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The solution structure of β,γ-dioxoalkyl(triphenyl)phosphonium salts

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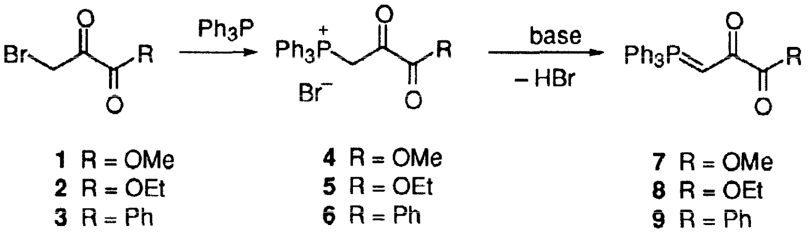
Absract

The simple phosphonium salts **4** and **5** have been fully characterised for the first time and are found by NMR spectroscopy to exist in $CDCl_3$ solution mainly as the *E* and *Z* enol structures **b** and **c**. The salt **6** exists as a mixture of the keto form **a** and one enol form assumed to be **b**. Similarly the bis(phosphonium salt) **16** exists entirely with one end in the keto form and the other in the enol form. The ylide/phosphonium salt **17** obtained from **16** by treatment with base also exists as an enol which is resistant to further deprotonation. Fully assigned ^{13}C NMR spectra are presented for all the structures involved.

Keywords: Phosphonium salts, NMR, Enols and derivatives, Ylides

In a recent paper we described the thermal extrusion of triphenylphosphine oxide from the β,γ-dioxo phosphorus ylides **7–9** using flash vacuum pyrolysis and also their use in the construction of tetraoxo ylides and hexaoxo bis(ylides)[1]. Although the ylides **7–9** are well known [2,3], they have generally been prepared by a one-pot procedure involving formation of the phosphonium salts **4–6** and their *in situ* treatment with base. For this reason these salts have scarcely been characterised and in fact, for **6**, elemental analysis, mp and UV data appear in the literature [3], while there are no data at all for **4** and **5**. A later paper reported an unusual IR absorption for **6** which was attributed to an enol form [4]. In this paper we describe the isolation and full characterisation of the salts **4–6** including their ^{31}P, ^{1}H and ^{13}C NMR spectra from which it is clear that they exist in $CDCl_3$ solution predominantly as mixtures of hydrogen-bonded enol forms.



The three phosphonium salts **4–6** were readily prepared in quantitative yield by reaction of the corresponding α-bromo-1,2-dicarbonyl compounds **1–3** with triphenylphosphine in toluene at room temperature. Although these gave correct elemental analysis data, their

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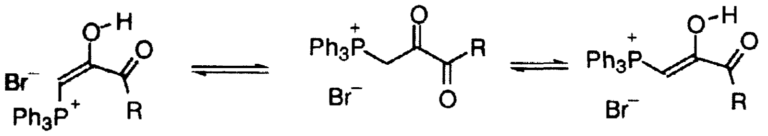
NMR spectra proved to be unexpectedly complex with **4** and **5** giving three ^{31}P NMR signals and **6** giving two. Careful analysis of the ^{1}H and ^{13}C NMR spectra led to the conclusion that, for **4** and **5**, the expected structure **a** is accompanied by the *Z* and *E* enol forms **b** and **c** while, for **6**, form **a** and either **b** or **c** is present.



4–6c **4–6a** **4–6b**

It was not possible to unambiguously determine which enol corresponded to **b** and which to **c** but it seems more likely that the isomers with δ_P 17.2–17.4 which were the major forms for **4** and **5** and the only one for **6** correspond to the less sterically hindered isomers **b**. This is also supported by the larger coupling from phosphorus to C_γ observed for the **b** isomers. Making this assumption, the ratios were **4a** (10%) / **4b** (54%) / **4c** (36%), **5a** (15%) / **5b** (46%) / **5c** (39%) and **6a** (42%) / **6b** (58%). The ^{13}C NMR data for **4–6** form a highly consistent pattern as shown in Table 1 and the occurrence of =CH signals at δ_C 80–84 provides ready confirmation of the enol structures.

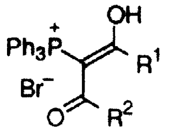
Table 1: NMR Spectra of phosphonium salts **4–6**, **16** and **17**, δ_P and δ_C (J_{P-C})

			δ_C			P–Phenyl			
	R	δ_P	$C\alpha$	$C\beta$	$C\gamma$	C–1	C–2	C–3	C–4
4a	OMe	21.1	37.0 (58)	185.5 (5)	159.5 (6)	117.7 (89)	133.9 (10)	130.4 (14)	135.2
4b	OMe	17.2	83.2 (105)	162.3	161.0 (16)	121.5 (95)	133.4 (11)	129.9 (14)	134.2 (2)
4c	OMe	15.0	82.5 (95)	162.3	164.2 (7)	119.1 (93)	134.0 (11)	130.4 (14)	135.0
5a	OEt	21.2	36.9 (57)	185.5 (5)	159.6 (6)	117.7 (89)	134.0 (11)	130.4 (13)	135.2
5b	OEt	17.3	83.1 (105)	162.7	160.6 (16)	121.8 (95)	133.4 (11)	129.8 (13)	134.1
5c	OEt	15.0	82.1 (95)	162.7	163.8 (7)	119.3 (93)	133.1 (10)	130.4 (13)	135.0
6a	Ph	22.3	36.4 (56)	188.9 (21)	192.5	118.3 (89)	134.0 (10)	130.3 (13)	135.1 (2)
6b	Ph	17.4	80.4 (106)	171.8	171.6	121.4 (94)	133.5 (11)	129.6 (13)	134.0 (3)
16-keto end		20.4	40.2 (60)	190.8 (6)	—	118.4 (89)	134.6 (11)	130.6 (13)	135.3 (2)
16-enol end		15.0	85.8 (92)	167.9 (13)	—	120.4 (93)	133.8 (11)	129.9 (13)	134.2 (2)
17-enol end		16.7	109.9 (89, 3)	158.5 (2)	—	117.5 (91)	133.6 (11)	130.8 (13)	135.7 (1)
17-ylide end		12.8	65.0 (104)	174.7 (18, 3)	—	124.4 (92)	133.0 (11)	129.3 (12)	132.9

Additional signals due to R: **4a** 54.0; **4b/4c** 53.8, 53.3; **5a** 63.9, 13.9; **5b/5c** 63.9, 63.1, 14.2, 13.6; **6a/6b** 135.0, 134.7, 133.3, (4ry), 131.5 (2C), 130.8 (4ry),130.4 (2C), 128.7 (2C), 128.4 (2C).

As far as we are aware this is the first example of the existence of stable enol forms for β,γ-dioxophosphonium salts although the phenomenon has been reported for β,β'-dioxo- [5,6]

and α-phosphino-β-oxo-phosphonium salts **10** and **11** [7]. It has also been shown that β-iminophosphonium salts may exist mainly in the enamine form **12** [8,9].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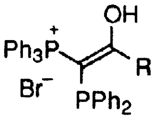
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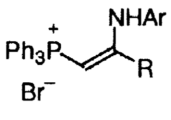
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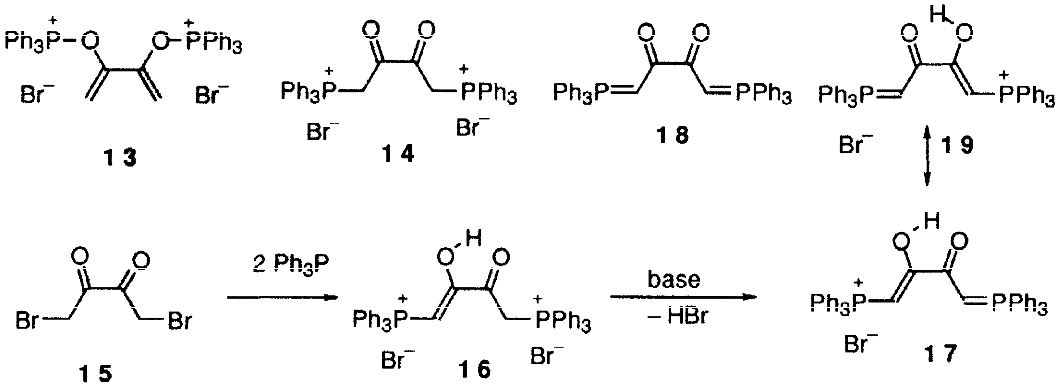
In view of these results it was of particular interest to examine the bis(phosphonium salt) formed from triphenylphosphine and 1,4-dibromobutanedione **15**. Shevchuk and coworkers reported that carrying out the reaction in toluene gave a quantitative yield of the bis(enol phosphonium salt) **13** which could then be converted into the more conventional structure **14** by heating in boiling acetone [10]. The enol structure **13** was proposed on the basis of UV and IR measurements and the earlier report of such a structure from reaction of chlorodiphenylmethyl phenyl ketone with triphenylphosphine [11], but no NMR data were reported.



In our hands, reaction of **15** with triphenylphosphine at room temperature gave a white solid but examination of this by ^{31}P NMR spectroscopy showed at least twenty signals. When it was boiled in acetone according to the literature procedure a solid did precipitate in 32% yield which gave analytical data in agreement with expectation for **14**. We therefore believe that acetone does not bring about isomerisation of **13** but simply affords a convenient method for separation of the product from the complex mixture formed in the initial reaction. The ^{31}P NMR spectrum of the product showed doublets at δ_P 20.4 and 15.0 indicative of two non-equivalent phosphorus atoms coupling to each other and thus ruling out structure **14**. This was confirmed by the ^{1}H and ^{13}C NMR data (Table 1) which clearly showed the compound to exist in solution entirely as the structure **16** with one end in the enol form and one in the keto form. The data for the keto and enol parts of the molecule are in excellent agreement with the patterns already established for **4**–**6**.

Shevchuk and coworkers described the reaction of the bis(phosphonium salt) with two equiv. of sodium ethoxide in ethanol to give the bis(ylide) **18** [10]. We were unable to reproduce this result but found that treatment of **16** with an excess of aqueous sodium hydroxide gave the ylide/phosphonium salt **17** which again exists entirely as an enol form

(Table 1). It is interesting to note that, in this case, two of the carbons are coupled to both phosphorus atoms. In an attempt to form **18**, we treated **17** with butyllithium in THF but, rather remarkably, this resulted in recovery of the unchanged starting material. The structure of **17** is obviously very stable. If it were not for the association of the bromide counter-ion with one phosphorus atom the whole structure would be symmetrical as indicated by the possible resonance form **19**. The observed spectra show that transfer of the bromide from one end of the molecule to the other does not occur on the NMR time scale.

The IR spectra for all five compounds were recorded both in solution and as KBr discs. In each case the solution spectra showed a single broad OH stretch peak in the range 3350–3450 cm^{-1}. For **4** and **5** the solid state spectra also showed a peak at this position but this was now accompanied by two broad peaks at 2640 and 2440–2420 cm^{-1} which would appear to indicate extensive hydrogen bonding. The occurrence of peaks in this range has previously been attributed to hydrogen bonded enol forms for the β,β'-dioxophosphonium salts [5,6]. The solid state spectrum of **6** was dominated by broad twin peaks at 3450 and 3400 cm^{-1} but there was also significant absorption down to 2400 cm^{-1}. The solid state spectrum of **16** showed OH absorptions at 3400 cm^{-1} (broad), 2750 and 2600 while for **17** there was only a broad peak at 3350 cm^{-1}. From the significant differences between the solution and solid state spectra it would seem that the enol forms of these compounds also have the possibility of entering into intermolecular hydrogen bonding in the latter case leading to the observed extra absorptions.

Experimental

General

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. Infra red spectra were recorded in CH_2Cl_2 solution and as KBr discs on a Perkin Elmer Paragon 1000 FT instrument. NMR spectra were obtained for ^1H at 300 MHz and for ^{13}C at 75 MHz using a Bruker AM300 instrument, and for ^{31}P at 121.4 MHz using a Varian Gemini 2000 instrument. All spectra were run on solutions in $CDCl_3$ with internal Me_4Si as reference for ^1H and ^{13}C and external 85% H_3PO_4 as reference for ^{31}P. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz. Dry toluene and diethyl ether were prepared by storage over sodium wire. The acetone used was analytical reagent grade.

2-Methoxycarbonyl-2-oxoethyl(triphenyl)phosphonium bromide 4

A solution of methyl bromopyruvate **1** [12] (4.0 g, 22 mmol) in dry toluene (10 cm^3) was added dropwise to a solution of triphenylphosphine (5.7 g, 22 mmol) in dry toluene (50 cm^3) and the mixture stirred under a nitrogen atmosphere for 3 h. The mixture was evaporated and the residue triturated with dry diethyl ether to give the title compound in quantitative yield as colourless crystals, mp 152–153 °C (Found: C, 59.5; H, 4.5. $C_{22}H_{20}BrO_3P$ requires C, 59.6; H, 4.5%); ν_{max} /cm^{-1} (CH_2Cl_2) 3450, 1720, 1610, 1590, 1370, 1100, 995 and 820;

(KBr) 3440, 2640, 2440, 1720, 1630, 1610, 1590, 1425, 1370, 1230, 1130, 1100, 995, 980, 880, 820, 745, 720 and 680; δ_H **4a** 8.00–7.52 (15 H, m, Ph), 6.30 (2 H, d, *J* 12) and 3.41 (3 H, s, Me); **4b** 11.3 (1 H, br s, OH), 8.00–7.52 (15 H, m, Ph), 6.01 (1 H, d, *J* 16) and 3.94 (3 H, s, Me); **4c** 12.8 (1 H, br s, OH), 8.00–7.52 (15 H, m, Ph), 7.19 (1 H, d, *J* 13) and 3.86 (3 H, s, Me); δ_C see Table 1; δ_P +21.1 (10%, **4a**), +17.2 (54%, **4b**) and +15.0 (36%,**4c**).

2-Ethoxycarbonyl-2-oxoethyl(triphenyl)phosphonium bromide **5**

Reaction as above using ethyl bromopyruvate **2** [12] (4.5 g, 23 mmol) and triphenylphosphine (6.05 g, 23.1 mmol) gave the title compound in quantitative yield as colourless crystals, mp 160–161 °C (Found: C, 60.4; H, 4.8. $C_{27}H_{22}BrO_3P$ requires C, 60.4; H, 4.8%); ν_{max} /cm^{-1} (CH_2Cl_2) 3400, 1730, 1590, 1570, 1405, 1350, 1080, 1050 and 1000; (KBr) 3460, 2640, 2420, 1730, 1630, 1610, 1590, 1430, 1370, 1240, 1130, 1100, 1010, 990, 870, 820, 740, 720 and 690; δ_H **5a** 7.94–7.51 (15 H, m, Ph), 6.33 (2 H , d, *J* 12), 3.84 (2 H, q, *J* 7, OCH_2) and 1.02 (3 H, t, *J* 7, Me); **5b** 11.9 (1 H, br s, OH), 7.94–7.51 (15 H, m, Ph), 7.18 (1 H, d, *J* 13), 4.44 (2 H, q, *J* 7, OCH_2) and 1.45 (3 H, t, *J* 7, Me); **5c** 13.3 (1 H, br s, OH), 7.94–7.51 (15 H, m, Ph), 5.98 (1 H, d, *J* 16), 4.33 (2 H, q, *J* 7, OCH_2) and 1.37 (3 H, t, *J* 7, Me); δ_C see Table 1; δ_P +21.2 (15%, **5a**), +17.3 (46%, **5b**) and +15.0 (39%, **5c**).

2,3-Dioxo-3-phenylpropyl(triphenyl)phosphonium bromide **6**

Reaction as above using 3-bromo-1-phenylpropane-1,2-dione **3** [13] (4.0 g, 17.6 mmol) and triphenylphosphine (4.60 g, 17.6 mmol) gave the title compound in quantitative yield as yellow crystals, mp 108–110 °C (lit. [3], 104–105 °C); ν_{max} /cm^{-1} (CH_2Cl_2) 3450, 1705, 1650, 1580, 1430 and 1100; (KBr) 3450, 3400, 1705, 1650, 1580, 1485, 1430, 1370, 1310, 1220, 1100, 990, 890, 850, 810, 740, 720 and 690; δ_H **6a** 8.05–7.11 (20 H, m, Ph) and 6.45 (2 H, br d, *J* 13); **6b** 13.8 (1 H, br s, OH) and 8.05–7.11 (21 H, m, Ph and =CH); δ_C see Table 1; δ_P +22.3 (**6a**) and +17.4 (**6b**).

2,3-Dioxobutane-1,4-diylbis(triphenylphosphonium bromide) **16**

A solution of 1,4-dibromobutane-2,3-dione **15** [14] (5.0 g, 20.5 mmol) in acetone (40 cm^3) was added dropwise over 1 h to a solution of triphenylphosphine (12.0 g, 45.8 mmol) in acetone (80 cm^3) and the mixture stirred for 4 h at RT. The precipitate was filtered off to give an off-white powder. The crude product was redissolved in acetone, heated under reflux for 5 min. and left to cool. The precipitate which formed was filtered off to yield the pure product (1.6 g, 32%) as pale yellow crystals, mp 260–261 °C (decomp.) (lit. [10], 238–240 °C) (Found: C, 62.7; H, 4.7. $C_{40}H_{34}Br_2O_2P_2$ requires C, 62.5; H, 4.5%);ν_{max} /cm^{-1} (CH_2Cl_2) 3400, 1430, 1100 and 990; (KBr) 3400, 2750, 2600, 1660, 1580, 1470, 1430, 1310, 1100, 990, 840, 750, 720 and 690; δ_H 11.20 (1 H, br s, OH), 9.31 (1 H, t, *J* 18), 8.79 (1 H, dd, *J* 20, 18), 8.72–7.00 (30 H, m, Ph) and 7.10 (1 H, d, *J* 12); δ_C see Table 1; δ_P 20.4 (d, $^5J_{P-P}$ 3) and 15.0 (d, $^5J_{P-P}$ 3).

2,3-Dioxo-4-triphenylphosphoranylidenebutyl(triphenyl)phosphonium bromide **17**

To a stirred solution of the bis-phosphonium salt **16** (2.0 g, 2.6 mmol) in water (25 cm^3) was added sodium hydroxide (0.21 g, 5.2 mmol) in water (5 cm^3). The mixture was extracted with dichloromethane (2 x 25 cm^3) and the combined organic phase washed with water (25 cm^3), dried and evaporated to furnish the crude product as a yellow solid. Recrystallisation from ethyl acetate gave the title compound (1.54 g, 86%) as yellow crystals, mp 158–161 °C (Found: C, 69.5; H, 5.2. $C_{40}H_{33}BrO_2P_2$ requires C, 69.9; H, 4.8%); ν_{max} /cm^{-1} (CH_2Cl_2) 3350, 1590, 1530, 1480, 1430, 1390, 1180, 1110 and 830; (KBr) 3350, 1530, 1480, 1430, 1390, 1310, 1180, 1110, 990, 970, 860, 820, 750, 730 and 700; δ_H 8.72–7.00 (m, 30 H, Ph), 7.16 (1 H, d, J 20) and 4.40 (1 H, d, J 21, CHC=O) (enol H not apparent); δ_C see Table 1; δ_P +16.7 and +12.8.

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