CHEM 266 – Exam-1 **Name_____Keys_____**

(September 21st, 2017)

1. A 400 MHz spectrometer records protons that absorb at 3675, 3070, 2325 and 1880 Hz downfield from TMS. (8 pts)

(a) Determine the chemical shifts of each of these signals in ppm. (4 pts)

δ(ppm) = ($\nu_{sample} - \nu_{reference}$) /$\nu_{machine}$

δ_1 = 3675 Hz : 400 x 10^6 Hz = 9.19 x 10^{-6} = 9.19 ppm

δ_2 = 3070 Hz : 400 x 10^6 Hz = 7.68 x 10^{-6} = 7.68 ppm

δ_3 = 2325 Hz : 400 x 10^6 Hz = 5.81 x 10^{-6} = 5.81 ppm

δ_4 = 1880 Hz : 400 x 10^6 Hz = 4.70 x 10^{-6} = 4.70 ppm

(b) If the spectrum was recorded on a 60 MHz spectrometer, how far downfield (in hertz) from TMS would this proton absorb? (4 pts)

The chemical shift in ppm does not chance from a machine to another, only the frequency in Hz does.

Since : δ(ppm) = ($\nu_{sample} - \nu_{reference}$) /$\nu_{machine}$, it means that ν_{sample} = δ(ppm) x $\nu_{machine}$

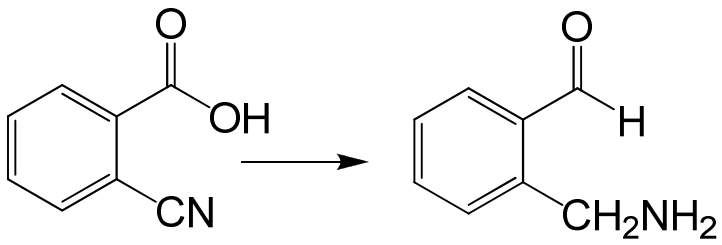
ν_1 = 9.19 x 10^{-6} x 60 x 10^6 Hz = 551.4 Hz

ν_2 = 7.68 x 10^{-6} x 60 x 10^6 Hz = 460.8 Hz

ν_3 = 5.81 x 10^{-6} x 60 x 10^6 Hz = 348.6 Hz

ν_4 = 4.70 x 10^{-6} x 60 x 10^6 Hz = 282 Hz

2. 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 reaction worked. (8 pts)



Starting material

$\bar{\upsilon}_{O\text{-}H\_Acid}$ = 2500 – 3300 cm^{-1}

$\bar{\upsilon}_{C\text{-}H\_Ar}$ = 3087 cm^{-1}

$\bar{\upsilon}_{CN}$ = 2135 cm^{-1}

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

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

$\bar{\upsilon}_{C\text{-}H\_Ar\_Bend}$ = 500 - 800 cm^{-1}

Product

$\bar{\upsilon}_{NH2}$ = 3300, 3200 cm^{-1}

$\bar{\upsilon}_{C\text{-}H\_Ar}$ = 3080 cm^{-1}

$\bar{\upsilon}_{C\text{-}Hsp3}$ = 2987 cm^{-1}

$\bar{\upsilon}_{C\text{-}H\_Aldehyde}$ = 2830, 2750 cm^{-1}

$\bar{\upsilon}_{C=O}$ = 1680 cm^{-1}

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

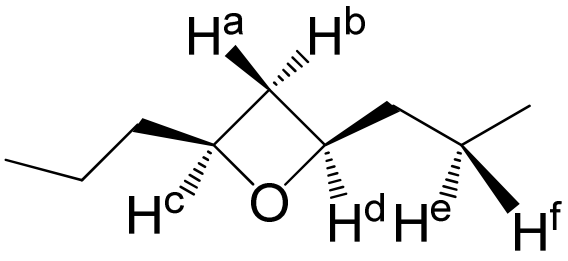
$\bar{\upsilon}_{C\text{-}N}$ = 1100 cm^{-1}

$\bar{\upsilon}_{C\text{-}H\_Ar\_Bend}$ = 500 - 800 cm^{-1}

Explain (3 pts)

The only similarities between the IR of the starting material and that of the product will be the carbonyl around 1680 cm^{-1}, the C-H aromatic around 3080 cm^{-1} and the C=C aromatic between 1450-1600 cm^{-1}. Otherwise, the broad signal of OH acid and the nitrile signal at 2135 cm^{-1} in the starting material will absent in the product, and will be replaced by the bidentate signal of NH_2 at 3300 and 3200 cm^{-1}, the signal of the $CHsp^3$ (2987 cm^{-1}) and the characteristic signal for the C-H aldehyde at 2830 and 2750 cm^{-1}. The presence of these latter signals in the IR of the product will indicate that the reaction did take place.

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



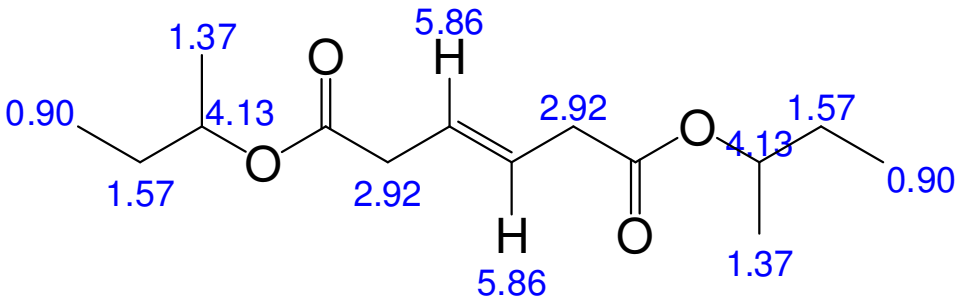
H^a and H^b are homotopic

H^c and H^d are enantiotopic

H^e and H^f are diastereotopic

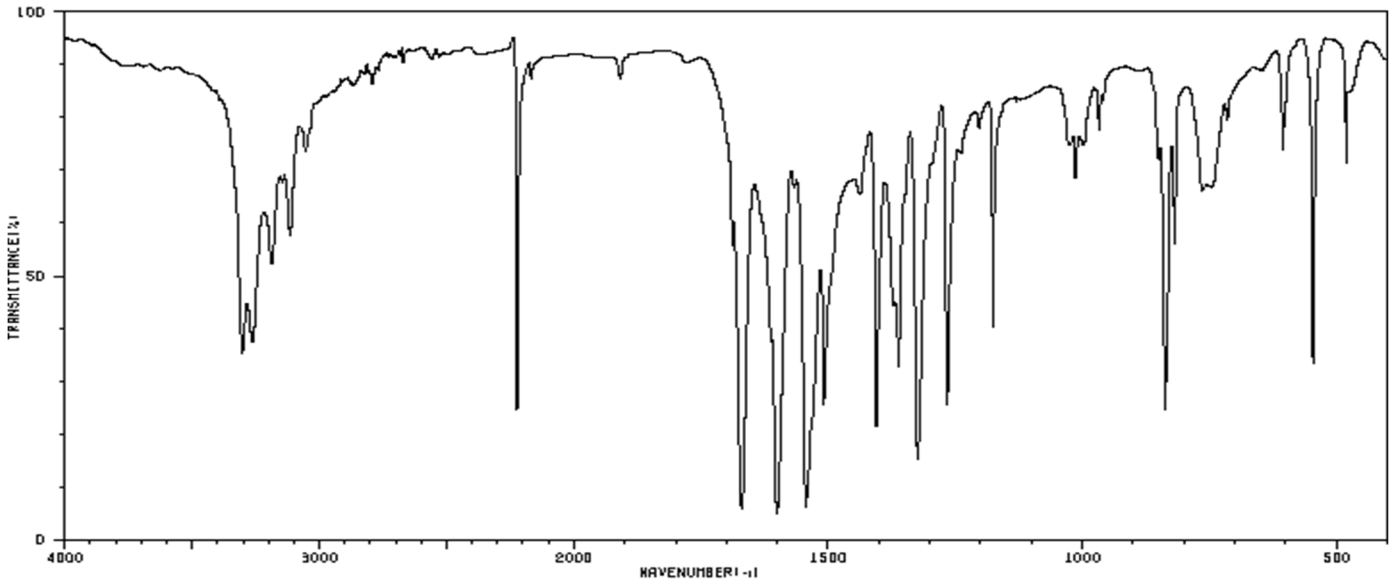
H^a and H^c are unrelated

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): 0.90 (3H, t), 1.37 (3H, d), 1.57 (2H, q*), 2.92 (2H, d), 4.13 (1H, m), 5.86 (1H, t)

5. (a) Identify the major signals and the corresponding bonds vibration present in the compound having the following IR spectrum; Molecular formula **$C_{13}H_{16}N_2O$** (7 pts)



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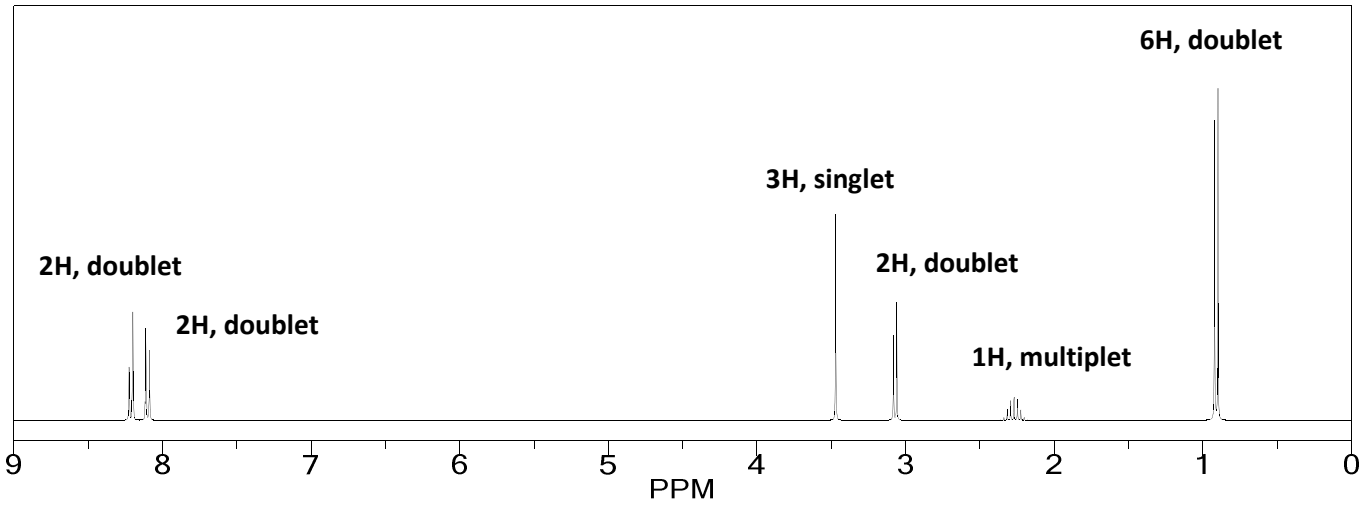
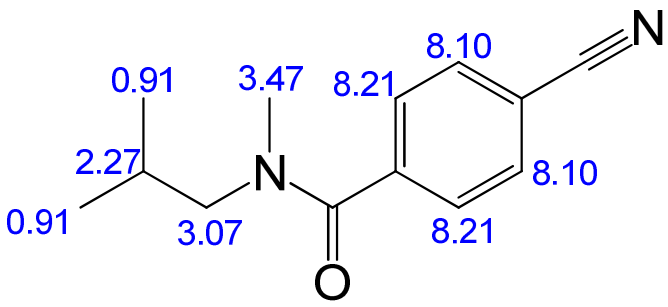
(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer.



Structure (4 pts) **REMOVED FROM THE EXAM**



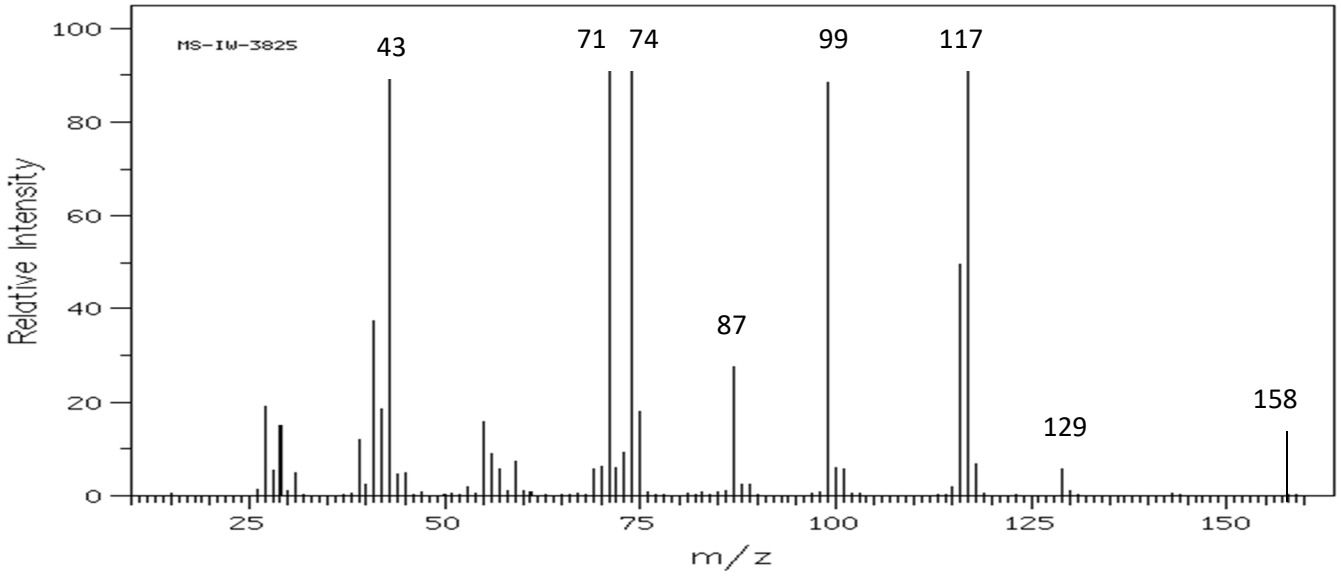
Explain (4 pts)

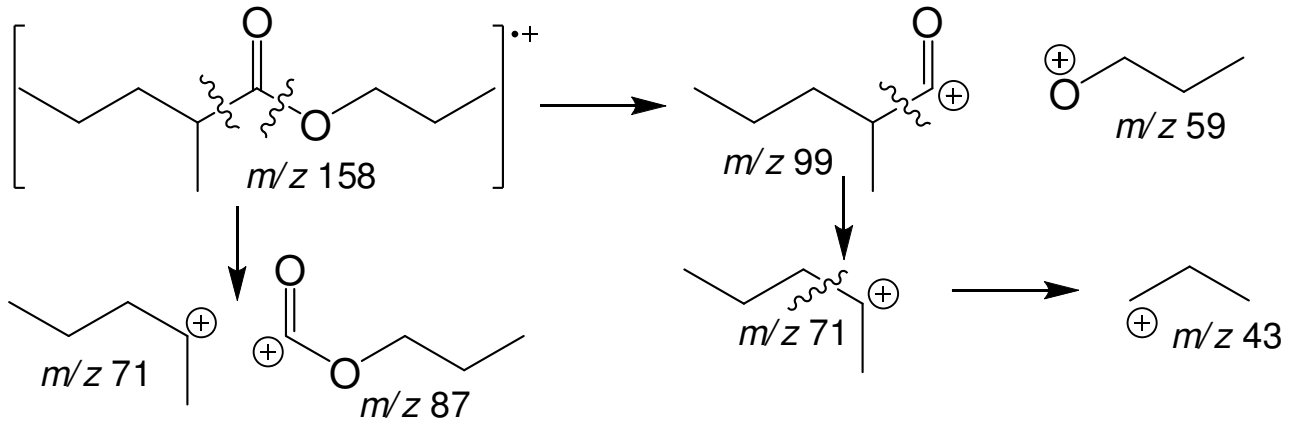
As the molecular formula of the compound is $C_{13}H_{16}N_2O$, the number of insaturation (NI) also known as hydrogen deficiency index (HDI) = 13 + 1 – ½ 16 + ½ 2 = 7 elements of insaturations.

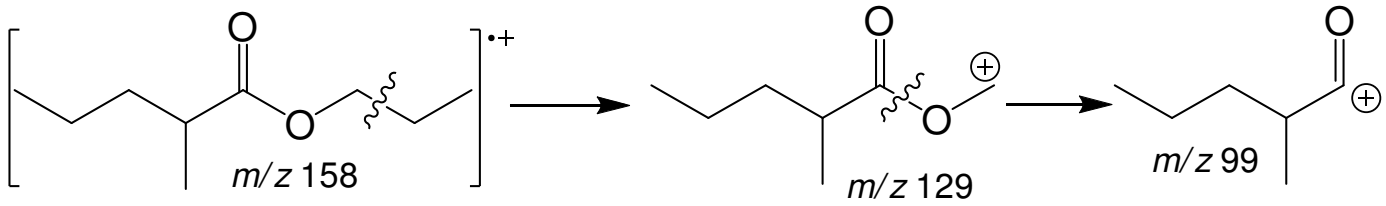
The IR spectrum has indicated that the molecule contains an aromatic ring (4 insaturations), a nitrile (2 insaturations) and a carbonyl (1 insaturation). As the wave number for the carbonyl is very low, this is indicative of a carbonyl of amide.

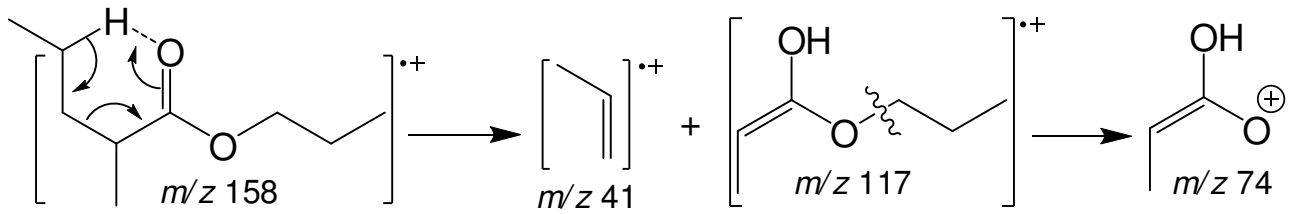
The proton NMR shows 2 doublets of 2H in the aromatic area indicative of a para-disubstituted benzene ring. Since these two signals are very deshielded, it indicates that neither the oxygen or the nitrogen atom is directly connected to the ring, instead the groups attached to the ring most be electron-withdrawing such as nitrile or the carbonyl of the amide. Since there is no signal for NH in the IR, the amide is fully substituted. This means that the deshielded 3H singlet at 4.47 ppm is attached to the nitrogen of the amide. The remaining 3 signals are 6H doublet corresponding to two CH_3 connected to the same CH, 2H doublet corresponding to CH_2 connected to a CH, and 1H multiplet corresponding to the CH connected both to the CH_2 and the two CH_3s. This part of the molecule corresponds to an isobutyl group. Since the 2H doublet signal is deshielded (3.07 ppm) it shows that this group is connected to the nitrogen of the amide, resulting in the above structure.

6. The mass spectrum showed below is that of propyl 2-methylvalerate (see structure). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 158, 129, 117, 99, 87, 74, 71 and 43 (you must show the fragmentation pattern to receive full credit) (7 pts).



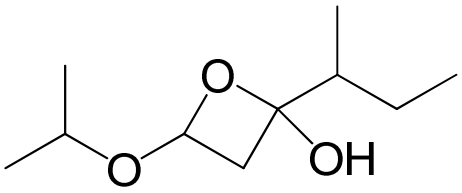






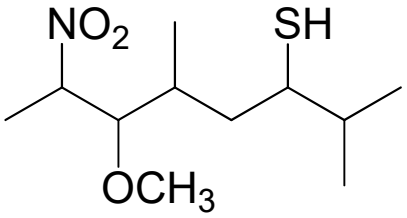
7. Name the following compounds (3 x 5 = 15 pts)

(a)



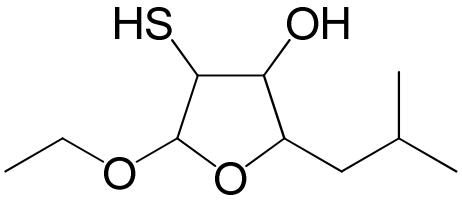
2-sec-butyl-4-isopropoxyoxetan-2-ol

(b)



6-methoxy-2,5-dimethyl-7-nitrooctane-3-thiol

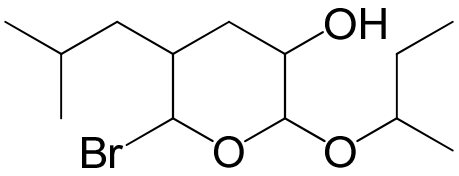
(c)



5-ethoxy-2-isobutyl-4-mercaptotetrahydrofuran-3-ol

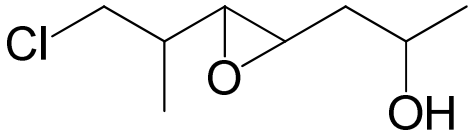
5-ethoxy-2-isobutyl-4-mercaptooxolan-3-ol

(d)



6-bromo-2-sec-butoxy-5-isobutyloxan-3-ol

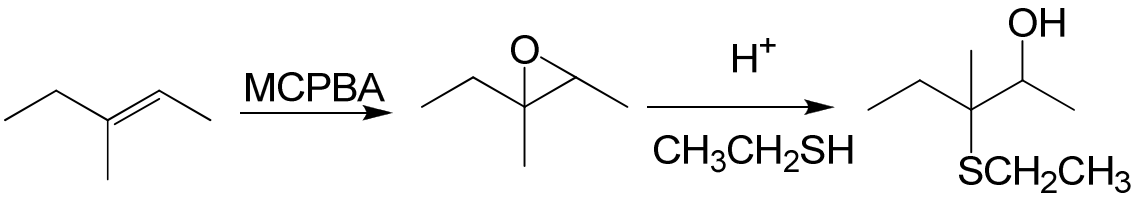
(e)



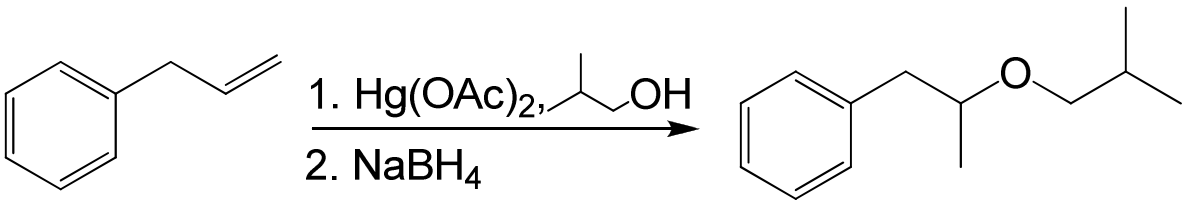
7-chloro-4,5-epoxy-6-methylheptan-2-ol

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

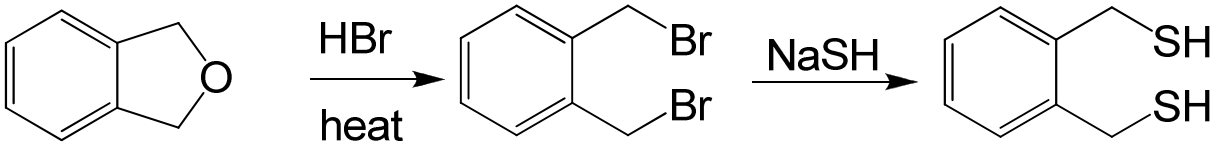
(a)



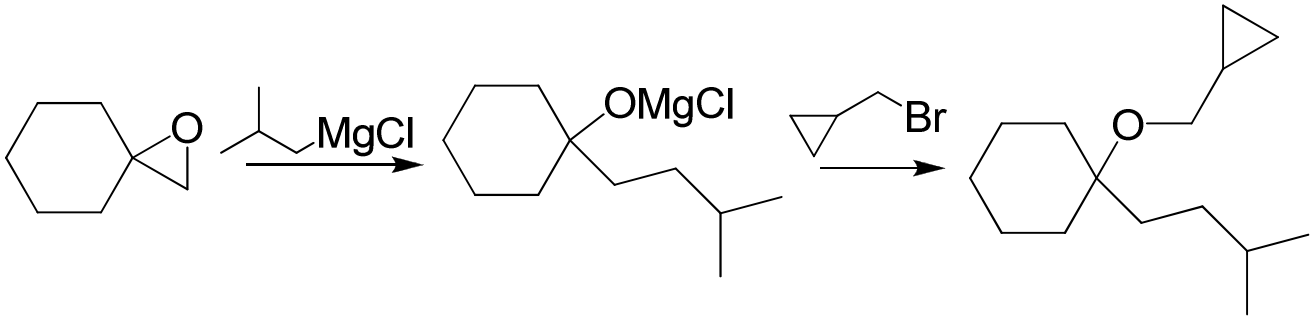
(b)



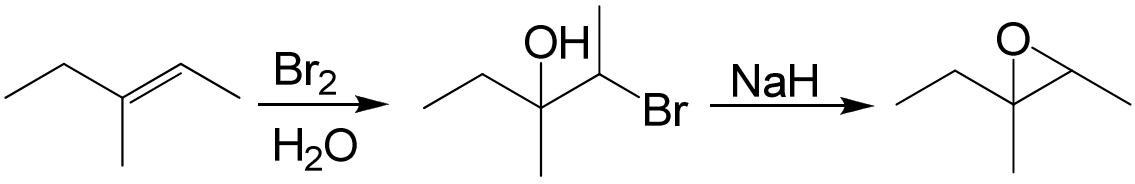
(c)



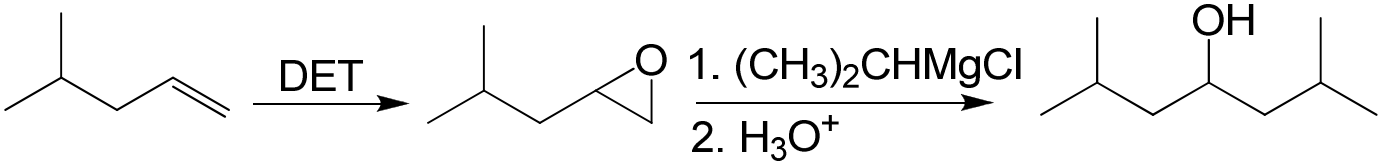
(d)



(e)

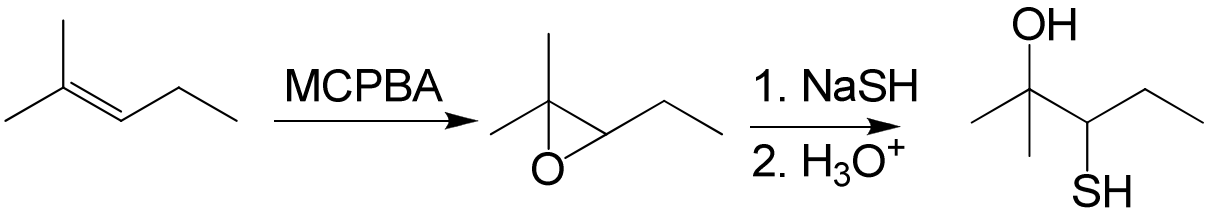


(f)

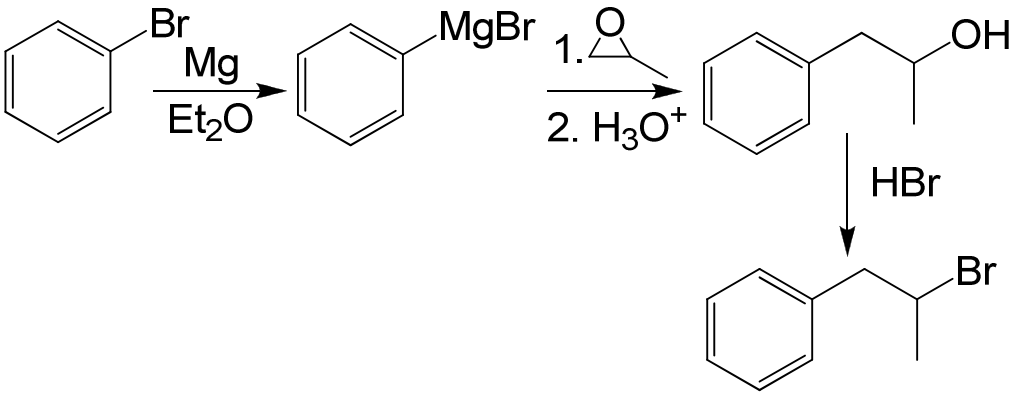


9. Show how you would synthesize each of the following compounds from the given starting material(s). You must draw keys intermediates to receive full credit (3 x 2 = 6 pts).

(a)



(b)



10. Draw a plausible mechanism for the reaction below (3 pts)