

Second Exam

Name (PRINT) \_\_\_\_\_  
Last, First

Chemistry 3332

Signature \_\_\_\_\_

March 21, 2003

SS# \_\_\_\_\_

**Please circle the name of your professor and class time where appropriate.**

Dr. Bean (T/Th 10 AM)

Dr. Cai

Dr. Bean (T/Th 5:30 PM)

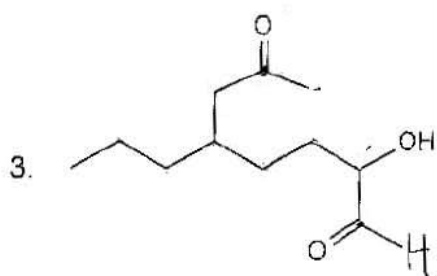
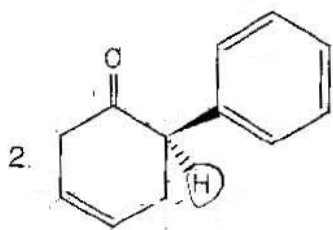
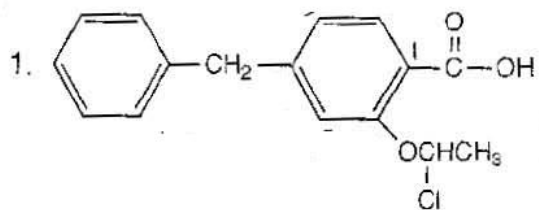
Page #	Score	
1. 12 pts.		
2. 9 pts.		
3. 9 pts.		
4. 12 pts.		
5. 18 pts.		
6. 15 pts.		
7. 15 pts.		
8. 10 pts.		

TOTAL \_\_\_\_\_

**Note: Present your student ID when you return the exam booklet**

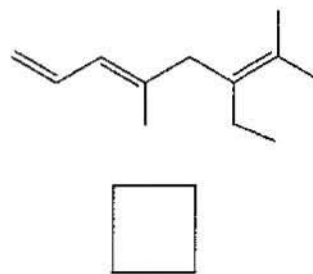
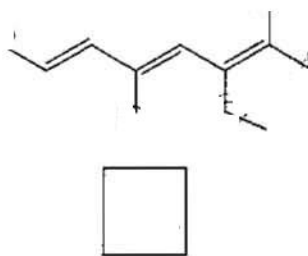
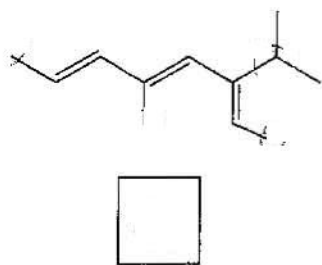
**A. Nomenclature:** ( 4 points each, total = 12 points)

Please provide an acceptable name for each of the following compounds.

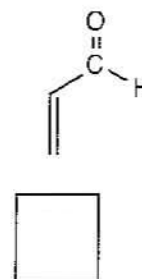
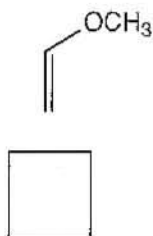
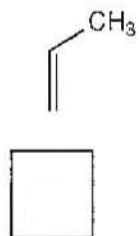


**B. Facts:** (18 points, 3 points each)

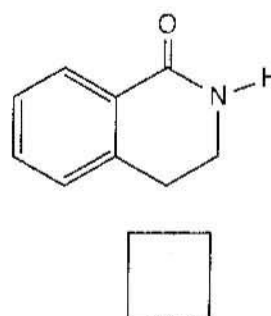
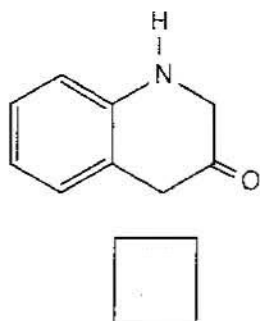
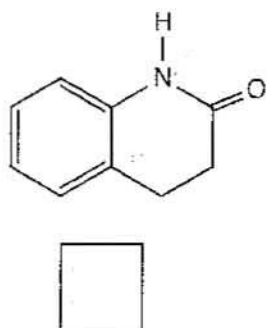
1. Place the compounds in increasing order of  $\lambda_{\max}$  (wavelength) for the  $\pi$  to  $\pi^*$  transition observed in the UV spectrum. (shortest wavelength = 1 | longest wavelength = 3)



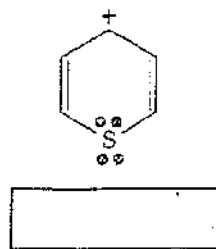
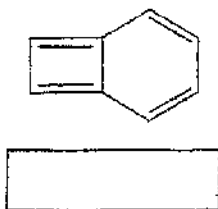
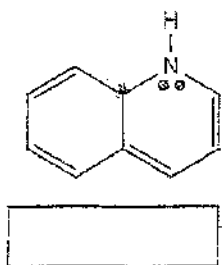
2. Place the compounds in order of increasing reactivity in a Diels-Alder reaction. (1 = least reactive, 3 = most reactive)



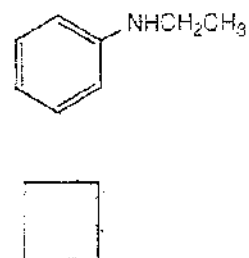
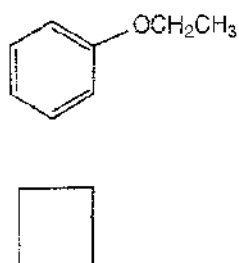
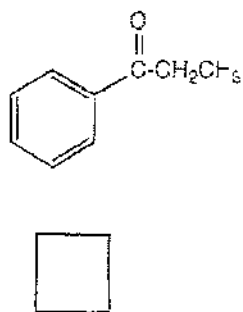
3. Place the compounds in order of increasing reaction rate with bromine in an electrophilic aromatic substitution reaction. (1 = slowest rate, 3 = fastest rate)



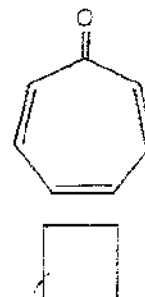
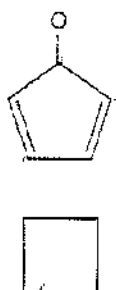
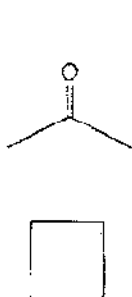
4. Label the compounds as aromatic, antiaromatic or nonaromatic. (You may assume all are planar.)



5. State whether the compounds will undergo Friedel-Crafts acylation (YES/NO).

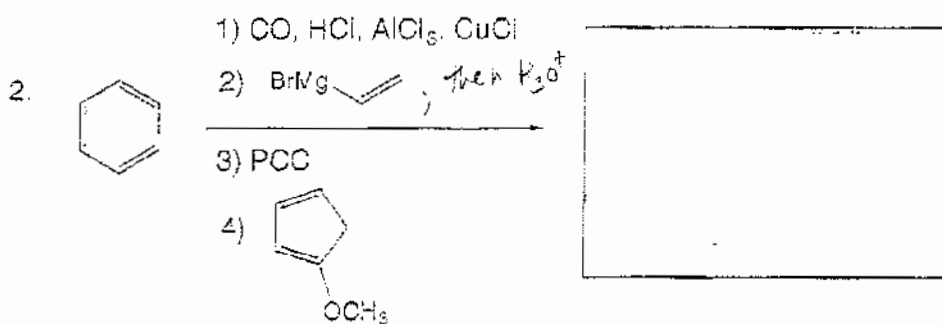
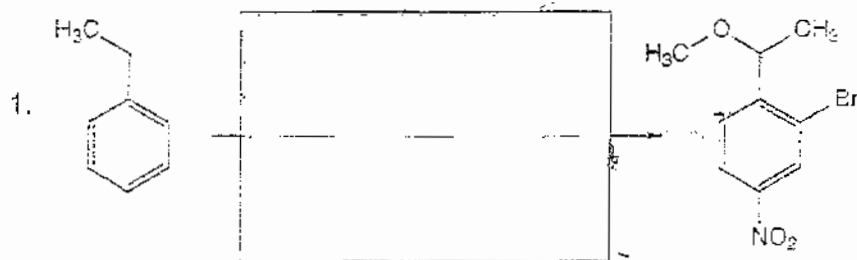


6. Place the ketones in order of increasing dipole moment. (1 = smallest, 3 = largest)



C. Reactions: (30 points, 6 pts. each)

Please provide the starting material, reagents, or major organic product(s) in the answer boxes. Be sure your drawing indicates **stereochemistry** if applicable. **Partial credit** is awarded only when intermediate products are shown below the reaction.



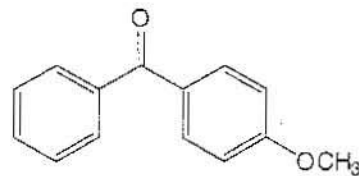
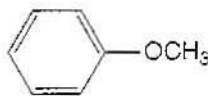
3.



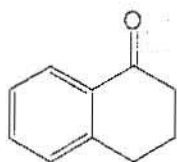
1)  $\text{KMnO}_4$ ,  $\text{NaOH}$ , warm  
2)  $\text{H}^+$

3)  $\text{SOCl}_2$

4)  $\text{AlCl}_3$ ,



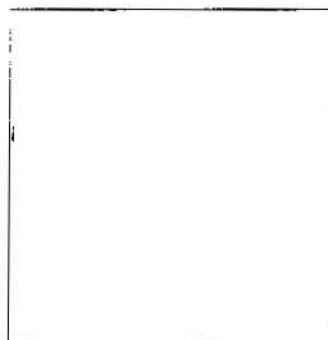
4.



1)  $\text{Na}$ ,  $\text{NH}_3$  (*l*),  $\text{CH}_3\text{CH}_2\text{OH}$

2)  $\text{O}_3$

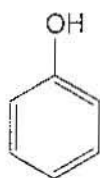
3)  $(\text{CH}_3)_2\text{S}$



+



5.

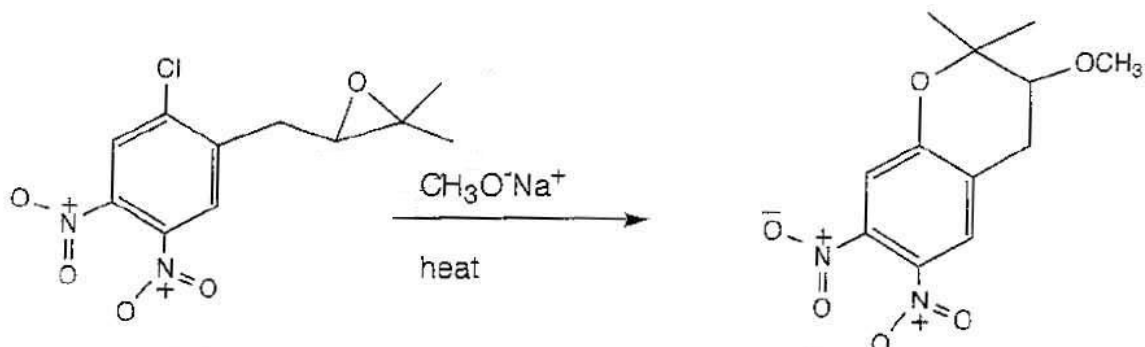


1)  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$



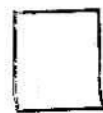
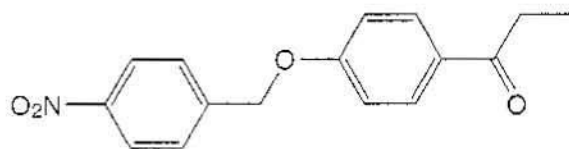
**D. Mechanism:** 15 points

Provide a reasonable mechanism for the reaction below. Use curved arrows to indicate "electron flow." Show all intermediates and formal charges. If there is more than one resonance contributor, you must show the "best" (i.e., lowest energy) structure.



**E. Synthesis** (15 points)

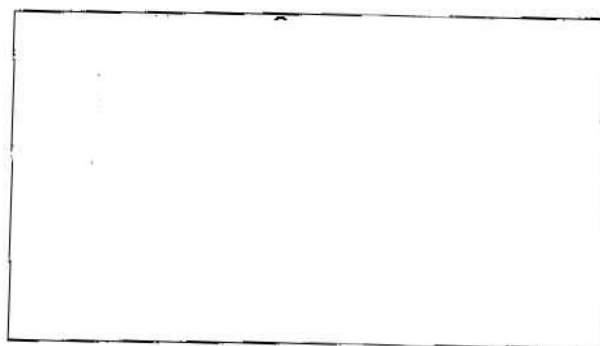
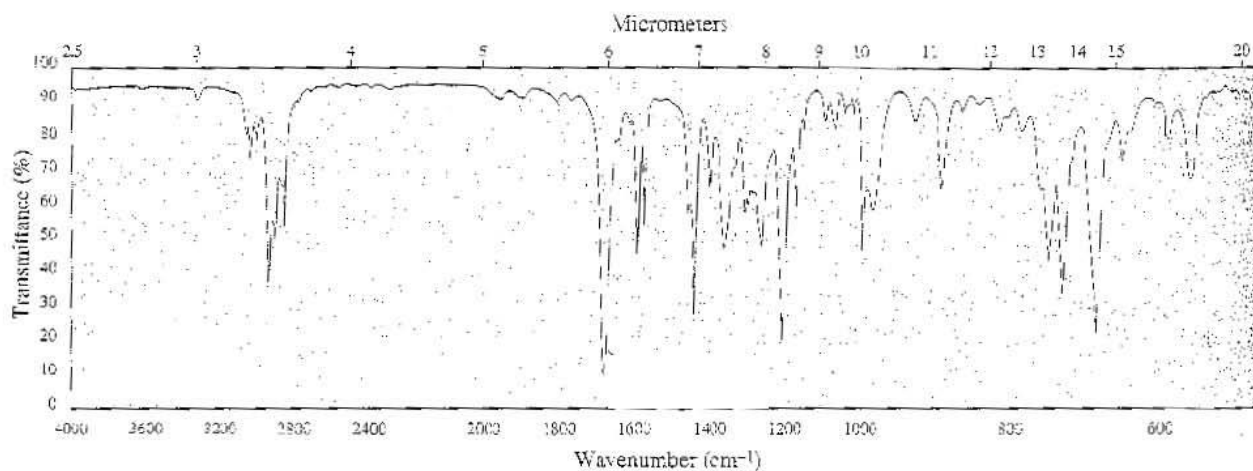
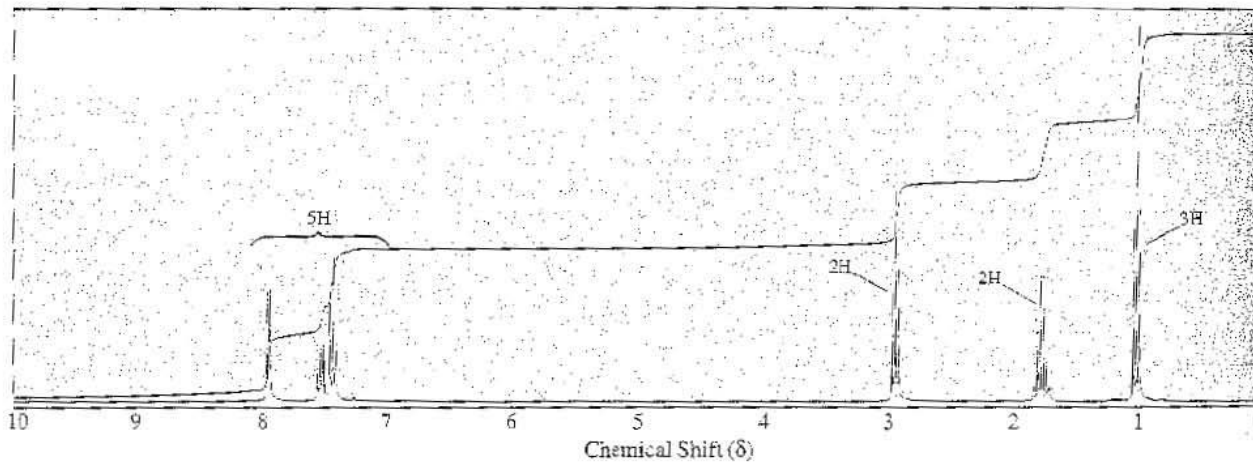
Synthesize the compound below using any of the following reagents: alkanes, alkenes, alkynes or alcohols of two carbons or less, benzene, any oxidizing or reducing agents, any inorganic reagents, and any peroxyacids.





**F. Spectroscopy: (10 points)**

A compound with the formula  $C_{10}H_{12}O$  exhibits the IR and  $^1H$  NMR shown below. Please identify this compound and draw the structure in the box provided below.



**TABLE 13.2** Characteristic infrared absorptions of groups

GROUP	FREQUENCY RANGE (cm <sup>-1</sup> )	INTENSITY <sup>a</sup>
<b>A. Alkyl</b>		
C—H (stretching)	2853–2962	(m–s)
Isopropyl, —CH(CH <sub>3</sub> ) <sub>2</sub>	1380–1385	(s)
	and 1365–1370	(s)
<i>tert</i> -Butyl, —C(CH <sub>3</sub> ) <sub>3</sub>	1385–1395	(m)
	and ~1365	(s)
<b>B. Alkenyl</b>		
C—H (stretching)	3010–3095	(m)
C=C (stretching)	1620–1680	(v)
R—CH=CH <sub>2</sub>	985–1000	(s)
	and 905–920	(s)
R <sub>2</sub> C=CH <sub>2</sub>	880–900	(s)
<i>cis</i> -RCH=CHR	675–730	(s)
<i>trans</i> -RCH=CHR	960–975	(s)
	(out-of-plane C—H bendings)	
<b>C. Alkynyl</b>		
≡C—H (stretching)	~3300	(s)
C≡C (stretching)	2100–2260	(v)
<b>D. Aromatic</b>		
Ar—H (stretching)	~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)		
Monosubstituted	690–710	(very s)
	and 730–770	(very s)
<i>o</i> Disubstituted	735–770	(s)
<i>m</i> Disubstituted	680–725	(s)
	and 750–810	(very s)
<i>p</i> Disubstituted	800–840	(very s)
<b>E. Alcohols, Phenols, and Carboxylic Acids</b>		
O—H (stretching)		
Alcohols, phenols (dilute solutions)	3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)	3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)	2500–3000	(broad, v)
<b>F. Aldehydes, Ketones, Esters, and Carboxylic Acids</b>		
C=O (stretching)	1630–1780	(s)
Aldehydes	1690–1740	(s)
Ketones	1680–1750	(s)
Esters	1735–1750	(s)
Carboxylic acids	1710–1780	(s)
Amides	1630–1690	(s)
<b>G. Amines</b>		
N—H	3300–3500	(m)
<b>H. Nitriles</b>		
C≡N	2220–2260	(m)

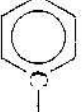
<sup>a</sup> Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

**TABLE 13.3** Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT ( $\delta$ , ppm)
1° Alkyl, RCH <sub>3</sub>	0.8–1.0
2° Alkyl, RCH <sub>2</sub> R	1.2–1.4
3° Alkyl, R <sub>3</sub> CH	1.4–1.7
Allylic, R <sub>2</sub> C=C—CH <sub>2</sub> , R	1.6–1.9
Ketone, RCCH <sub>3</sub> , O	2.1–2.6
Benzylic, ArCH <sub>2</sub>	2.2–2.5
Acetylenic, RC≡CH	2.5–3.1
Alkyl iodide, RCH <sub>2</sub> I	3.1–3.3
Ether, ROCH <sub>2</sub> R	3.3–3.9
Alcohol, HOCH <sub>2</sub> R	3.3–4.0
Alkyl bromide, RCH <sub>2</sub> Br	3.4–3.6
Alkyl chloride, RCH <sub>2</sub> Cl	3.6–3.8
Vinyllic, R <sub>2</sub> C=CH <sub>2</sub>	4.6–5.0
Vinyllic, R <sub>2</sub> C=CH R	5.2–5.7
Aromatic, ArH	6.0–9.5
Aldehyde, RCH O	9.5–9.6
Alcohol hydroxyl, ROH	0.5–6.0 <sup>a</sup>
Amino, R—NH <sub>2</sub>	1.0–5.0 <sup>a</sup>
Phenolic, ArOH	4.5–7.7 <sup>a</sup>
Carboxylic, RCOH O	10–13 <sup>a</sup>

<sup>a</sup> The chemical shifts of these protons vary in different solvents and with temperature and concentration.

**TABLE 13.4** Approximate carbon-13 chemical shifts

TYPE OF CARBON ATOM	CHEMICAL SHIFT ( $\delta$ , ppm)
1° Alkyl, RCH <sub>3</sub>	0–40
2° Alkyl, RCH <sub>2</sub> R	10–50
3° Alkyl, RCHR <sub>2</sub>	15–50
Alkyl halide or amine, —C—X (X = Cl, Br, or N—)	10–65
Alcohol or ether, —C—O	50–90
Alkyne, —C≡	60–90
Alkene, >C=	100–170
Aryl, 	100–170
Nitriles, —C≡N	120–130
Amides, —C—N O	150–180
Carboxylic acids, esters, —C—O O	160–185
Aldehydes, ketones, —C— O	182–215

# PERIODIC TABLE OF THE ELEMENTS

Noble gases

Group	Atomic number		Symbol		Atomic weight	
IA	6	Name	C	Symbol	Atomic weight	Atomic weight
1	Hydrogen 1		Carbon 6		12.011	
2	Helium 2					
3	Lithium 3					
4	Beryllium 4					
5	Boron 5					
6	Carbon 6					
7	Nitrogen 7					
8	Oxygen 8					
9	Fluorine 9					
10	Neon 10					
11	Sodium 11					
12	Magnesium 12					
13	Aluminum 13					
14	Silicon 14					
15	Phosphorus 15					
16	Sulfur 16					
17	Chlorine 17					
18	Argon 18					
19	Potassium 19					
20	Calcium 20					
21	Scandium 21					
22	Titanium 22					
23	Vanadium 23					
24	Chromium 24					
25	Manganese 25					
26	Iron 26					
27	Cobalt 27					
28	Nickel 28					
29	Copper 29					
30	Zinc 30					
31	Gallium 31					
32	Germanium 32					
33	Arsenic 33					
34	Selenium 34					
35	Bromine 35					
36	Krypton 36					
37	Rubidium 37					
38	Strontium 38					
39	Yttrium 39					
40	Zirconium 40					
41	Niobium 41					
42	Molybdenum 42					
43	Technetium 43					
44	Ruthenium 44					
45	Rhodium 45					
46	Palladium 46					
47	Silver 47					
48	Cadmium 48					
49	Indium 49					
50	Tin 50					
51	Antimony 51					
52	Tellurium 52					
53	Iodine 53					
54	Xenon 54					
55	Cesium 55					
56	Barium 56					
57	Lanthanum 57					
58	Cerium 58					
59	Praseodymium 59					
60	Neodymium 60					
61	Promethium 61					
62	Samarium 62					
63	Europium 63					
64	Gadolinium 64					
65	Terbium 65					
66	Dysprosium 66					
67	Hoium 67					
68	Erbium 68					
69	Thulium 69					
70	Ytterbium 70					
71	Lutetium 71					

\*Lanthanide series

†Actinide series

\*Numbers in parentheses are mass numbers of the most stable or best-known isotope of radioactive elements.