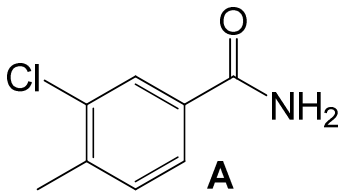
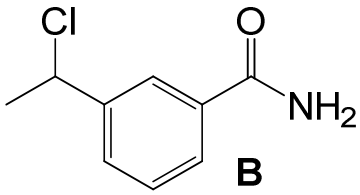
CHEM 266 - Homework 1 **Name_____Keys_____**

(Due on Wednesday, February 21, 2018 at the beginning of the class, no late return, no exam under my office's door will be accepted)

1. Can IR be used to distinguish between the following compounds? Explain your answer (2 pts)



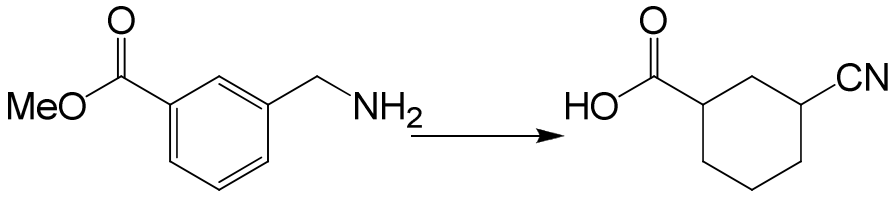
A



B

Both compounds will displayed the same signals for NH_2, (3400, 3500 cm^{-1}), $CHsp^2$ (3100 cm^{-1}), $CHsp^3$ (2950 cm^{-1}), conjugated C=O (1680 cm^{-1}) and C=C_aromatic (1600 cm^{-1}), thus it will be impossible to distinguish them by IR.

2. You have performed the reaction below in the lab. List all the signals observed in the IR spectrum of the starting material and in the IR spectrum of the product. Explain how IR can be used to tell whether the reaction took place or not.



IR vibrational signals (5 pts)

Starting material

$\bar{\upsilon}_{N-H}$ = 3350, 3400 cm^{-1}

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

$\bar{\upsilon}_{C-Hsp3}$ = 2960 cm^{-1}

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

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

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

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

$\bar{\upsilon}_{C-HAr\_bend}$ = 600 cm^{-1}

Product

$\bar{\upsilon}_{O-H}$ = 2500 – 3500 cm^{-1}

$\bar{\upsilon}_{C-Hsp3}$ = 2970 cm^{-1}

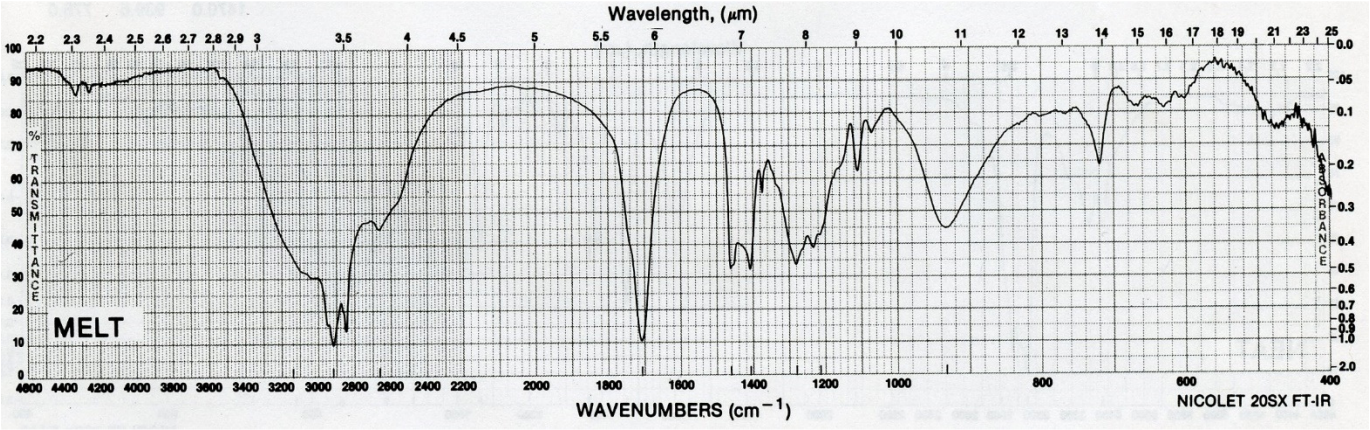
$\bar{\upsilon}_{CN}$ = 2260 cm^{-1}

$\bar{\upsilon}_{C=O}$ = 1735 cm^{-1}

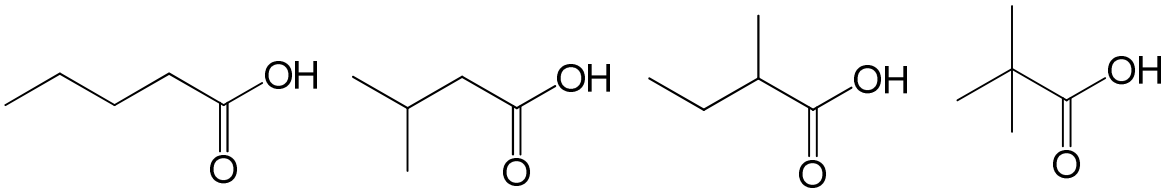
Explain (2 pts)

The signals for NH2, CH_aromatic, C=C_aromatic found in the spectrum of the starting material will be absent in the IR spectrum of the product. Instead, they will be replaced by the broad signal for OH of acid, and the CN signal. The C=O signal in the product, which is not conjugated like the one in the starting material, will appear at a much higher wave number (1735 cm^{-1}) as compare to the same signal in the starting material (1680 cm^{-1}). The presence of these signals will help tell whether the reaction worked or not.

3. The compound with the IR spectrum below has a molecular formula of **$C_5H_{10}O_2$**. Propose **two** structures consistent with the IR spectrum and explain your answer.



Structures (4 pts)



Explain (2 pts)

HDI = 5 + 1 – 10/2 = 1

The only signals from the IR indicate the presence of a broad OH for carboxylic acid, corroborated by the signal of C=O around 1800 cm^{-1}. This explains the only element of insaturation found in the molecule. Since there is no other functional group in the molecule, the compound is a saturated carboxylic acid, which is consistent with the above listed structures.

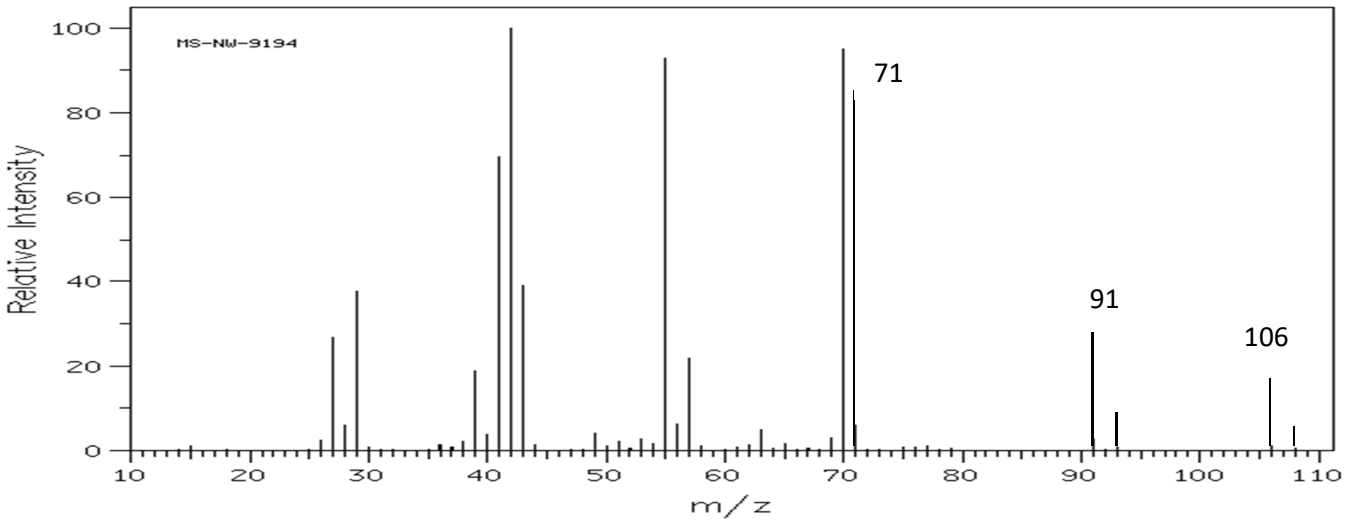
4. Both **$C_6H_{13}NO_2$** and **$C_5H_9NO_3$** have the same nominal mass of 131. Show how these compounds can be distinguished by the *m/z* ratio of their molecular ions in high-resolution mass spectrometry (C 12.0107; O 15.9994; H 1.00794; N 14.0067) (3 pts)

$C_6H_{13}NO_2$ = 6 x 12.0107 + 13 x 1.00794 + 14.0067 + 2 x 15.9994 = 131.17292

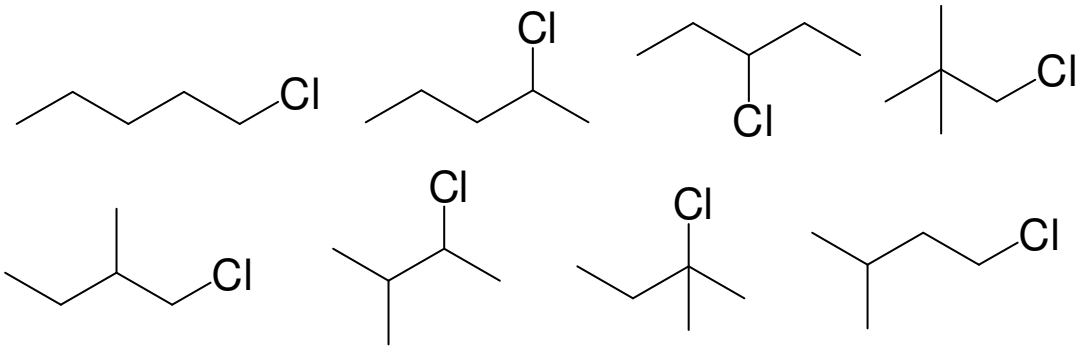
$C_5H_9NO_3$ = 5 x 12.0107 + 9 x 1.00794 + 14.0067 + 3 x 15.9994 = 131.12986

Although both compounds have the same nominal mass, at high resolution, the masses for these compounds are different by (131.17292 - 131.12986 = 0.04934) mass unit.

5. Propose **three (03)** possible structures that can produce the mass spectrum given below and explain your answer (**beside carbon and hydrogen, this molecule contains only one other atom**)



Structures (3 pts)

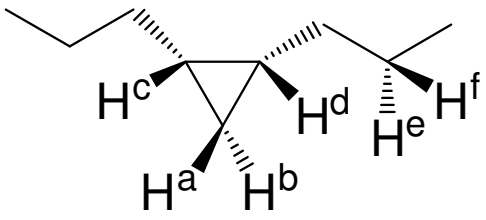


Explain (3 pts)

This compound has a molecular mass at *m/z* 106 and a M+2 which is a third of M+, indicative of the presence of a chlorine atom. The signal at 91 represent a loss of CH_3 (106 – 91 = 15). While the signal at m/z 71, represents the loss of the chlorine atom (106 – 35 = 71).

Since the molecule contains only one other atom than carbon and hydrogen, the fragment at *m/z* 71 represent the hydrocarbon part of the molecule.
If the compound no insaturation, 71 will correspond to $CH_3(CH_2)_n$- meaning that 71 = 14n + 15.
So, n = (71-15)/14 = 4. So, the formula of the compound $CH_3(CH_2)_4$-Cl. This formula is consistent with all the structure above listed.

6. State the relationship between the **protons labelled** in the structure below (as: homotopic, enantiotopic, diastereotopic or unrelated). (1 x 5 = 5 pts)



H^a and H^b are_____**Homotopic**_____

H^b and H^c are _____**Unrelated**_____

H^c and H^d are _____**Enantiotopic**_____

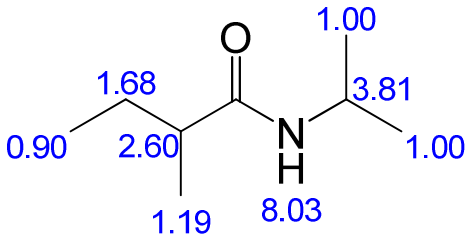
H^d and H^e are_____**Unrelated**_____

H^f and H^e are _____**Diastereotopic**_____

7. A compound with a molecular formula **$C_8H_{17}NO$** has the ^{1}H-NMR data listed below. The compound displays characteristic bands around 3454, 2950 and 1685 cm^{-1} in its IR spectrum. Elucidate the structure of this compound and explain your answer.

^{1}H NMR (δ): 0.90 (3H, triplet), 1.00 (6H, doublet), 1.19 (3H, doublet), 1.68 (2H, quintet), 2.60 (1H, multiplet), 3.81 (1H, multiplet), 8.03 (1H, broad singlet).

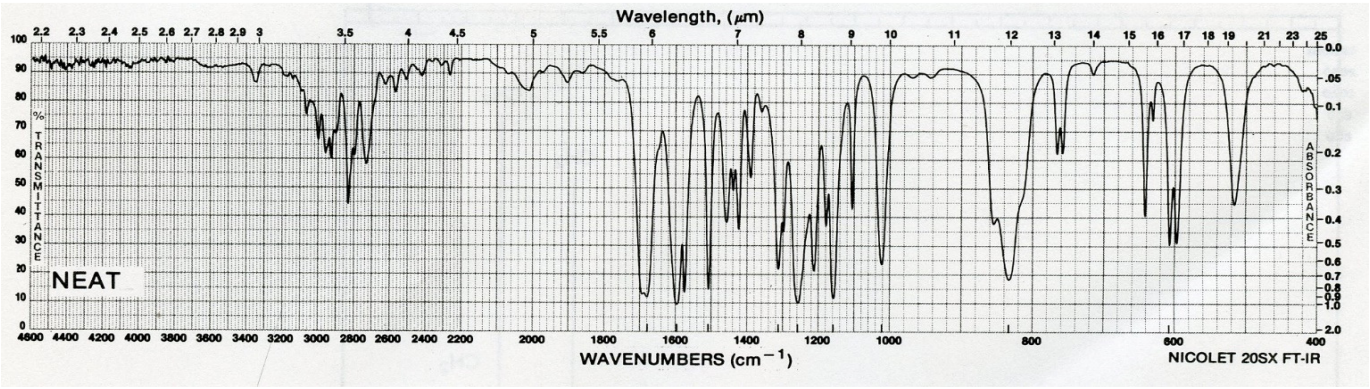
Structures (4 pts)



Explain (2 pts)

HDI = 8 + 1 – 17/2 + ½ = 1. The molecule has just one element of insaturation, and the IR indicates the presence of NH, CHsp^3 and C=O, which is conjugated. Since there is just one element of insaturation in the molecule corresponding to C=O, the carbonyl can only be conjugated to the NH, resulting in an amide functional group (-CO-NH-). At 0.9 ppm the molecule display a triplet of 3H corresponding to a CH_3 connected to CH_2. At 1.0 ppm 6H doublet correspond to CH_3-CH-CH_3, while the 3H doublet at 1.19 correspond to a CH_3 connected to a CH. The only 2H present in the molecule is a quintet at 1.68 ppm, corresponding to a CH_3 connected to a CH_2 and a CH, this CH corresponds to the multiplet at 2.60 ppm, which is also connected to the CH_3 at 1.19 ppm. This indicates that the above CH_3-CH-CH_3 group is connected to the nitrogen of the amide, while the H attached to the nitrogen atom appear as a broad singlet at 8.03 ppm. All these data are consistent with the above structure

8. (a) Identify the major signals and the corresponding bond types present in the compound having the following IR spectrum; Molecular formula **$C_{12}H_{16}O_2$** (3 pts)



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

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

$\bar{\upsilon}_{C\text{-}H\_aldehyde}$ = 2820 and 2740 cm^{-1}

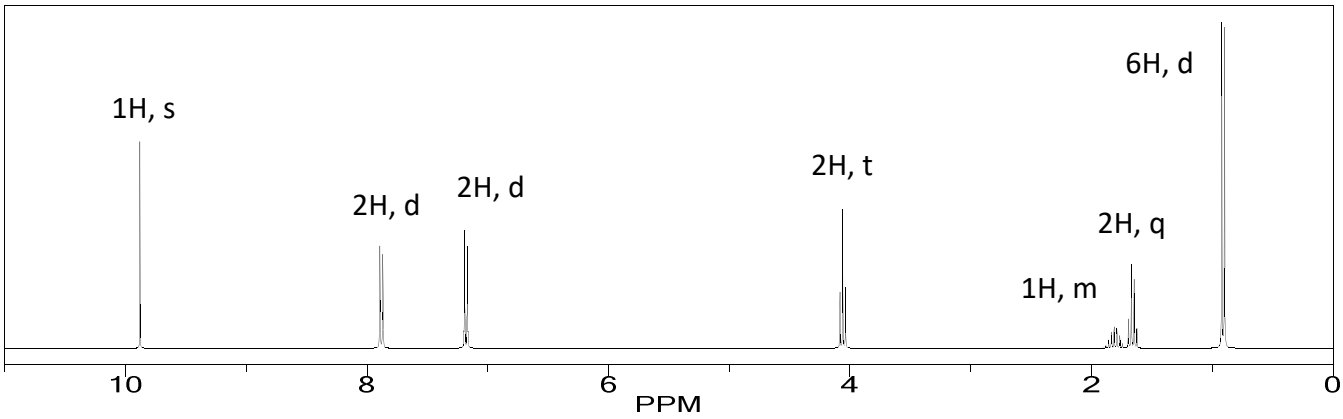
$\bar{\upsilon}_{C=O}$ = 1698 cm^{-1}

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

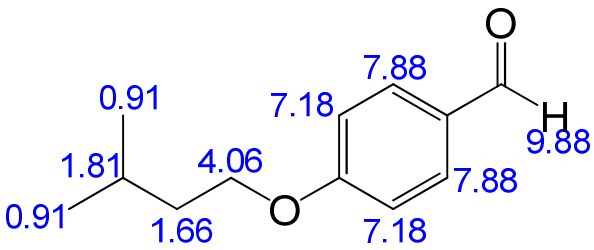
$\bar{\upsilon}_{C\text{-}O}$ = 1050 cm^{-1}

$\bar{\upsilon}_{C\text{-}H\_Aromatic\_bend}$ = 600 - 800 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.



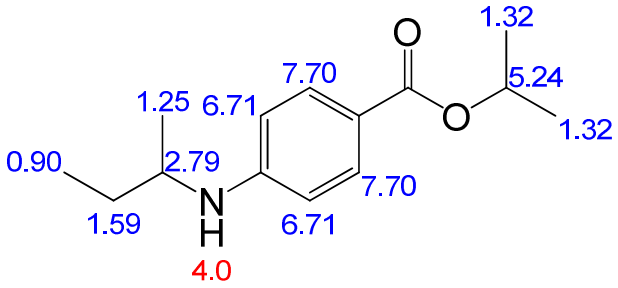
Structure (3 pts)



Explain (2 pts)

HDI = 12 + 1 – 16/2 = 5. The IR spectrum indicates the presence of an aromatic ring and a carbonyl of an aldehyde accounting for the 5 elements of insaturation. The carbonyl appeared to be directly connected to the aromatic ring as indicated by the low wave number as a result of the conjugation. The 1H-NMR display the H of aldehyde at 9.88 ppm. It also display 2 doublets of 2H in the aromatic region corresponding to a para-disubstituted aromatic ring. Since the aldehyde is directly connected to the aromatic ring, it occupies one side of the para-disubstituted system.
The spectrum also display triplet of 2H corresponding to a CH_2 connected to another CH_2. This latter CH_2 (1.66 ppm) appeared to be also connected to a CH and thus display a quartet of 2H. The only CH of the molecule is must also be connected to two CH_3 groups as indicates by the doublet of 6H at 0.91 ppm. Since the triplet of 2H appeared at 4.06, it must be connected to an oxygen atom, resulting in the observed deshielding effect. All these data are consistent with the above structure.

9. Predict the number of signals expected, their chemical shifts, their multiplicity, and the number of protons under each signal in the ^{1}H-NMR spectrum of the following compound (3 pts)



δ_{ppm} = 0.90 (3H, triplet), 1.25 (3H, doublet), 1.32 (6H, doublet), 1.59 (2H, quintet), 2.79 (1H, multiplet), 4.0 (1H, broad singlet), 5.24 (1H, multiplet), 6.71 (2H, doublet), 7.70 (2H, doublet).

10. The mass spectrum below is that of 1-phenylhexan-2-one (see structure below). Provide a structure for the fragments at m/z 176, 134, 120, 91, 85, 57, 41 and29 (**You must show the fragmentation pattern**) (0. 5 x 8 = 4 pts)