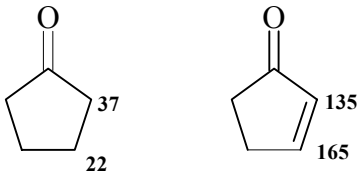
Chem 2P21 Assignment 1 Name: _____
Due Monday, Jan. 20, 5 pm

ID Number:_____

For all the questions on this assignment, please NEATLY provide your answers on loose leaf paper.

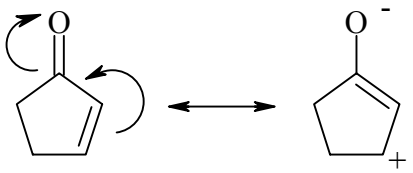
1. In cyclohexanone, chemical shifts decrease the further one goes from the carbonyl group (which is what one expects); however in cyclohexenone, one observes the opposite. Provide an explanation for this. (4 marks)



net 15 ppm drop net 30 ppm gain

The saturated molecule exhibits the normal inductive effect through the σ-bond.

In the unsaturated molecule, not only is this going on through the σ-framework, but the presence of conjugated double bonds means the two π systems are delocalised:

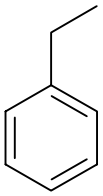


minor contributor

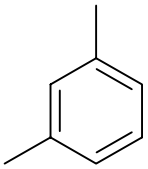
As positive charge builds up on a nucleus, it becomes deshielded relative to 0 ppm, and exhibits a downfield shift. Thus, the carbon that feels positive charge *via* resonance is deshielded (slightly) compared to one that is not.

2. Since ^{13}C NMR lacks spin-spin coupling information, it may be a belief that it is less important than spin-coupled methods in the assignment of structures. However, the simple ability to "see" the carbons in a molecule should not be underestimated.

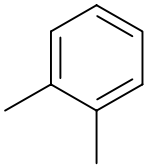
Explain how the following isomeric aromatics can be identified using ^{13}C NMR *only*.
(4 marks)



ethybenzene

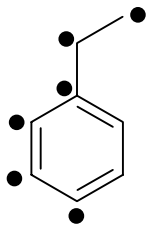


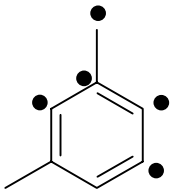
meta-xylene

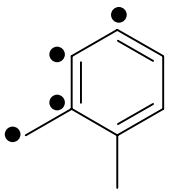


ortho-xylene

The ^{13}C spectra of ethylbenzene exhibits 6 peaks, while meta-xylene's spectrum shows 5 peaks, and ortho-xylene's shows only 4.

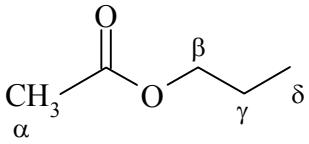




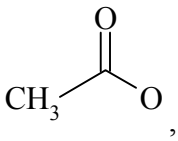


3. On the back of this page is the ^{1}H NMR spectrum of an ester, $C_5H_{10}O_2$, compound A. Determine the structure of compound A, rationalise and assign the peaks to the appropriate hydrogens, and rationalise the observed splittings. (10 marks)

Peak ppm	Peak Integration	Peak multiplicity	Assignment
0.95	48.7/33.2 = 1.47 = 3	triplet	δ
1.65	33.3/33.2 = 1.00 = 2	sextet	γ
2.05	48.4/33.2 = 1.46 = 3	singlet	α
4.05	33.2/33.2 = 1.00 = 2	triplet	β

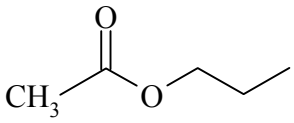


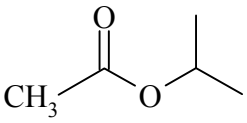
The peak at 2.05 is clearly a methyl group (integrates to 3) next to a carbonyl (2.05 ppm), which is confirmed by the fact that it is a singlet (uncoupled).

This confirms this much of the structure: 

, $C_2H_3O_2$

The remaining atoms are C_3H_7, either a propyl or *iso*-propyl group.





expect	expect
2H triplet around 4	1H septet around 4
2H triple quartet	6H singlet
3H triplet	

observed
2H triplet around 4
2H sextet
3H triplet

The reason why γ is a sextet and not a (3+1)(2+1) = 12 peak multiplet must be because the J values ($J_{\beta\gamma}$ and $J_{\gamma\delta}$) are similar (see Good Problem 9.9), so the N+1 rule predicts (3+2+1) = 6 peaks (a sextet).

4. Compound B has the chemical formula C_7H_8O. From the IR, ^{13}C and ^{1}H NMR of compound B, determine its structure, rationalise and assign the relevant peaks in each spectrum (IR, ^{13}C and ^{1}H NMR), and rationalise the splittings in the ^{1}H NMR. (12 marks)

Scan the IR quickly:

IR suggests no O-H bond present
IR suggests no C=O bond present
IR suggests there are sp^2 C-H bonds (3003 cm^{-1})
IR suggests there are sp3 C-H bonds (2957 cm^{-1})
IR suggests there are C=C bonds (1601 cm^{-1})

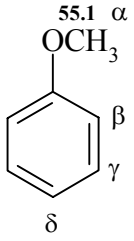
Look at ^{13}C NMR next:

5 peaks indicate 5 different types of carbon (the three peaks are 77 ppm are $CDCl_3$ solvent; impurity!)

1 peak at 55.1 ppm, this is one of the ether carbons. R-**C**-O-R
4 peaks in the alkene/aromatic region (individual assignments of these peaks not marked)

Finally examine ^{1}H NMR:

Peak ppm	Peak Integration	Peak multiplicity	Assignment
3.8	63.8/41.1 = 1.55 = 3	singlet	α
6.9	60.6/41.1 = 1.47 = 3	triplet (not clean)	β and δ **
7.4	41.1/41.1 = 1.00 = 2	triplet	γ **



** = these assignments not marked