CHEM 303
Organic Chemistry II
Problem Set V
Chapter 16
Answers

1) $A$ and $B$ are isomeric dicarbonyl compounds of the molecular formula $C_5H_8O_2$. The $^1$H-NMR spectrum of $A$ contains a singlet at $\delta 2.05$ ppm, and another singlet at $\delta 5.40$ ppm. The $^1$H-NMR spectrum of $B$ contains three signals: a singlet at $\delta 2.30$ ppm, a triplet at $\delta 1.10$ ppm, and a quartet at $\delta 2.70$ ppm. Suggest structures for $A$ and $B$.

From the molecular formula, we find that both $A$ and $B$ have 2 degrees of unsaturation, which is taken up with the two carbonyls (given information).

Compound $A$ therefore, must be fairly symmetric. The singlet at $\delta 2.05$ is pretty indicative of a $\text{CH}_3$ next to a carbonyl, and the singlet at $\delta 5.40$ looks like it could be next to two electron-withdrawing groups. All this makes me think we have $\text{2,4-pentanedione}$, $\text{CH}_3\text{C(O)CH}_2\text{C(O)CH}_3$ here.

Compound $B$ having a triplet at $\delta 1.10$ tells me that we have a methyl group next to a methylene, which itself seems to be near an electron-withdrawing group. The quartet verifies this assumption. The singlet at $\delta 2.30$ is probably a methyl next to an electron-withdrawing group. All told, I think we have $\text{2,3-pentanedione}$, $\text{CH}_3\text{C(O)C(O)CH}_2\text{CH}_3$.

2) Linamarin is a potentially toxic substance that releases hydrogen cyanide in aqueous acid. Suggest a mechanism for this reaction.

Well, here’s the mechanism.
Essentially, it is just the hydrolysis of an acetal, with the added benefit of one of the resultant alcohols being a cyanohydrin, which itself can hydrolyze in acid.

3) The preparation of each of the following compounds requires protection of a carbonyl functionality at some stage of the synthesis. Provide feasible sequences to construct these molecules using the indicated starting materials and any other necessary reagents.
This one is pretty straight-forward:
Again, fairly straight-forward:

1) t-BuLi
2) CuBr
3) PhCH₂Cl
4) H₃O⁺
The first two steps make the Gilman reagent (lithium dialkylcuprate), which allows for alkyl halide coupling, and then we hydrolyze off the protecting group.

4) When the epoxide shown below was treated with CH$_3$O$^-$ followed by an acidic work-up, a compound of the molecular formula C$_6$H$_{12}$O$_3$ was formed as the major product. Its $^1$H-NMR spectrum exhibited signals at $\delta$1.07 (t, 3H), 2.60 (q, 2H), 3.41 (s, 6H), 4.50 (s, 1H) ppm, and a strong absorption was seen at 1730 cm$^{-1}$ in its IR spectrum. Propose a structure for this molecule, and explain how it could have been formed under these reaction conditions i.e. propose a mechanism

![Epoxide Structure](image)

The IR peak at 1730 cm$^{-1}$ tells us right away that we have a carbonyl group; looking at the starting material, I’m going to go out on a limb (not really) and say we have a ketone. Now to work on structure, and then the mechanism.

The NMR data suggests a fairly normal methyl next to a methylene ($\delta$1.07, t, 3H). The methylene is next to the methyl (no kidding!) and an electro-withdrawing group, which is no doubt the carbonyl. Thus far we have: CH$_3$CH$_2$C(O). The 6H singlet at 3.41 is two methyl groups on an electronegative atom, so this signal is the methoxyls. Finally a down-field 1H singlet is a methine near two electronegative atoms, or O$_2$C. Putting it all together, we get:

![Proposed Structure](image)

Now to the mechanism:
5) An oxidation reaction was performed on 3-phenyl-1,2-propanediol, with the intention of producing the corresponding dicarbonyl compound. Upon examination of the reaction product by $^{13}$C-NMR, it quickly became apparent that only one carbonyl carbon was present. Using the $^{13}$C and $^1$H NMR data provided, suggest a reasonable structure for the observed product.

$^1$H-NMR: \(\delta 9.22 \text{ (s, 1H)}, 7.83 \text{ (d, 2H)}, 7.3-7.4 \text{ (m, 3H)}, 6.4 \text{ (broad s, 1H)}, 6.2 \text{ (s, 1H)} \) ppm

$^{13}$C-NMR: \(\delta 122.8, 128.7, 129.3, 130.4, 133.5, 148.7, 188.3 \) ppm

Well, the $^1$H-NMR clearly shows an aldehyde hydrogen ($\delta 9.22$, s, 1H) plus the usual array of aromatic protons. The $^{13}$C-NMR tells us we have eight different carbon atoms, so there must be a bit of symmetry operating. The shift at \(\delta 188.3\) is confirming of the presence of a carbonyl. What is revealing is that there are no chemical shifts indicative of any alkyl positions! All the $^1$H shifts are those of vinyl and/or aryl protons, and the same can be said for the $^{13}$C shifts. The total number of hydrogens accounted for from the $^1$H-NMR is 8; there were 12 in the original compound, and two would be expected to have been lost per oxidation. Therefore, it looks as if both oxidations worked! Now the question becomes: where is the second carbonyl? If we look at the structure we expected
we see an $\alpha$-keto-aldehyde. This may not tell us much, but gives us a hint in explaining two things from the $^1$H-NMR spectrum: the broad singlet at $\delta 6.4$, and the singlet at $\delta 6.2$. The broad singlet seems like an $\text{–OH}$ group, and the (sharper) singlet upfield of the broad one is right in the vinyl range. Putting these together into a sensible structure, we obtain:

which, as shown, can engage in intramolecular hydrogen bonding to stabilize the enol. The extension of conjugation doesn’t hurt, either.