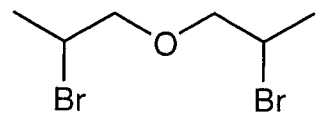
CHEM 3332 - EXAM 1

Bean - Cai - 1
Chem 3332

A. Nomenclature (3 points each; 9 total points)

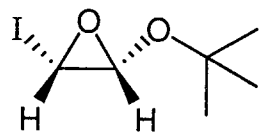
Please provide an acceptable name for each of the following compounds, noting stereochemistry where appropriate.

1.



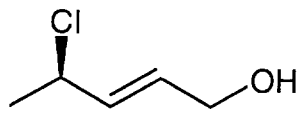
_____

2.



_____

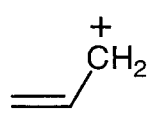
3.

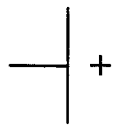


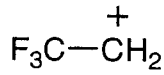
_____

B. Facts (1 point for every blank; 19 total points)

1. Rank the stability of the following cations from lowest (**1**) to highest (**3**).

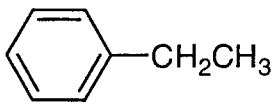


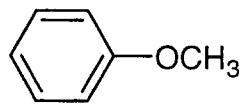


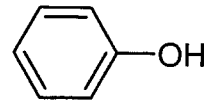


____ ____ ____

2. Rank the boiling points of the following molecules from lowest (**1**) to highest (**3**).

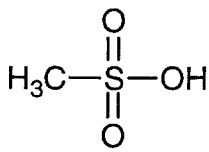


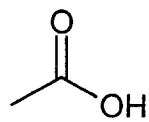


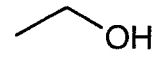


____ ____ ____

3. Rank the pK_a value of the following molecules from lowest (**1**) to highest (**3**).

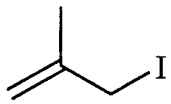


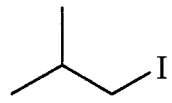


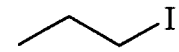


____ ____ ____

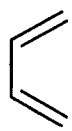
4. Rank these molecules from slowest (**1**) to fastest (**3**) in their rate of reaction with $NaOCH_3$.

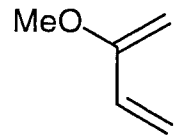


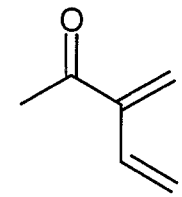




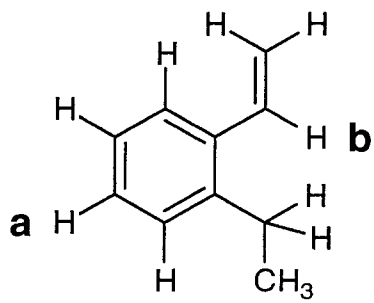
5. Rank the following molecules from slowest (**1**) to fastest (**3**) in their rate of Diels-Alder reactivity.







6. Answer the following questions for the molecule shown below and place the answers in the appropriate boxes. (i) How many distinct proton types are present in the molecule? (ii) How many signals would appear in the proton-decoupled ^{13}C NMR spectrum? (iii) & (iv) What are the theoretically predicted multiplicities (splitting patterns) of the signals for protons **a** and **b**?



(i) number of distinct proton types: ☐

(ii) number of carbon signals: ☐

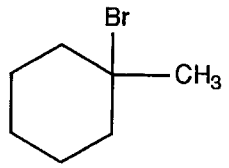
(iii) multiplicity of H_a: ☐

(iv) multiplicity of H_b: ☐

☐

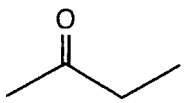
C. Reactions: Total = 30 points, 5 points each
Please provide the starting material or major product in the answer box. Be sure your drawing indicates stereochemistry if applicable. Partial credit is awarded only when intermediate products are shown below the reaction.

1.



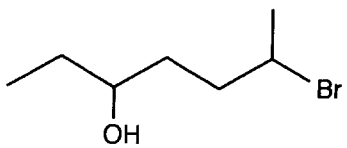
1. $(CH_3)_3CO^- K^+$
2. NBS/ 65 °C
3. NaCN

2.



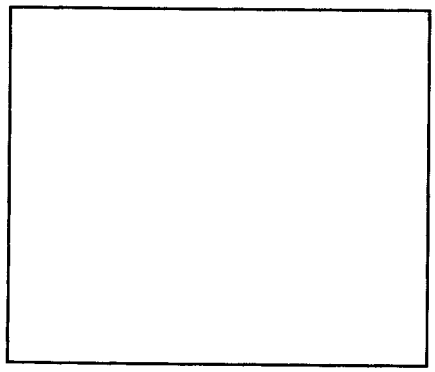
1. CH_3MgBr
2. H_2SO_4 / Heat
3. MCPBA
4. CH_3CH_2OH / H^+

3.

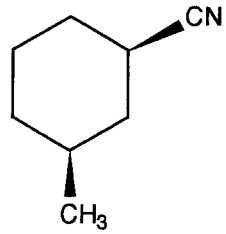


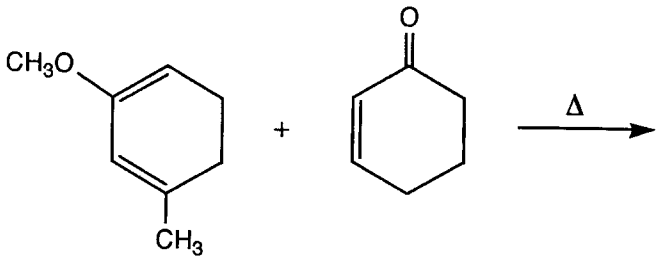
1. $(CH_3)_3CO^- K^+$ / Heat
2. HI (xs)
3. $CH_3CH_2O^- Na^+$

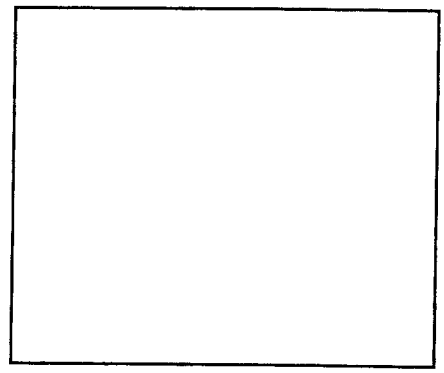
C_7H_{12}

4. 

1. PBr_3
2. NaCN

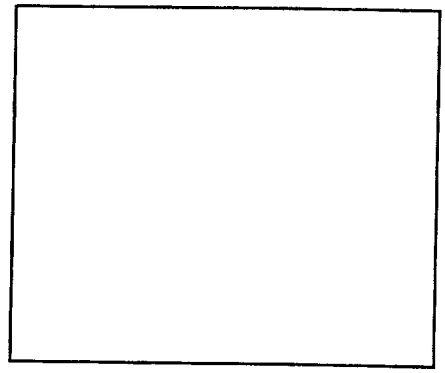


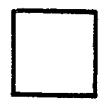
5. 



6. H-C≡C-CH_2CH_3

1. Sia_2BH
2. H_2O_2 / ^-OH
3. CH_3CH_2-C≡C $^-Na^+$
4. H_3O^+
5. PCC

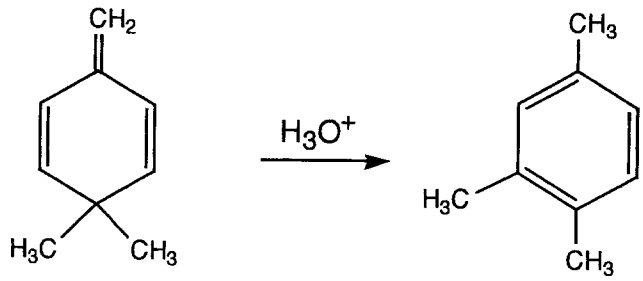




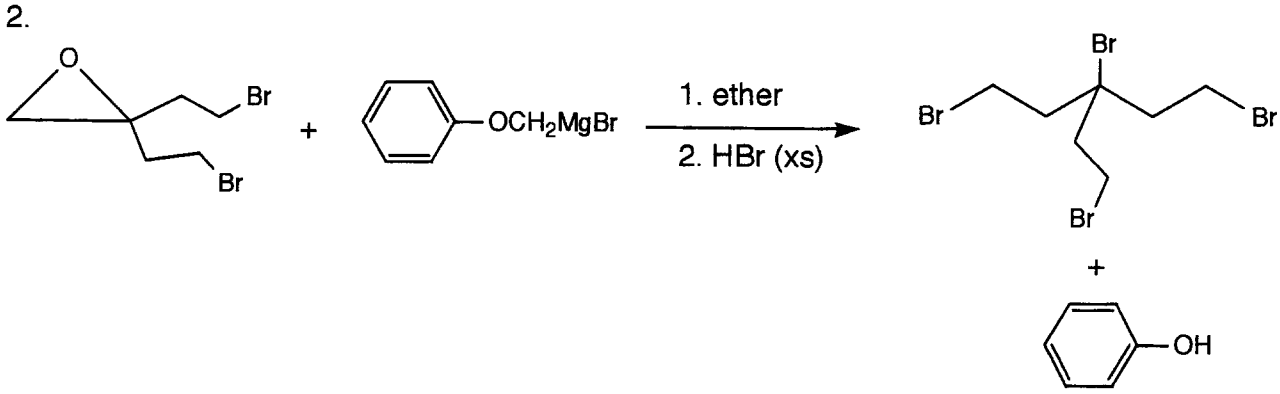
D. Mechanisms: (9 points each)

Provide clear mechanisms for reactions 1 and 2. Use curved arrows to indicate "electron flow". Remember to show only one step at a time. **Show all intermediates and all formal charges**. If there is more than one resonance structure, you must show the "best" (i.e. lowest energy) structure.

1.

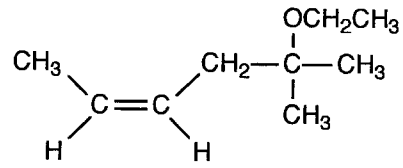


2.



E. Synthesis: (14 points)

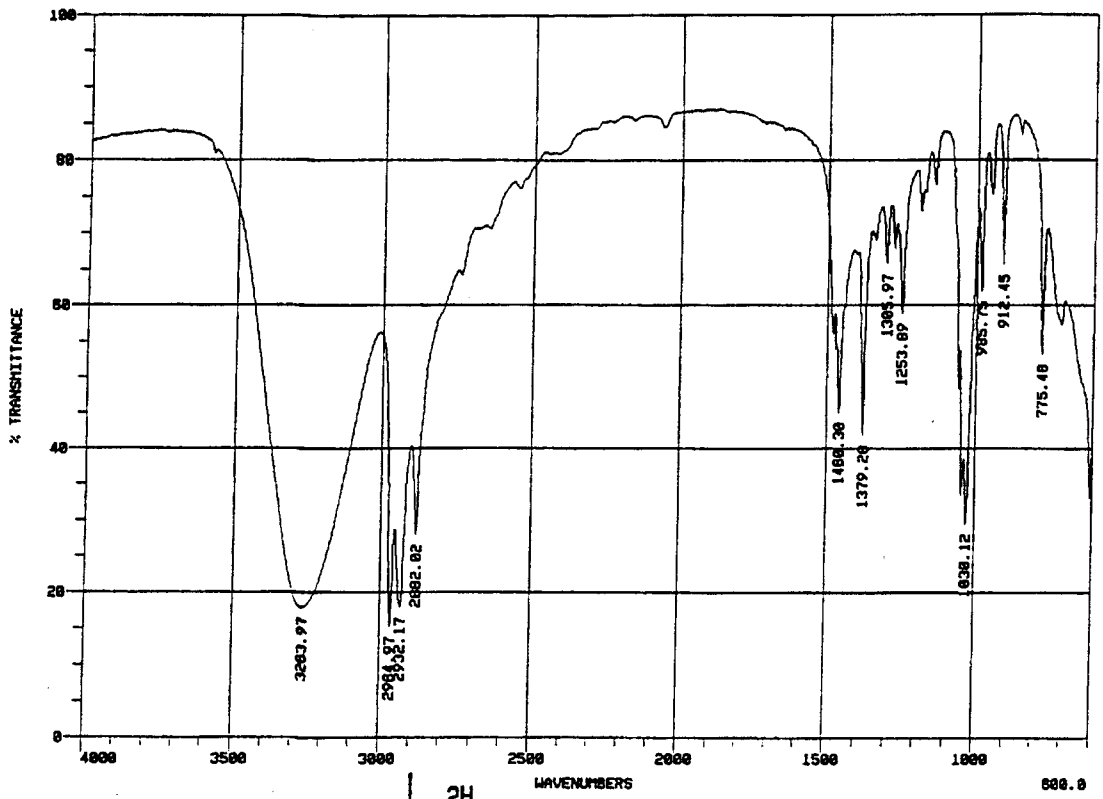
Synthesize the molecule below using any of the following reagents: alkanes, alkenes or alcohols of **three carbons or less**, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids.



F. Spectroscopy: 10 Points

A compound with the formula $\mathbf{C_7H_{16}O_2}$ exhibits the IR, ^1H NMR, and proton-decoupled ^{13}C NMR spectra shown on the following page. Please identify this compound and draw the structure in the box provided below.

MF $C_7H_{16}O_2$


% TRANSMITTANCE
WAVENUMBERS
3283.97
2964.87
2932.17
2882.82
1468.30
1379.20
1303.97
1253.89
938.12
912.45
775.48

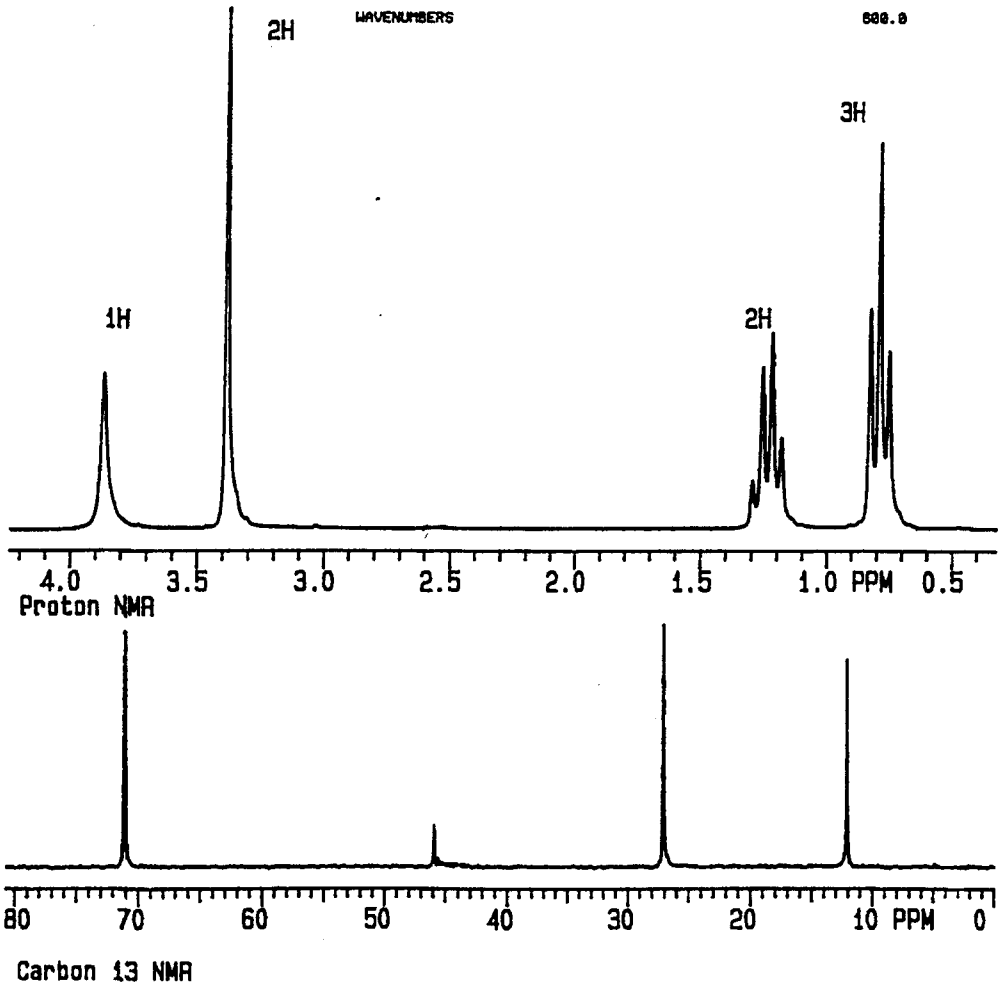

2H
3H
1H
2H
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5
Proton NMR
80
70
60
50
40
30
20
10 PPM
0
Carbon 13 NMR

TABLE 13.2 Characteristic infrared absorptions of groups

GROUP		FREQUENCY RANGE (cm^{-1})	INTENSITY[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $-CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $-C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
$R-CH=CH_2$	(out-of-plane C—H bendings)	985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$		880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o Disubstituted		735–770	(s)
m Disubstituted		680–725	(s)
	and	750–810	(very s)
p Disubstituted		800–840	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
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)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
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)
G. Amines			
N—H		3300–3500	(m)
H. Nitriles			
C≡N		2220–2260	(m)

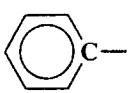
[a] Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

TABLE 13.3 Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Ketone, $RC(=O)CH_3$	2.1–2.6
Benzylic, $ArCH_3$	2.2–2.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl chloride, RCH_2Cl	3.6–3.8
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Aldehyde, $RC(=O)H$	9.5–9.6
Alcohol hydroxyl, ROH	0.5–6.0[a]
Amino, $R{-}NH_2$	1.0–5.0[a]
Phenolic, ArOH	4.5–7.7[a]
Carboxylic, $RC(=O)OH$	10–13[a]

[a] 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 (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-\overset{|}{\underset{|}{C}}-X$ (X = Cl, Br, or $-\overset{|}{N}-$)	10–65
Alcohol or ether, $-\overset{|}{\underset{|}{C}}-O$	50–90
Alkyne, $-C{\equiv}$	60–90
Alkene, $\diagdown C{=}$	100–170
Aryl,  C—	100–170
Nitriles, $-C{\equiv}N$	120–130
Amides, $-C(=O)-N-$	150–180
Carboxylic acids, esters, $-C(=O)-O$	160–185
Aldehydes, ketones, $-C(=O)-$	182–215