The Reaction of Diphenylphosphine Oxide and Diphenylphosphine with Dialkyl Azodicarboxylates

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Diphenylphosphine oxide reacts rapidly with azodicarboxylates to give 1:1 diphenylphosphinoylhydrazine-1,2-dicarboxylate adducts. Structural analysis shows that the diethyl compound crystallises in space group $P\bar{1}$, $a = 12.197(5)$, $b = 9.507(3)$, $c = 8.503(6)$ Å, $\alpha = 85.83(5)$, $\beta = 76.91(6)$, $\gamma = 75.61(3)°$ and the diisopropyl compound crystallises in space group $P2_1/c$, $a = 21.344(6)$, $b = 9.702(2)$, $c = 10.929(4)$ Å, $\beta = 104.71(3)°$. The solid state conformations of the two molecules differ. In the diisopropyl structure the nitrogen protons and phosphorus oxygen atoms lie *trans* to each other whereas in the diethyl structure they are *cis*. ^{1}H and ^{13}C NMR spectroscopic studies reveal a high degree of hindered rotation. The mechanism of the reaction is discussed. Unexpectedly, diphenylphosphine and diisopropyl azodicarboxylate react slowly to give a complex mixture of products.

As part of a general investigation into the mechanism of the Mitsunobu reaction,[1] we have examined the reaction of secondary phosphines and phosphine oxides with azodicarboxylates. Generally, phosphine oxides are produced as by-products under Mitsunobu conditions and do not react further with azodicarboxylates. However, diphenylphosphine oxide was found to react with dialkyl azodicarboxylates in a manner similar to that previously reported[2] for alkyl phosphites and phosphinites to yield 1:1 adducts. Unlike the products from these latter reactions which were viscous oils, the diphenylphosphine oxide adducts were stable solids which could be readily crystallised allowing unambiguous crystallographic assignment of their structures.

Results and Discussion

Diphenylphosphine oxide and diisopropyl or diethyl azodicarboxylate react cleanly and rapidly to give 1:1 diphenylphosphinoylhydrazine-1,2-dicarboxylate adducts which have been characterised by NMR spectroscopy and X-ray crystallographic structural analysis. Molecules of the two compounds are shown in Fig. 1 and relevant bond distances and angles listed in Tables 1 and 2. The solid state conformations of the two molecules differ. In the diisopropyl structure **1**, the H(21) and phosphorus oxygen atoms lie *trans* to each other whereas in the diethyl structure **2**, they are *cis*. This conformational change and the diminished bulk of the diethyl substituent permits rotation of the phenyl ring (201–206) in the diethyl compound about the P–C(201) axis towards orthogonality with both the phenyl ring (101–106) and the azodicarboxylate assembly (Fig. 1) [O–P–C(201)–C(202) = −4.8° for **1**, −43.8° for **2**].

Solid state ^{13}C NMR spectra show the expected number of signals for each compound. The solution ^{1}H and ^{13}C NMR spectra of both adducts, however, display more than the expected number of signals. By way of example, four major and three minor sets of methyl doublets were observed in the ^{1}H NMR spectrum of **1**. In addition, a shoulder on one of the peaks suggested the presence of an eighth signal. This complexity has been attributed to the presence of *syn* and *anti* rotamers about the 'amide' and P(O)N moiety,[6] eight such rotamers being possible. The more stable rotamers (by virtue of superior hydrogen bonding or reduced steric interaction) will each

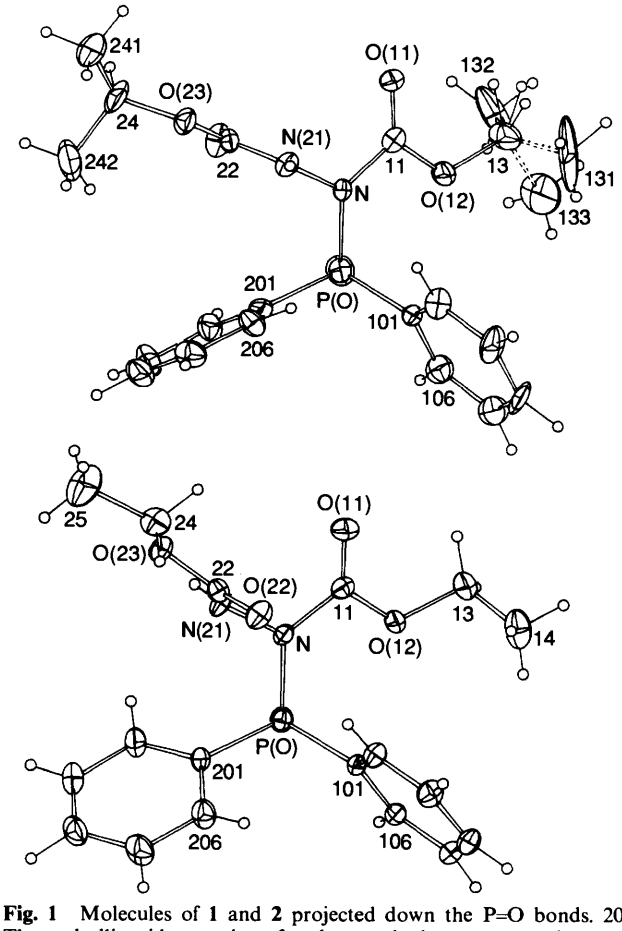


Fig. 1 Molecules of **1** and **2** projected down the P=O bonds. 20% Thermal ellipsoids are given for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

contribute to the NMR spectrum. It should be noted that another possible source of rotational isomerism is hindered rotation about the N–N bond as suggested by the existence of *cis* and *trans* PNNH conformations in the crystal structures. However, such conformational changes might be expected to result in different ^{31}P chemical shifts and no evidence for this

Table 1 Relevant interatomic distances (Å) for **1** and **2**

	1	2
P–C(101	1.77(1)	1.783(4)
P–C(201)	1.82(1)	1.796(4)
P–O	1.457(7)	1.472(3)
P–N	1.70(1)	1.710(4)
N–C(11)	1.41(2)	1.399(6)
N–N(21)	1.39(1)	1.397(6)
C(11)–O(11)	1.18(2)	1.187(6)
C(11)–O(12)	1.33(2)	1.332(6)
O(12)–C(13)	1.45(2)	1.454(6)
N(21)–C(22)	1.34(2)	1.352(6)
C(22)–O(22)	1.19(2)	1.193(5)
C(22)–O(23)	1.36(1)	1.337(6)
O(23)–C(24)	1.43(2)	1.451(8)

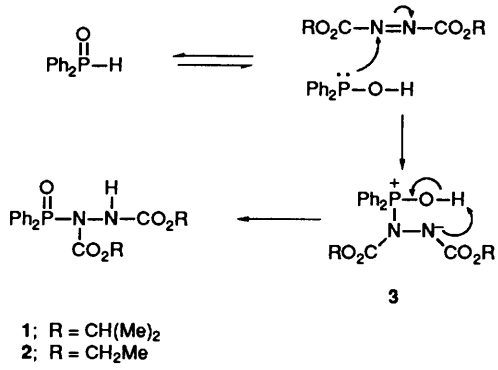
Table 2 Relevant interbond angles (degrees) for **1** and **2**

	1	2
C(101)–P–C(201)	107.3(5)	107.5(2)
C(101)–P–O	113.9(5)	114.9(2)
C(101)–P–N	104.7(6)	104.7(2)
C(201)–P–O	112.1(5)	111.2(2)
C(201)–P–N	102.9(5)	104.7(2)
O–P–N	115.0(5)	113.1(2)
P–C(101)–C(102)	125(1)	122.2(4)
P–C(101)–C(106)	117(2)	118.8(3)
P–C(201)–C(202)	115.4(8)	118.9(3)
P–C(201)–C(206)	123.3(9)	121.1(3)
P–N–C(11)	121.5(8)	124.2(3)
P–N–N(21)	122.4(7)	120.9(3)
C(11)–N–N(21)	115.3(9)	114.4(4)
N–C(11)–O(11)	125(1)	125.3(5)
N–C(11)–O(12)	107(1)	108.0(4)
O(11)–C(11)–O(12)	128(1)	126.7(4)
C(11)–O(12)–C(13)	120(1)	117.2(5)
N–N(21)–C(22)	118.9(9)	118.1(3)
N(21)–C(22)–O(22)	127(1)	125.3(5)
N(21)–C(22)–O(23)	105(1)	108.2(3)
O(22)–C(22)–O(23)	128(1)	126.5(5)
C(22)–O(23)–C(24)	116(1)	115.7(4)

was obtained. A single sharp ^{31}P resonance at *ca.* 30 ppm was observed for **1** and **2** in several different solvents (see Experimental section). Also, when recorded in 2:1 benzene–TFA (trifluoroacetic acid), both **1** and **2** gave a ^{31}P chemical shift of +42.7 ppm, consistent with protonation of the phosphoryl oxygen.

Morrison[2] has reported similar 1:1 adducts following treatment of triethyl phosphite or diethyl phosphite with diethyl azodicarboxylate. The product oils were characterised by degradative techniques and believed to be diethyl *N*-alkyl-*N'*-bis(alkoxy)phosphorylhydrazine dicarboxylates, formed *via N*-phosphonium salts.[7] Ginsburg[8] and co-workers have proposed alternative structures for these compounds, suspecting them to be derived from the corresponding *O*-phosphonium salt. Mitsunobu[9] has also reported an analogous reaction involving diethyl *N,N*-diethylphosphoramidite, though again no firm structural information was presented. The crystalline material afforded after treatment of azodicarboxylates with diphenylphosphine oxide permits an insight into the probable structure of Morrison's and Mitsunobu's compounds, assuming a similar reaction pathway is being followed.

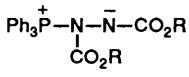
We suggest that the reaction between diphenylphosphine oxide and azodicarboxylates occurs as shown in Scheme 1. Although the equilibrium concentration of the diphenylphosphinous acid tautomer would be expected to be quite low, such a species should be strongly nucleophilic due to the 'alpha' effect.[10] Moreover, the betaine **3** might well catalyse the tautomerisation step (due to the acidic proton) so that the



Scheme 1

reaction is autocatalytic. It is also possible that **3** catalyses the addition of the diphenylphosphine oxide by removal of the acidic proton to generate $Ph_2(O)P-$, which would be expected to undergo rapid nucleophilic addition to the azodicarboxylate.

The mechanism depicted in Scheme 1 is analogous to betaine formation in the Mitsunobu reaction. Here, tertiary phosphines such as triphenylphosphine and tributylphosphine react rapidly and irreversibly[11] with azodicarboxylates to give betaines of the type **4**. These reactions are essentially instantaneous in THF at 0 °C.



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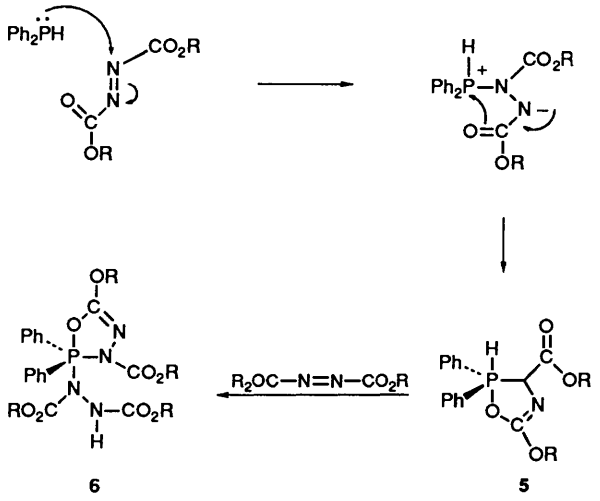
In contrast to the reactions with triphenylphosphine and diphenylphosphine oxide, we have found that there was no immediate reaction between diphenylphosphine and diisopropyl azodicarboxylate in THF (tetrahydrofuran) at 0 °C. After 24 h at 25 °C, ^{31}P NMR spectroscopy showed that the major species present in the reaction mixture was diphenylphosphine (45%) ($\delta_P = -40.2$). Numerous minor peaks were present in the spectrum between +64 and −40 ppm. The most intense of these were located at $\delta_P = +28.5$ and −38.3 in a ratio of 1:2. After a further week at 4 °C, the diphenylphosphine peak had decreased to about 18%, while the two peaks at +28.5 and −38.3 accounted for 6 and 36% of the total phosphorus content respectively. The minor peak at +28.5 ppm has been assigned to the 1:1 adduct **1**, prepared independently from diphenylphosphine oxide and the azodicarboxylate as described above. This product may arise from oxidation of the diphenylphosphine to the oxide (possibly by adventitious oxygen in the reaction mixture) followed by reaction with the azodicarboxylate. The other major signal at −38.3 ppm has been tentatively assigned to the phosphorane **6**, presumably formed following addition of **5** across diisopropyl azodicarboxylate as depicted in Scheme 2.

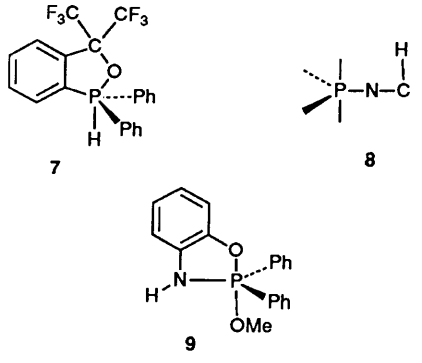
Although mediation by **5** is possible and one example of a phosphorane incorporating a P–H bond in the apical position is known (7 δ_P −49.45 in THF),[12] the proton resonating at 6.82 ppm with $^1J_{PH} = 266$ Hz, no such feature was evident in the ^1H NMR spectrum of a reaction mixture recorded in deuteriated benzene. (The ^{31}P NMR recorded prior to the ^1H NMR was similar in most aspects to the THF reaction already described.) A doublet was however apparent at 7.69 ppm with a coupling of 36.2 Hz. Moreover, integration revealed that the ratio of this doublet to the doublet of unchanged diphenylphosphine was identical with that obtained for a postulated penta-coordinated adduct and diphenylphosphine by ^{31}P NMR. The small coupling suggested that **6** may be the actual species observed by NMR. Three bond J_{PH} values of between 2 and 15 Hz have been reported for the phosphorane fragment



Scheme 2

8.[13] These values are very sensitive to changes in the bond angles in ring systems. The larger value observed here may reflect the different geometries between the PNNH fragment of **6** compared with the PNCH moiety in **8**.

Further support for the structure **6** is provided by the chemical shift of phosphoranes containing five-membered rings. These compounds generally resonate some 20–40 ppm downfield from their acyclic analogues.[14] For example, the chemical shift of the triphenylphosphorane derived from catechol occurs at −21.1 ppm, whereas the acyclic analogue, diphenoxytriphenylphosphorane, is observed at −66 ppm in THF.[1d,15] By analogy, the chemical shift of **6** would also be expected to lie between −20 and −40 ppm. Interestingly, the related *O,N*-phosphane **9** exhibits a ^{31}P chemical shift value of −36.0 ppm in $CDCl_3$.[16]



The very slow reaction between diphenylphosphine and diisopropyl azodicarboxylate was surprising even though secondary phosphines are known[17] to be less nucleophilic than tertiary phosphines. This difference in reactivity is most likely due to the differences in inductive effects which also result in substantial differences between the pK_a values for these phosphines (Ph_3P, 2.73; Ph_2PH, 0.03).[18] However, other factors such as polarisibility and delocalisation of the phosphorus lone pair into the phenyl rings may also be involved.

Experimental

All reagents and solvents were carefully dried prior to use. Diphenylphosphine, diisopropyl azodicarboxylate and diethyl azodicarboxylate were commercially available (Aldrich) and not further purified. Low resolution mass spectra were recorded on a Kratos MS-25 spectrometer. Elemental analyses were performed by the Microanalytical Service, University of Queensland or by the Australian Microanalytical Service, Victoria. M.p.s were determined using a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Jasco IR-810 spectrometer. Samples for ^{31}P NMR were prepared by dissolving either diphenylphosphine (0.36 mmol) or diphenylphosphine oxide (0.36 mmol) in THF (tetrahydrofuran) (3 cm^3) under nitrogen in a 10 mm NMR tube and cooling to 0 °C or −78 °C respectively prior to the addition of the dialkyl azodicarboxylate (1 equiv.). The tube was stoppered, sealed with Parafilm, and shaken vigorously before the ^{31}P NMR spectrum was recorded. Spectra were recorded on a Bruker CXP-300 spectrometer at 10 °C and acquired using a 45° flip angle, 3 s recycle delay and 0.33 s acquisition time with gated decoupling. Negative ^{31}P chemical shifts are upfield of external phosphoric acid (85%). ^{1}H and ^{13}C NMR spectra were recorded as [^{2}H]$_5$-pyridine solutions on a Bruker WM-250 instrument at room temperature using tetramethylsilane as an internal standard. *J* values are given in Hz. Solid state ^{13}C spectra were obtained on a Bruker CXP-300 spectrometer at 76.46 MHz using ^{1}H–^{13}C cross-polarization with total suppression of spinning side bands and a 10 s recycle delay. Samples were packed in Kel-F rotors and spun at speeds of between 3.0 and 4.0 kHz at the magic angle. A sweep width of 20 kHz with a total acquisition time of 51 ms was used. The FIDs were zero filled to 4 K and transformed with an experimental line broadening of 15 Hz. Chemical shift data are referenced to an external adamantane standard.

Preparation of Compounds.—Diphenylphosphine oxide. Diphenylphosphinous chloride (6 g) in carbon tetrachloride (30 cm^3) was treated with water (0.5 cm^3, added dropwise over 30 min) under nitrogen. The mixture was stirred for a further 6 h and allowed to stand overnight during which time a white solid had precipitated. The precipitate was filtered off and dissolved in chloroform. The solution was extracted with aqueous sodium hydrogen carbonate, washed with water, dried and evaporated under reduced pressure. The resultant oil was kept at 4 °C until crystallisation was complete; m.p. 50–52 °C (lit.,[3] 53–56 °C).

Diisopropyl Diphenylphosphinoylhydrazine-1,2-dicarboxylate **1**.—Diphenylphosphine oxide (268 mg) was dissolved in anhydrous THF (6 cm^3) under a stream of nitrogen. The solution was cooled to −78 °C and diisopropyl azodicarboxylate (262 mm^3) added. The reaction was left to warm slowly to room temperature overnight, during which time the initial orange–yellow hue became colourless. This mixture was allowed to stand at 25 °C for a further hour before the solvent was evaporated, ether added and the product filtered. Recrystallisation from ethyl acetate–hexane yielded the *title compound* **1** as white prisms (400 mg, 75%); m.p. 203–210 °C (Found: C, 59.0; H, 6.3; N, 6.7. $C_{20}H_{25}N_2O_5P$ requires C, 59.4; H, 6.2; N, 6.9%); ν_{max}(KBr)/cm^{-1} 3175 (NH), 1755 and 1725 (C=O, esters) and 1250 (P=O); δ_H([^{2}H]$_5$-pyridine) 0.75, 0.89, 0.99, 1.03, 1.10, 1.33 and 1.44 [7 d, 12 H, *J* 6.3, CH_3s (ratio 1:1:4:4:1:4)], 4.89, 5.03 and 5.18 [at least 3 septets, 2 H, *J* 6.3, CHs (ratio 1:7:7)], 5.5–6.0 (br, 1 H, NH), 7.38–7.54 (m, 6 H, ArH), 8.26–8.34 (m, 2 H, ArH) and 8.60–8.69 (m, 2 H, ArH); δ_C([^{2}H]$_5$-pyridine) 21.15, 21.32, 21.56, 21.95, 22.17 and 22.27 [6 s, CH_3s (ratio 1:1.2:11:8:1:7)], 69.36, 69.77 and 71.71 [three s, CHs (ratio 5:1:3)], 128.59, 128.80, 128. 88, 129.09 (ArC); 130.97 and 133.05 (d, *J* 131, ipso C), 132.35 and 134.41 (d, *J* 129, *ipso* C), 132.54, 132.61, 132.75 and 132.89 (ArC), 155.47 and 155.65 (d, *J* 11, PNC) and 157.39 (s, PNNC); δ_C (solid state) 20.5 and 22.4 [$(CH_3)_2$CHOCONH], 21.7 and 22.7 [$(CH_3)_2$COCONP], 66.7 [CHOCONP), 72.2 (CHOCONH),

Table 3 Non-hydrogen atom coordinates for **1**

Atom	*x*	*y*	*z*
P	0.7590(1)	0.3672(4)	0.6197(3)
C(101)	0.7968(5)	0.503(1)	0.556(1)
C(102)	0.8174(6)	0.493(1)	0.447(1)
C(103)	0.8431(7)	0.608(2)	0.405(1)
C(104)	0.8473(7)	0.732(2)	0.465(2)
C(105)	0.8252(8)	0.742(2)	0.573(2)
C(106)	0.8002(6)	0.628(2)	0.615(1)
C(201)	0.6750(5)	0.361(1)	0.529(1)
C(202)	0.6293(6)	0.358(1)	0.601(1)
C(203)	0.5640(6)	0.360(2)	0.538(2)
C(204)	0.5461(6)	0.363(2)	0.408(2)
C(205)	0.5913(7)	0.366(2)	0.341(1)
C(206)	0.6565(5)	0.368(1)	0.403(1)
O	0.7651(3)	0.3796(8)	0.7551(6)
N	0.7907(5)	0.2202(9)	0.5747(9)
C(11)	0.8549(7)	0.180(1)	0.631(1)
O(11)	0.8766(4)	0.0699(8)	0.6207(9)
O(12)	0.8851(4)	0.2876(8)	0.6954(8)
C(13)	0.9526(8)	0.277(2)	0.763(2)
C(131)[a]	0.995(1)	0.357(6)	0.709(3)
C(132)[a]	0.958(1)	0.238(4)	0.889(3)
C(133)[a]	0.963(2)	0.417(4)	0.840(6)
N(21)	0.7525(4)	0.122(1)	0.4975(7)
C(22)	0.7175(5)	0.035(1)	0.549(1)
O(22)	0.7133(4)	0.0351(8)	0.6548(7)
O(23)	0.6849(4)	−0.0462(8)	0.4512(7)
C(24)	0.6409(7)	−0.144(1)	0.482(1)
C(241)	0.6352(7)	−0.257(2)	0.386(2)
C(242)	0.5773(7)	−0.071(2)	0.473(2)

[a] Population = 0.6667.

Table 4 Non-hydrogen atom coordinates for **2**

Atom	*x*	*y*	*z*
P	0.108 56(9)	0.2539(1)	0.5057(1)
C(101)	0.2018(3)	0.0832(4)	0.4385(4)
C(102)	0.3161(4)	0.0437(5)	0.4520(6)
C(103)	0.3837(5)	−0.0909(6)	0.4069(6)
C(104)	0.3388(5)	−0.1886(6)	0.3461(6)
C(105)	0.2252(5)	−0.1519(6)	0.3330(6)
C(106)	0.1563(4)	−0.0158(5)	0.3769(5)
C(201)	0.0757(3)	0.2482(5)	0.7225(5)
C(202)	−0.0081(4)	0.3580(6)	0.8039(6)
C(203)	−0.0445(5)	0.3476(7)	0.9705(7)
C(204)	0.0014(5)	0.2315(7)	1.0537(7)
C(205)	0.0830(6)	0.1212(7)	0.9739(7)
C(206)	0.1214(5)	0.1272(6)	0.8065(7)
O	0.0021(2)	0.2959(3)	0.4421(3)
N	0.1941(3)	0.3751(3)	0.4548(4)
C(11)	0.2542(4)	0.3974(5)	0.2978(6)
O(11)	0.3128(3)	0.4821(4)	0.2598(4)
O(12)	0.2327(3)	0.3087(3)	0.2005(3)
C(13)	0.2975(7)	0.3019(7)	0.0340(7)
C(131)	0.3751(9)	0.156(1)	0.005(1)
N(21)	0.1965(3)	0.4738(4)	0.5672(5)
C(22)	0.2963(4)	0.4598(5)	0.6176(5)
O(22)	0.3762(3)	0.3561(3)	0.5975(4)
O(23)	0.2874(2)	0.5792(3)	0.6982(3)
C(24)	0.3927(5)	0.5924(7)	0.7417(8)
C(25)	0.360(1)	0.720(1)	0.847(2)

127.4, 130.2, 131.7, 132.6, 133.2, 134.3 and 136.8 (ArC) and 155.7 (two COs); δ_P(THF, 10 °C) 28.5; (benzene, 10 °C) 31.3; (pyridine, 10 °C) 30.4; *m/z* 404 (M^+), 1.4%.

Diethyl Diphenylphosphinoylhydrazine-1,2-dicarboxylate **2**.—This compound was prepared using the same procedure as described for the diisopropyl analogue **1**. Recrystallisation from ethyl acetate afforded the *title compound* **2** (83%). M.p. 157–165 °C (Found: C, 57.8; H, 5.6; N, 7.5. $C_{18}H_{21}N_2O_5P$ requires C, 57.5; H, 5.6; N, 7.5%); δ_H([^{2}H]$_5$-pyridine) 0.77, 0.84, 1.01, 1.10 and 1.26 (5 t, 6 H, *J* 7, CH_3s (ratio 40:5:40:1:5), 3.91–4.35 (m, 4 H, CH_2s), 5.0–5.5 (br, 1 H, NH), 7.37–7.57 (m, 6 H, ArH), 8.21–8.35 (m, 3 H, ArH) and 8.56–8.65 (m, 2 H, ArH); δ_C([^{2}H]$_5$-pyridine) 13.82 (*C*H_3CH$_2$OCONP), 14.61 (*C*H_3C-H_2OCONH), 61.79 (*C*H_2OCONP), 63.35 (*C*H_2OCONH), 128.61, 128.82, 128.91 and 129.11 (ArC), 130.87 (*ipso* C), 131.97 and 134.03 (d, *J* 129, *ipso* C), 132.64, 132.70, 132.80 and 132.87 (ArC), 159.7 and 156.18 (d, *J* 13, PNC) and 157.77 (s, PNNC); δ_C(solid state) 13.0 (*C*H_3CH$_2$OCONP), 14.3 (*C*H_3CH$_2$-OCONH), 61.6 (*C*H_2OCONP), 62.8 (*C*H_2OCONH), 128.1, 129.8, 131.1 and 134.9 (ArC) and 155.2 (2 COs); δ_P(THF, 10 °C) 28.8; (benzene, 10 °C) 32.3; (pyridine, 10 °C) 30.9; *m/z* 376 (M^+), 4.0%.

Structure Determinations.—Unique data sets were measured at *ca.* 295 K using an Enraf-Nonius CAD-4 four-circle diffractometer in conventional $2\theta/\theta$ scan mode to $2\theta_{max}$ 50°. Monochromatic Mo-K_α radiation was employed (λ = 0.71069 Å); *N* independent reflections were obtained, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement without absorption correction after direct methods solution of the structures. Anisotropic thermal parameters were refined for the non-hydrogen atoms. Residuals at convergence, *R*, *R'* are quoted on |*F*|; statistical reflection weights derivative of σ^2 $(I) = [\sigma^2$ $(I)_{diff} + 0.0004$ σ^4 $(I)_{diff}]$ were employed. Neutral complex scattering factors were used;[4] computation used the XTAL 2.4 program system[5] implemented by S. R. Hall. Non-hydrogen atom coordinates are given in Tables 3 and 4. Additional material available from the Cambridge Crystallographic Centre comprises H-atom coordinates, ligand geometries and thermal parameters.*

Crystal Data for **1**. $C_{20}H_{25}N_2O_5P$, Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a = 21.344(6), b = 9.702(2), c = 10.929(4) Å, β = 104.71(3)°, U 2189 Å^3. D_c (Z = 4) = 1.23 g cm^{-3}, $F(000)$ = 856; μ_{Mo} = 1.2 cm^{-1}; specimen: 0.08 × 0.15 × 0.22 mm; N = 3855, N_o = 1029; R = 0.062, R' = 0.055.

Crystal Data for **2**. $C_{18}H_{21}N_2O_5P$, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 12.197(5), b = 9.507(3), c = 8.503(6) Å, α = 85.83(5), β = 76.91(6), γ = 75.61(3)°, U 929.9 Å^3; D_c (Z = 2) = 1.34 g cm^{-3}, $F(000)$ = 396; μ_{Mo} = 1.3 cm^{-1}; specimen: 0.25 × 0.13 × 0.13 mm; N = 3262, N_0 = 1866; R = 0.047, R' = 0.046.

Abnormal Features/variations in procedure. In the diethyl derivative, data quality permitted refinement of hydrogen atoms in (x,y,z,U_{iso}). In the diisopropyl derivative, data was much weaker and poorer in quality, possibly as a consequence of disorder in one of the isopropyl substituents and the reduced crystal size; $(x,y,z,U_{iso})_H$ were included in the refinement constrained at estimated values.

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* For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, Issue 1, 1991.

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