

Seat No. _____

Name _____
(Please print your name and **circle** your last name)

CHEMISTRY 331A

EXAM IV

Monday, December 8, 2008

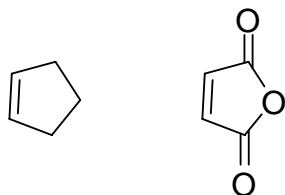
- I. (10 points) _____
- II. (16 points) _____
- III. (12 points) _____
- IV. (5 points) _____
- V. (16 points) _____
- VI. (5 points) _____
- VII. (10 points) _____
- VIII. (8 points) _____
- IX. (10 points) _____
- X. (8 points) _____

TOTAL (100 points) _____

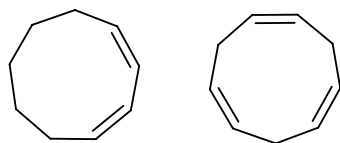
I. (10 pts.) In an electron-impact, magnetic-sector mass spectrometer a high-energy electron strikes an organic molecule and creates a _____
 _____ (two words) which is then focused, accelerated and analyzed according to its _____. The molecular ions of alcohols, amines and ketones tend to fragment by _____. Ionization of molecules which decompose when heated in a vacuum can be accomplished by either _____ or _____. Molecular absorption of IR light occurs when the light's energy matches that of a _____ of the molecule. Only _____ molecules absorb in the UV region. This electronic absorption is from _____ to _____ nm. This energy gap decreases with increased _____.

II. (16 pts.) **Circle** the member of each pair which

A. Will be the better dienophile



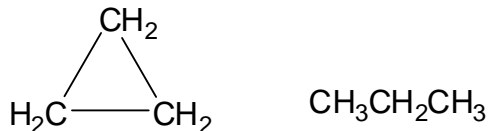
B. Will absorb light of λ 200 – 400 nm.



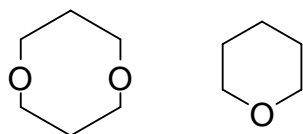
C. is more stable



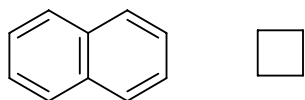
D. will have the largest H–H coupling constant (J_{HH})



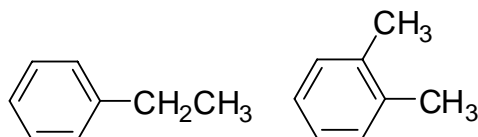
E. Will have one pentet and one triplet in its $^1\text{H-NMR}$ spectrum.



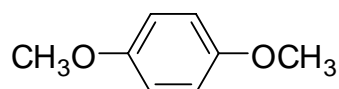
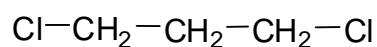
F. Will have 8 equivalent H's



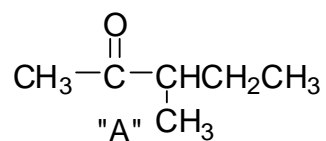
G. Will have 4 ^{13}C absorptions in its ^{13}C -NMR spectrum



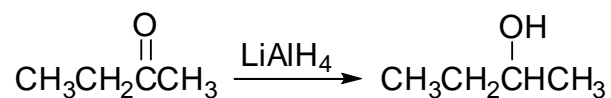
H. Will have 3 ^{13}C -peaks in ^{13}C -NMR, with two well downfield of the other one.



III. (12 pts.) The mass spectrum of 3-methyl-2-pentanone ("A") shows significant ions at M/Z 100, 85, 72 and 43. Show a reasonable structure for each ion.



IV. (5 pts.) In one sentence (or less) tell how you would use IR spectroscopy to determine when the following reaction is complete (i.e. when all of the ketone is converted).



V. (16 pts.) Identify two of the following three compounds from the spectral data provided.
CLEARLY CROSS OUT THE ONE YOU WISH TO OMIT!

A. $C_5H_{11}Cl$

^{13}C -NMR	72 δ	1H NMR	1.0 δ (t, 3H)
	39 δ		1.5 δ (s, 6H)
	33 δ		1.7 δ (q, 2H)
	10 δ		

B. C_7H_8O

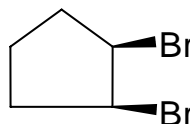
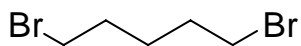
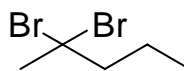
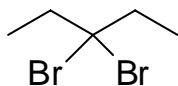
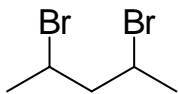
1H -NMR	2.4 δ (s, 1H)	IR: Broad strong peak
	4.6 δ (s, 2H)	in 3200-3500 cm^{-1}
	7.3 δ (m, 5H)	region

C. $C_{11}H_{16}O$

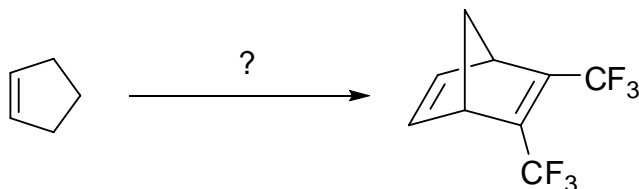
1H -NMR	1.0 δ (d, 6H, J=6 Hz)
	1.7 δ (septet, 1H, J=6 Hz)
	2.9 δ (s, 3 H)
	4.6 δ (s, 2 H)
	7.1 δ (d, 2H, J = 4 Hz)
	7.3 δ (d, 2H, J = 4 Hz)

VI. (5 pts.) Circle the structure that best fits the following ^{13}C -NMR data:

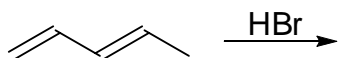
29 δ , 31 δ , 45 δ , 49 δ , 86 δ



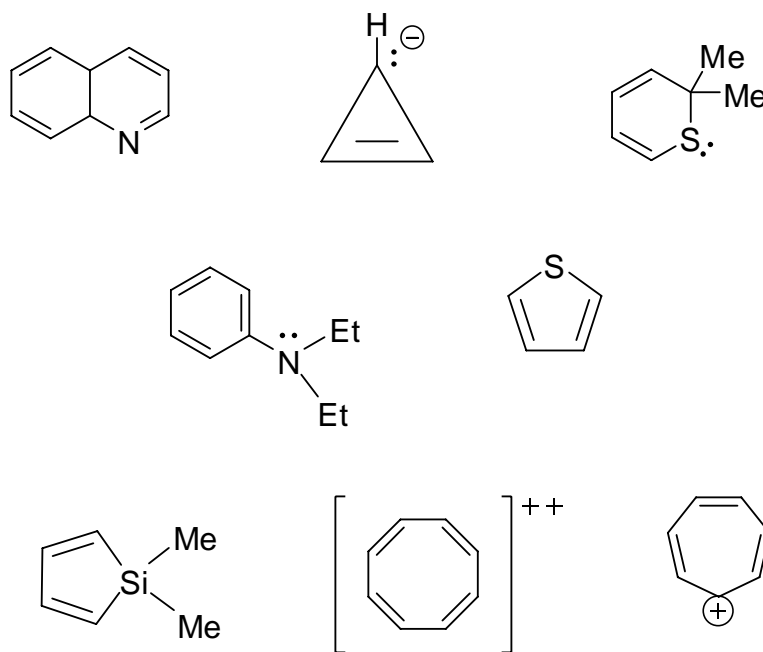
VII. (10 pts.) Starting with cyclopentene, and assuming the availability of all necessary reagents, show how you would perform the following synthetic transformation.



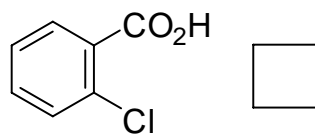
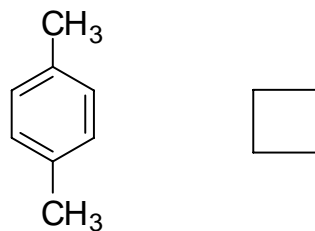
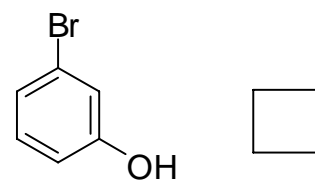
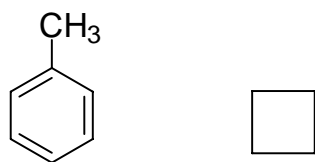
VIII. (8 pts.) Draw all of the monobromo products resulting from the addition of HBr to 1,3-pentadiene.



IX. (10 pts.) Circle each of the following compounds which would be expected to display aromatic characteristics.



X. (8 pts.) Match the following names and structures by placing the corresponding number in the box.



- 1) quinoline
- 2) p-bromophenol
- 3) o-chlorobenzoic acid
- 4) β -viagra
- 5) m-toluene
- 6) p-xylene
- 7) toluene
- 8) m-bromophenol
- 9) melamine

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton	Chemical shift δ , ppm	
Cyclopropane	0.2	
Primary	$\begin{array}{c} \text{H} \\ \\ \text{RC}-\text{H} \end{array}$	0.9
	$\begin{array}{c} \text{H} \\ \\ \text{H} \\ \\ \text{R}_2\text{C}-\text{H} \end{array}$	1.3
Tertiary	$\text{R}_3\text{C}-\text{H}$	1.5
Vinylc	$\text{C}=\text{C}-\text{H}$	4.6-5.9
Acetylenic	$\text{C}\equiv\text{C}-\text{H}$	2-3
Aromatic	$\text{Ar}-\text{H}$	6-8.5
Benzylic	$\text{Ar}-\text{C}-\text{H}$	2.2-3
Allylic	$\text{C}=\text{C}-\text{C}-\text{H}$	1.7
Fluorides	$\text{H}-\text{C}-\text{F}$	4-4.5
Chlorides	$\text{H}-\text{C}-\text{Cl}$	3-4
Bromides	$\text{H}-\text{C}-\text{Br}$	2.5-4
Iodides	$\text{H}-\text{C}-\text{I}$	2-4
Alcohols	$\text{H}-\text{C}-\text{OH}$	3.4-4
Ethers	$\text{H}-\text{C}-\text{OR}$	3.3-4
Esters	$\text{RCOO}-\text{C}-\text{H}$	3.7-4.1
Esters	$\text{H}-\text{C}-\text{COOR}$	2-2.2
Acids	$\text{H}-\text{C}-\text{COOH}$	2-2.6
Carbonyl compounds	$\text{H}-\text{C}-\text{C}=\text{O}$	2-2.7

Aldehydic	$\begin{array}{c} \text{H} \\ \\ \text{RC}=\text{O} \end{array}$	9-10
	$\text{RO}-\text{H}$	1-5.5
Phenolic	$\text{ArO}-\text{H}$	4-12
Enolic	$\text{C}=\text{C}-\text{O}-\text{H}$	15-17
Carboxylic	$\text{RCOO}-\text{H}$	10.5-12

Amino	$\begin{array}{c} \text{H} \\ \\ \text{RN}-\text{H} \end{array}$	1-5
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DEPT 90 CH
 DEPT 135 CH, CH₃ positive signal
 CH₂ negative signal

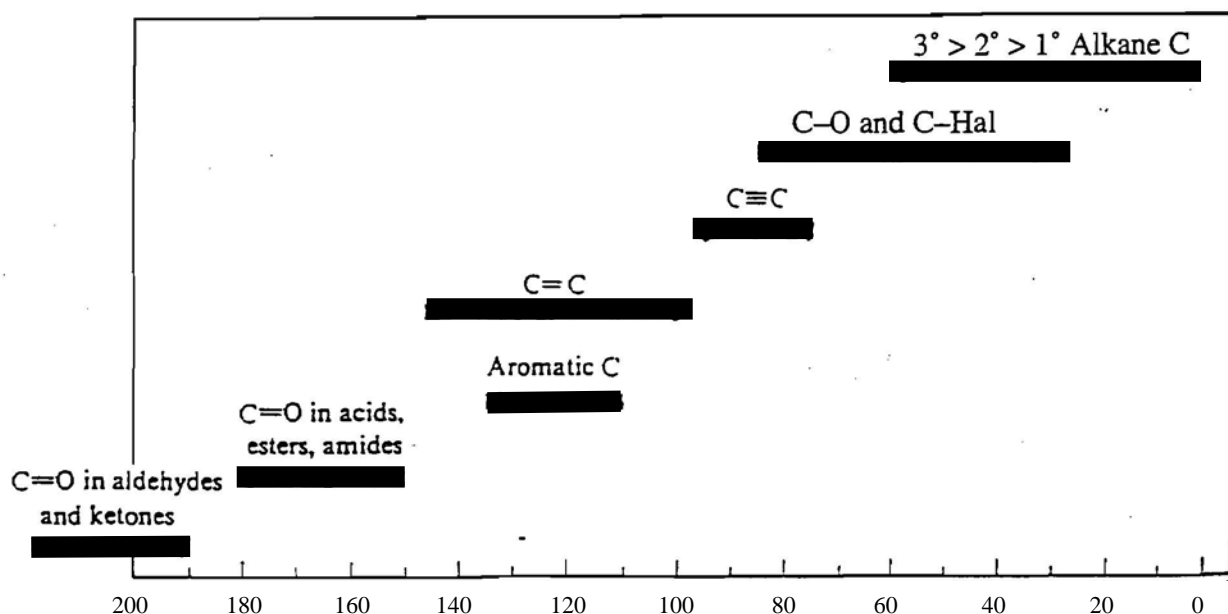
CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES

Bond	Compound type	Frequency range, cm ⁻¹
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 ₂	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											3A 13	4A 14	5A 15	6A 16	7A 17	8A 18 He 4.00
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 ¹³C in various kinds of compounds.