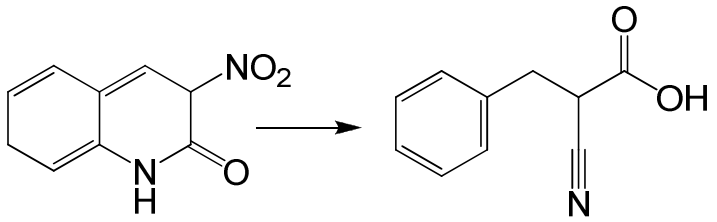
CHEM 266 – Exam-1 **Name_____Keys_____**

Spring 2018 (February 28th, 2018)

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

$\bar{\upsilon}_{N-H}$ = 3350 cm^{-1}

$\bar{\upsilon}_{C-Hsp2}$ = 3050 cm^{-1}

$\bar{\upsilon}_{C-Hsp3}$ = 2980 cm^{-1}

$\bar{\upsilon}_{C=O}$ = 1685 cm^{-1}

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

$\bar{\upsilon}_{NO2}$ = 1350 and 1510 cm^{-1}

Product

$\bar{\upsilon}_{O-H\_acid}$ = 2550 - 3500 cm^{-1}

$\bar{\upsilon}_{C-Hsp2}$ = 3100 cm^{-1}

$\bar{\upsilon}_{C-Hsp3}$ = 2950 cm^{-1}

$\bar{\upsilon}_{CN}$ = 2250 cm^{-1}

$\bar{\upsilon}_{C=O}$ = 1720 cm^{-1}

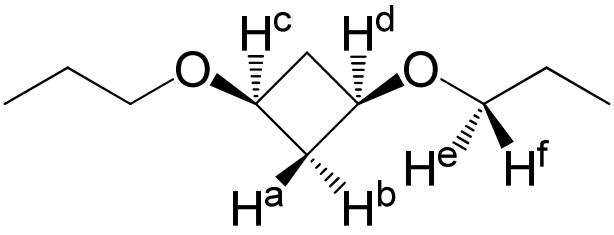
$\bar{\upsilon}_{C=C\_Ar}$ = 1600, 1450 cm^{-1}

$\bar{\upsilon}_{C-H\_bend}$ = 650 cm^{-1}

Explain (3 pts)

Both the starting material and the product will show a signal for CHsp^2 and CHsp^3, that will also show signals for C=C conjugated systems as well as a signal for C=O. However, the product will show in addition to the signal at 1600 cm^{-1}, some signal around 1450 cm^{-1} for C=C. Furthermore, the C=O signal in the starting material will have a smaller wave number (1685 cm^{-1}) than that in the product (1720 cm^{-1})due to the resonance. There will be some differences in the finger print area as well, as the NO_2 signals in the starting material's spectrum is replaced by the bending of CH aromatic in the product. However, the most obvious changes will be the replacement of a sharp small signal of the NH bond (3350 cm^{-1}), by the broad signal of OH of acids (2550 – 3500 cm^{-1}), as well as the appearance of the signal of CN (2250 cm^{-1}) in the IR of the product.

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



H^a and H^b Homotopic

H^c and H^d Homotopic

H^e and H^f Enantiotopic

H^c and H^f Unrelated

3. A 600 MHz spectrometer records protons that absorb at 8.02 ppm, 6.87 ppm, 5.33 ppm and 3.78 ppm. (10 pts)

(a) How far downfield (in hertz) from TMS would these protons absorb? (4 pts)

δ(ppm) = ν_s / ν_M meaning the ν_s = δ(ppm) x ν_M

ν_1 = 8.02 x 10^{-6} x 600 x 10^6 Hz = 4812 Hz

ν_2 = 6.87 x 10^{-6} x 600 x 10^6 Hz = 4122 Hz

ν_3 = 5.33 x 10^{-6} x 600 x 10^6 Hz = 3198 Hz

ν_4 = 3.78 x 10^{-6} x 600 x 10^6 Hz = 2268 Hz

(b) If the spectrum was recorded on a 200 MHz spectrometer, what will be the chemical shifts (in ppm) for the signal above listed (question a)? (2 pts)

The chemical shifts will be the same:

δ_1 = 8.02 ppm, δ_2 = 6.87 ppm, δ_3 = 5.33 ppm and δ_4 = 3.78 ppm

(c) At 200 MHz, how far downfield (in hertz) from TMS would these protons absorb? (4 pts)

δ(ppm) = ν_s / ν_M meaning the ν_s = δ(ppm) x ν_M

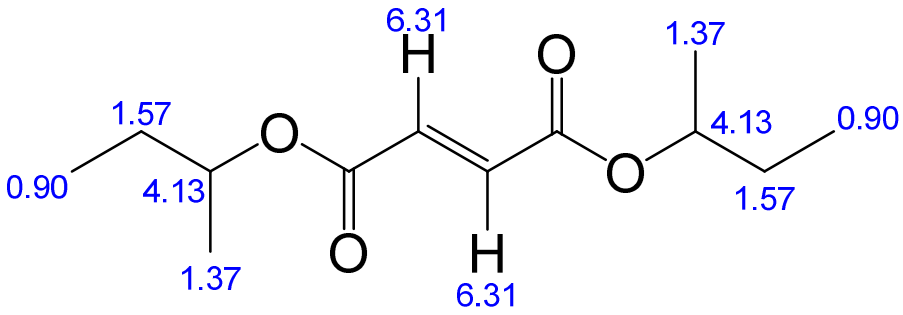
ν_1 = 8.02 x 10^{-6} x 200 x 10^6 Hz = 1604 Hz

ν_2 = 6.87 x 10^{-6} x 200 x 10^6 Hz = 1374 Hz

ν_3 = 5.33 x 10^{-6} x 200 x 10^6 Hz = 1066 Hz

ν_4 = 3.78 x 10^{-6} x 200 x 10^6 Hz = 756 Hz

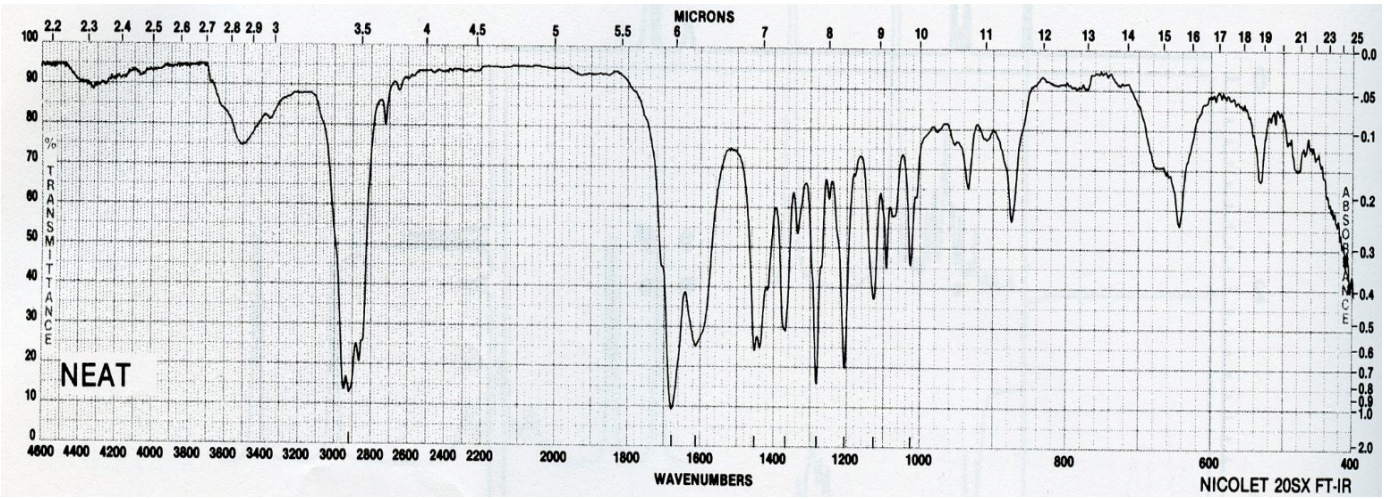
4. Predict the signals expected, their chemical shifts, their splitting, and their relative intensity in the ^{1}H-NMR spectrum of the following compound. (5 pts)



δ(ppm) = 0.90 (3H, triplet), 1.37 (3H, doublet), 1.57 (2H, quintet), 4.13 (1H, multiplet), 6.31 (1H, singlet)

One can also multiply the number of protons by 2.

5. (a) Identify the major signals and the corresponding bonds vibration present in the compound having the following IR spectrum; Molecular formula **$C_{13}H_{19}NO_2$** (8 pts)



$\bar{\upsilon}_{N-H}$ = 3350 cm^{-1}

$\bar{\upsilon}_{C-Hsp3}$ = 2980 cm^{-1}

$\bar{\upsilon}_{C=C\_Ar}$ = 1600, 1450 cm^{-1}

$\bar{\upsilon}_{C-N}$ = 1100 cm^{-1}

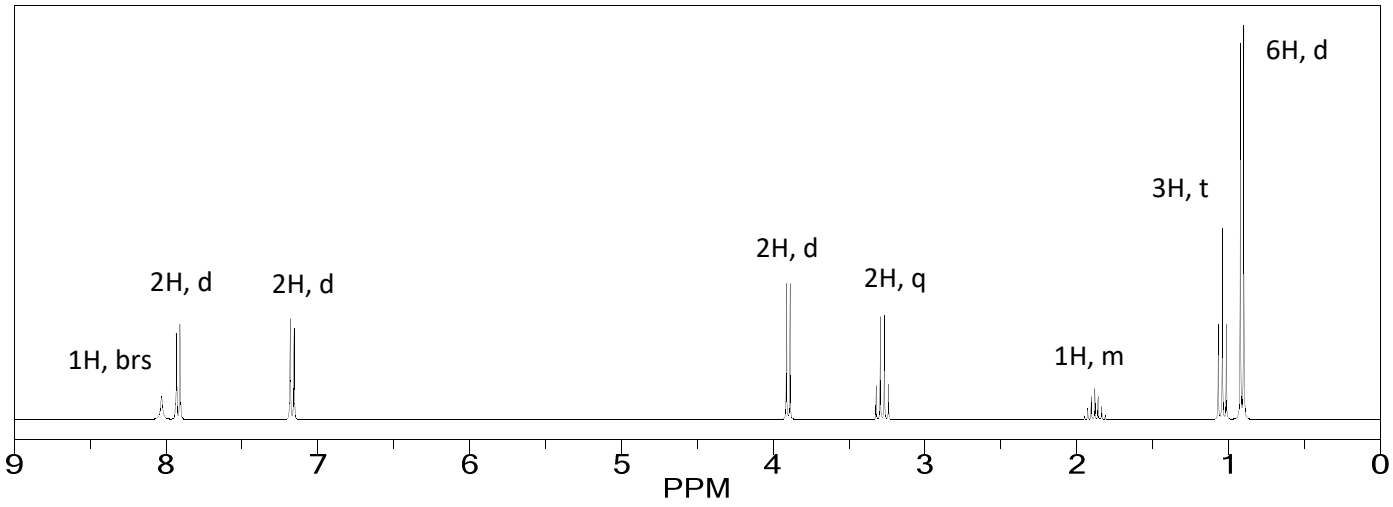
$\bar{\upsilon}_{C-Hsp2}$ = 3050 cm^{-1}

$\bar{\upsilon}_{C=O}$ = 1685 cm^{-1}

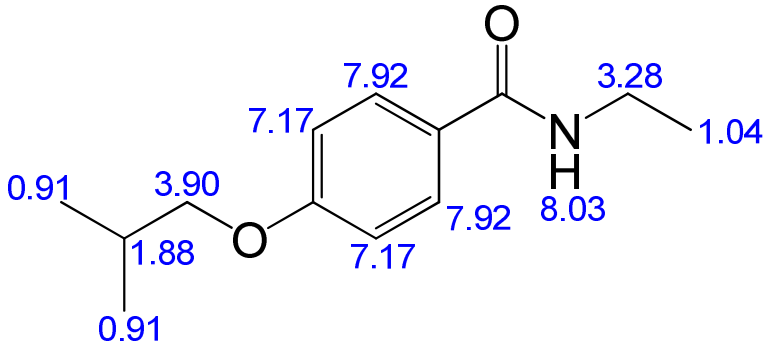
$\bar{\upsilon}_{C-O}$ = 1050 cm^{-1}

$\bar{\upsilon}_{C-H\_bend}$ = 620 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)



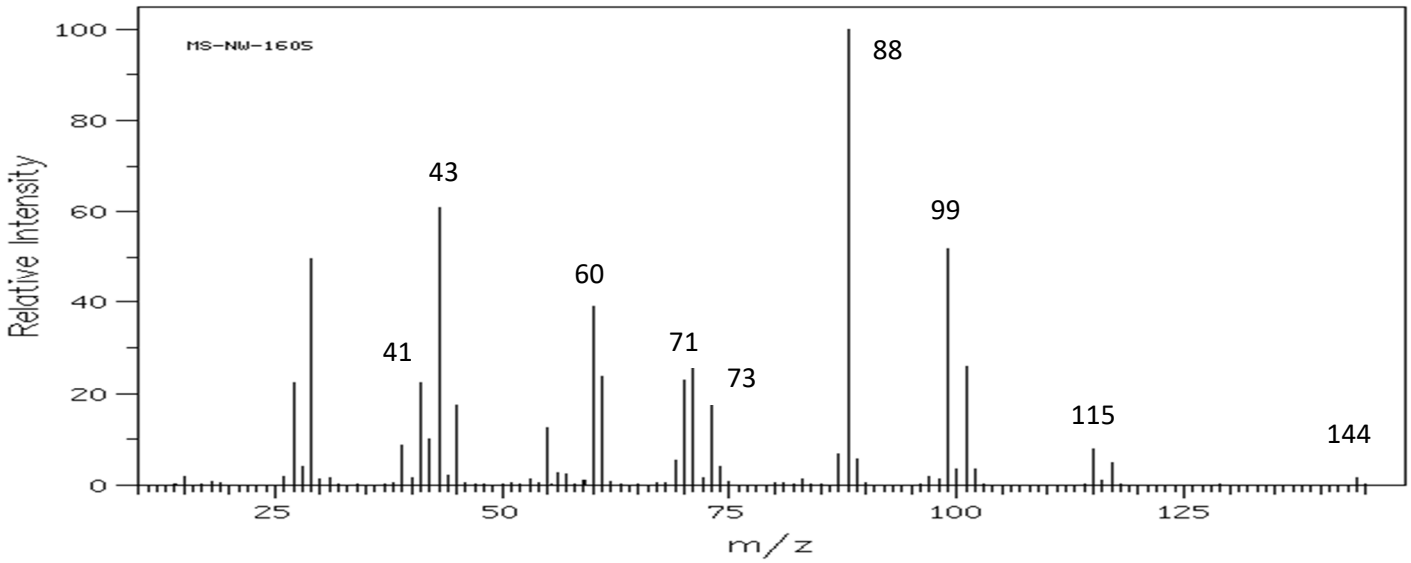
Explain (4 pts)

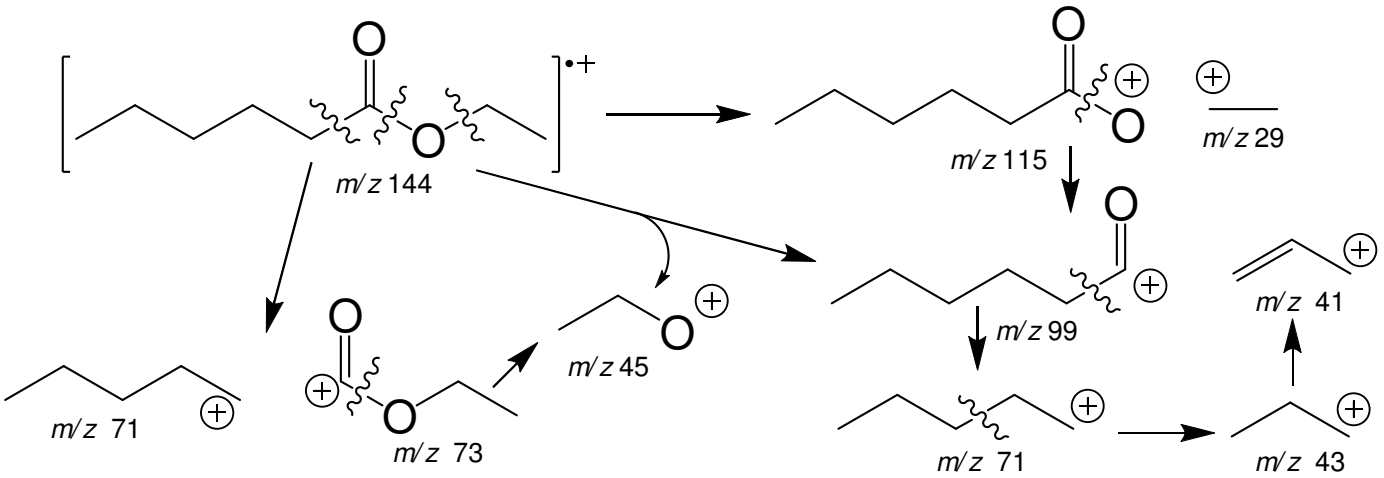
$C_{13}H_{19}NO_2$ HDI = 13 + 1 - ½ (19) + ½ = 5 elements of insaturations.

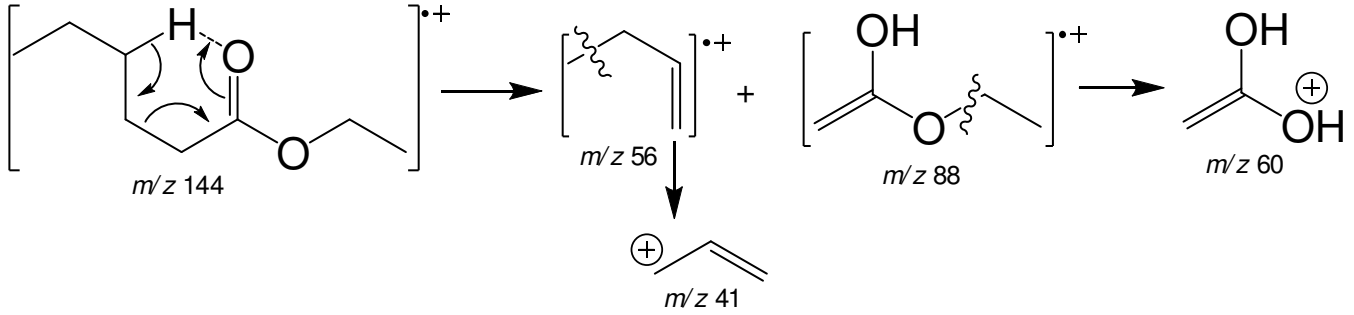
The IR spectrum indicates that the molecule contains an aromatic ring, a conjugated carbonyl and NH that suggests the presence of an amide functional group.

The ^{1}H-NMR spectrum shows a broad singlet at 8.03 ppm corresponding to the H of the nitrogen of the amide. The two doublet of 2H in the aromatic area is indicative of a *para*-disubstituted aromatic ring. The doublet of 2H around 3.90 ppm corresponds to a CH_2 attached to an oxygen atom as well as to a CH. The CH is also attached to 2 CH_3 groups as indicated by the multiplet of 1H at 1.88 ppm and a doublet of 6H around 0.91 ppm. This correspond to an isopropoxy group. The remaining of the signals are a quartet of 2H around 3.28 ppm and the triplet of 3H at 1.04 ppm corresponding to an ethyl group attached to the nitrogen of the amide. So, the isopropoxy group and the N-ethyl amide group are attached to the two sides of the para-disubstituted aromatic system, resulting in the above structure.

6. The mass spectrum showed below is that of ethyl hexanoate (see structure). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 144, 115, 99, 88, 73, 71, 60, 43 and 41 (you must show the fragmentation pattern to receive full credit) (8 pts).

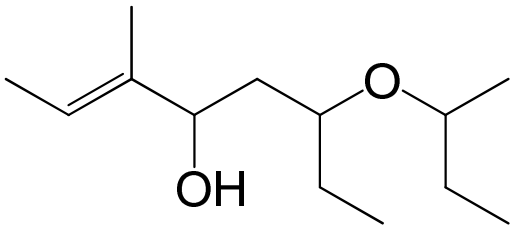






7. Name the following compounds (3 x 4 = 12 pts)

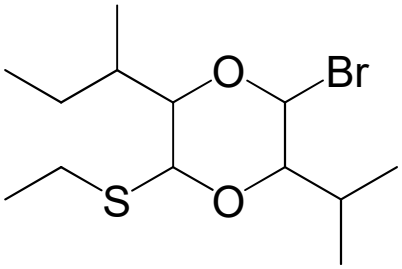
(a)



6-sec-butoxy-3-methyloct-2-en-4-ol

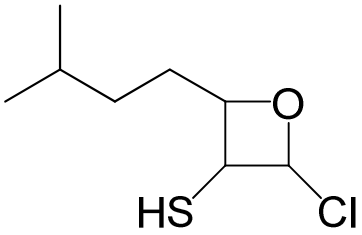
Or 3-methyl-6-(1-methylpropyloxy) oct-2-en-4-ol

(b)



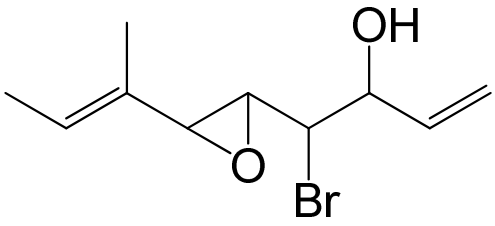
2-bromo-6-sec-butyl-5-(ethylthio)-3-isopropyl-1,4-dioxane

(c)



2-chloro-4-isopentyloxetane-3-thiol

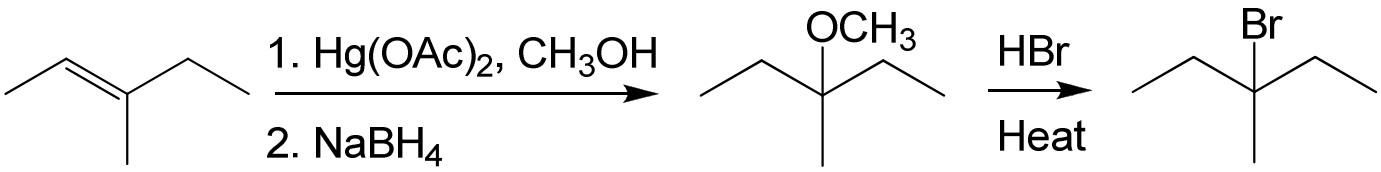
(d)



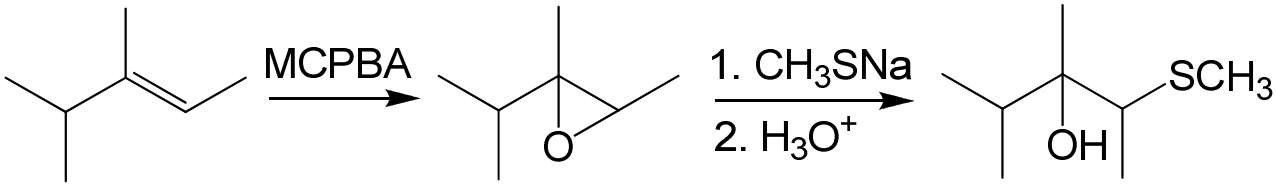
4-bromo-5,6-epoxy-7-methylnona-1,7-dien-3-ol

8. Predict the major product(s) expected from the following reaction sequences (3 x 6 = 18 pts)

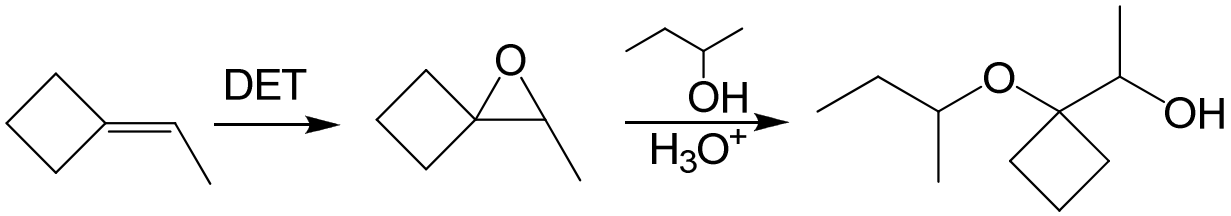
(a)



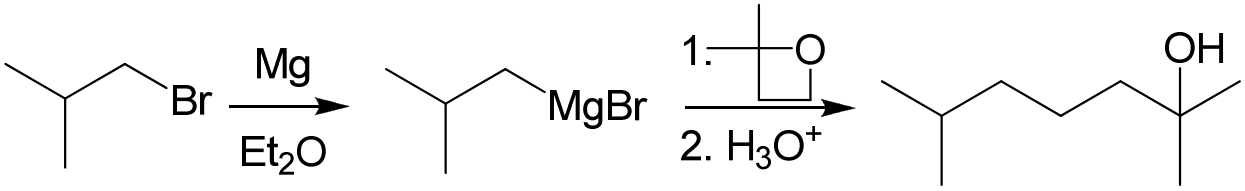
(b)



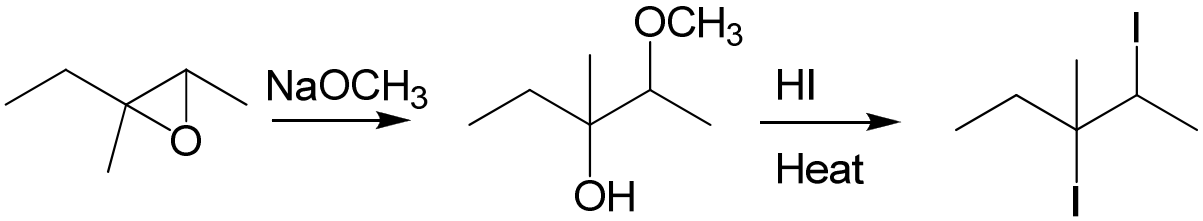
(c)



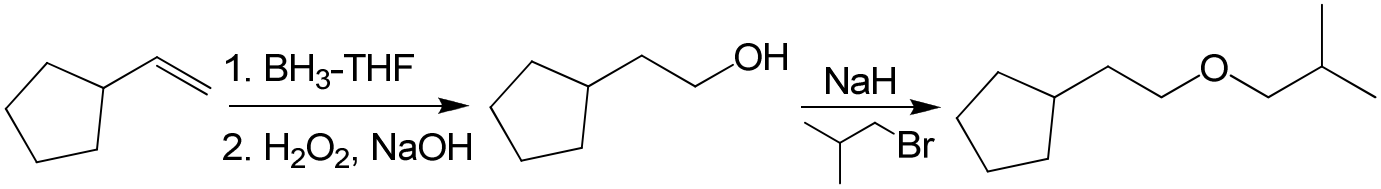
(d)



(e)

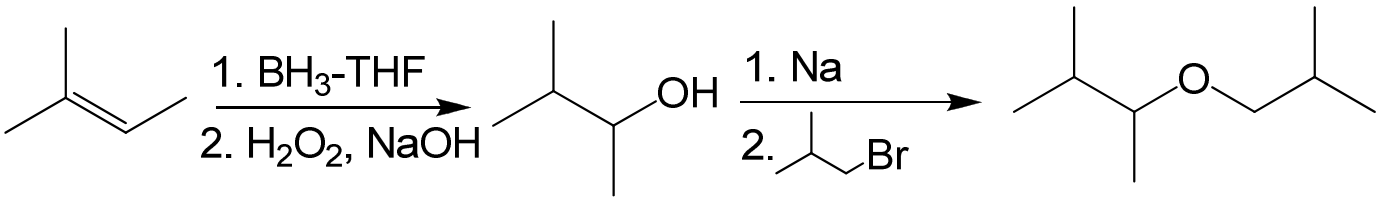


(f)

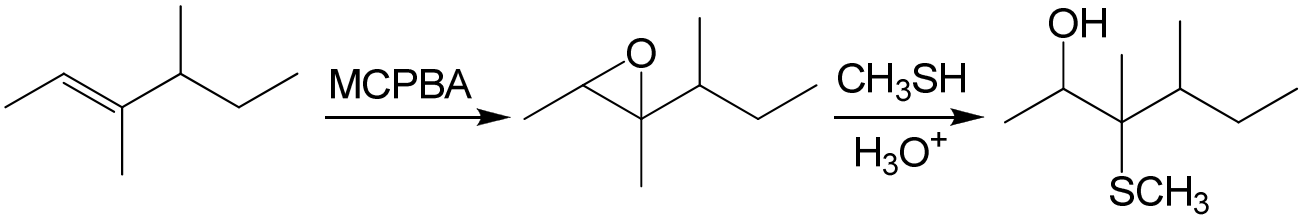


9. Show how you would synthesize each of the following compounds from the given starting material(s). **You must show all the intermediates to receive full credit** (3 x 3 = 9 pts)

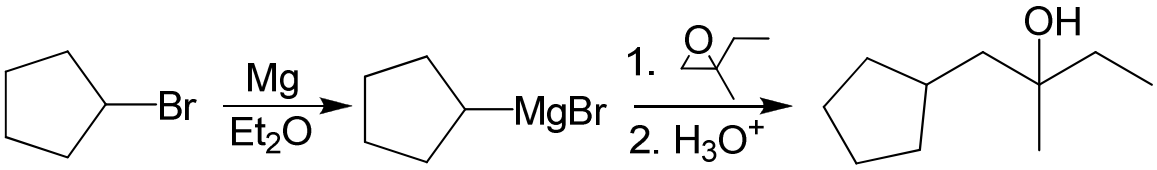
(a)



(b)



(c)



10. Propose a mechanism consistent with the following reaction (**you must show all the intermediates, and arrows indicating the electron flow to receive full credit**) (4 pts)