Protonation of a β-Diketone; an Intramolecular Hydrogen Bond with an Extremely Deshielded Proton

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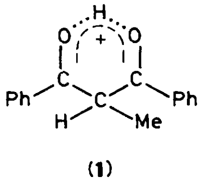
Studies of the protonation of 1,3-diphenyl-2-methylpropane-1,3-dione in HBr/CF_2Br_2 show that the proton is held between the oxo groups in an unusual hydrogen bond, giving rise to a ^1H n.m.r. signal at δ 21.44 with a negative Δδ(H,D) value.

^1H N.m.r. has been used widely in studies of the properties of hydrogen-bonded protons. Of particular importance are correlations of the chemical shift and the isotope effect on the chemical shift [Δδ(H,D)] with the potential function and with the strength of the hydrogen bond.[1] We now report our studies with protonated 1,3-diphenyl-2-methylpropane-1,3-dione (**1**), which exhibits an extreme value for the chemical shift of the hydrogen-bonded proton.

The ^1H n.m.r. spectrum† of a solution of 1,3-diphenyl-2-methylpropane-1,3-dione (*ca.* 0.5 mol dm^{-3}) in CF_2Br_2 at 298 K shows that the dioxo form is present, giving signals at δ 7.91—7.36 (m, 10 H, arom.), 5.13 (q, 1 H, CH), and 1.54 (d, 3 H, Me), with less than *ca.* 3% of the enol form. For solutions of 1,3-diphenyl-2-methylpropane-1,3-dione (0.061 mol dm^{-3}) in CF_2Br_2 with HBr (1.38 mol dm^{-3}) at 258 K, small shifts of the methyl doublet and the methine quartet to 1.55 and 5.25, respectively, are observed. The HBr resonance is found at δ −2.23. As the temperature of the solution is lowered by 10 K intervals down to 158 K, these signals are shifted further downfield. However the major change in the spectrum is the appearance of a new signal at δ 21.4. The signal is first observed at *ca.* 180 K as a broad peak, but as the temperature is lowered the line sharpens and this is accompanied by a sharpening in the HBr signal. The new signal, integrating for one proton and observed at 21.44 ± 0.02 at 158 K, is assigned to the hydrogen-bonded proton held between the oxo groups as in (**1**). At this temperature the methyl and methine signals are found at δ 2.05 and 6.15, respectively, the aromatic resonances appear at 7.5—8.5, and the HBr signal is found at −2.34.

Previously[2] we have observed the formation of a 1-bromo alcohol from the reaction of 1,1,1-trifluoropropan-2-one with HBr in CF_2Br_2. This species was characterised by the



(**1**)

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† Spectra were taken with a Bruker WM 250 spectrometer with variable temperature unit; ^1H, ^2H, and ^{13}C spectra were run at 250.13, 38.4, and 62.9 MHz, respectively. The internal lock was 10% CD_2Cl_2. The ^1H spectra were measured relative to Me_4Si and the ^2H spectra were referenced to CD_2Cl_2 at δ 5.30 p.p.m. Solutions were prepared in a dry box.

observation of a ^{13}C n.m.r. signal at 86.5 p.p.m., assigned to C(OH)Br. The ^{13}C spectrum of solutions of 1,3-diphenyl-2-methylpropane-1,3-dione (0.5 mol dm^{-3}) showed peaks at 196.5 (C=O); 136.3, 133.4, 129.0, and 128.8 (arom.); 51.5 (2-carbon); and 14.4 (CH_3). In the presence of HBr, downfield shifts of 2.5 and 1.1 p.p.m. were observed for the carbonyl and methyl resonances, respectively, and an upfield shift of 2.4 p.p.m. for the 2-carbon. The nature of these signals was confirmed by the DEPT sequence, and no resonance in the region 80—100 p.p.m. was found which would correspond to a 1-bromo alcohol.

The acid–base behaviour of 1,3-diphenyl-2-methylpropane-1,3-dione differs from that observed for other β-diketones. The diketones previously studied exist chiefly in the enol form and monoprotonation leads to a protonated enol with the positive charge delocalised over the allylic system.[3] The contrasting behaviour of 1,3-diphenyl-2-methylpropane-1,3-dione may be largely a consequence of the 2-methyl substituent; one manifestation of this is the destabilisation of the planar enol as compared with the diketone. In the solid state the diketone exists in a *cis* conformation with a torsion angle of 89° between the carbonyl groups.[4] In solution, formation of the planar enol is still unfavourable, but protonation of the diketone does occur and may bring the carbonyl groups closer to planarity. One of the factors favouring the protonated diketone is the intramolecular hydrogen bond which forms. The extreme value of the chemical shift of the proton [even higher shift than that for the hydrogen phthalate ion (δ 21.0)[1]] indicates an unusual environment. To probe this further we have measured the isotope effect on the chemical shift.

To introduce deuterium into the hydrogen-bond site, CH_3OD was added to the solutions. Our previous studies[5] have shown that alcohols in CF_2Br_2 in the presence of HBr undergo protonation and exchange but are otherwise chemically stable. The ^{2}H spectrum of solutions of 1,3-diphenyl-2-methylpropane-1,3-dione (0.092 mol dm^{-3}) with HBr (2.00 mol dm^{-3}) and CH_3OD (0.89 mol dm^{-3}) in CF_2Br_2 showed a chemical shift for the hydrogen-bonded deuteron at 21.7 ± 0.15. The calculated isotope effect on the chemical shift [$\Delta\delta$(H,D)] is therefore -0.26 ± 0.15.

The observed chemical shift for the intramolecularly hydrogen-bonded proton in (**1**) and the $\Delta\delta$(H,D) value show that we are dealing with a rather unusual hydrogen bond. Negative or small positive isotope effects on the chemical shifts of intramolecularly hydrogen-bonded protons have been observed in a limited number of cases previously: bifluoride anion,[1] phthalate and maleate monoanions,[1] and inside-protonated 1,6-diazabicyclo[4.4.4]tetradecane.[6] In each case, single minimum potential functions have been inferred and the hydrogen bond in (**1**) can be similarly described. The O-to-O distance in (**1**) must be a key factor in determining the single minimum potential and the extreme value of the chemical shift. In the solid state[4] the O-to-O distance in the diketone is long (318.9 pm) and presumably shortens on protonation. In further work it will be attempted to vary the O-to-O distance by use of different substituents at the 2-position and to investigate the effect on the properties of this unique hydrogen bond.

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