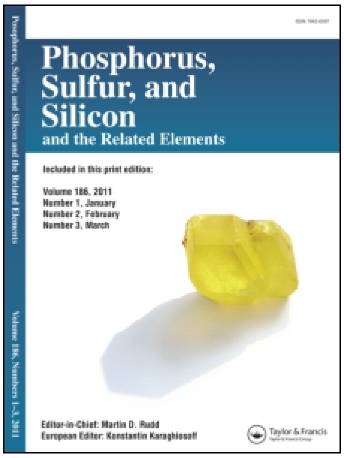

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DIETHYL 1-SUBSTITUTED 2-OXO-ETHYLPHOSPHONATES AND THE LITHIUM SALTS AND ZINC COMPLEX OF THEIR ENOL TAUTOMERS

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DIETHYL 1-SUBSTITUTED 2-OXO-ETHYLPHOSPHONATES AND THE LITHIUM SALTS AND ZINC COMPLEX OF THEIR ENOL TAUTOMERS

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The lithium salts of diethyl-(1-methyl-2-oxoethyl)phosphonate 1 and diethyl-(2-oxo-1-phenylethyl)phosphonate 2 (3 and 4 respectively) as well as the zinc complex of ester 2 (5) are synthesized and characterized. The lithium salt 3 exists as a mixture of (*Z*)- and (*E*)-forms, while the lithium salt 4 and zinc complex 5 have (*Z*)-chelate structure.

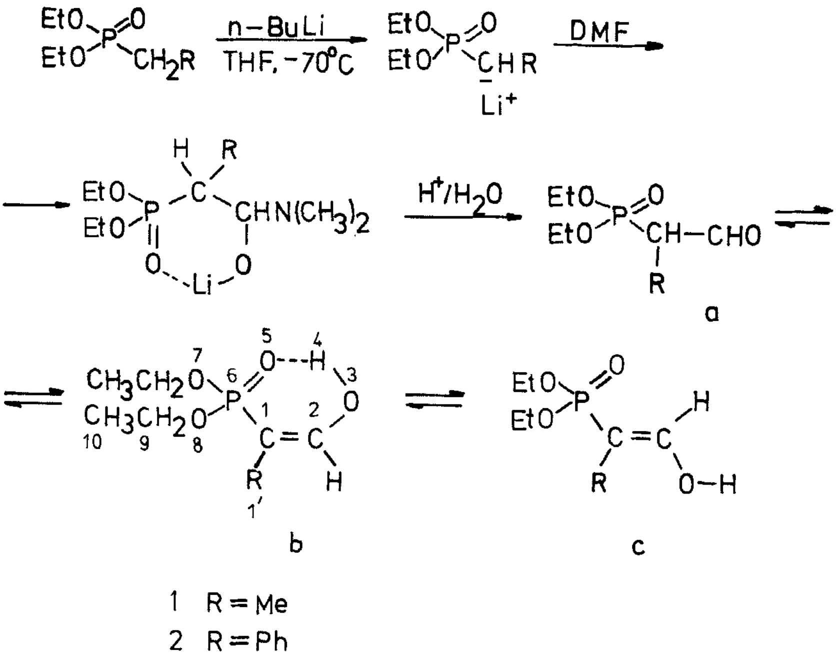
Key words: Diethyl 1-substituted 2-oxo-ethylphosphonates; lithium salt; zinc complex; keto-enol tautomerism.

INTRODUCTION

In previous papers[1,2] we studied the reactivity of diethylphosphonoacetaldehyde in autoaldol reactions, condensation reactions with amines and complex formation. We showed that at room temperature and below the aldehyde is stable and that its lithium salt and zinc complex can be isolated, while at elevated temperature an autoaldol condensation reaction takes place. In order to avoid the process of autoaldol condensation when the metallation is carried out with basic reagents, in the present work we investigated phosphonoacetaldehydes substituted in α-position, namely the diethyl ester of 1-methyl-2-oxoethylphosphonic acid 1[3,4] and the diethyl ester of 2-oxo-1-phenylethylphosphonic acid 2.[5,6] Now we report the synthesis of the lithium salts of esters 1 and 2 as well as of the zinc complex of the ester 2. Although the keto-enol equilibrium of phosphonoacetaldehydes has been investigated by IR and NMR[7–12] there are some contradictions concerning their configuration in different solvents.

RESULTS AND DISCUSSION

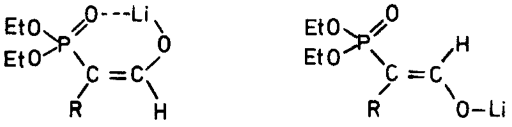
The phosphonoacetaldehyde 1 was obtained according to the route shown in the Scheme, using dimethylformamide (DMF) as the formylating reagent.[3] The phosphonoacetaldehyde 2 was obtained analogously to 1, but using ethyl formate as formylating reagent.[5]



Scheme

The lithium salts 3 and 4 (Figure 1) were obtained using *n*-butyllithium at −70°C in tetrahydrofuran and isolated in pure state. The white crystalline salts were hygroscopic and soluble in highly polar solvents. The IR spectra of salts 3 and 4 in nujol contained absorptions at 1580 cm^{-1} and 1550 cm^{-1} respectively due to C═C valence vibrations, thus complexation producing low frequency shifts of 55 and 85 cm^{-1} of these bands in respect to 1 and 2. According to the IR and NMR data the salt 3 was found to be a mixture of (*Z*)-form 3b and (*E*)-form 3c. The band at 1175 cm^{-1} corresponds to the PO group in chelate 3b and the band at 1230 cm^{-1}—to the PO group in (*E*)-enolate 3c, which is in agreement with literature data for metal complexes of β-ketophosphonates.[13]

NMR studies of vinylphosphonates have shown vicinal couplings from phosphorus to the β-hydrogens to be large (30–45 Hz) when trans orientated and smaller (5–13 Hz) when cis orientated.[9,10] Thus the large value of the $^3J_{HP}$ 41.35 Hz of the doublet at δ 7.91 ppm was attributed to (*Z*)-enolate 3b (trans orientated P and H atoms), while the smaller value of the $^3J_{HP}$ 7.5 Hz of the doublet at δ 7.96 ppm—to (*E*)-enolate 3c. The ratio 3b/3c, determined on the basis of these signals was 1:2 in the isolated crystalline product, washed with ether. The configuration of 3b



b c

3 R=Me
4 R=Ph

FIGURE 1 (*Z*)- and (*E*)-structure of the lithium salts of 1 and 2.

TABLE I
^{31}P NMR data in CDCl$_3$ of phosphonates 1, 2, 3, 4 and 5

Compound	(ppm)	J_{HP} (Hz)
1a	23.05 24.50[a]	9.8
1c	27.09 26.60[a]	9.8
2a	17.90	
2c	23.86	9.8
3b	32.58	39.2
3c	37.69	10.2
4b	27.90	40.3
5	27.36	43.9

[a] In DMSO.

and 3c were confirmed by ^{31}P NMR (see Table I), where $^3J_{HP}$ in nondecoupled spectra were 39.2 and 10.2 Hz respectively. In ^{13}C NMR of 3 the smaller value of $^2J_{PC\text{-}2}$ (11.7 Hz) in 3b and the larger value of $^2J_{PC\text{-}2}$ (26.3 Hz) in 3c are in agreement with the literature data for (*Z*)- and (*E*)-metal complexes of diethyl (2-oxopropyl)phosphonate.[14]

The relative proportions of the two isomers 3b and 3c may be due to the position of the equilibrium between the (*Z*)- and (*E*)-enols in the reacting ligand or to the interconversion 3b $\rightleftharpoons$ 3c. Investigations on this problem are in course.

The IR and NMR (^{1}H, ^{13}C and ^{31}P) spectral data of 4 were consistent with a (*Z*)-chelate structure 4b. The absorption of PO group at 1175 cm^{-1} as well as the large value of $^3J_{HP}$ in ^{1}H and ^{31}P nondecoupled spectra (40.6 and 40.3 Hz respectively) and the small one of $^3J_{PC\text{-}2}$ (6.1 Hz) in ^{13}C NMR spectra prove (*Z*)-chelate structure with transorientated phosphorus and hydrogen atoms.

With a view to obtain comparative data for the complexation ability of β-oxophosphonates 1, 2 and the unsubstituted phosphonoacetaldehyde 6 (R=H) the synthesis of the zinc complexes of esters 1 and 2 was attempted, using zinc acetate dihydrate in anhyrous methanol (ratio ligand:acetate = 2:1). The ester 1 did not react with zinc acetate under these conditions,† while the ester 2 gave the complex 5 quantitatively. Its structure was established by ^{1}H, ^{31}P and ^{13}C NMR spectra and confirmed by elemental analysis and IR spectra.

The presence of an acetate group was indicated by the ^{1}H NMR signal at δ 2.06

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†Starting 1 and oligomers were isolated.

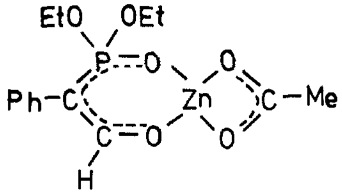

FIGURE 2 Possible structure of the complex 5 with a coordination number 4 for the metal.

ppm corresponding to the acetate methyl group and appropriate ^{13}C NMR signals at δ 180.98 and 23.61 ppm. The large value of $^{3}J_{HP}$ 41.4 Hz in ^{1}H and 43.9 Hz in ^{31}P nondecoupled spectra establishes trans orientated phosphorus and hydrogen atoms. Figure 2 shows a possible structure of the complex 5 with a coordination number 4 for the metal.

The present experimental data concerning the reactivity of α-substituted phosphonoacetaldehydes 1 and 2, compared to our previous data for unsubstituted phosphonoacetaldehyde 6,[1] indicate the lowest reactivity for 1 in the complexation reaction due to its lower acidity, as well as the highest activity in the aldol condensation (the highest basicity of the conjugated anion).

The stereochemistry of the starting phosphonoacetaldehydes 1 and 2 was investigated by IR and NMR spectroscopy. The IR (nujol and film) and NMR ($CDCl_3$) spectral data of the ester 1 indicate it to be a mixture of aldehyde 1a and (*E*)-enolic tautomer 1c, with (*E*)-enol predominating. In IR spectra we accept the bands at 1635 cm^{-1} and 2730 cm^{-1} to be characteristic for C=C and OH groups in (*E*)-enols and 1600 cm^{-1} for C=C group in (*Z*)-enols in accordance with References 8, 11, 15 and on the opposite of Reference 12. The IR spectra of 2 in nujol showed a predominance of (*E*)-enol 2c, the (*Z*)-enol 2b being less than 10% and the aldehyde form 2a is absent. In 0.025 M solution of tetrachloromethane for 6 hours the equilibrium 2a $\rightleftharpoons$ 2b $\rightleftharpoons$ 2c is shifted to the (*Z*)-enol 2b: immediately after dissolving the ratio 2a:2b:2c was 1:5:5.7; six hours later it was 1:7.9:0. The ^{31}P NMR ($CDCl_3$) spectra of phosphonates 1 and 2 contained signals at δ 27.09 and 23.86 ppm respectively, both of which appeared as doublets in the nondecoupled spectra with J_{HP} 9.8 Hz, and thus are attributed to the (*E*)-enolic tautomers 1c and 2c on the basis of the reduced magnitude of the vicinal HP coupling constants. Weaker signals at 23.05‡ (in 1) and 17.9 ppm (in 2) are attributed to the aldehyde forms 1a and 2a.

Thus unlike β-dicarbonyl compounds intermolecular hydrogen bonding in (*E*)-tautomers of the phosphonates appear to have a similar stabilising effect as the intramolecular hydrogen bonding in the (*Z*)-tautomers. This can be understood on the basis that phosphorus acts as a barrier to through-conjugation and therefore there is little difference in the resonance stabilisation of the two isomers.

EXPERIMENTAL

The ligands 1[3] and 2[5] were prepared by literature methods. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL FX 90Q spectrometer. The ^{31}P [H] spectra were recorded at 36.23 MHz in 10 mm

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‡Lit.[3] 20.2.

tube, referenced to external 85% aq. H_3PO_4. The IR spectra were registered on Specord-71 IR. The solvents tetrahydrofuran, diethyl ether and hexane were dried by distillation from sodium-benzophenone. The reactions of **1** and **2** with butyllithium were carried out under argon.

Sometimes an impurity in the starting diethyl ester of benzylphosphonic acid was observed in the spectra of **2** (δ_H, $CDCl_3$, 3.15, 2H, d, J_{HP} 21.6, CH_2; δ_C 33.53 CH_2, J_{CP} 138.7; ^{31}P 26.68, lit.[16] 25.0, J_{CP} 137.4).

2-Diethoxyphosphonyl-propene-1-olato-lithium **3**. To a solution of *n*-butyllithium (5 mmol, 1.6 M in hexane) in 2 ml of THF, cooled to −70°C, diethyl 2-oxo-1-methyl-ethylphosphonate **1** (0.97 g, 5 mmol) in 5 ml of THF was added dropwise under argon. The reaction mixture was stirred for 90 minutes at −70°C and left overnight at −20°C. The precipitate was filtered off under argon, washed with ether and dried in vacuum. The yield of salt **3** was 0.70 g (70%), m.p. above 300°C. The product is soluble in DMSO, methanol and insoluble in THF, $CHCl_3$ and acetone.

$C_7H_{14}O_4PLi$ (200.0) Calc. %: C, 42.02; H, 7.06; Li, 3.46. Found %: C, 42.00; H, 7.12; Li, 3.40: ν_{max} (nujol)/cm^{-1} 1020 and 1050 (P—O—C), 1175 (P=O in **3b**), 1220 (P=O in **3c**), 1580 (C=C).

3b: (δ(ppm), J(Hz)) ^1H NMR (90 MHz; $CDCl_3$) δ: 1.18 (6H, dt,[a] C-Me), 1.44 (3 H, d, J_{HP} 13.5, 1′-Me), 3.75 (4 H, m,[a] OCH_2), 7.91 (1 H, d, J_{HP} 41.35, 2-CH); ^{13}C NMR δ_C 13.19 (methyl, J_{CP} 13.27, C'_1), 16.37[b] (methyl, J_{CP} 7.2, C-10), 59.10 (methylene, J_{CP} 4.3, C-9), 68.23 (C-1),[c] 176.3 (methine, J_{CP} 11.7, C-2).

3c: ^1H NMR, δ: 1.18 (6 H, dt,[a] C-Me), 1.38 (3 H, d, J_{HP} 14.4, 1′-Me), 3.75 (4 H, m,[a] OCH_2), 7.96 (1 H, d, J_{HP} 7.5, 2-CH); ^{13}C NMR δ_C 8.96 (methyl, J_{CP} 10.35, C'_1), 16.37[b] (methyl, J_{CP} 7.2, C-10), 58.56 (methylene, J_{CP} 4.3, C-9), 77.54 (quaternary, J_{CP} 192.5, C-1), 172.2 (methine, J_{CP} 26.3, C-2).

(Z)-2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato-lithium **4b**. To a solution of 4.3 mmol of *n*-butyllithium (1.6 M in hexane) in 2 ml of THF at −70°C, diethyl ester of 2-oxo-1-phenyl-ethylphosphonic acid **2** (1.03 g, 4 mmol) in 4 ml of THF was added dropwise under argon. The reaction mixture was stirred at this temperature for 2 hours and left at 20°C overnight. The solvent was removed in vacuum and the oil stirred with 15 ml of hexane. The precipitate was filtered off, washed with hexane and dried in vacuum to give **4b** (0.97 g, 93%), m.p. 115–118°C. After recrystallisation from hexane-ether 3:1 the m.p. was 125–126°C; yield 0.75 g (77%). **4b** is soluble in ether, $CHCl_3$, DMSO and insoluble in hexane.

$C_{12}H_{16}O_4PLi$ (262.1) Calc. %: C, 54.99; H, 6.14; Li, 2.64. Found %: C, 55.30; H, 6.32; Li, 2.60; ν_{max} (nujol)/cm^{-1} 1020 and 1050 (P—O—C), 1175 (P=O), 1550 (C=C); ^1H NMR (90 MHz; $CDCl_3$) δ: 1.13 (6 H, dt, J_{HH} 6.7, J_{HP} 5, C—Me), 3.97 (4 H, m, OCH_2), 6.93–7.49 (5 H, m, Ph), 8.33 (1 H, d, J_{HP} 40.56, 2-CH); ^{13}C NMR, δ: 16.1 (methyl, J_{CP} 7.2, C-10), 61.0 (methylene, J_{CP} 4.5, C-9), 90.4 (quaternary, J_{CP} 184.4, C-1), 124.10 (methine, C-*p*), 127.85 (methine, C-*m*), 127.85 (methine, C-*o*), 138.97 (quaternary, J_{CP} 11.7, C-*i*), 178.41 (methine, J_{CP} 6.1, C-2).

(Z)-2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato-zinc-acetate **5**. $Zn(OOCCH_3)_2 \cdot 2H_2O$ (0.44 g, 2 mmol) in 4 ml of methanol was added dropwise to a solution of diethyl ester of 2-oxo-1-phenyl-ethylphosphonic acid **2** (1.03 g, 4 mmol) in 3 ml of methanol. The reaction mixture was stirred for 10 hours at room temperature and concentrated to 5 ml. The crystals were filtered off, washed with ether and dried in vacuum to give **5** (0.72 g, 95%), m.p. 155–157°C. Compound **5** is soluble in DMSO, $CHCl_3$, THF and insoluble in ether, hexane and water.

$C_{14}H_{19}O_6PZn$ (379.6) Calc. %: C, 44.30; H, 5.04; Zn, 17.22. Found %: C, 44.53; H, 5.22; Zn, 17.17; ν_{max} (nujol)/cm^{-1} 1020 and 1050 (P—O—C), 1175 (P=O), 1550 (C=C); ^1H NMR (90 MHz; $CDCl_3$) δ: 1.18 (6 H, t, J_{HH} 6.6, C-Me), 2.06 (3 H, s, Me-acetate), 4.03 (4 H, m, OCH_2), 6.87–7.43 (5 H, m, Ph), 8.0 (1 H, d, J_{HP} 41.40, 2-CH); ^{13}C NMR δ: 16.03 (methyl, J_{CP} 7.2, C-10), 23.61 (methyl, Me-acetate), 62.27 (methylene, J_{CP} 4.3, C-9), 94.0 (quaternary, J_{CP} 179.9, C-1), 125.64 (methine, C-*p*), 127.91 (methine, C-*m*), 128.17 (methine, C-*o*), 136.7 (quaternary, J_{CP} 10.1, C-*i*), 172.39 (methine, C-2), 180.98 (quaternary, C in COO).

Diethyl-(1-methyl-2-oxoethyl)phosphonate **1**. **1a**[d]: ^{13}C NMR ($CDCl_3$) δ: 7.55 (methyl, J_{CP} 5.6, C'_1), 16.07, 16.20 and 16.33[e] (methyl, C-10), 47.25 (methine, J_{CP} 130.2, C-1), 62.75 (methylene, J_{CP} 5.8, C-9), 196.0 (formyl, J_{CP} 4.5, C-2).

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[a] The ^1H NMR signal for the methyl and methylene groups of **3b** and **3c** overlap.

[b] The ^{13}C NMR signal for methyl groups of **3b** and **3c** overlap.

[c] Only half of the doublet was observed.

[d] The ^1H NMR spectra of aldehyde **1a** corresponded to the published data,[3] with exception of $^3J_{HP}$ 23.5 (1′-Me), while in Lit.[3] it is 18.

[e] The ^1H NMR signals for two methyl groups of **1a** and **1c** tautomers overlap.

1c: ^{1}H NMR (90 MHz; CDCl$_3$)^f δ: 1.31^c (6 H, dt, J_{HH} 6.8, C-Me), 1.67 (3 H, dd, J_{HH} 1.3, J_{HP} 14.6, 1′-Me), 4.09 (4 H, qi, J_{HH} = J_{HP} 7, OCH$_2$), 7.34 (1 H, dd, J_{HH} 1.3, J_{HP} 10.6, 2-CH), 10.5 (1 H, br s, OH); ^{13}C NMR, δ: 8.23 (methyl, J_{CP} 7.2, C_1'), 61.28 (methylene, J_{CP} 2, C-9), 92.96 (quaternary, J_{CP} 112.5, C-1), 155.94 (methine, J_{CP} 29.2, C-2).

Diethyl-(2-oxo-1-phenylethyl)phosphonate 2. **2a**: ^{1}H NMR (90 MHz; CDCl$_3$) δ: 1.22^c (6 H, t, J_{HH} = J_{HP} 6.6, C-Me), 3.62 (1 H, dd, J_{HP} 11.6, 1-CH), 3.92–4.26 (4 H, m, OCH$_2$), 7.11–7.56 (5 H, m, Ph), 9.78 (1 H, s, 2-CHO); ^{13}C NMR δ: 16.39^e (methyl, J_{CP} 5.9, C-10), 62.7 (methylene, J_{CP} 5.8, C-9), 60.28^g (methine, J_{CP} 128.6, C-1), 194.05 (formyl, C-2), 127.07–130.19 (Ph).

2c: ^{1}H NMR (90 MHz; CDCl$_3$) δ: 1.22^c (6 H, t, J_{HP} = J_{HH} 6.6, C-Me), 4.02 (4 H, qi, J_{HH} = J_{HP} 7, OCH$_2$), 7.11–7.56 (5 H, m, Ph), 7.79 (1 H, d, J_{HP} 11.26, 2-CH), 10.99 (1 H, br s, OH); ^{13}C NMR δ: 16.39^e (methyl, J_{CP} 5.9, C-10), 62.1^g (methylene, J_{CP} 4.3, C-9), 98.4 (quaternary, J_{CP} 115.1, C-1), 127.07–130.19 (Ph), 162.96 (methine, J_{CP} 5.8, C-2).

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[f] ^{1}H NMR of 1 in CCl$_4$ see in Reference 11.

[g] Tentative assignment.