CH 336
Midterm Exam 1
Friday, April 22, 2016 Name___KEY_____

Answers in RED.

You may use a molecular model kit, but no other notes or material with chemical information. Electronic gadgets (including but not limited to: calculators, phones, MP3 players, smart watches) are prohibited; we may ask you to leave electronic watches at the front of the room or in your backpack for the exam period.

Please ask questions if a question is not clear.

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]				

*Lanthanide series	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
**Actinide series	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]

Score Table:

Section I _____/20

Section II _____/25

Section III _____/20

Section IV _____/21

Srction V _____/14

Total: _____/100

Table 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules

Type of hydrogen[a]	Chemical shift δ in ppm	
Primary alkyl, RCH_3	0.8–1.0	Alkane and alkane-like hydrogens
Secondary alkyl, RCH_2R'	1.2–1.4	
Tertiary alkyl, R_3CH	1.4–1.7	
Allylic (next to a double bond), $R_2C{=}C(CH_3)R'$	1.6–1.9	Hydrogens adjacent to unsaturated functional groups
Benzylic (next to a benzene ring), $ArCH_2R$	2.2–2.5	
Ketone, $RCCH_3$ (O)	2.1–2.6	
Alkyne, $RC{\equiv}CH$	1.7–3.1	
Chloroalkane, RCH_2Cl	3.6–3.8	Hydrogens adjacent to electronegative atoms
Bromoalkane, RCH_2Br	3.4–3.6	
Iodoalkane, RCH_2I	3.1–3.3	
Ether, RCH_2OR'	3.3–3.9	
Alcohol, RCH_2OH	3.3–4.0	
Terminal alkene, $R_2C{=}CH_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $R_2C{=}CH(R')$	5.2–5.7	
Aromatic, ArH	6.0–9.5	
Aldehyde, RCH (O)	9.5–9.9	
Alcoholic hydroxy, ROH	0.5–5.0	(variable)
Thiol, RSH	0.5–5.0	(variable)
Amine, RNH_2	0.5–5.0	(variable)

[a] R, R′, alkyl groups; Ar, aromatic group (not argon).

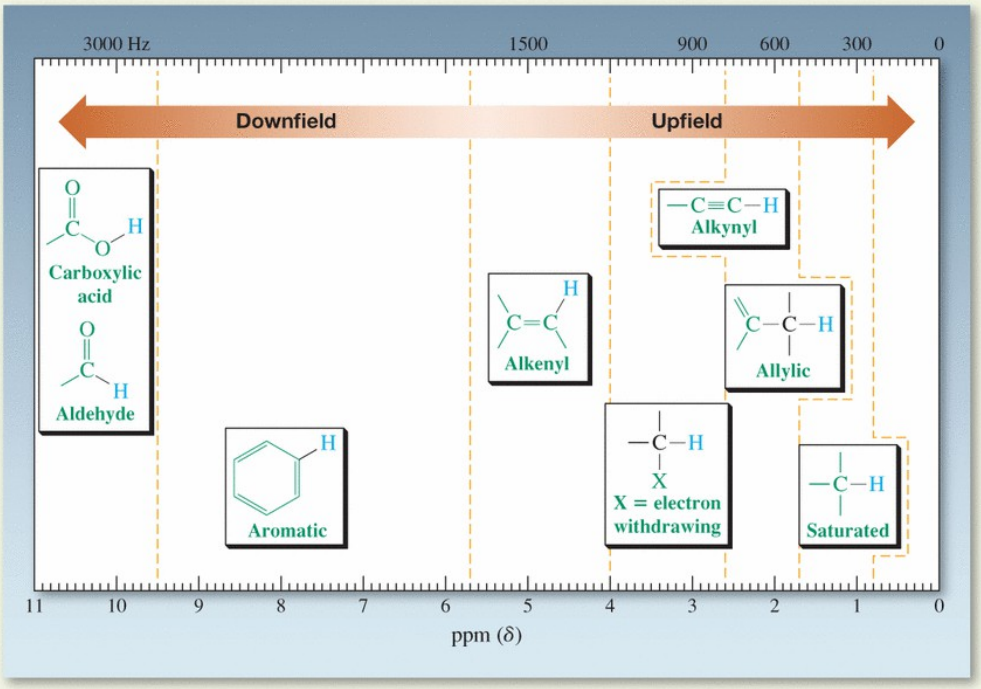
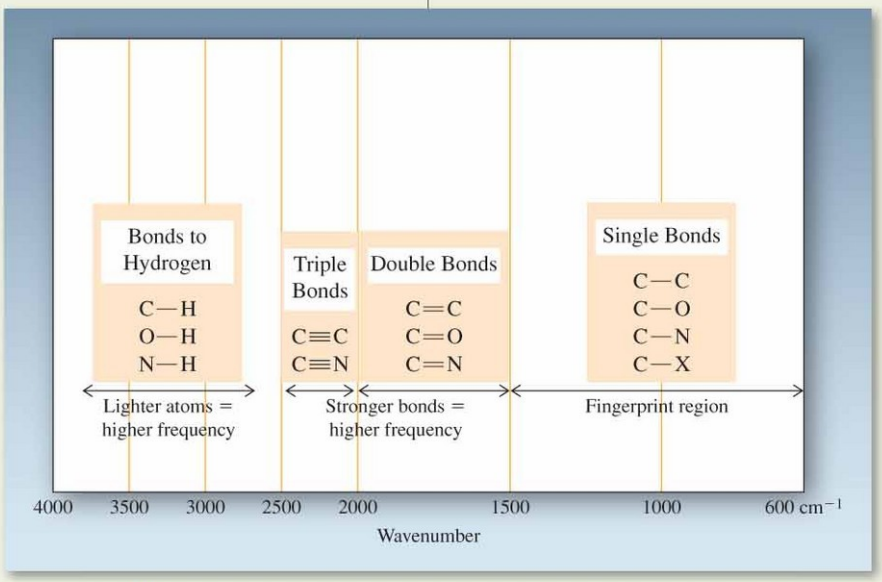


Table 11-4 Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or Functional Group	$\tilde{\nu}$ (cm^{-1})	Bond or Functional Group	$\tilde{\nu}$ (cm^{-1})
RO—H (alcohols)	3200–3650	RC≡N (nitriles)	2220–2260
RCO—H (carboxylic acids)	2500–3300	RCH, RCR′ (aldehydes, ketones)	1690–1750
R_2N—H (amines)	3250–3500	RCOR′ (esters)	1735–1750
RC≡C—H (alkynes)	3260–3330	RCOH (carboxylic acids)	1710–1760
C=C (alkenes)	3050–3150	C=C (alkenes)	1620–1680
—C—H (alkanes)	2840–3000	RC—OR′ (alcohols, ethers)	1000–1260
RC≡CH (alkynes)	2100–2260		



Increasing wavenumber (energy)

Section I (4 points each) Select the best answer among the possibilities given and circle it.

1. How does the dipole moment 3-pentanone compare with that of diethyl ether?

a. 3-Pentanone > diethyl ether because the C=O double bond is more polarized.

b. Diethyl ether > 3-pentanone because there are 2 C-O bonds.

c. Both are equal, because each has a C-O bond.

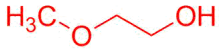
d. As neutral molecules, both lack a dipole moment.

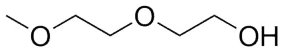
2. Select the structure that best matches the following spectroscopic data.

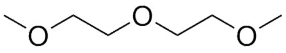
IR (cm^{-1}): 3200-3600, s, br; 2931 s; 2911 s; 2883 m; 2829 m; 1458 m; 1408 m; 1368 m; 1196 m; 1124 s; 1066 s; 1019 m; 891 m; 835 m.

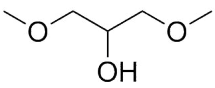
^{1}H NMR (ppm): 3.71 t, 2H, J = 7 Hz
3.52 t, 2H, J = 7 Hz
3.40 s, 3H
3.21 br s, 1H (disappears on shaking with D_2O)

^{13}C NMR (ppm): 74.21, 61.55, 58.91

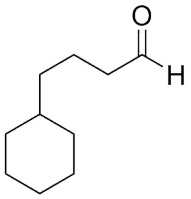
a. 

b. 

c. 

d. 

3. Select the best name for the following compound.



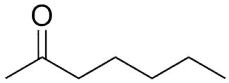
a. 4-phenylbutanal

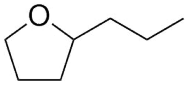
b. 4-cyclohexylbutyl ketone hydride

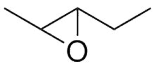
c. 4-cyclohexylbutanal

d. 4-cyclohexylbutanol (all students get full credit because of exam error)

4. Select the structure whose name is both 2-pentyloxirane, or 1-heptene oxide.

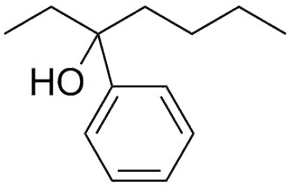
a. 

b. 

c. 

d. 

5. The best set of reactants to form 3-phenyl-3-heptanol (shown) are



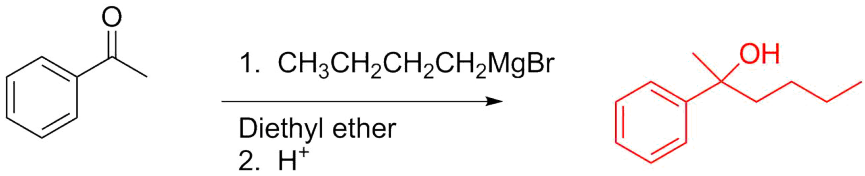
a. 3-heptanone plus $NaBH_4$ in one step, followed by H+.

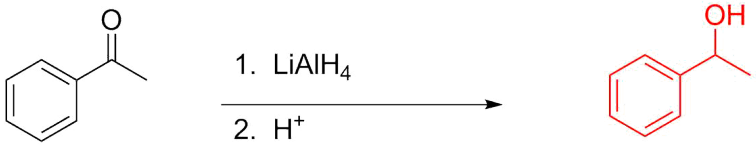
b. 3-heptanone plus C_6H_5MgBr in one step, followed by H^+.

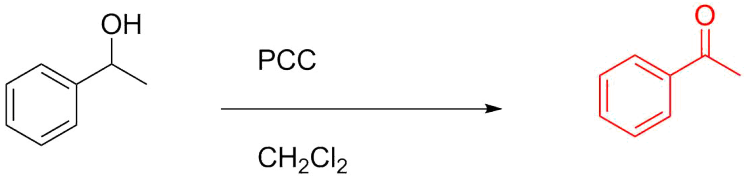
c. Benzoic acid plus one mole of ethylmagnesium bromide, then one mole of butylmagnesium bromide.

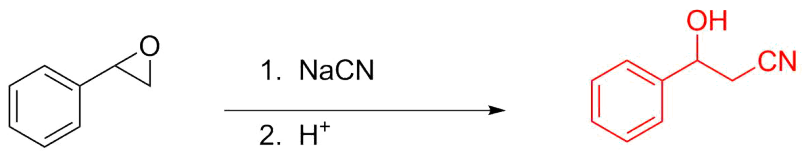
d. 3-phenylheptane plus Jones' reagent.

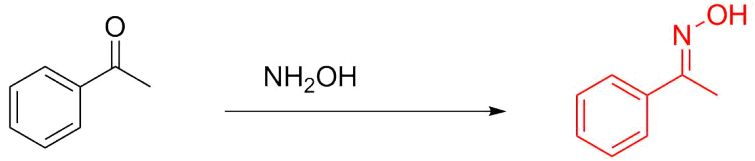
Section II. (5 points each) Draw the major organic product for each of the following reactions.

6. 

7. 

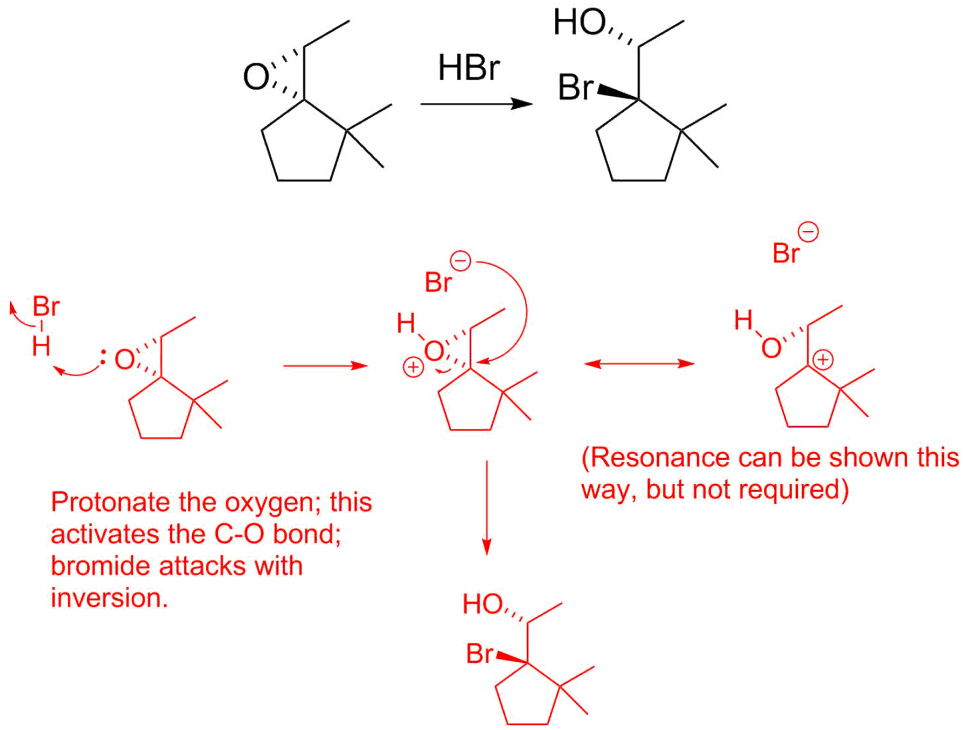
8. 

9. 

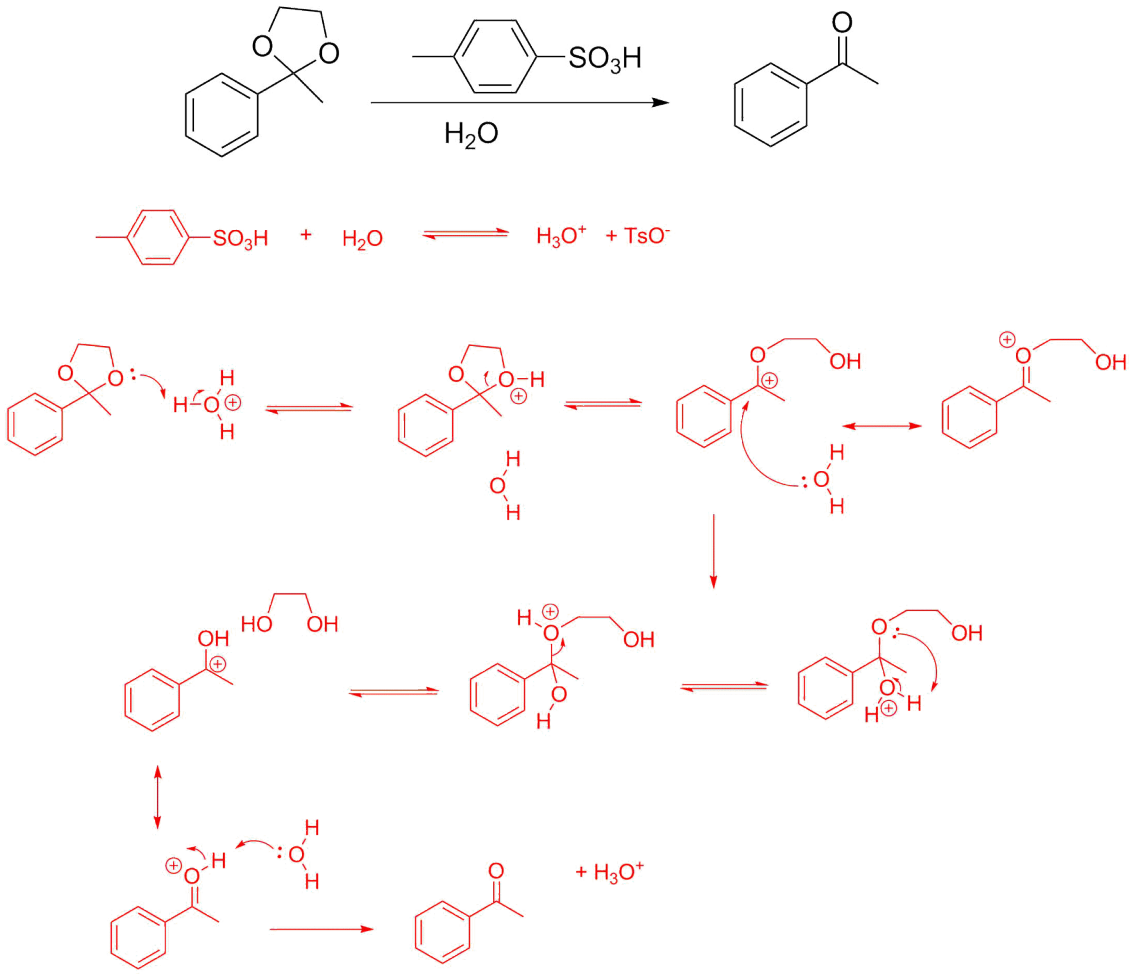
10. 

Section III. (10 points each) Write a mechanism for each of the following two transformations. Use electron-pushing arrows correctly, designate lone pairs where necessary, and make sure charges are correctly shown. If resonance is a stabilizing influence for any structure, show appropriate resonance forms.

11.



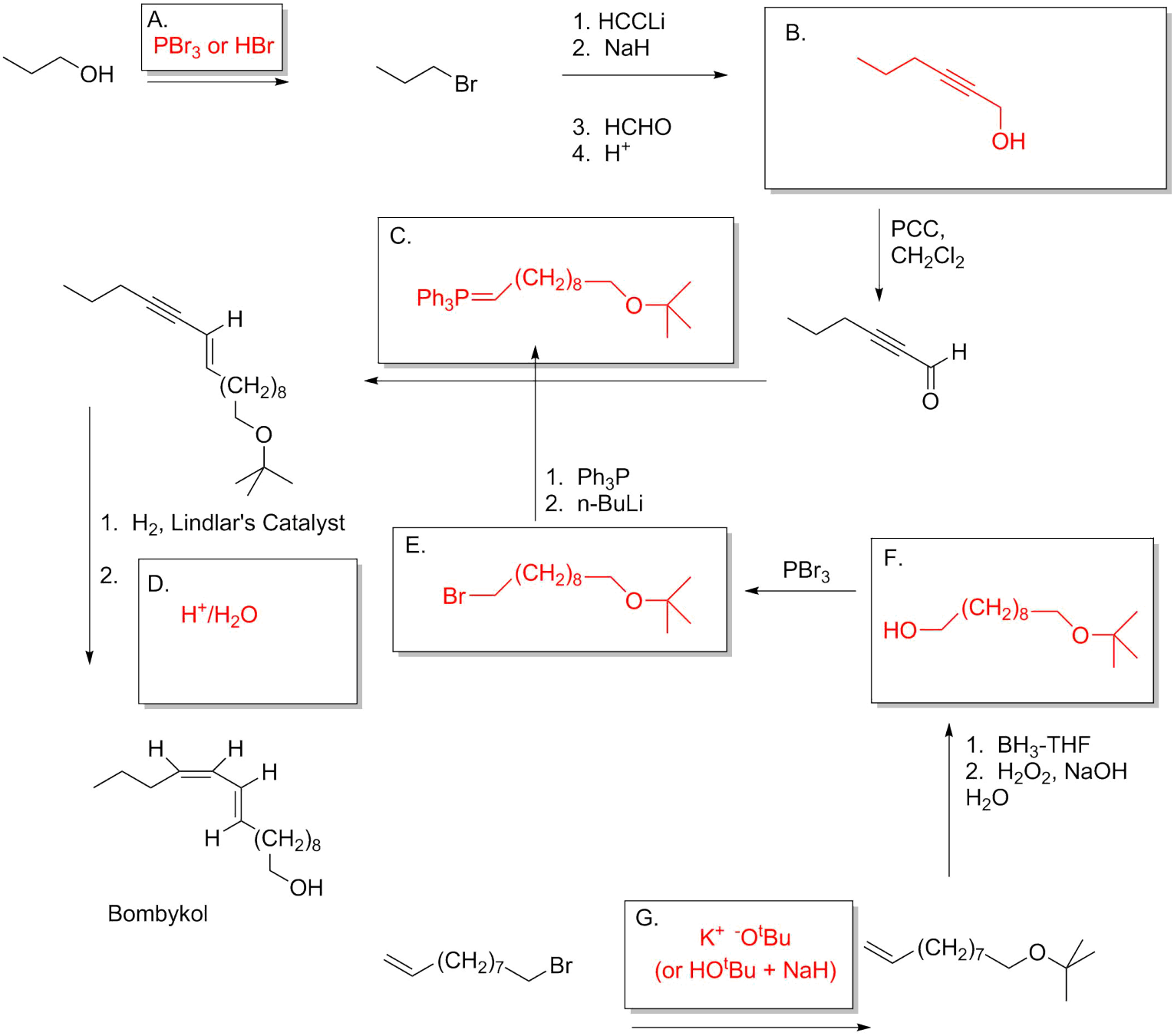
12.



Section IV. (21 points)

13. Fill in the boxes with the correct organic structure or set of reagents/conditions to complete the following multistep synthesis of bambykol, an insect hormone secreted by the silk moth.

Answers A, C, D, and G are all reagents; answers B, E and F are intermediate isolated compounds.



Section V.

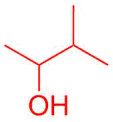
14. (14 points) *trans*-2-Butene is epoxidized with mCPBA to a product **A** which then reacts with $LiCuMe_2$ (followed by acid workup) to give a new product **B** having an IR spectrum that has a strong, broad peak between 3300-3600 cm^{-1}. Reaction of **B** with Jones' reagent gives a new compound **C** that shows the 3 spectra displayed on the following page; the mass spectrum has important peaks at m/z = 86, 71, 43 and 41.

Draw structures for **A**, **B** and **C**. Explain the reaction chemistry and/or the spectral assignment to allow assignment of partial credit.

A = 

(epoxidation product of *trans*-2-butene)

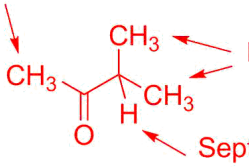
$LiCuMe_2$
(Nucleophilic ring opening followed by protonation)

B = 

O-H appears at 3300-3600 cm^{-1} in the IR spectrum

Jones' reagent oxidizes the 2° alcohol to a ketone

Singlet at
2.14 ppm

C = 

Doublet at 1.12 ppm

Septet at 2.57 ppm (next to C=O)

C=O IR stretch at 1730 cm^{-1}

C=O carbon at 212 ppm;
three alkyl carbons (41, 28, 19 ppm)

Spectra for **C** (IR, ^{1}H NMR, ^{13}C NMR):