Seat No. _____ LAST NAME WST

Section _____ FIRST NAME _____

PLEASE REMOVE LAST PAGE OF EXAM BEFORE PRINTING YOUR NAME ON THE BACK OF PAGE 8.
THERE ARE 9 PAGES TO THIS EXAM. CHECK TO MAKE SURE YOU HAVE A COMPLETE EXAM.

CHEMISTRY 331

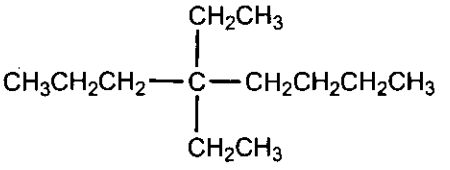
EXAM V

Spring 2009
April 24, 2009

I.	(16 points)	_____
II.	(12 points)	_____
III.	(9 points)	_____
IV.	A, B & C (21 points)	_____
	D, E & F (21 points)	_____
V.	(21 points)	_____
TOTAL	(100 points)	_____

THE FINAL EXAM IS SCHEDULED FOR TUESDAY, MAY 5 FROM 7:30-9:30 A.M.

I. (16 pts.) A. (8 pts.) The mass spectrum of hydrocarbon **A** (molecular formula is $C_{12}H_{26}$) shows a parent peak and several strong fragmentation peaks at lower *m/z* values. (**See the last page for a Periodic Table of the Elements.**)



A

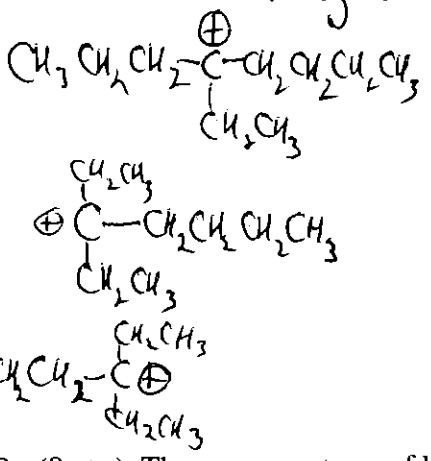
math error −1 pt

1. (3 pts.) What is the *m/z* value for the parent peak? 170

$C_{12}H_{26}$ C $12 \times 12 = 144$, H $26 \times 1 = 26$, $144 + 26 = 170$

2. (5 pts.) Give the expected structure and the *m/z* value for one of the major positively charged fragments. Any one of the following

3 pts only 1 pt if not +



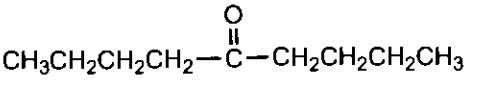
$170 - C_2H_5 = 170 - 29 = 141^+$

$170 - C_3H_7 = 170 - 43 = 127^+$

$170 - C_4H_9 = 170 - 57 = 113^+$

2 pts

B. (8 pts.) The mass spectrum of ketone **B** (molecular formula is $C_9H_{18}O$) shows a parent peak and a very strong fragmentation peak at lower *m/z* values.

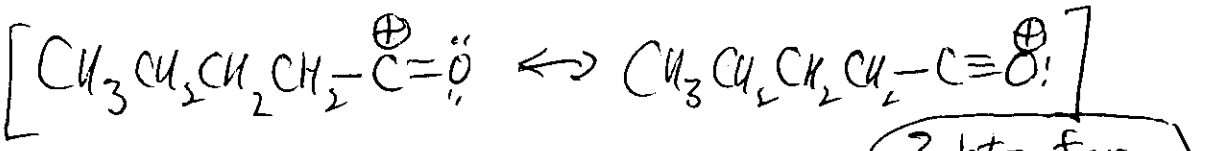


B

3. (3 pts.) What is the *m/z* value for the parent peak? 142

$C_9H_{18}O$ C $= 12 \times 9 = 108$, H $= 18 \times 18 = 18$, O $= 16 \times 1 = 16$, $108 + 18 + 16 = 142$

4. (5 pts.) Give the expected structure and the *m/z* value for the major positively charged fragment.

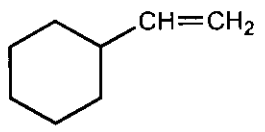


C_5H_9O C $5 \times 12 = 60$
H $9 \times 1 = 9$
O $1 \times 16 = 16$
85 — 2 pts

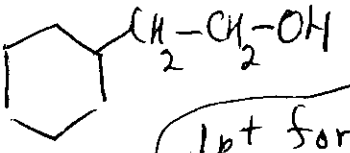
3 pts for either structure

II. (12 pts) Complete the following equations, giving all organic product(s). **No stereochemistry required.**

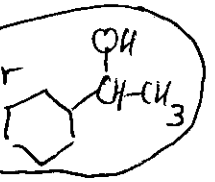
A.



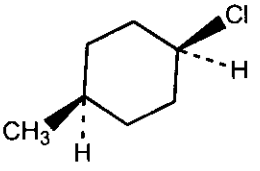
1) BH_3/THF
2) H_2O_2, ^-OH



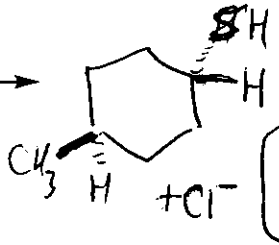
1 pt for



B.

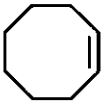


^-SH

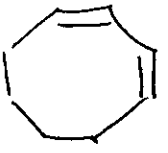


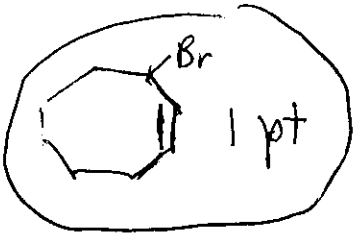
(stereochemistry need not be shown)

C.



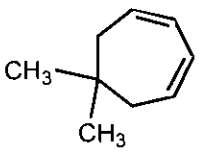
1) NBS/hv
2) alcoholic KOH
or
NaOEt/EtOH



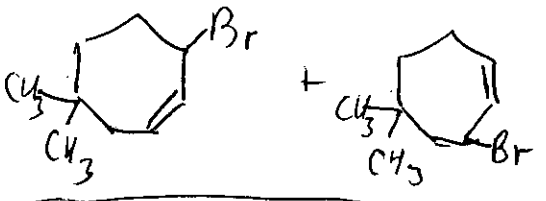


1 pt

D.

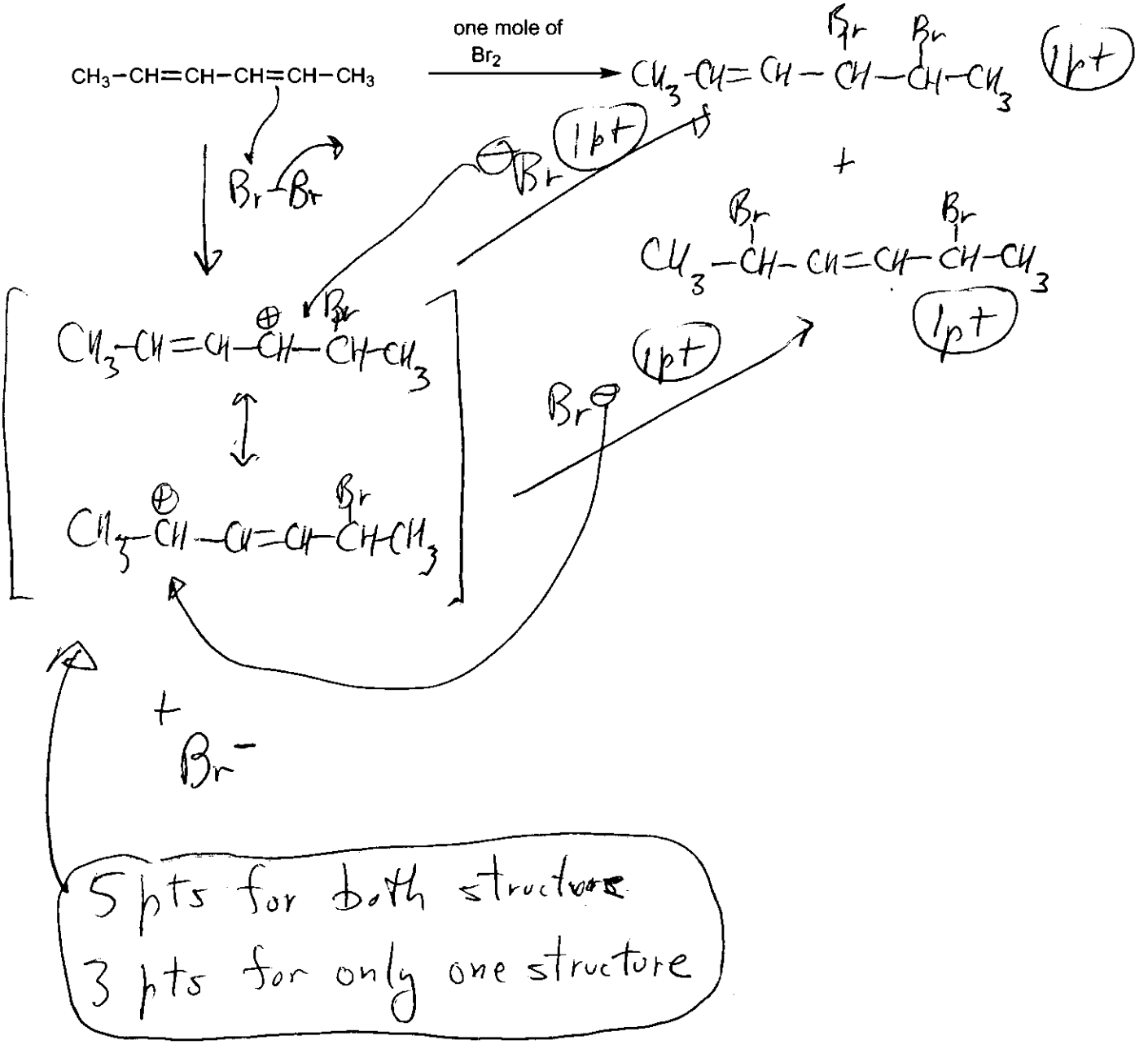


HBr



2 products = 3 pts
1 product = 1 pt

III. (9 pts) Give the product(s) (neglect stereochemistry) and draw a stepwise mechanism for the following reaction (include all important resonance structures).

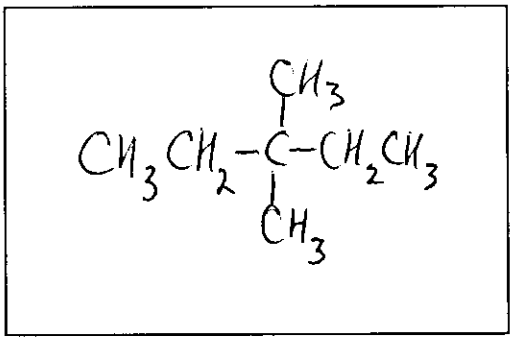


IV. (42 pts) For each of the following compounds, propose a structure in the box provided that fits the data presented.

A. (7 pts) C_7H_{16}

^{1}H NMR:
- δ 1.2 (4H, quartet)
- δ 0.8 (6H, singlet)
- δ 0.78 (6H, triplet)

Broadband-decoupled ^{13}C NMR:
- δ 33.72
- δ 32.75
- δ 26.20
- δ 8.36

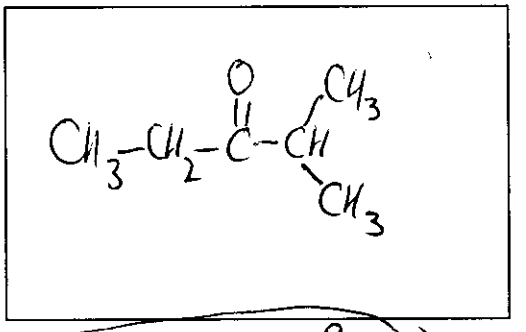


B. (7 pts) $C_6H_{12}O$

^{1}H NMR:
- δ 2.6 (1H, septet)
- δ 2.5 (2H, quartet)
- δ 1.1 (6H, doublet)
- δ 1.05 (3H, triplet)

Broadband-decoupled ^{13}C NMR:
- δ 215.19
- δ 40.58
- δ 53.40
- δ 18.38
- δ 7.89

IR: 1710 cm^{-1}



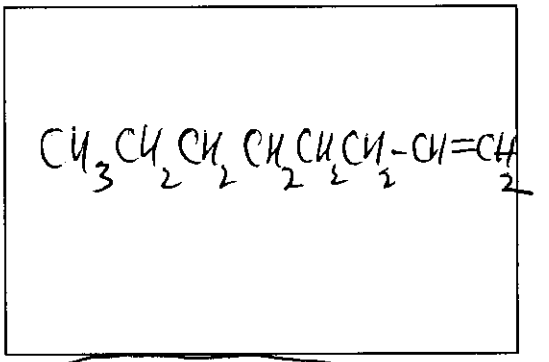
2 pts for -C-

C. (7 pts) C_8H_{16}

^{1}H NMR:
- δ 5.8 (1H, multiplet)
- δ 4.9 (2H, multiplet)
- δ 2.0 (2H, multiplet)
- δ 1.3 (8H, multiplet)
- δ 0.9 (3H, triplet)

Broadband-decoupled ^{13}C NMR:

δ 139.19	δ 29.01
δ 114.05	δ 28.88
δ 33.87	δ 22.67
δ 31.81	δ 14.06

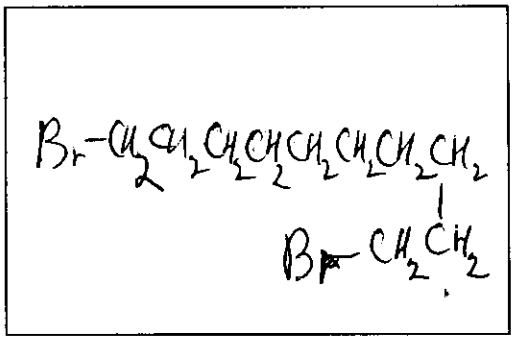


2 pts for C=C

D. (7 pts) $C_{10}H_{20}Br_2$

^{1}H NMR:
- δ 3.4 (4H, triplet)
- δ 1.8 (4H, multiplet)
- δ 1.4 (12H, multiplet)

Broadband-decoupled ^{13}C NMR:
- δ 33.91
- δ 32.79
- δ 29.28
- δ 28.68
- δ 28.12

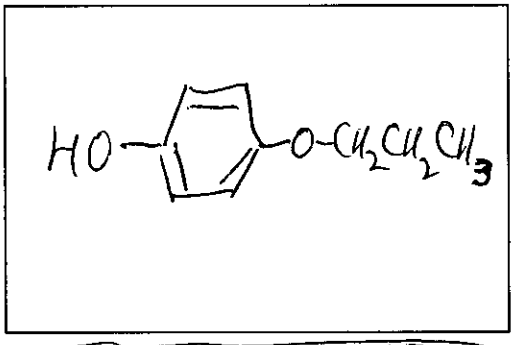


E. (7 pts) $C_9H_{12}O_2$

^{1}H NMR:
- δ 8.9 (1H, broad singlet)
- δ 6.7 (4H, multiplet)
- δ 3.8 (2H, triplet)
- δ 1.7 (2H, multiplet)
- δ 0.9 (3H, triplet)

Broadband-decoupled ^{13}C NMR:
- δ 151.45
- δ 151.02
- δ 115.62
- δ 115.29
- δ 69.41
- δ 22.17
- δ 10.36

1R: 3500 cm^{-1}
1100 cm^{-1}



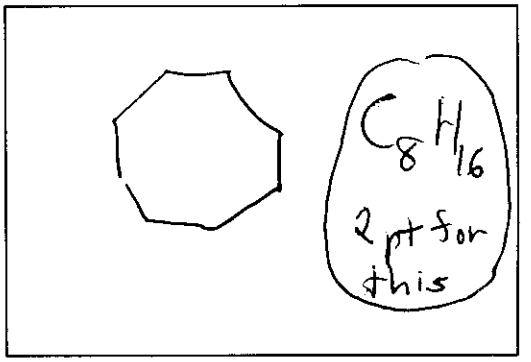
2 pts for benzene ring
2 pts for -OH

F. (7 pts) The following compound, a hydrocarbon, is characterized by a ^{1}H NMR spectrum that shows only a single peak (a singlet) and a ^{13}C NMR spectrum that shows only a single peak. The chemical shifts of the NMR signals are given. The mass spectrum of the hydrocarbon shows a parent peak at m/z = 112. Write the correct structure for the compound in the box provided.

$C_8 = 8 \times 12 = 96$
$112 - 96 = 16$
$\therefore C_8H_{16}$
C_7 would be C_7H_{28} (impossible)
C_9 would be C_9H_4 (would not fit data)

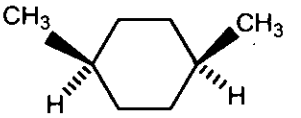
^{1}H NMR:
- δ 1.6 (singlet)

Broadband-decoupled ^{13}C NMR:
- δ 27.50



V. (21 pts) Circle the correct answer (think carefully).

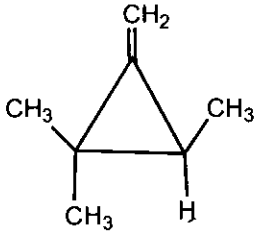
A. How many signals are present in the broadband-decoupled ^{13}C NMR spectrum of



?

1.) 2 (2.) 3 3.) 4 4.) 6

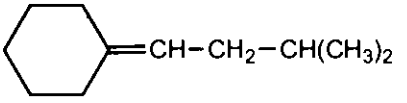
B. How many signals are present in the ^{1}H NMR spectrum of



?

1.) 3 2.) 4 3.) 5 (4.) 6

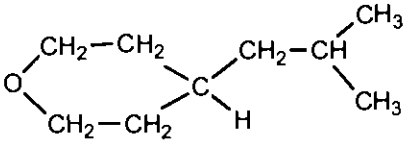
C. How many signals are present in the broadband-decoupled ^{13}C NMR spectrum of



?

1.) 8 2.) 9 (3.) 10 4.) 11

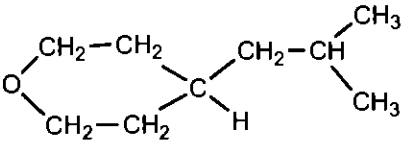
D. The DEPT 90 ^{13}C NMR spectrum of



would show how many signals?

1.) 1 (2.) 2 3.) 4 4.) 5

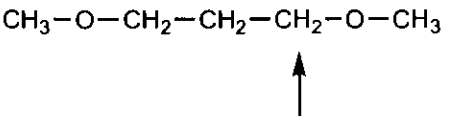
E. The DEPT 135 ^{13}C NMR spectrum of



would show how many positive and how many negative signals?

1.) 2 positive, 2 negative
2.) 2 positive, 3 negative
3.) 3 positive, 3 negative
4.) 4 positive, 5 negative

F. What multiplicity (splitting pattern) is observed in the ^{1}H NMR spectrum for the indicated hydrogen?



1.) Singlet
2.) Doublet
3.) Triplet
4.) Quartet

G. For chlorine and bromine the natural abundance of isotopes is 75.8% ^{35}Cl and 24.2% ^{37}Cl and 50.7 % ^{79}Br and 49.3% ^{81}Br. The molecular ion region of the mass spectrum of which compound would be expected to show three peaks at m/z = 112, m/z = 114, and m/z = 116?

1.) C_3H_5Br
2.) $C_3H_6Br_2$
3.) $C_3H_6Cl_2$
4.) $C_3H_5Cl_3$

C $3 \times 12 = 36$
H $6 \times 1 = 6$
Cl $2 \times 35 = 70$
112