

Seat No. \_\_\_\_\_

LAST NAME \_\_\_\_\_

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 2007  
April 20, 2007

I. (16 points) \_\_\_\_\_

II. (13 points) \_\_\_\_\_

III. ( 8 points) \_\_\_\_\_

IV. A, B & C (21 points) \_\_\_\_\_

D, E & F (21 points) \_\_\_\_\_

V. (21 points) \_\_\_\_\_

TOTAL (100 points) \_\_\_\_\_

The Final Exam is scheduled for Monday, April 30, from 7:30-9:30 A.M.

First 4 exams scores (**to be filled in by graders**). Best 4 (including score above) will be counted in your final score.

\_\_\_\_\_ I

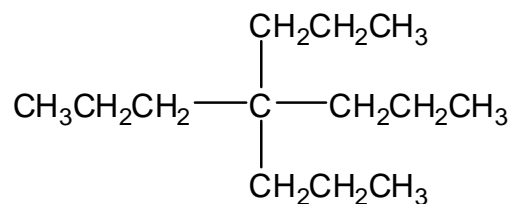
\_\_\_\_\_ II

\_\_\_\_\_ III

\_\_\_\_\_ IV

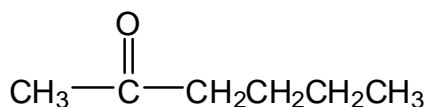
\_\_\_\_\_ # of quizzes  
taken (Maximum  
score = 10)

- I. (16 pts.) A. (8 pts.) The mass spectrum of hydrocarbon **A** (molecular formula is  $C_{13}H_{28}$ ) shows a parent peak and a strong fragmentation peak at lower  $m/z$  values. (See the last page for a Periodic Table of the Elements.)

**A**

- (3 pts.) What is the  $m/z$  value for the parent peak? \_\_\_\_\_
- (5 pts.) Give the expected structure and the  $m/z$  value for the major positively charged fragment.

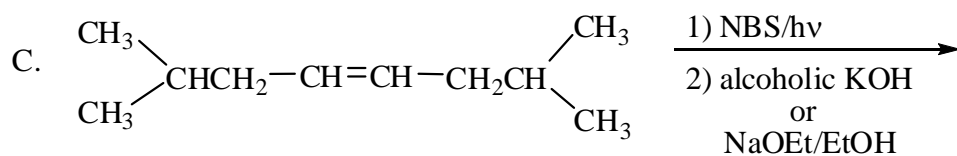
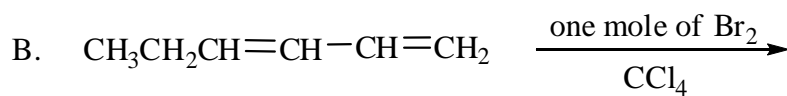
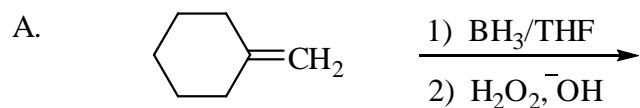
- B. (8 pts.) The mass spectrum of ketone **B** (molecular formula is  $C_6H_{12}O$ ) shows a parent peak and two very strong fragmentation peaks at lower  $m/z$  values.

**B**

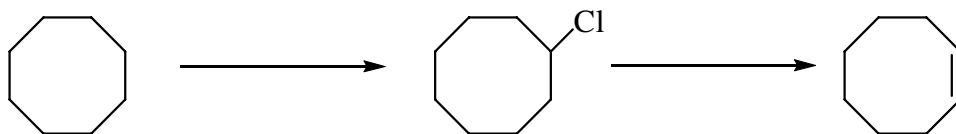
- (3 pts.) What is the  $m/z$  value for the parent peak? \_\_\_\_\_

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

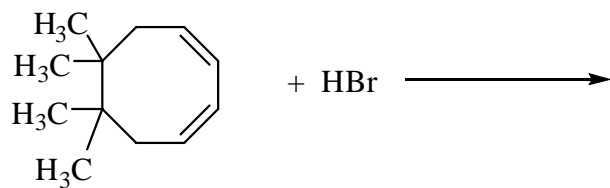
II. (13 pts) Complete the following equations, giving all organic product(s). **No stereochemistry required.**



D. (4 pts) Give the reactants for the following reactions.



- III. (8 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)



$^1\text{H}$  NMR:

$\delta$  3.9 (2H, singlet)

$\delta$  2.7 (2H, quartet)

$\delta$  1.1 (3H, triplet)

Broadband-decoupled  $^{13}\text{C}$  NMR:

$\delta$  202.60

$\delta$  34.09

$\delta$  33.16

$\delta$  7.93

IR:  $1710\text{cm}^{-1}$

B. (7 pts)



$^1\text{H}$  NMR:

$\delta$  2.3 (2H, singlet)

$\delta$  2.1 (3H, singlet)

$\delta$  1.0 (9H, singlet)

Broadband-decoupled  $^{13}\text{C}$  NMR:

$\delta$  208.38

$\delta$  56.00

$\delta$  32.30

$\delta$  30.91

$\delta$  29.77

IR:  $1710\text{cm}^{-1}$

C. (7 pts)



$^1\text{H}$  NMR:

$\delta$  2.4 (2H, triplet)

$\delta$  2.1 (3H, singlet)

$\delta$  1.6 (2H, multiplet)

$\delta$  1.3 (6H, multiplet)

$\delta$  0.9 (3H, triplet)

Broadband-decoupled  $^{13}\text{C}$  NMR:

$\delta$  209.58       $\delta$  29.77

$\delta$  44.67       $\delta$  24.80

$\delta$  32.48       $\delta$  23.35

$\delta$  30.54       $\delta$  14.80

IR:  $1710\text{cm}^{-1}$

D. (7 pts)  $C_7H_4Cl_4O$

$^1H$  NMR:  
 $\delta$  7.4 (1H, singlet)  
 $\delta$  3.9 (3H, singlet)  
 Broadband-decoupled  $^{13}C$  NMR:  
 $\delta$  154.54  
 $\delta$  131.94  
 $\delta$  127.38  
 $\delta$  126.33  
 $\delta$  60.75  
 IR:  $1100\text{ cm}^{-1}$



E. (7 pts)  $C_8H_{14}$

$^1H$  NMR:  
 $\delta$  5.8 (2H, multiplet)  
 $\delta$  5.0 (4H, multiplet)  
 $\delta$  2.1 (4H, multiplet)  
 $\delta$  1.4 (4H, multiplet)  
 Broadband-decoupled  $^{13}C$  NMR:  
 $\delta$  138.89  
 $\delta$  114.25  
 $\delta$  33.65  
 $\delta$  28.43



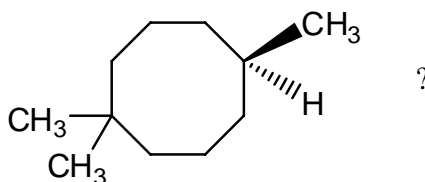
F. (7 pts) The following compound is characterized by a  $^1H$  NMR spectrum that consists of only a single peak (a singlet) having the chemical shift indicated. Some additional data are given. Write the correct structure for the compound (either of two structures will get full credit) in the appropriate box.

$C_8H_{12}O_2$   
 $^1H$  NMR:  
 $\delta$  1.3 (12H, singlet)  
 Broadband-decoupled  $^{13}C$  NMR:  
 $\delta$  215.42  
 $\delta$  70.37  
 $\delta$  18.82  
 IR:  $1750\text{ cm}^{-1}$



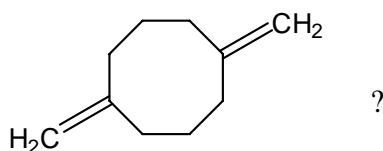
V. (21 pts) Circle the correct answer (think carefully).

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



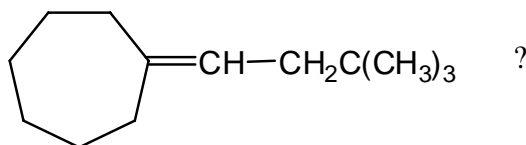
- 1.) 7                      2.) 8                      3.) 10                      4.) 11

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



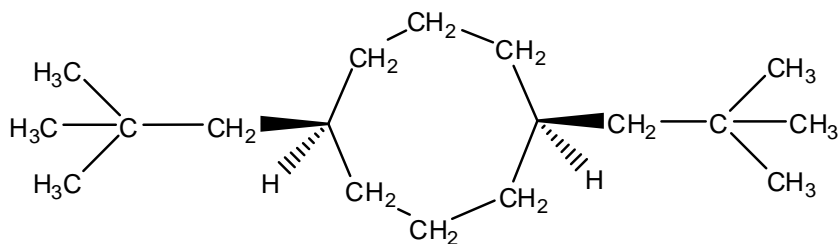
- 1.) 3                      2.) 4                      3.) 5                      4.) 6

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



- 1.) 8                      2.) 9                      3.) 11                      4.) 12

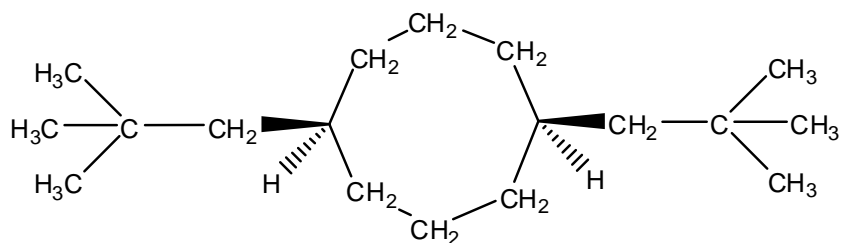
D. The DEPT 90  $^{13}\text{C}$  NMR spectrum of



would show how many signals?

- 1.) 1                      2.) 2                      3.) 4                      4.) 5

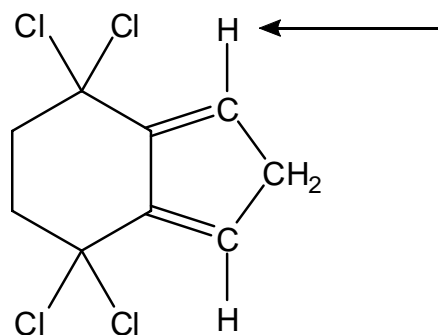
E. The DEPT 135  $^{13}\text{C}$  NMR spectrum of



would show how many positive and how many negative signals?

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

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



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

G. The natural abundance of bromine isotopes is 50.7%  $^{79}\text{Br}$  and 49.3%  $^{81}\text{Br}$ . The molecular ion region of the mass spectrum of compound **G** would be expected to show



**G**

- One peak at  $m/z = 202$
- Two peaks at  $m/z = 200$  and  $m/z = 202$
- Two peaks at  $m/z = 200$  and  $m/z = 204$
- Three peaks at  $m/z = 200$ ,  $m/z = 202$ , and  $m/z = 204$

**CHARACTERISTIC PROTON CHEMICAL SHIFTS**

Type of proton	Chemical shift $\delta$ , ppm
Cyclopropane	0.2
Primary	0.9
Secondary	1.3
Tertiary	1.5
Vinylic	4.6-5.9
Acetylenic	2-3
Aromatic	6-8.5
Benzylic	2.2-3
Allylic	1.7
Fluorides	4-4.5
Chlorides	3-4
Bromides	2.5-4
Iodides	2-4
Alcohols	3.4-4
Ethers	3.3-4
Esters	3.7-4.1
Esters	2-2.2
Acids	2-2.6
Carbonyl compounds	2-2.7

Aldehydic	9-10
Hydroxylic	1-5.5
Phenolic	4-12
Enolic	15-17
Carboxylic	10.5-12
Amino	1-5
DEPT 90	CH
DEPT 135	CH, CH <sub>3</sub> positive signal CH <sub>2</sub> negative signal

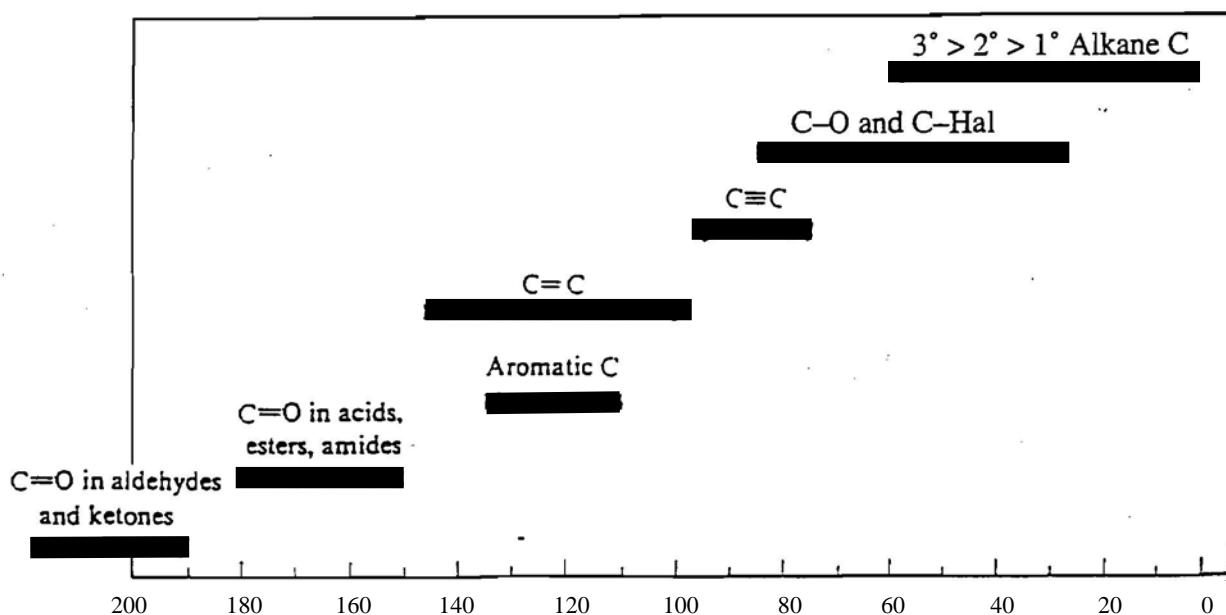
**CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES**

Bond	Compound type	Frequency range, cm <sup>-1</sup>
C—H	Alkanes	2850-2960
C—H	Alkenes	1350-1470
C—H	Aromatic rings	3020-3080 ( <i>m</i> ) 675-1000
C—H	Alkynes	3000-3100 ( <i>m</i> ) 675-870
C=C	Alkenes	3300
C≡C	Alkynes	1640-1680 ( <i>v</i> )
C—C	Aromatic rings	2100-2260 ( <i>v</i> )
C—O	Alcohols, ethers, carboxylic acids, esters	1500, 1600 ( <i>v</i> )
C=O	Aldehydes, ketones, carboxylic acids, esters	1080-1300
O—H	Monomeric alcohols, phenols	1690-1760
	Hydrogen-bonded alcohols, phenols	3610-3640 ( <i>v</i> )
	Carboxylic acids	3200-3600 ( <i>broad</i> )
N—H	Amines	2500-3000 ( <i>broad</i> )
C—N	Amines	3300-3500 ( <i>m</i> )
C≡N	Nitriles	1180-1360
—NO <sub>2</sub>	Nitro compounds	2210-2260 ( <i>v</i> ) 1515-1560 1345-1385

\*All bands strong unless marked: *m*, moderate; *v*, variable.

**Abbreviated Periodic Table**

1A 1 H 1.01	2A 2 He 4.00	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18										
3 Li 6.94	4 Be 9.01	5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2										
11 Na 23.0	12 Mg 24.3	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8 9 10	1B 11	2B 12	13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9		
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8



Chemical shifts for <sup>13</sup>C in various kinds of compounds.