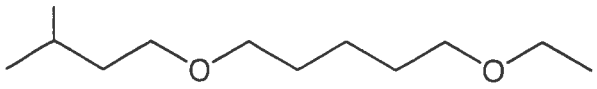
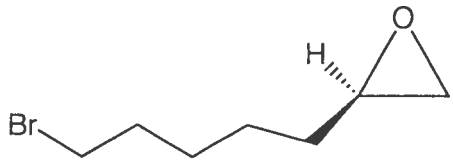
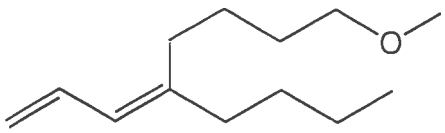
Alt Exam 1, 3p

A. Nomenclature: (12 points)

Give an acceptable name for each of the following compounds. Be sure to indicate the **stereochemistry** where appropriate.

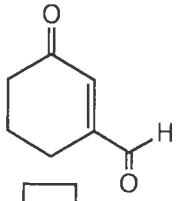
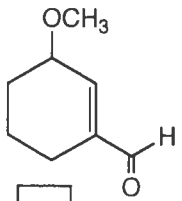
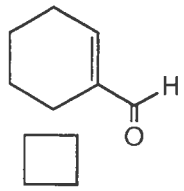
1. 

2. 

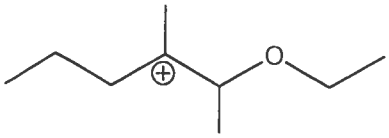
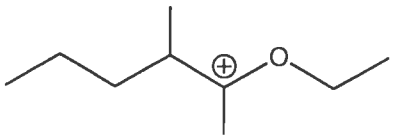
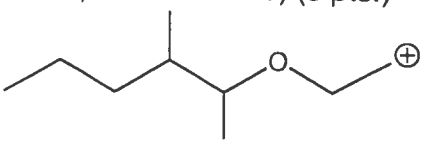
3. 

B. Facts: Total points = 16

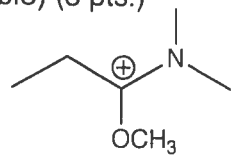
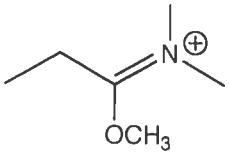
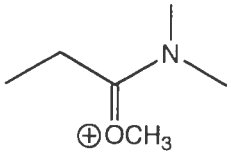
1. Place the following compounds in order of increasing reactivity in a Diels-Alder reaction. (1=least reactive, 3=most reactive) (3 pts)

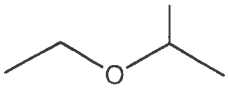
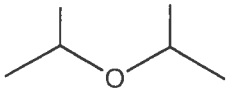
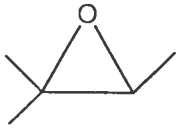
2. Place the following cations in order of increasing stability. (1=least stable, 3=most stable) (3 pts.)

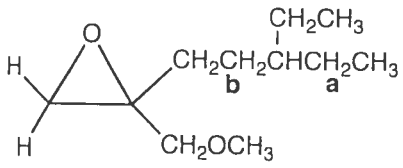
3. Place the following resonance contributors in order of increasing stability. (1=least stable, 3=most stable) (3 pts.)

4. Rank the following compounds in order increasing reaction rate with HBr. (1=slowest rate, 3=fastest rate) (3 pts)

5. Answer the following questions for the molecule below and place the answers in the appropriate boxes. (i) How many distinct types of protons are present in the molecule? (ii) How many distinct carbons are present? (iii) What is the theoretically predicited multiplicity(splitting pattern) of the signal for proton **a**? (iv) What is the multiplicity of the signal for carbon **b** in the proton-coupled ^{13}C NMR? (4 pts.)



(i) # of proton types ☐

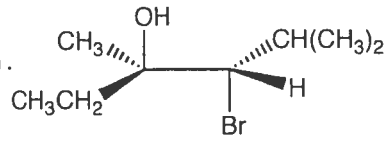
(ii) # of carbon types ☐

(iii) multiplicity of H**a** ☐

(iv) multiplicity of C**b** ☐

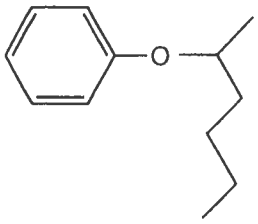
C. Reactions: Total = 36 points, 6 points each
Please provide the major product in the answer box unless indicated otherwise. Indicate **stereochemistry** with wedges and dashes if applicable. Partial credit is awarded only when intermediate products in a multi-step reaction are shown below the reaction.

1.



1.NaOH
2. $CH_3-C\equiv C:^-\ Na^+$, then H_3O^+

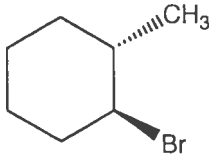
2.

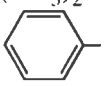


HI (1 eq) / heat

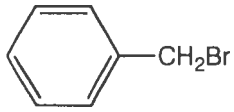
+

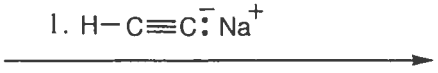
3.

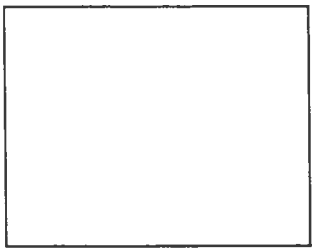


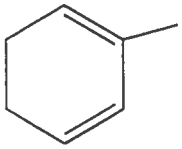
1. $CH_3CH_2O^-\ Na^+$
2. O_3
3. $(CH_3)_2S$
4. 

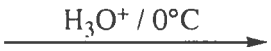
, then H_3O^+

4. 

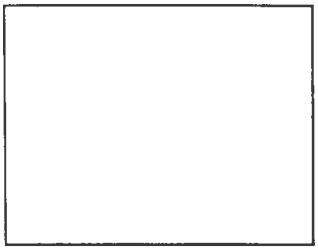




5. 

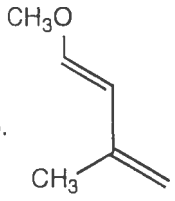


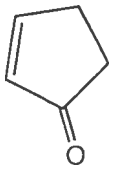
+

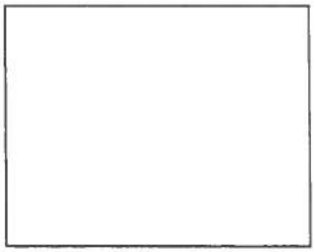


Major product

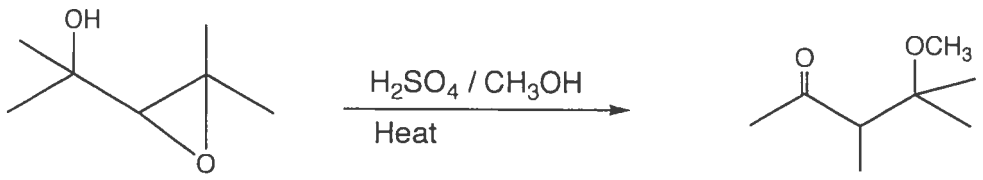
Minor Product

6. 

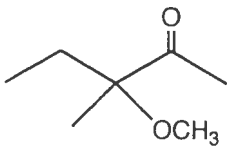
+ 



D. Mechanism: (12 points)
Provide a clear mechanism to explain the formation of the product. Use curved arrows to indicate "electron flow". Remember to show only one step at a time. **Show all intermediates and all formal charges.**
Do not show transition states!

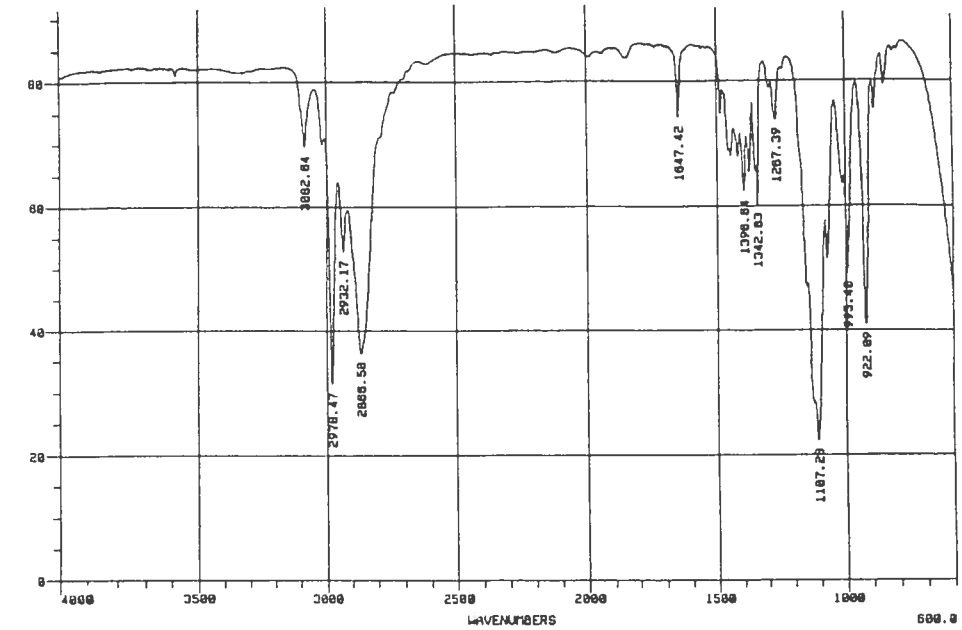


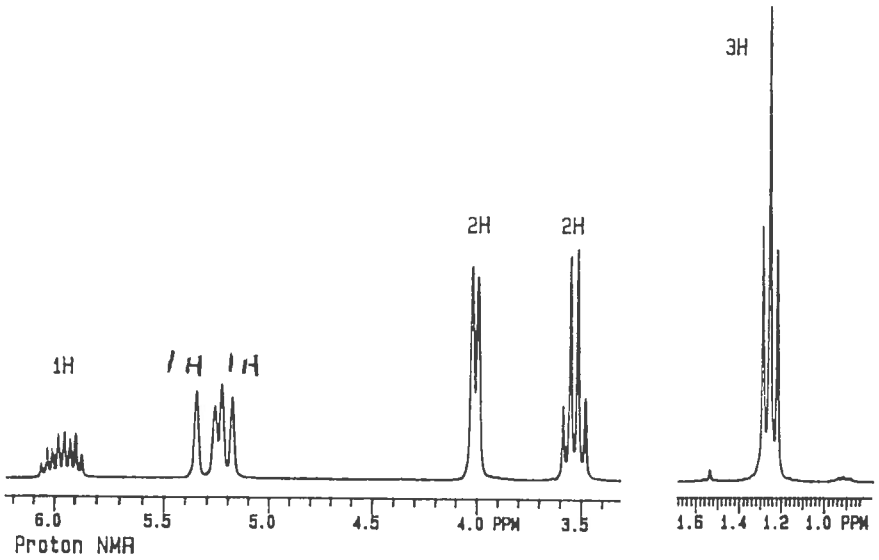
E. Synthesis: 12 Points
Synthesize the molecule below using any of the following reagents: alcohols, alkanes, and/or alkenes of **four carbons or less**, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids.

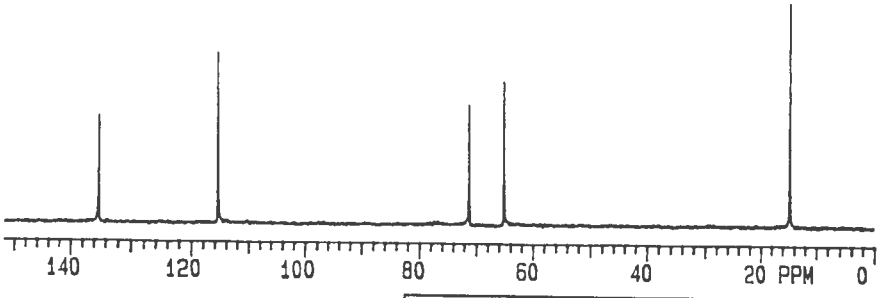


F. Spectroscopy: 12 Points

A compound with the formula $C_5H_{10}O$ exhibits the IR, ^1H NMR and proton decoupled ^{13}C NMR spectra shown below. Please identify this compound and draw the structure in the box provided below.







WebElements: the periodic table on the world-wide web

http://www.webelements.com/

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

Key

element name
atomic number
symbol
atomic weight (mean relative mass)

*lanthanoids	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**actinoids	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements 110-112 and 114 so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings aluminum and cesium are normal while in the UK and elsewhere the common spelling is sulphur.

Group labels: the numeric system (1-18) used here is the current IUPAC convention.

Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2001 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope.

Spring 2012
First Exam

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, ~ = approximate

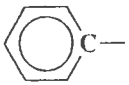
Spring 2012
Final Exam

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, $>C{=}$	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