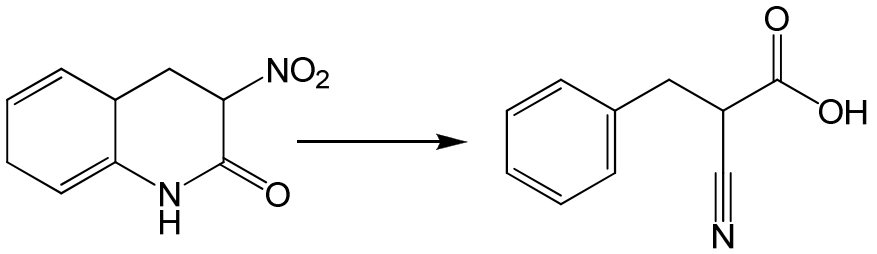
CHEM 266 – Exam-1 **Name_____Keys_____**

Fall 2016 (September 20th, 2016)

1. You have just performed the following transformation in the lab; predict the type of bonds corresponding to the major signals found in the IR spectra of both the product and the reactant. Explain how IR spectroscopy could be used to check if the transformation is successful. (7 pts)

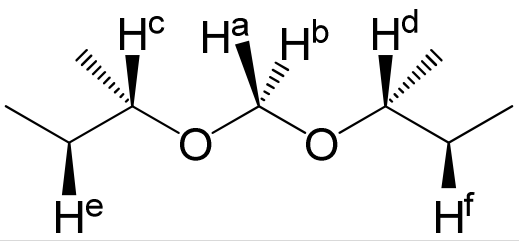


Reactant	Product
$\ddot{\upsilon}_{NH}$ = 3300 cm^{-1}	$\ddot{\upsilon}_{OH\_acid}$ = 2500 - 3300 cm^{-1}
$\ddot{\upsilon}_{CHsp2}$ = 3100 cm^{-1}	$\ddot{\upsilon}_{CHsp2}$ = 3100 cm^{-1}
$\ddot{\upsilon}_{CHsp2}$ = 2950 cm^{-1}	$\ddot{\upsilon}_{CHsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C=O}$ = 1680 cm^{-1}	$\ddot{\upsilon}_{CN}$ = 2200 cm^{-1}
$\ddot{\upsilon}_{C=C}$ = 1620 cm^{-1}	$\ddot{\upsilon}_{C=O}$ = 1700 cm^{-1}
$\ddot{\upsilon}_{NO2}$ = 1330 and 1560cm^{-1}	$\ddot{\upsilon}_{C=CAromatic}$ = 1600 - 1450 cm^{-1}
	$\ddot{\upsilon}_{CH\_Ar\_bend}$ = 600 - 800 cm^{-1}

Explain (3 pts)

The most obvious differences will be the replacement of the sharp signal of NH around 3300 cm^{-1} in the spectrum of the starting material by the broad signal of O-H acid around 2500 – 3300 cm^{-1} in the spectrum of the product. The appearance of a signal of CN around 2200 cm^{-1} in the spectrum of the product (not present in that of the starting material) will also be noticeable. Although the signal of NO_2 from the starting material will also disappear, it might or might not be easy to notice due to the fact that it appears in the fingerprint area.

2. State the relationship between the protons indicated in the structure below (as: homotopic, enantiotopic, diastereotopic, or unrelated). (2 x 4 = 8 pts)



H^a and H^b **Equivalent**

H^c and H^d **Enantiotopic**

H^e and H^f **Enantiotopic**

H^c and H^f **Unrelated**

3. A 900 MHz spectrometer records protons that absorb at 7.84 ppm, 6.96 ppm, 5.54 ppm, 2.78 ppm and 1.15 ppm. (10 pts)

(a) How far downfield (in hertz) from TMS would these protons absorb? (5 pts)

$7.84 \times 10^{-6} \times 900 \times 10^{6}$ Hz = 7056 Hz

$6.96 \times 10^{-6} \times 900 \times 10^{6}$ Hz = 6264 Hz

$5.54 \times 10^{-6} \times 900 \times 10^{6}$ Hz = 4986 Hz

$2.78 \times 10^{-6} \times 900 \times 10^{6}$ Hz = 2502 Hz

$1.15 \times 10^{-6} \times 900 \times 10^{6}$ Hz = 1035 Hz

(b) If the spectrum was recorded on a 400 MHz spectrometer, How far downfield (in hertz) from TMS would these protons absorb? (5 pts)

Regardless of the instrument, the chemical shifts are the same.

$7.84 \times 10^{-6} \times 400 \times 10^{6}$ Hz = 3136 Hz

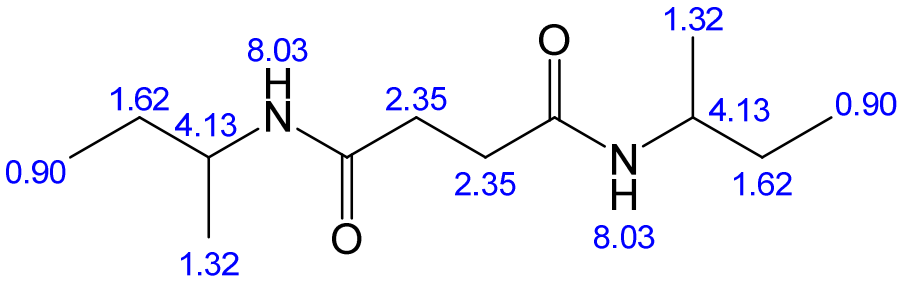
$6.96 \times 10^{-6} \times 400 \times 10^{6}$ Hz = 2784 Hz

$5.54 \times 10^{-6} \times 400 \times 10^{6}$ Hz = 2216 Hz

$2.78 \times 10^{-6} \times 400 \times 10^{6}$ Hz = 1112 Hz

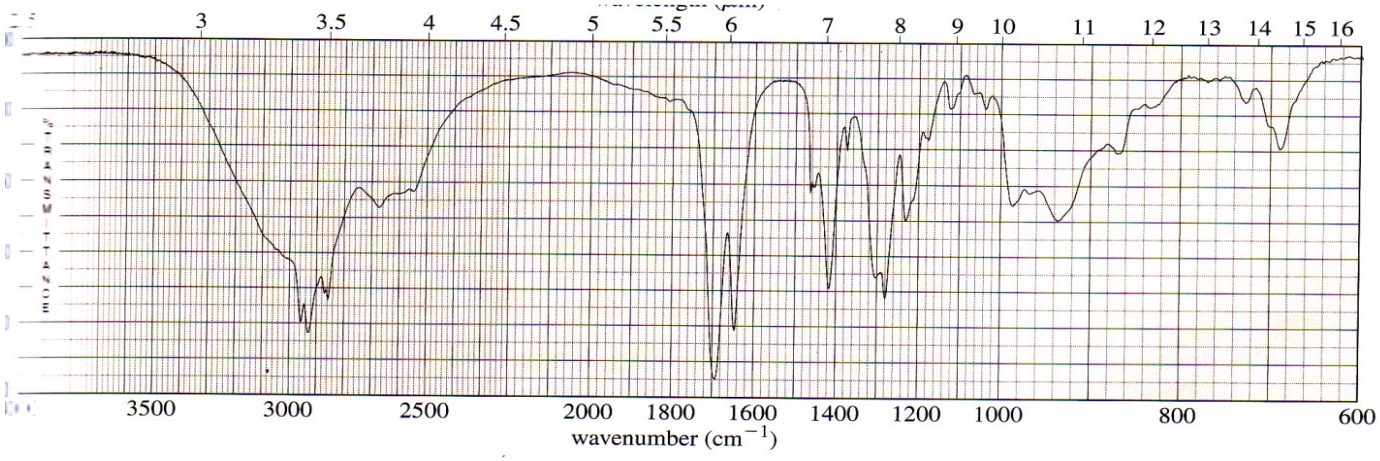
$1.15 \times 10^{-6} \times 400 \times 10^{6}$ Hz = 460 Hz

4. Predict the number of signals expected, their splitting, their relative area and their relative intensity in the ^{1}H-NMR spectrum of the following compound. (6 pts)



δ(ppm): 0.9 (6H, t), 1.32 (6H, d), 1.62 (4H, m or quintet), 2.35 (4H, s), 4.13 (2H, m), 8.03 (2H, brs)

5. (a) Identify the major signals and the corresponding bonds vibration present in the compound having the following IR spectrum; Molecular formula **$C_{11}H_{15}NO_2$** (8 pts)



$\ddot{\upsilon}_{NH}$ = 3300 cm^{-1}

$\ddot{\upsilon}_{OH\_acid}$ = 2500 - 3300 cm^{-1}

$\ddot{\upsilon}_{CHsp2}$ = 3100 cm^{-1}

$\ddot{\upsilon}_{CHsp3}$ = 2910 cm^{-1}

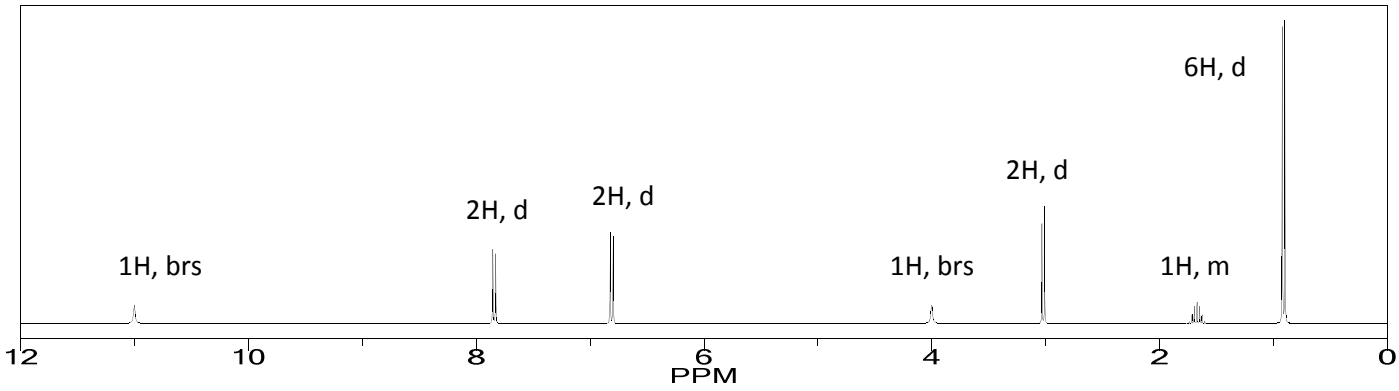
$\ddot{\upsilon}_{C=O}$ = 1700 cm^{-1}

$\ddot{\upsilon}_{C=C}$ = 145 - 1600 cm^{-1}

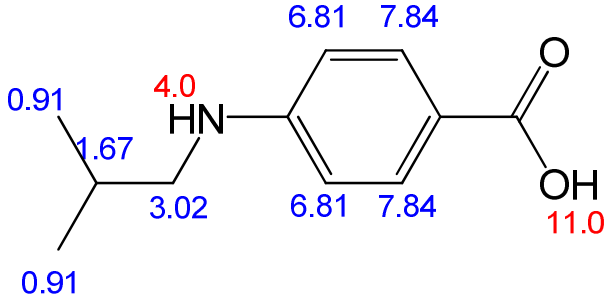
$\ddot{\upsilon}_{C-N}$ = 1200 cm^{-1}

$\ddot{\upsilon}_{CH\_bending}$ = 1200 cm^{-1}

(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer.



Structure (4 pts)

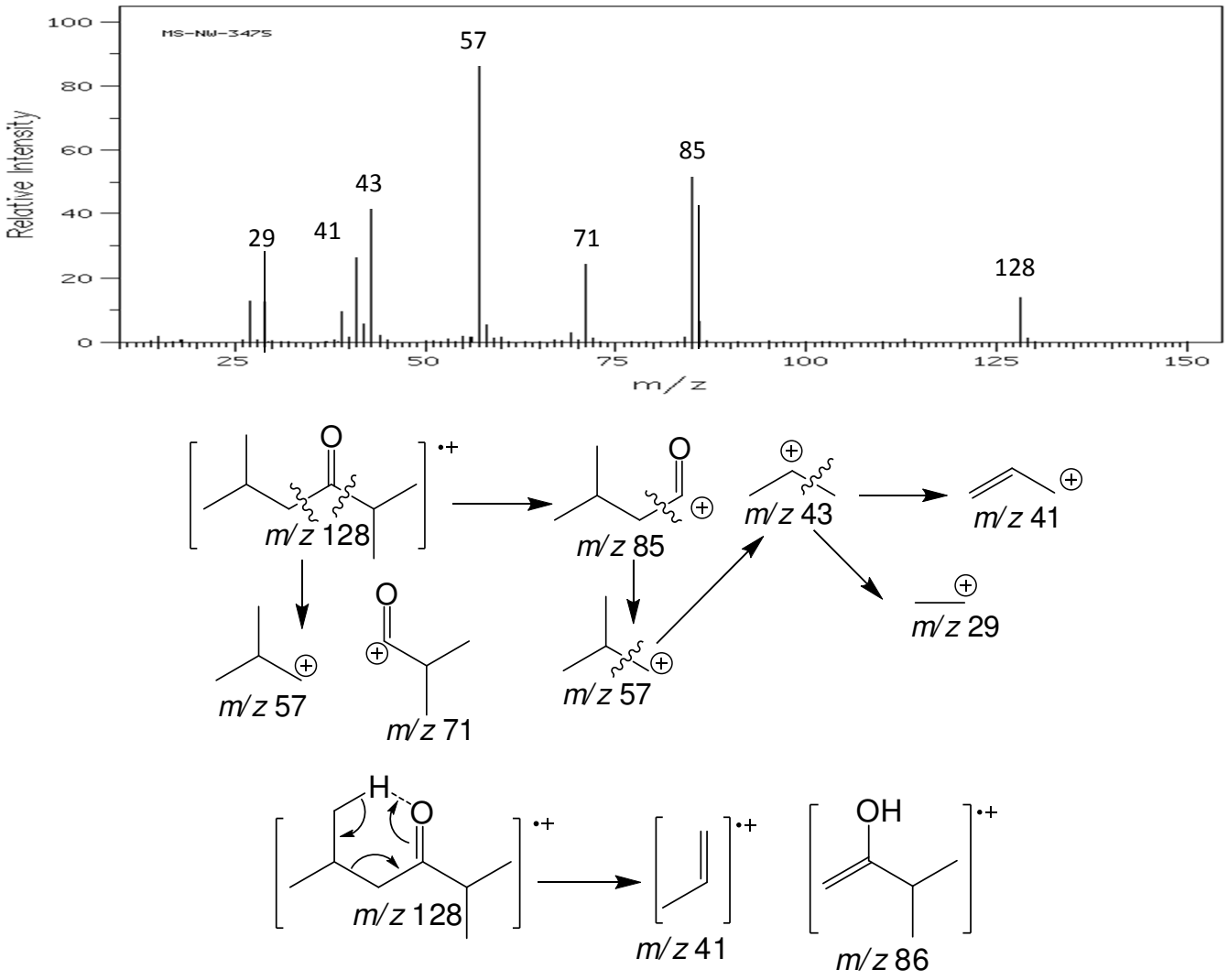


Explain (5 pts)

nI = 11+1 – 15/2 + ½ = 5 element of insaturation

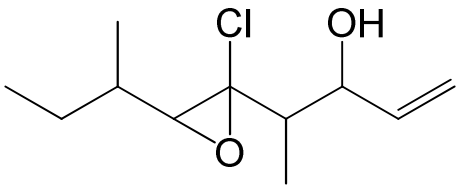
The IR indicates the presence of an aromatic ring and a carboxylic acid that account for the observed degree of insaturation. The NMR spectrum shows a broad singlet at 11 ppm attributable to the H of the carboxylic acid, 2 doublets of 2H corresponding to a para-disubstituted aromatic system. The same spectrum shows a doublet of 2H, a multiplet of 1H and a doublet of 6H all corresponding to a CH_2 connected to a CH which is connected to $2CH_3$. This corresponds to an isobutyl group. The fact that the CH_2 is so deshielded and the some protons of the aromatic ring are very shielded (2H, d at 6.81 ppm) suggest that the NH (broad singlet at 4 ppm) is connect to the aromatic ring and to the CH_2 of the isobutyl. The other side of the para-disubstituted aromatic ring is connected to the carboxylic acid, leading to the above chemical structure.

6. The mass spectrum showed below is that of octan-2-one (see structure). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 128, 86, 85, 71, 57, 43, 41 and 29 (you must show the fragmentation pattern to receive full credit) (7 pts).



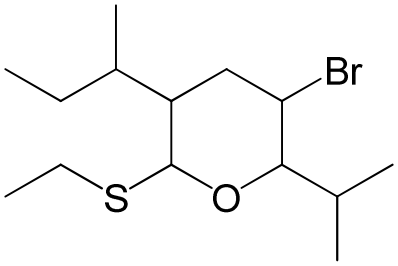
7. Name the following compounds (3 x 4 = 12 pts)

(a)



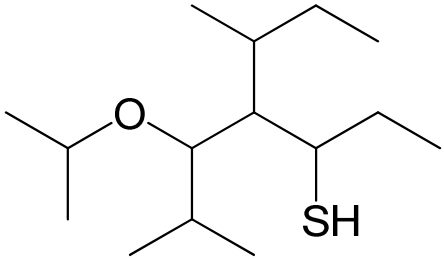
5-chloro-5,6-epoxy-4,7-dimethylnon-1-en-3-ol

(b)



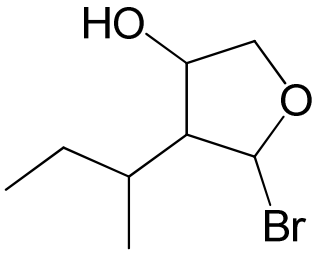
5-bromo-3-sec-butyl-2-ethylthio-6-isopropyloxane

(c)



4-sec-butyl-5-isopropoxy-6-methylheptane-3-thiol

(d)

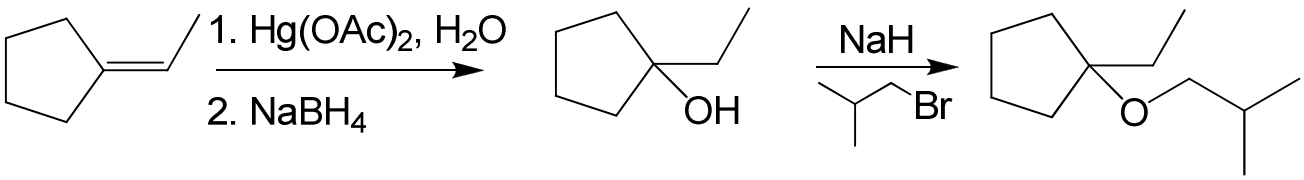


5-bromo-4-sec-butyltetrahydrofuran-3-ol

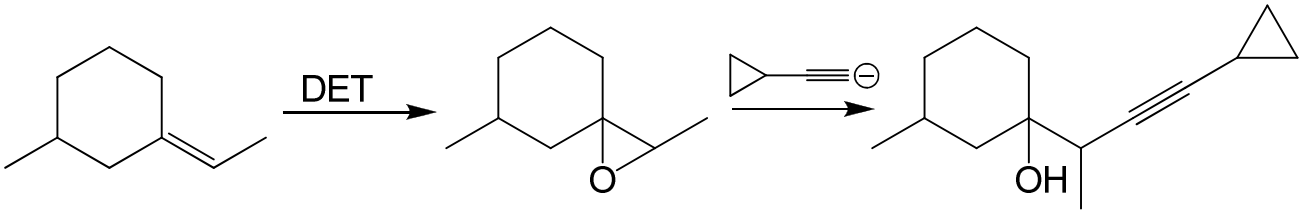
Or 5-bromo-4-sec-butyloxolan-3-ol

8. Predict the major product(s) expected from the following reaction sequences (3.5 x 6 = 21 pts)

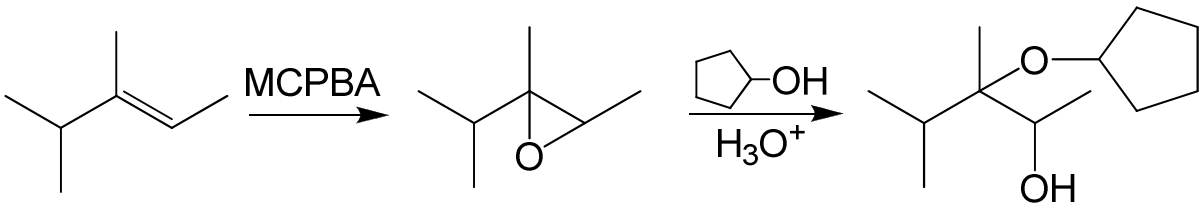
(a)



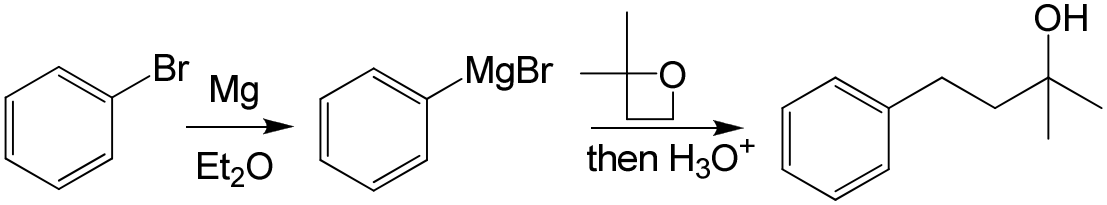
(b)



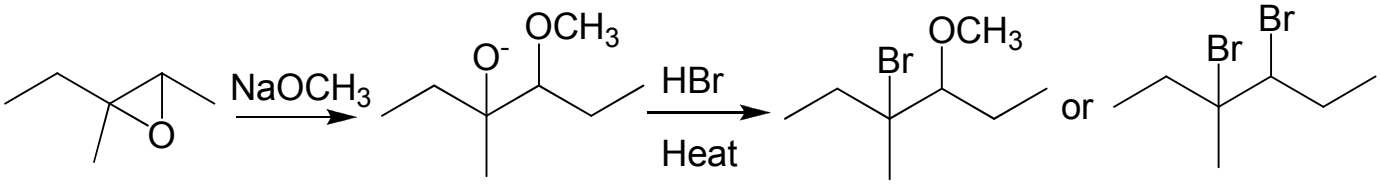
(c)



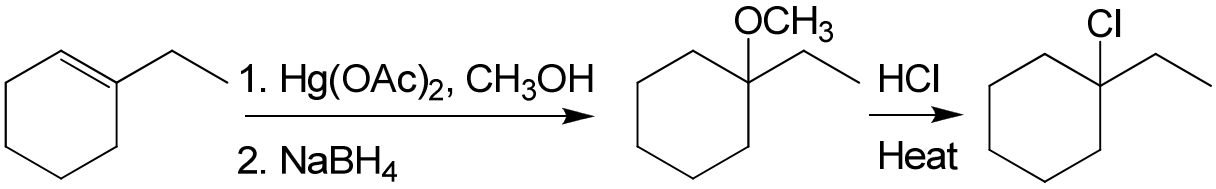
(d)



(e)

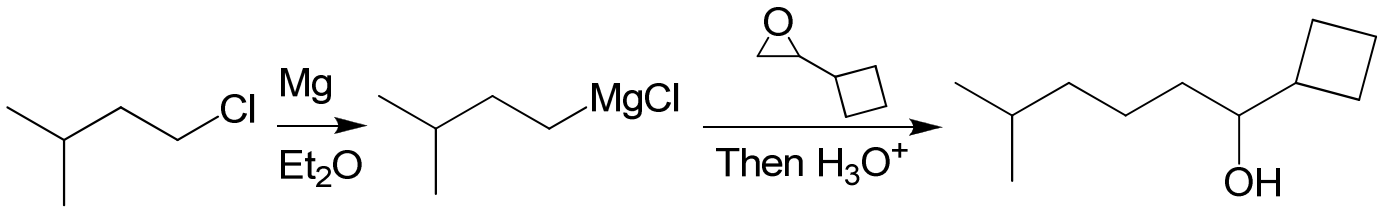


(f)

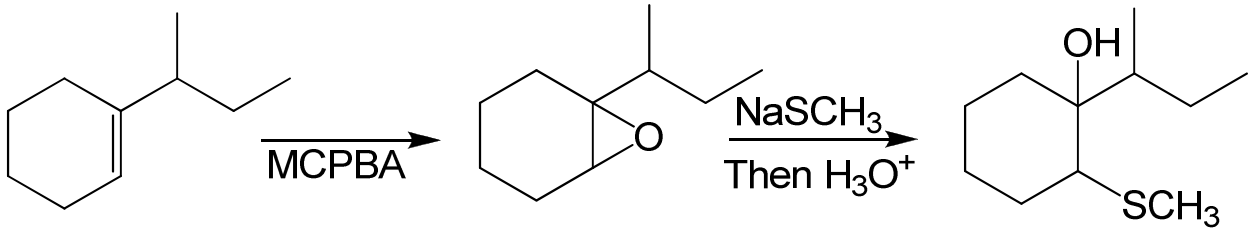


9. Show how you would synthesize each of the following compounds from the given starting material(s). You must draw keys intermediates to receive full credit (3 x 3 = 9 pts).

(a)



(b)



(c)