Seat No. ______________ Name KEY ______________
(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)	______________

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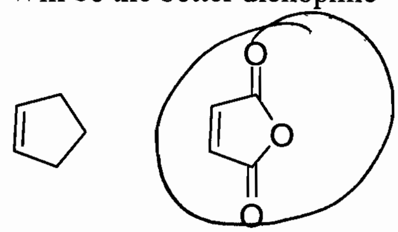
TOTAL (100 points) ______________

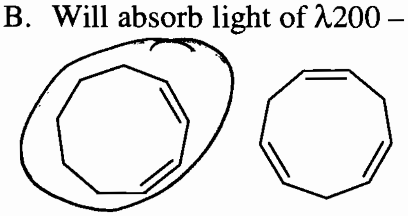
I. (10 pts.) In an electron-impact, magnetic-sector mass spectrometer a high-energy electron strikes an organic molecule and creates a radical cation (two words) which is then focused, accelerated and analyzed according to its mass (to charge). The molecular ions of alcohols, amines and ketones tend to fragment by α-cleavage. Ionization of molecules which decompose when heated in a vacuum can be accomplished by either MALDI or ESI. Molecular absorption of IR light occurs when the light's energy matches that of a vibration of the molecule. Only conjugated molecules absorb in the UV region. This electronic absorption is from ~200 to ~400 nm. This energy gap decreases with increased conjugation.

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

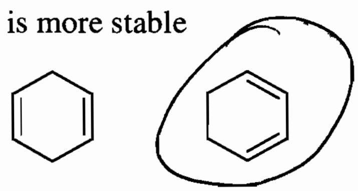
A. Will be the better dienophile



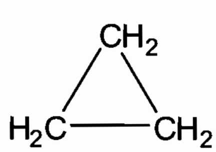
B. Will absorb light of λ200 – 400 nm.



C. is more stable

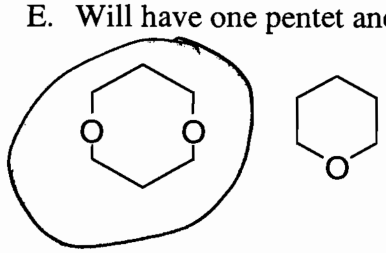


D. will have the largest H–H coupling constant (J_{HH})

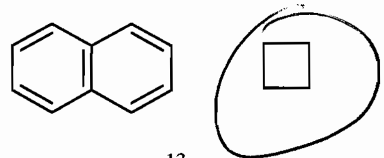


$CH_3CH_2CH_3$

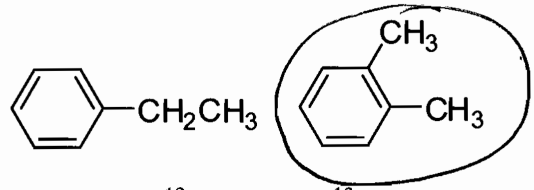
E. Will have one pentet and one triplet in its [1]H-NMR spectrum.



F. Will have 8 equivalent H's

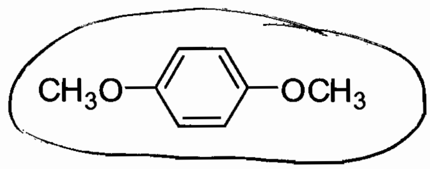


G. Will have 4 ^{13}C absorptions in its ^{13}C-NMR spectrum

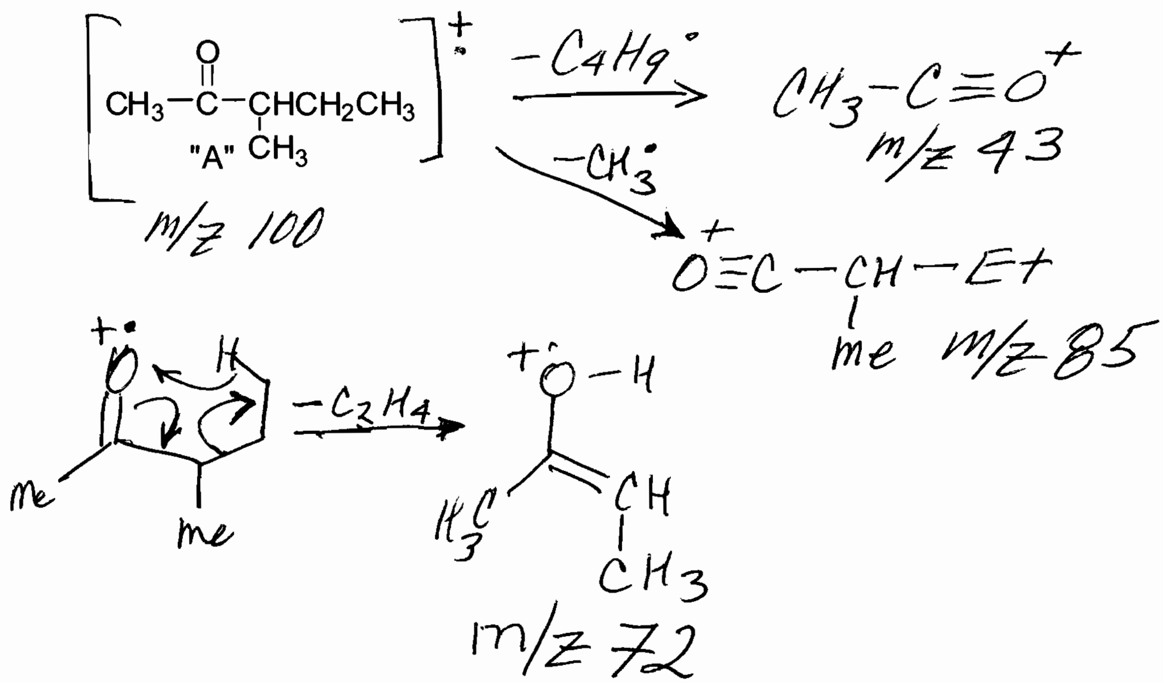


H. Will have 3 ^{13}C-peaks in ^{13}C-NMR, with two well downfield of the other one.

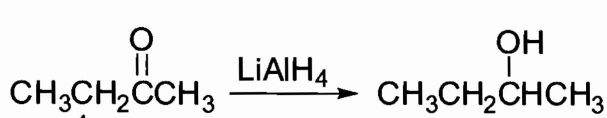
$Cl-CH_2-CH_2-CH_2-Cl$



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).

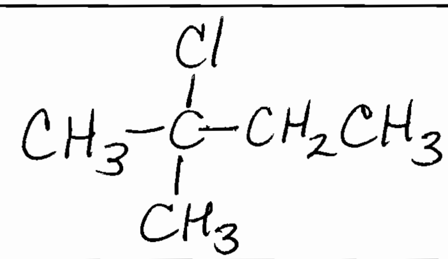


The broad, strong O-H band around 3400 cm⁻¹ stops growing.

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

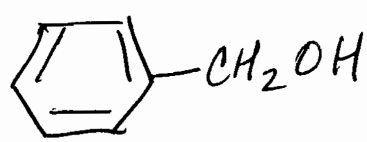
A. $C_5H_{11}Cl$

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



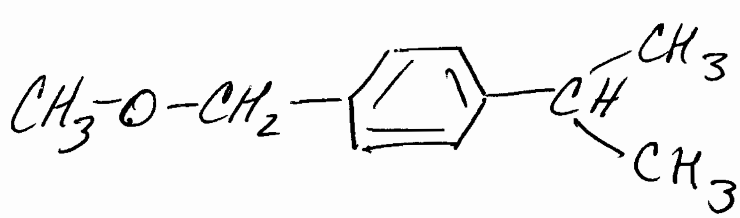
B. C_7H_8O

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



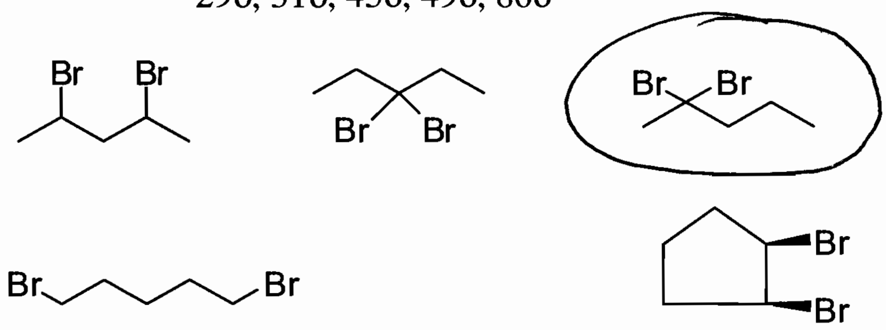
C. $C_{11}H_{16}O$

^{1}H-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)

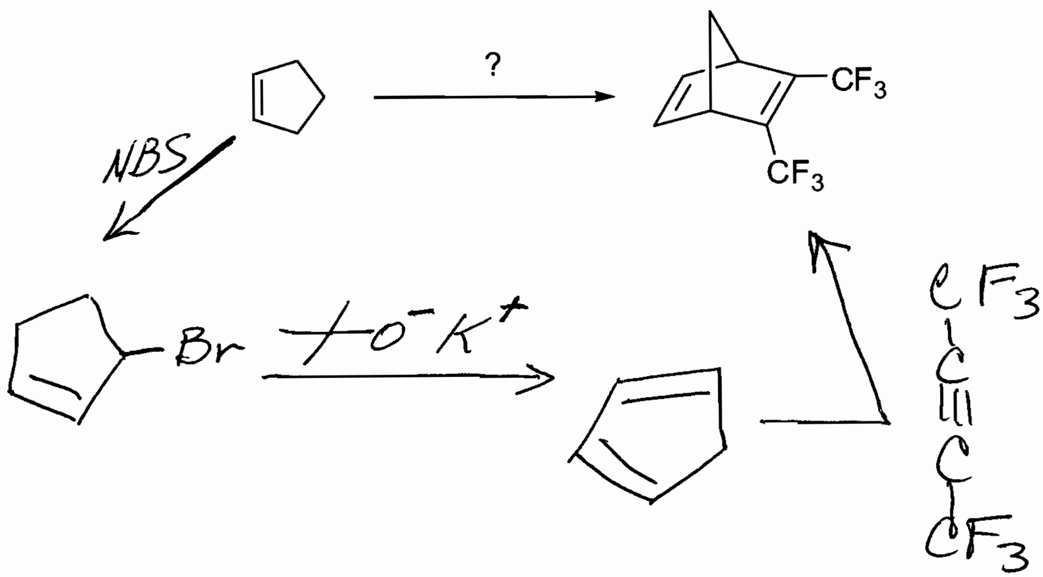


VI. (5 pts.) Circle the structure that best fits the following ^{13}C-NMR data:

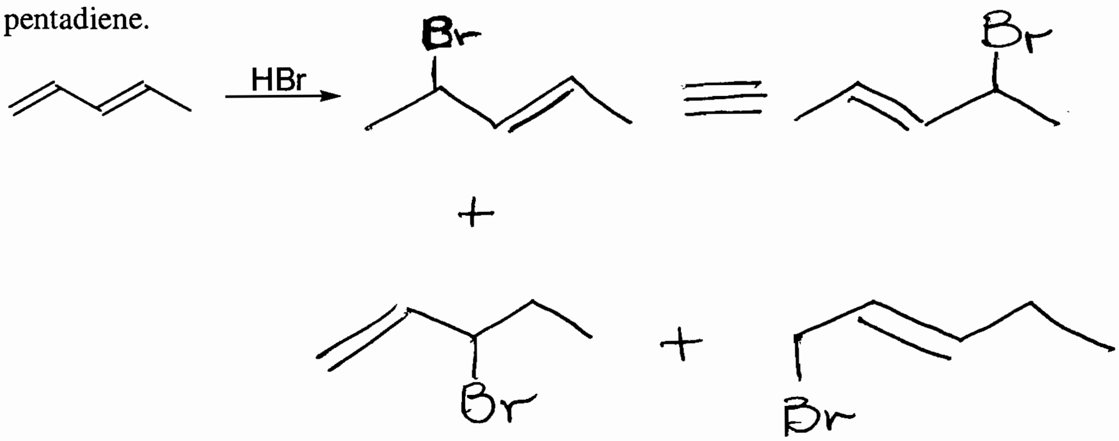
$29\delta, 31\delta, 45\delta, 49\delta, 86\delta$



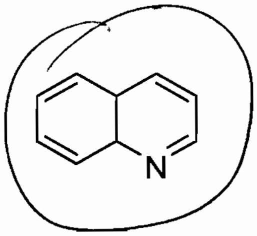
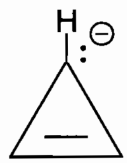
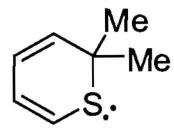
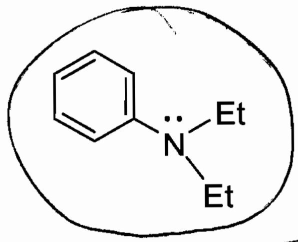
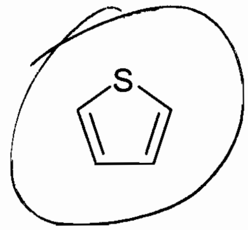
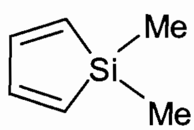
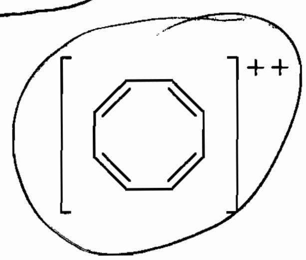
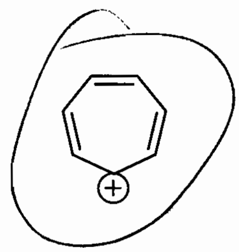
VII. (10 pts.) Starting with cyclopentene, and assuming the availability of all necessary reagents, show how you would perform the following synthetic transformation.



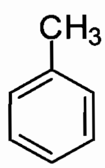
VIII. (8 pts.) Draw all of the monobromo products resulting from the addition of HBr to 1,3-pentadiene.

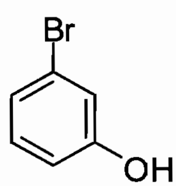


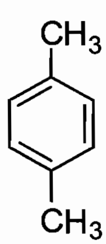
IX. (10 pts.) Circle each of the following compounds which would be expected to display aromatic characteristics.

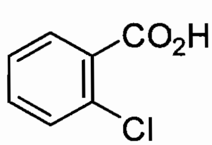









X. (8 pts.) Match the following names and structures by placing the corresponding number in the box.


[7]


[8]


[6]


[3]

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	H | RC—H | H	0.9
Secondary	H | R_2C—H	1.3
Tertiary	R_3C—H	1.5
Vinylic	C=C—H	4.6-5.9
Acetylenic	C≡C—H	2-3
Aromatic	Ar—H	6-8.5
Benzylic	Ar—C—H	2.2-3
Allylic	C=C—C—H	1.7
Fluorides	H—C—F	4-4.5
Chlorides	H—C—Cl	3-4
Bromides	H—C—Br	2.5-4
Iodides	H—C—I	2-4
Alcohols	H—C—OH	3.4-4
Ethers	H—C—OR	3.3-4
Esters	RCOO—C—H	3.7-4.1
Esters	H—C—COOR	2-2.2
Acids	H—C—COOH	2-2.6
Carbonyl compounds	H—C—C=O	2-2.7
Aldehyclic	H | RC=O	9-10
Hydroxylic	RO—H	1-5.5
Phenolic	ArO—H	4-12
Enolic	C=C—O—H	15-17
Carboxylic	RCOO—H	10.5-12
Amino	H | RN—H	1-5

DEPT 90 CH
DEPT 135 CH, CH_3 positive signal
CH_2 negative signal

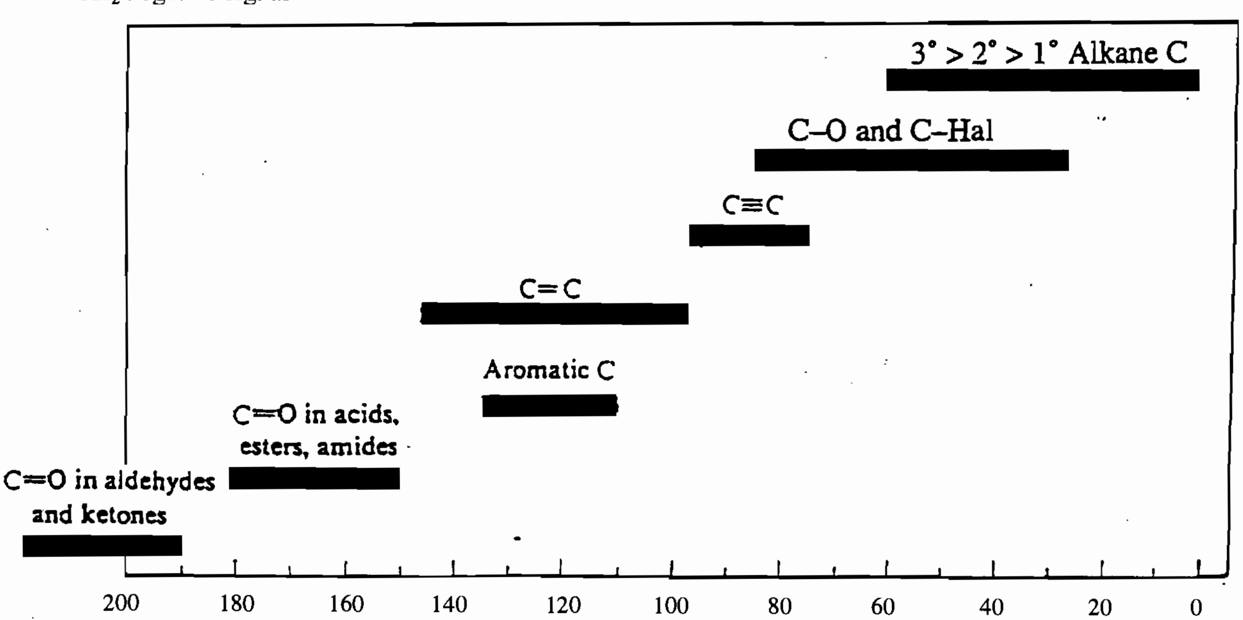
Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C—H	Alkanes	2850-2960 1350-1470
C—H	Alkenes	3020-3080 (*m*) 675-1000
C—H	Aromatic rings	3000-3100 (*m*) 675-870
C—H	Alkynes	3300
C=C	Alkenes	1640-1680 (*v*)
C≡C	Alkynes	2100-2260 (*v*)
C—C	Aromatic rings	1500, 1600 (*v*)
C—O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O—H	Monomeric alcohols, phenols	3610-3640 (*v*)
	Hydrogen-bonded alcohols, phenols	3200-3600 (*broad*)
	Carboxylic acids	2500-3000 (*broad*)
N—H	Amines	3300-3500 (*m*)
C—N	Amines	1180-1360
C≡N	Nitriles	2210-2260 (*v*)
—NO_2	Nitro compounds	1515-1560 1345-1385

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

Abbreviated Periodic Table

1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 H 1.01																	2 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											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 ^{13}C in various kinds of compounds.