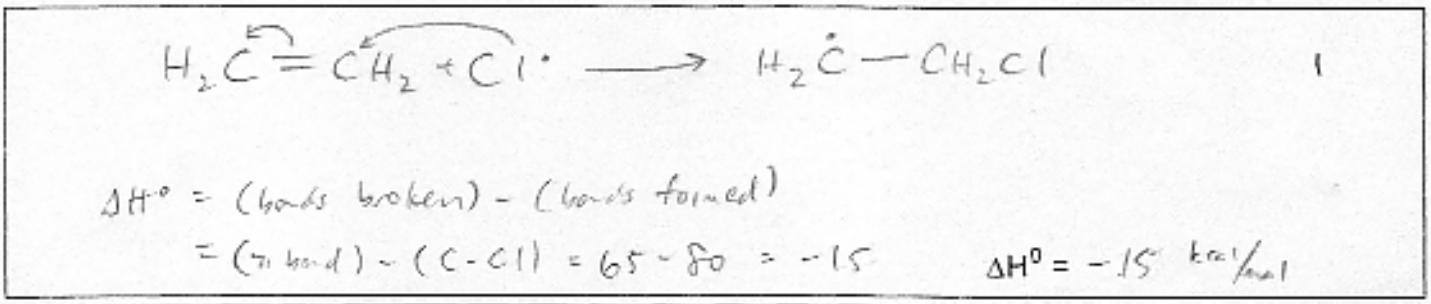
(ii) write the two propagation steps for the reaction (b) and calculate the ΔH^0 for each step



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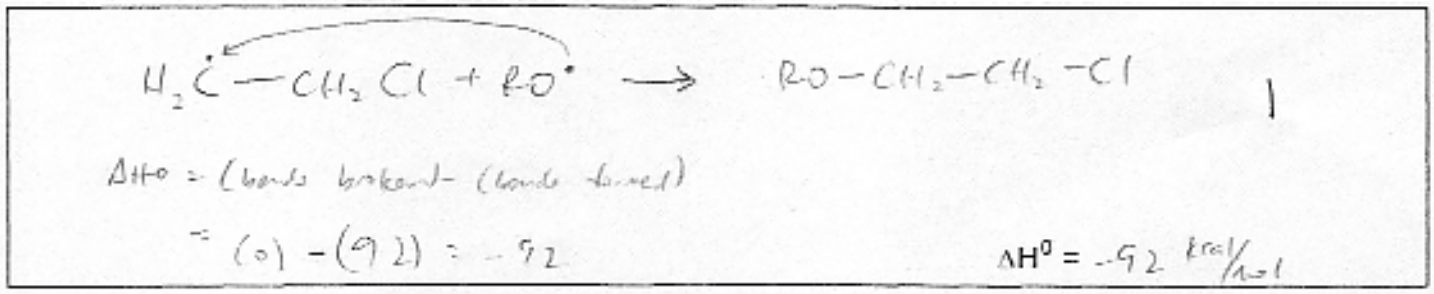

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(iii) Explain why only one of the two reactions (**specify which one**) takes place at room temperature

Reaction (b) can take place at room temperature because its net ΔH° is lower. This is governed by the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. As ΔH° decreases, the T needed to make the reaction spontaneous decreases as well.

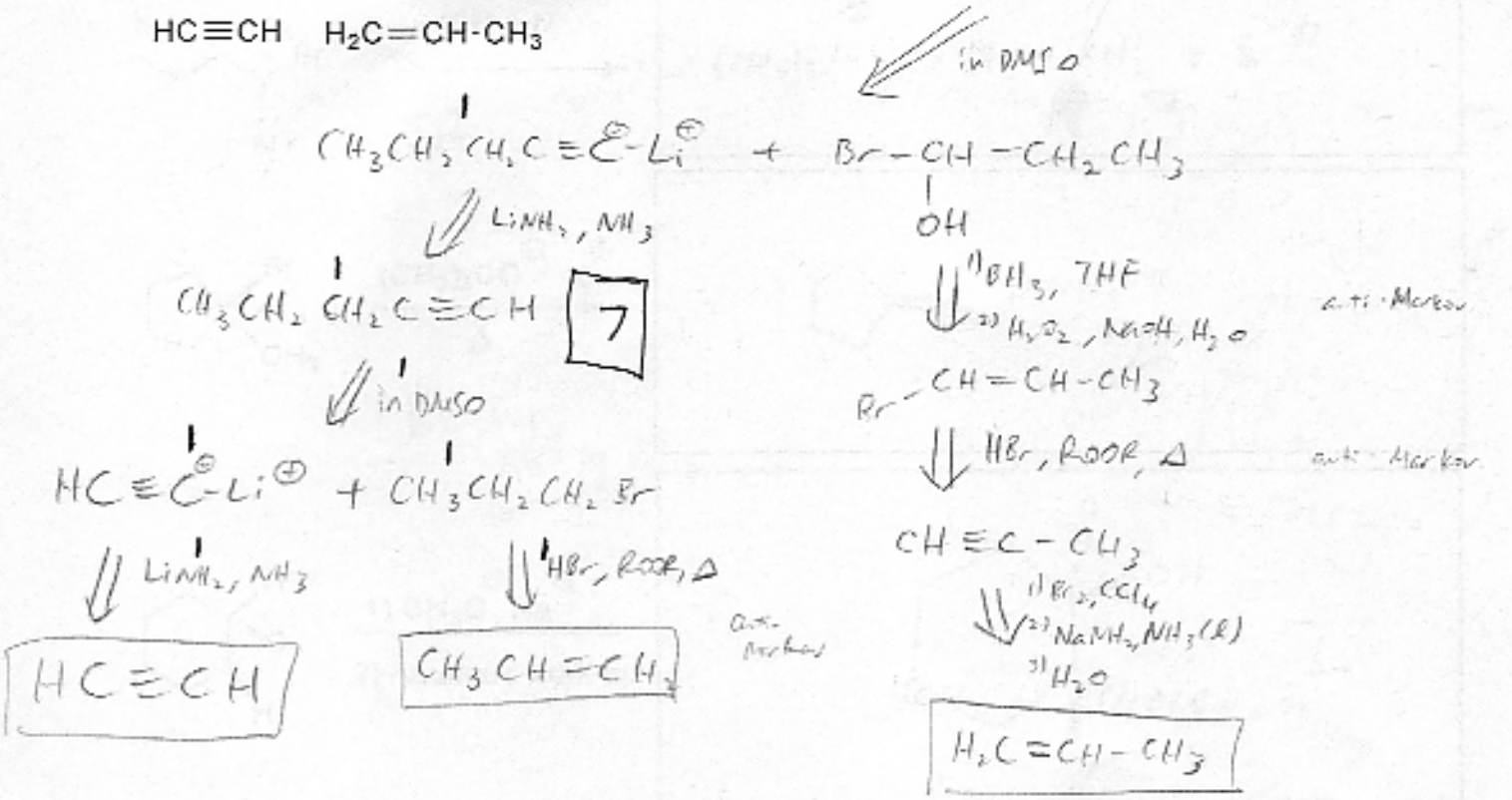
7

0

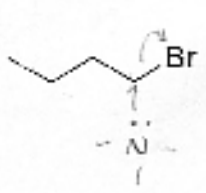
10. (15 Points) Propose a step-by-step synthesis of $CH_3CH_2CH_2C{\equiv}C-\underset{\underset{OH}{|}}{CH}-CH_2CH_3$

from ethyne and propene as the sole sources of C atoms

$HC{\equiv}CH$ $H_2C{=}CH\text{-}CH_3$



11. (18 Points). Complete the following reactions showing the major product(s) or reagents. Show clear stereochemistry where relevant.

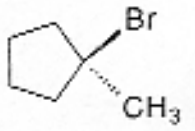


$(CH_3)_3N$

S_N2 ... ?

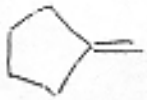
$(CH_3)_3\overset{\oplus}{N}CH_2CH_2CH_2CH_3 + Br^{\ominus}$

3



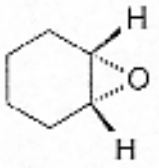
$(CH_3)_3CO^{\ominus}\ K^{\oplus}$

Δ



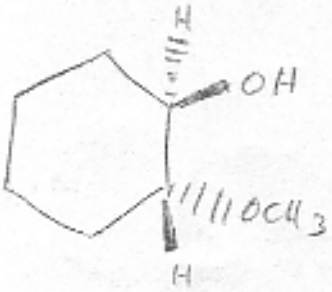
2

E2 but BBS- Hofmann Rule



1) $CH_3O^{\ominus}\ Na^{\oplus}$

2) Aqueous work-up



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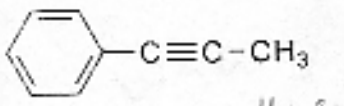
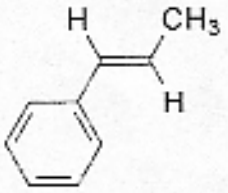


have alkene

1) $Na, NH_3(\ell)$

2) H_2O

2

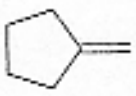


$H_3C-C\equiv C-CH_3$

HBr (1 equiv.)

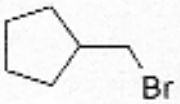
$H_3C-CH=CBr-CH_3$

1



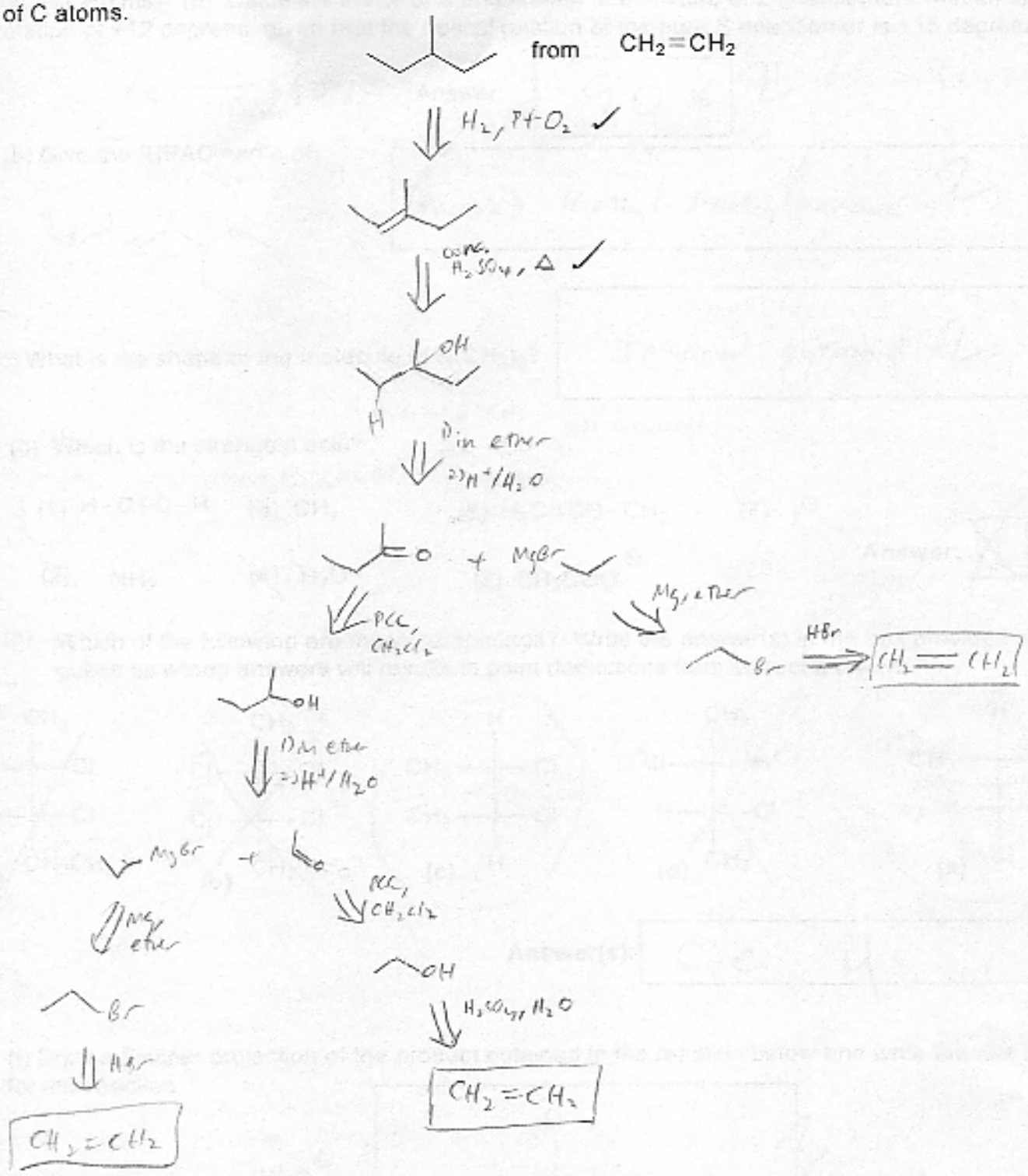
HBr, ROOR, Δ

3



/13

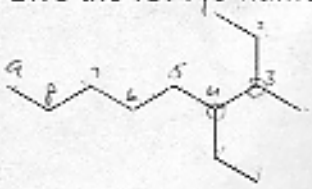
12. (14 Points) Propose a synthesis of 3-methylpentane from ethene used as the sole source of C atoms.



13. (17 Points) (a) Calculate the % of S enantiomer in a mixture of 2 enantiomers with an optical rotation of +12 degrees, given that the optical rotation of the pure S enantiomer is +15 degrees.

$ee = \frac{+12}{+15} = 80\%$ Answer: 90 % 2 80% + ½(20%)

(b) Give the IUPAC name of:



(racemic) 4-ethyl-3-methylnonane 2

(c) What is the shape of the molecule of $N(CH_3)_3$? trigonal pyramid 2

$H_3C-\ddot{N}-CH_3$ (not tetrahedral)
CH_3

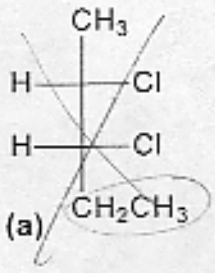
(d) Which is the strongest acid?

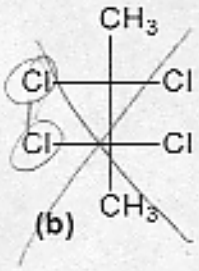
(1) $H-C\equiv C-H$ (3) CH_4 (5) $H_2C=CH-CH_3$ (7) $I^{\ominus}$

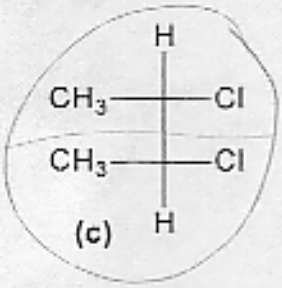
(2) NH_3 (4) H_2O (6) $CH_3COO^{\ominus}$

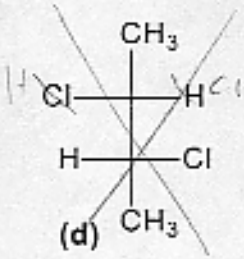
Answer:

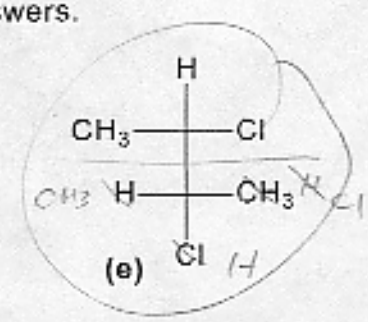
(e) Which of the following are meso compounds? Write the answer(s) in the box provided but do not guess as wrong answers will results in point deductions from correct answers.







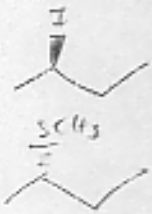


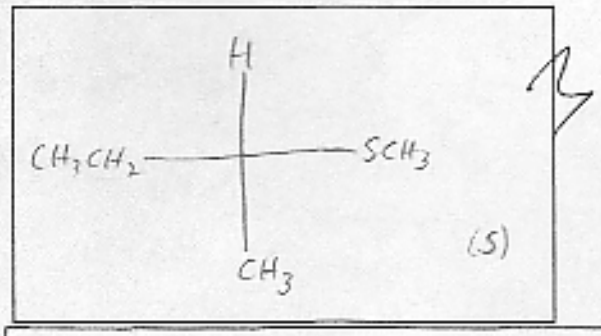


Answer(s): C, e 4

(f) Draw a Fischer projection of the product obtained in the reaction below and write the rate law for this reaction.

(R)-2-iodobutane $\xrightarrow[DMF]{CH_3S^{\ominus}}$





2

Answer: Rate = $[CH_3S^{\ominus}][(R)\text{-2-iodobutane}]$ 1

14