CHE 173
Winter, 2005
Quiz 1 Answer Key

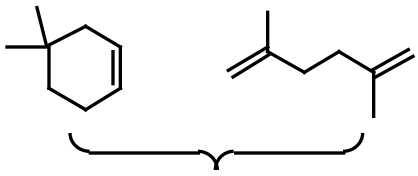
Name_____

Section: 201 202 203 204 205
M T W Th F
(circle one)

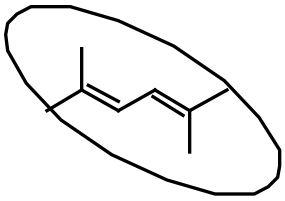
1. Briefly explain what spectroscopy is in general, and describe how one specific type of spectroscopy (or spectrometry) works in the determination of organic structures. (5 points)

   Spectroscopy is the study of the absorption of electromagnetic radiation by a compound. Different types of spectroscopy involve absorption of different types of e.m. radiation (see notes for specifics).

2. Which of the C_8H_{14} isomers shown below would you expect to absorb UV radiation? Explain. (5 points)



These are NOT conjugated systems and will not absorb in the UV range.

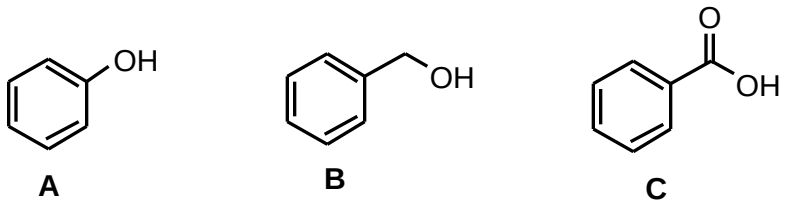


This one IS conjugated and will absorb UV.

3. The λ_{max} values for the π -> π^* transitions for three compounds are shown below. For which compound is the HOMO-LUMO gap the smallest? Explain. (5 points)

   Since the HOMO-LUMO gap is defined by ΔE and ΔE is proportional to $1/\lambda$, the longer the λ, the lower the ΔE and the smaller the HOMO-LUMO gap. Thus, the compound with $\lambda_{max} = 223$ has the smallest HOMO-LUMO gap.

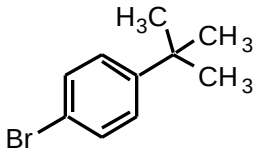
4. Describe the characteristic IR absorption bands that could allow you to distinguish between the compounds shown below. (5 points)



A **B** **C**

They will all have a strong absorption band at ~3450 cm-1 from the O-H bonds. Compound B will show an absorption band at around 2900 cm-1 from the sp3 C-H bonds. Compound C will show a strong absorption band at ~1750 cm-1 for the carbonyl bond.

5. For the compound shown below, (a) draw what the mass spectrum would look like, including the molecular ion and the base peak; (b) calculate the index of hydrogen deficiency (IHD), showing your calculation, or explain what the IHD is for this molecule. (10 points)



The molecular formula is C10H13Br, so the molecular ion is at 212 and the M+2 peak (which is almost equal in intensity) is at 214. The easiest way for the molecular ion to fragment is by loss of a methyl radical (CH_3) to give base peaks at 197 and 199 (there are TWO, because Br is still present in the fragment).

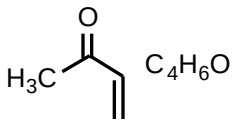
IHD = 1/2 [2 (10) + 2 -13 -1] = 4 (or, three double bonds and a ring!)

6. A compound gives a mass spectrum with a molecular ion peak at m/z = 70 (with no M + 2 peak) and a base peak at m/z = 55. When an IR spectrum is taken of this sample, it shows absorption bands at 3100 cm^{-1}, 2900 cm^{-1}, 1775 cm^{-1} (a very strong band), and 1640 cm^{-1}. The compound is also found to be UV-active (absorbs UV radiation). Suggest a possible structure for this compound, and explain your answer. (10 points)

The molecular weight is 70, a small, even number which suggests there are no nitrogen atoms in the molecule. There is no significant M+2 peak in the MS, so

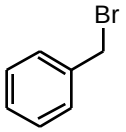
there are no Br or Cl atoms in the molecule. The base peak results from loss of a methyl radical (M-15=55). The IR tells us the following:
Absorption band at 3100 = CH stretch where C is sp2 hybridized
Absorption band at 2900 = CH stretch where C is sp3 hybridized
Absorption band at 1775 = carbonyl present (C=O)
Absorption band at 1640 = C=C present

The fact that the compound is UV active, suggests there is a conjugated system of π electrons. The following structure is realistic:

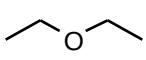


7. What is unique about the mass spectrum shown below? Can you suggest a plausible structure for the sample? (5 points)

A significant M+2 peak indicates the presence of a Br atom in the molecule. The base peak at m/z = 91 suggests a benzylic carbocation fragment. The compound is most likely:



8. For the molecule shown below (diethyl ether), (a) how many signals would you expect to find in the ^{1}H NMR spectrum? (b) identify the most shielded and least shielded protons. (5 points)



(a) there should be 2 signals in the ^{1}H NMR spectrum (there are two sets of protons)
(b) the methyl protons are more shielded than the methylene protons