The Formation of 2-Oxopropyl-2-oxopropylidenediphenylphosphorane. Crystal and Molecular Structure of its Lithium Enolate

Olyana Angelova, Emil M. G. Kirilov, Marko Kirilov, and Galin Petrov *
Department of Chemistry, Kliment Ochridsky University of Sofia, 1126 Sofia, boul. Anton Ivanov 1, Bulgaria
José Kaneti *
Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria
Josef Macicek
Institute of Applied Mineralogy, Bulgarian Academy of Sciences, 1000 Sofia, Bulgaria

An assignment of the constitution of the compound obtained in the reaction of Ph_2PSiMe_3 with $BrCH_2COCH_3$ (1) is made. Subsequent dehydrobromination is reported to give 2-oxopropyl-2-oxopropylidenediphenylphosphorane (4) instead of diphenylphosphinoacetone (2). Lithiation of (4) yields the corresponding enolate (6). The crystal and molecular structure of (6) has been resolved by X-ray diffraction analysis, and spectroscopic properties of (4) are interpreted on the basis of MNDO calculations.

Several syntheses[1-4] of 2-oxopropyl(diphenyl)phosphine [diphenylphosphinoacetone (2)] have been described previously. Scheme 1 shows one such synthesis reported which yields products having somewhat contradictory properties. Compound (2) has been reported to be a liquid, with b.p. 138 °C at 0.03 Torr.†[1-3] A solid product (m.p. 93–95 °C) has been obtained by Brunner and co-workers.[4] The latter method is followed here since it was reported to yield compound (2) more directly and under milder conditions than other methods.

Results and Discussion

Our [1]H n.m.r. and i.r. spectroscopic data for the intermediate shown in Scheme 1, and for the final product, are approximately the same as the published values,[4] but are more complex. A ratio of 10:4:6 for the integrated intensities in the [1]H n.m.r. spectrum of the intermediate was observed instead of 10:2:3:1, which is the ratio expected for the analysis suggested by Brunner.[4] No absorption corresponding to a P–H stretching vibration in the 2 100–2 450 cm^{-1} region was present in our i.r. spectra. We thus found no spectroscopic evidence for the presence of a PH group in the intermediate (3).

The [1]H n.m.r. spectrum of our final product, (4), showed two broad singlets in the non-aromatic region at 2.17 and 4.09 ppm. The latter resonance is due to exchangeable protons (shown by treatment with D_2O). For compound (2) one would expect a proton integral ratio of 10:2:3, whereas we observed 10:3:6. These findings led us to the idea that the reaction between $Ph_2P–SiMe_3$ and bromoacetone, under strictly maintained conditions, proceeeds along an alternative pathway to yield bis(2-oxopropyl)diphenylphosphonium bromide (3) and, after dehydrobromination, 2-oxopropyl-2-oxopropylidene phosphorane (4), Scheme 2.

The intermediate and the final product of Scheme 2, were further verified by a more thorough investigation. In the mass spectrum of the intermediate (3), the peak with the highest intensity, *ca.* 90, appears at m/z 298. This corresponds to compound (4) (Calc. M 298). The occurrence of this fragment is attributed to thermal decomposition of (3), M 379, which loses HBr, M 81. For the intermediate of Scheme 1, with M 323 (Calc.) the peak for the fragment obtained by dehydrobromination should appear at m/z 242. Instead, a smaller peak, of intensity *ca.* 20 and with no bromine-isotope pattern, is observed at m/z 320, this was not assigned in the present work.
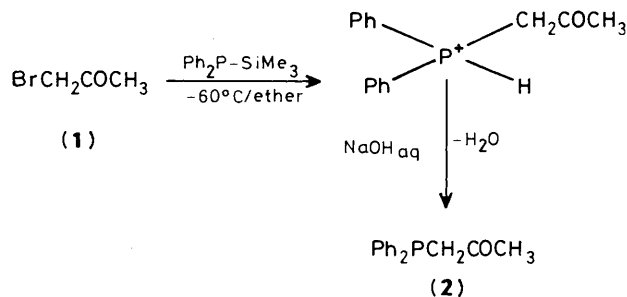
Scheme 1. The reaction of bromoacetone and diphenyltrimethysilyl phosphine, according to Brunner.[4]
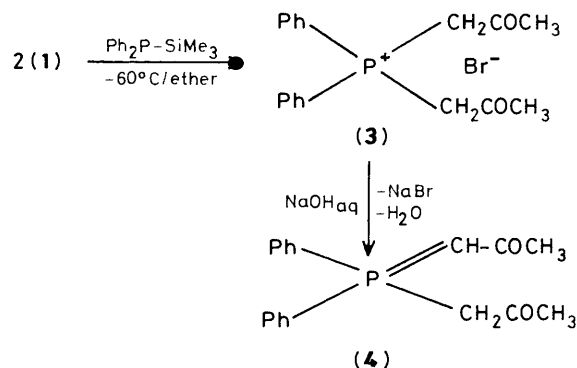
Scheme 2. The reaction of bromoacetone and diphenyltri(methylsilyl)-phosphine.

The observed proton-integral ratio 10:3:6 for the intermediate is consistent with the phosphonium bromide structure, (3). The broad features in the [1]H n.m.r. spectrum of the final product might be attributed to slow proton exchange due to prototropy (Scheme 3).

Proton exchange of the above type has been reported for phosphoranes containing the fragment $P(=CH)CH_2$.[5-8] In these cases the prototropy is explained in terms of catalytic participation of proton donors from the solvent and formation of intermediate phosphonium salts.[8] The high J_{PC} value (88.8
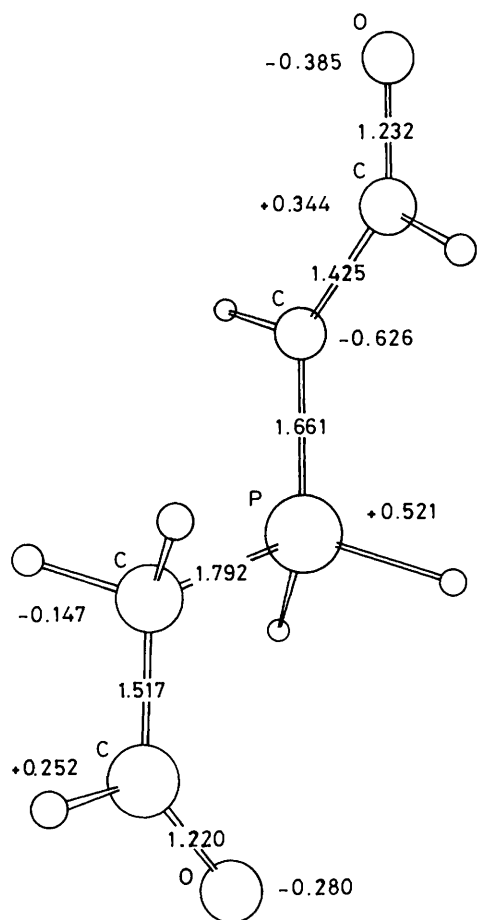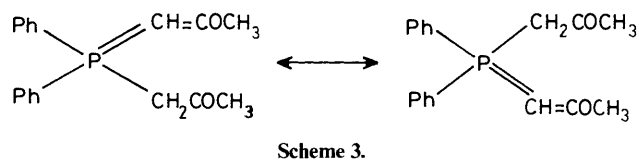
† 1 Torr = 133.32 Pa.

Figure 1. MNDO optimized structure of the model 2-oxoethyl-2-oxo-ethylidenephosphorane: calculated atomic charges and bond lengths.
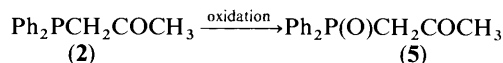

Scheme 3.

Hz), for the aromatic carbon directly bonded to phosphorus, in the ^{13}C n.m.r. spectrum of (4) indicates a hypervalent structure of ylide type.[9] The slow exchange process, also observed in the ^1H n.m.r. spectrum, gives rise to broad ^{13}C signals for the methine and methylene carbon atoms, and to another broad signal for the two methyl groups, additionally split due to P–C coupling.

The i.r. spectrum of our final product did not show the single intense carbonyl peak expected for a phosphinoacetone. Instead, we observed an additional intense absorption at 1 530 cm^{-1}. An attempt to model the vibrational spectrum of phosphinoacetone by MNDO calculations[11] [v_{CO}(Calc.) = 1 713 cm^{-1}] did not explain the additional, intense peak close to the carbonyl region. We therefore investigated the vibrational spectra of two other model molecules, 2-oxoethyl-2-oxoethyl-idene- and 2-oxo-propyl-2-oxopropylidene-phosphoranes, by further MNDO calculations. The two models indeed provide for a split vibrational pattern in the carbonyl region, calculated frequencies 1 621 and 1 718 cm^{-1}. Therefore, we assign the 1 530 cm^{-1} peak to the carbonyl stretching vibration in an ylide fragment, P=CHCOCH$_3$, of (4). The extraordinary lowering of the carbonyl frequency in similar ylides has been attributed to the strong resonance conjugation.[10] An alternative, although

essentially equivalent, interpretation is suggested by our MNDO calculations. The calculated atomic net charges (MNDO), and the elongated C=O bond are characteristic of a quasi-carbanionic structure, responsible for the observed low carbonyl vibrational frequency, Figure 1.

To prove the structure of (2), Brunner and co-workers[4] carried out oxidation of the alleged phosphine to the corresponding phosphine oxide (5), Scheme 5. Another well known property of phosphonium ylides is their hydrolysis,[12] which also yields phosphine oxides. We isolated (5) by treating the phosphorane (4) with aqueous NaOH. Our m.p. determinations and spectroscopic data for (5) are the same as the literature values.[13,14] Traces of phosphine oxide (5) were also obtained in some of the work-up procedures of (4). Obviously, partial hydrolysis occurs during the dehydrobromination procedure, as shown below.

$$Ph_2PCH_2COCH_3 \xrightarrow{\text{oxidation}} Ph_2P(O)CH_2COCH_3$$
$$\text{(2)} \qquad\qquad\qquad \text{(5)}$$
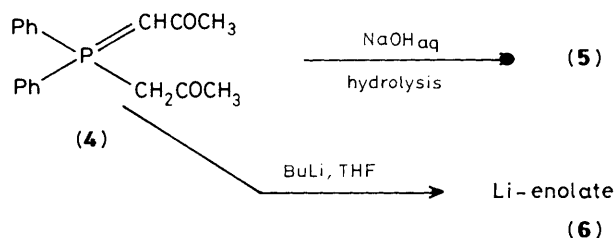
Scheme 4.

Scheme 5.

The reliability of the proposed reaction schemes is definitively confirmed by an X-ray diffraction analysis of (6). The crystals, prepared for this analysis, were actually formed from the centrosymmetric dimer of (6), $Li_2L_2(THF)_2$ where L is the phosphorane ligand $Ph_2P(CHCOCH_3)_2$, (see Figure 2) and additional solvating THF molecules, in the ratio 1:2. The enolised phosphorane ligand associates with lithium in a bidentate fashion to form eight-membered rings. Essential atomic parameters of the refined structure are listed in Table 1, and selected bond lengths and angles are given in Table 2. A characteristic feature of the observed dimeric structure is the rhomboidal bridgewise Li–O connection between two mono-meric fragments. The latter are arranged in a propeller-like fashion around the central Li–O rhombus, together with two THF molecules, each associated with a lithium atom. The ligand rings may be considered to consist of two planar O–C(CH$_3$)–C–P fragments, with a dihedral angle of 117.2° between the planes. The phosphorus atom is in a distorted tetrahedral environment. The most significant deviation from the tetrahedral angle is observed for the C(1)–P–C(1′) angle, 122.1°. The tilting angle between the phenyl rings is 99.3°.

The lithium atom is thus tetrahedrally co-ordinated to four oxygen atoms, one of which is contributed by a co-ordinated THF molecule [Li–O(F) distance 2.03 Å]. Additional solvating tetrahydrofuran molecules fill the space between the voluminous complexes and are planarly disordered in the structure. Their interaction with the rest of the structure is by van der Waals' bonding. A perspective drawing of the dimeric lithium enolate of 2-oxopropyl-2-oxopropylidenediphenylphosphorane is given in Figure 2.

We have demonstrated that the reaction of diphenyltrimethyl-silylphosphine with bromoacetone yields 2-oxopropyl-2-oxo-propylidenediphenylphosphorane (4), and not the 2-oxopropyl-diphenylphosphine (2), claimed by Brunner. The latter may possibly take part in the reaction as a transient intermediate, which quaternizes readily with the excess bromoacetone, to

(6)
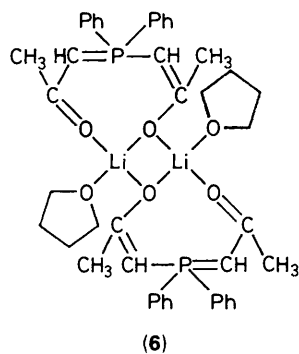
Table 1. Atomic co-ordinates (with esds in parentheses) for compound (6)

Atom	x	y	z
P	0.209 7(4)	0.002 3(4)	0.134 7(3)
C(1)	0.321(2)	0.008(1)	0.219(1)
C(2)	0.417(2)	0.065(1)	0.214(1)
C(3)	0.508(2)	0.067(2)	0.295(1)
O	0.429(1)	0.114 4(8)	0.145 4(8)
C(1')	0.210(1)	−0.072(1)	0.040(1)
C(2')	0.292(2)	−0.076(1)	−0.015(1)
C(3')	0.286(2)	−0.147(1)	−0.095(1)
O'	0.386(1)	−0.032 1(8)	−0.072(8)
C(1a)	0.101(1)	−0.046(1)	0.195(1)
C(2a)	−0.001(2)	0.001(2)	0.293(1)
C(3a)	−0.086(2)	−0.037(1)	0.250(1)
C(4a)	−0.072(2)	−0.124(2)	0.287(2)
C(5a)	0.031(2)	−0.174(1)	0.283(1)
C(6a)	0.115(2)	−0.134(1)	0.232(1)
C(1b)	0.165(1)	0.114(1)	0.097(1)
C(2b)	0.112(2)	0.128(1)	0.009(1)
C(3b)	0.069(2)	0.215(2)	−0.016(1)
C(4b)	0.074(2)	0.284(2)	0.051(1)
C(5b)	0.127(2)	0.271(1)	0.136(1)
C(6b)	0.172(2)	0.185(1)	0.162(1)
O(F)	0.438(1)	0.180(1)	−0.057(1)
C(F1)	0.371(2)	0.255(2)	−0.049(2)
C(F2)	0.319(2)	0.282(2)	−0.147(2)
C(F3)	0.389(3)	0.223(2)	−0.205(2)
C(F4)	0.457(3)	0.163(2)	−0.149(2)
C(D1)ᵃ	0.263(3)	0.010(3)	0.518(3)
C(D2)ᵃ	0.153(3)	0.011(3)	0.472(3)
C(D3)ᵃ	0.160(2)	0.105(3)	0.437(2)
C(D4)ᵃ	0.270(3)	0.139(2)	0.459(3)
C(D5)ᵃ	0.330(2)	0.077(3)	0.513(2)
Li	0.460(3)	0.079(3)	0.037(3)

ᵃ Atoms include a disordered oxygen.

Table 2. Selected bond lengths/Å and angles/° of the dimer of lithium 2-oxopropyl-2-oxopropylidenediphenylphosphorane (6).

Li–O	1.76(4)	Li–O″	2.05(4)
Li–O′	1.94(4)	Li–O(F)	2.03(5)
P–C(1)	1.73(2)	P–C(1b)	1.79(3)
P–C(1a)	1.80(2)	P–C1')	1.79(2)
C(1)–C(2)	1.43(3)	C(2')–C(3')	1.58(3)
C(2)–C(3)	1.53(3)	C(2)–O	1.27(2)
C(1')–C(2')	1.33(3)	C(2')–O'	1.29(2)
O–Li–O'	115(2)	O'–Li–O″	92(2)
O–Li–O″	125(3)	O'–Li–O(F)	112(2)
O–Li(F)–O	112(3)	O″–Li–O(F)	99(2)
C(1)–P–C(1')	122.4(9)	C(1')–P–C(1b)	109.7(8)
C(1)–P–C(1a)	101.3(9)	C(1a)–P–C(1b)	107.9(9)
C(1)–P–C(1b)	111.4(9)	P–C(1)–C(2)	124(1)
C(1')–P–C(1a)	102.5(9)	P–C(1')–C(2')	125(1)
C(1)–C(2)–C(3)	118(2)	C(1')–C(2')–C(3')	121(2)
C(1)–C(2)–O	122(2)	C(1')–C(2')–O'	128(2)
C(3)–C(2)–O	119(2)	C(3')–C(2')–O'	111(2)

Figure 2. The crystal structure of dimer lithium enolate of 2-oxopropyl-(2-oxopropylidene)diphenylphosphorane (6).
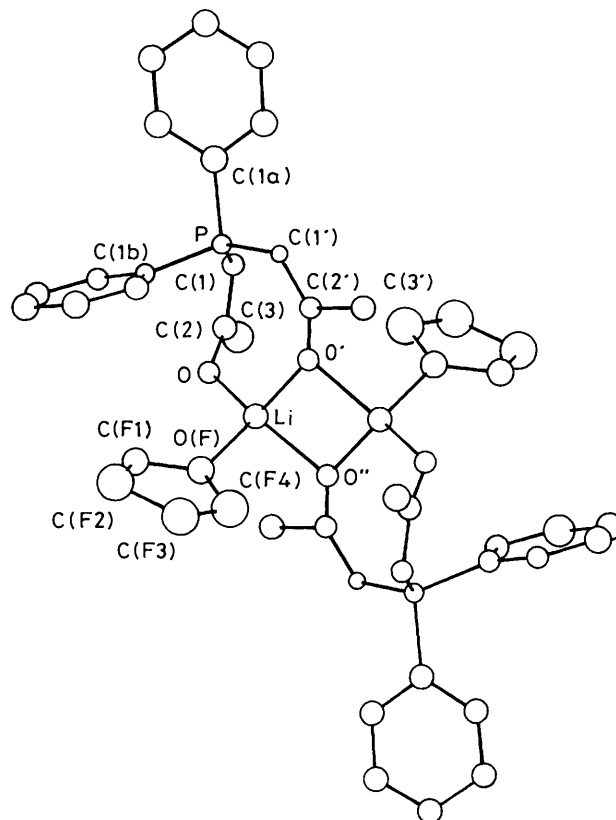
yield the isolable phosphonium bromide (3). We are now undertaking further studies of phosphoranes, using the clarified synthetic procedure.

Experimental

I.r. spectra were recorded on SPECORD 71 IR and UR 20, Carl Zeiss, Jena, spectrometers for KBr pellets. N.m.r. spectra were run on TESLA BI 487, 80 MHz (^{1}H), and Bruker WP 250, 250 MHz (^{1}H), and 62.9 MHz (^{13}C) instruments. SiMe$_4$ was used as an internal standard. The mass spectra were run on a JEOL JMS D300 at 70 eV and a source temperature of 170 °C. M.p.s were determined on a Kofler hot-stage microscope and are uncorrected. All experiments with phosphines and lithium

compounds were carried out under argon atmosphere in water-free solvents.

Compounds (3) and (4) were obtained by the procedure described previously by Brunner et al.[4]

Bis(2-oxopropyl)diphenylphosphonium Bromide (**3**).—M.p. 201–203 °C after recrystallization from EtOH (lit.,[4] 200–202 °C); v_{max} 1 720 cm^{-1} (CO), (lit.,[4] 1 720 cm^{-1}); δ_H(80 MHz; CDCl$_3$) 2.36 (6 H), 5.40 (4 H), and 7.35–7.91 (10 H) [lit.,[4] δ(60

MHz; CDCl$_3$, SiMe$_4$) 2.39 (d, J_{PH} 2 Hz, CH$_3$), 5.41 (d, J_{PH} 12 Hz, CH$_2$), and 7.31–8.09 (m, arom.)]. [Found: C, 55.9; H, 5.1. Calc. for C$_{15}$H$_{16}$BrOP (1): C, 55.74; H, 4.99%; Calc. for C$_{18}$H$_{20}$BrOP (3): C, 56.95; H, 5.28%]; m/z no M^+, 320 (20%), 298 (95), 283 (100), 201 (30), 183 (28), 155 (17), and 43 (30).

2-Oxopropyl(2-oxopropylidene)diphenylphosphorane **(4).**— M.p. 119–121 °C (THF), (lit.,[4] 93–95 °C); v_{max} 1 400 (P=C), 1 530 (ylide CO), and 1 720 cm^{-1} (CO) (lit.,[4] 1 720 cm^{-1} only); δ_H(250 MHz) 2.17 (6 H, d, J_{PH} 1.5 Hz, CH$_3$), 4.09 (3 H, br s, CH and CH$_2$, D$_2$O exchangeable), 7.40–7.71 (10 H, multiplet, C$_6$H$_5$) [lit.,[4] δ(60 MHz; CDCl$_3$; SiMe$_4$) 2.14 (s, CH$_3$), 4.16 (s, CH$_2$), and 7.28–7.86 (m, C$_6$H$_5$)]; δ_C 30.14 (br d, J_{PC} 7.4 Hz, CH$_3$), 45.78 (br d, J_{PC} 77.7 Hz, CH and CH$_2$), 125.01 (d, J_{PC} 11.1 Hz, C$_{meta}$), 126.7 (d, J_{PC} 88.8 Hz, C$_{ipso}$), 132.01 (d, J_{PC} 11.1 Hz, C$_{ortho}$), 132.3 (s, C$_{para}$), and 196.7 (CO).

2-Oxopropyl(diphenyl)phosphine Oxide, **(5).**—δ_H (250 MHz; CDCl$_3$) 2.32 (s, 3 H, CH$_3$), 3.60 (d, 2 H, J_{PH} 14 Hz, CH$_2$), and 7.4–7.8 (m, 10 H, C$_6$H$_5$).

Bis[(μ-4,4-diphenyl-4λ^5-phosphahepta-2,4-diene-2,6-dionato-(tetrahydrofuran)lithium]. **(6).**—Butyl-lithium (3.66 cm^3; 5 mmol; 15% hexane solution) was added dropwise to a solution of **(4)** (1.45 g 4.5 mmol) in THF (30 cm^3) and stirred vigorously then cooled to −60 °C. The colourless precipitate was filtered off and dissolved in THF (40 cm^3) under reflux. The product **(6)** crystallized as colourless prisms after the solution had been cooled to room temperature (1.85 g, 89.8%), m.p. 132–134 °C (THF); v_{max} 1 530 cm^{-1} (C–O and C=C, enolate) (Found: C, 69.9; H, 7.65. C$_{52}$H$_{68}$Li$_2$O$_8$P$_2$ requires C, 69.64; H, 7.59%).

X-Ray Structure Determination of **(6).**—*Crystal data:* C$_{52}$H$_{68}$Li$_2$O$_8$P$_2$, M 896.95. Monoclinic, $P2_1/n$; a = 11.932(7), b = 14.679(3), c = 14.815(3) Å, β = 95.97(3)°, V = 2 581(3) Å^3, Z = 2, D_x = 1.154 g cm^{-3}, λ(Mo-K_α) = 0.710 73 Å, μ = 1.28 cm^{-1}, $F(000)$ = 960, T = 295 K. The crystals were found to decompose rapidly when exposed to air, this necessitated careful handling under argon. A transparent colourless prismatic crystal with approximate dimensions 0.14 × 0.11 × 0.12 mm was selected, mounted in a thin-walled Liendemann capillary, and fixed with silicon grease. D_m was not determined. An Enraf–Nonius CAD-4 diffractometer with a graphite monochromator was used, scan type ω/2θ, scan rate of 6–7° min^{-1}, width (1.3 + 0.340 tanθ)°. Cell constants are derived from a least-squares treatment of 22 reflections with θ = 18.60°. A limited range of sinθ/λ < 0.549 (h: 0 to 13; k: 0 to 16; l: −16 to 16) was selected since the intensities at scattering angles larger than θ = 23° were too weak to measure. The intensities of three standard reflections were monitored every 1 h. After 19.2 h of X-ray exposure, the data collection was interrupted automatically, as the initial intensity drop cut-off

(FADING = 0.5) was reached. The experiment was then continued by forcing FADING to 0.2. After 27.0 h of irradiation, the total loss of intensity was 62.1%. The intensities of the 3 769 reflections collected, with the inclusion of those systematically disregarded in the space group $P2_1/n$ and also the equivalent reflections, were corrected for Lorentz and polarization effects, linear decay (maximum correction factor 1.635), and absorption (program EAC, maximum correction 99.98%, minimum correction 97.08%). 1 186 out of a total of 3 373 unique reflections, with $I > 2\sigma(I)$, were used in further calculations.

All attempts to solve the structure by direct methods (program MULTAN) proved unsuccessful. This was probably due to the limited number of good quality reflections. The position of the phosphorus atoms was determined from a 3D Patterson map, and used to generate a starting set of phases. Subsequent differential Fourier syntheses and matrix refinements on F with isotropic thermal parameters revealed the positions of all non-hydrogen atoms of the centrosymmetric dimer. An additional disordered THF molecule was also found, and the structure was isotropically refined to R_{iso} = 0.160. The anisotropic refinement converged at R = 0.133, R_w = 0.143, and S = 4.33, with unit weights. Maximum (Δ/σ) = 0.02: maximum, minimum residual densities were 0.49 and −0.62 Å^{-3}, respectively. No correction for extinction was applied. Atomic structure factors and complex coefficients were taken from the SDP V3.0 software package. The isotropic and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

References

1 Z. S. Novikova, N. V. Proskurina, L. I. Petrovskaja, I. V. Bogdanov, N. P. Galitskova, and I. F. Lutsenko, *Zh. Obshch. Khim*, 1967, **37**, 2028.

2 Z. S. Novikova, E. A. Efimova, and I. F. Lutsenko, *Zh. Obshch. Khim*, 1968, **38**, 2345.

3 Z. S. Novikova, N. P. Galitskova, V. A. Kozlov, and I. F. Lutsenko, *Zh. Obshch. Khim*, 1971, **41**, 831.

4 H. Brunner, M. Dylla, G. Hecht, and W. Pieronczyk, *Z. Naturforsch. Teil B*, 1982, 37, 404.

5 H. Schmidbaur and W. Tonich, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 448.

6 H. Schmidbaur and W. Tonich, *Chem. Ber.*, 1968, **101**, 604.

7 P. Crews, *J. Am. Chem. Soc.*, 1968, **90**, 2961.

8 H. Bestmann, G. H. Liberda, and J. P. Snider, *J. Am. Chem. Soc.*, 1968, **90**, 2963.

9 H. O. Kalinovsky, S. Berger, and S. Braun, '^{13}C N.m.r. Spektroskopie,' G. Thieme Verlag, Stuttgart, 1984, p. 532.

10 A. Dale and P. Froyen, *Acta Chem. Scand.*, 1970, **24**, 3772.

11 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4799; calculated frequencies are scaled by 400 cm^{-1}, see: M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa, W. Thiel, and Y. Yamaguchi, *J. Mol. Struct.*, 1978, **43**, 135.

12 L. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966.

13 B. A. Arbuzov, N. A. Polevaja, V. S. Vinogradov, and A. K. Shamsutdinova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 669.

14 M. Saunders and G. Burchmann, *Tetrahedron Lett.*, 1959, **1**, 8.

---

* For details of deposition of material at the Cambridge Crystallographic Data Centre, see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 2*, 1989, issue 1, p. xviii, paragraph 5.6.3.