

Reactivity and Chemoselectivity of Primary Z-β-Enamino-λ⁵-phosphazenes towards Electrophiles

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The multifunctional character of Z-β-enamino-λ⁵-phosphazenes (**2**) towards several electrophiles is shown. Thus, while hydrogen or alkyl halides react through the P=N double bond, affording β-enaminophosphonium salts (**3**) and (**4**), in the presence of a base, alkylation of the enamine moiety (**6**) occurs. Ethyl chloroformate acts as acylating agent of the enamino nitrogen and with bromine and triethylamine, α-bromoenamino phosphazenes (**8**) are obtained.

Enamines¹ are known to be useful intermediates in carbon-carbon and carbon-heteroatom bond formation yet their synthesis and reactivity has been little studied. In the last few years some primary enamines having electron-withdrawing substituents, e.g., sulphonyl,² nitro,³ imino,⁴ and cyano,⁵ have been prepared and their use in organic synthesis shown.

Recently we described the first synthesis of primary Z-β-enamino-λ⁵-phosphazenes (**2**) via α-lithiation of alkyldiaryl-λ⁵-phosphazenes (**1**) followed by reaction with arenenitriles, as well as their utility as key intermediates in the synthesis of phosphorus-containing heterocyclic compounds.⁷ The ability of compounds (**2**) to react through both reactive centres, λ⁵-phosphazene⁸ and enamine,¹ a feature which has already been observed in the preparation of 1-aza-4λ⁵-phosphinines,^{7a} prompted us to explore the chemoselectivity of (**2**) towards several reagents.

In a previous paper⁶ we reported the reactions of λ⁵-phosphazene derivatives of (**2**) with CO₂, and CS₂. Here, we report our results on the reactivity of (**2**) with other electrophiles (Schemes 1 and 2).

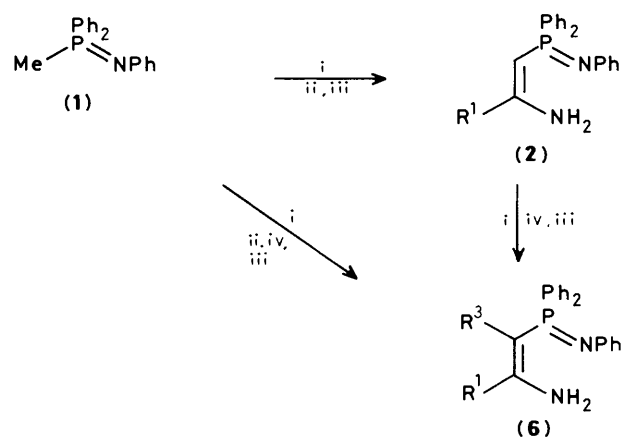
Results and Discussion

Treatment of compound (**2a**) with HI resulted in nitrogen protonation giving compound (**3**) (m.p. 164–165 °C, δ_P + 21.2 p.p.m.). Although the ¹³C n.m.r. spectrum confirmed that the framework of the enamine functionality remained intact, it did not allow the site of protonation (1 and/or 5-position) to be determined.

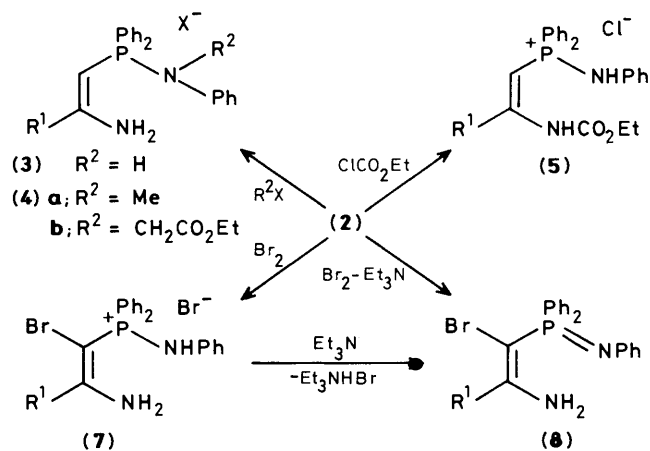
A single crystal X-ray analysis unequivocally established the structure of (**3**) and showed that selective protonation occurred at the λ⁵-phosphazene nitrogen (P–N bond length 1.622 Å). The bond angles for the C=C double bond are 125.7° and 122° and the torsion angles for the P=C–C–N and P=C–C–CAr are 16.3° and –162.4° respectively, values which corresponds with the appropriate sp² hybridization and Z-stereochemistry. The high basicity⁹ of λ⁵-phosphazenes could explain the nucleophilic attack by the P=N linkage rather than the primary enamino nitrogen atom.

Likewise, alkyl halides e.g., methyl iodide and ethyl bromoacetate, reacted with compound (**2**) to afford the N-alkyl-arylamino phosphonium salts (**4**) regioselectively in excellent yields. The high shift values of the ³¹P n.m.r. signals and the P–H (9.4 Hz) and P–C (5.9 Hz) coupling constants observed in ¹H- and ¹³C-n.m.r., respectively, for the methyl and methylene groups of the alkylating agent are fully consistent with the phosphonium salt structure (**4**).

The reaction of compound (**2**) with ethyl chloroformate led, as in the case of β-imino enamines,¹⁰ to exclusive ethoxy-



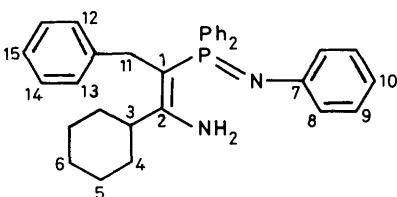
Scheme 1. Reagents and conditions: i, BuLi-THF, –70 °C; ii, R¹CN; iii, H₂O; iv, R³X.



Scheme 2.

carbonylation of the enamino nitrogen and formation of the phosphonium salt (**5**); the chemical shift at 21.3 p.p.m. similar to that found in compound (**3**) was assigned to the phosphorus and the doublets observed at 9.9 (²J_{PH} 7.1 Hz) and 4.5 (²J_{PH} 9.7 Hz) p.p.m. were assigned to the phenyl substituted amino and β-enamino hydrogens, respectively.

The reactivity of the β-enamino carbon of (**2**) was also investigated and it was found that metallation of (**2**) with butyl-

Table 1. Selected physical data for the compounds (2)—(8)^d


Compound	R ¹	R ²	R ³	M.p. (°C)	Yield (%)	I.r. (Nujol) ν _{max} . (cm ⁻¹)	CDCl ₃ (p.p.m.)		
							δ _H	δ _C	δ _P
(2b)	c-C ₆ H ₁₁			157—158	82	1 650	4.26 (d, ² J _{PH} 22.0 Hz, =CH); 5.93 (s, 1 H, NH)	71.2 (d, ¹ J _{PC} 115.5 Hz, C-1), 168.4 (C-2)	+4.7
(3)	4-MeC ₆ H ₄	H		164—165	98	1 640, 3 200, 3 280, 3 440	4.53 (d, 1 H, ² J _{PH} 22.1 Hz, =CH), 6.16 (s, 1 H, NH)	56.9 (d, ¹ J _{PC} 112.2 Hz, C-1), 164.3 (d, ² J _{PC} 1.1 Hz, C-2)	+21.2
(4a)	4-MeC ₆ H ₄	Me		Oil	98	1 630, 3 160, 3 300, 3 440	3.39 (d, 3 H, ³ J _{PH} 9.4 Hz, Me), 4.2 (d, 1 H, ² J _{PH} 17.3 Hz, =CH), 6.06 (s, 1 H, NH)	39.3 (d, ² J _{PC} 5.9 Hz Me), 60.7 (d, ¹ J _{PC} 119.6 Hz, C-1), 163.8 (C-2)	+36.0
(4b)	4-MeC ₆ H ₄	CH ₂ CO ₂ Et		Oil	97	1 600, 1 710, 2 500, 3 300	4.24 (d, 1 H, ² J _{PH} 18.3 Hz, =CH), 4.55 (d, 2 H, ³ J _{PH} 12.0 Hz, CH ₂), 6.79 (s, 1 H, NH)	52.0 (d, ² J _{PC} 8.8 Hz, CH ₂), 58.9 (d, ¹ J _{PC} 115.9 Hz, C-1), 165.0 (d, ² J _{PC} 0.7 Hz, C-2), 168.9 (d, ³ J _{PC} 1.2 Hz, CO)	+37.0
(5)	4-MeC ₆ H ₄			Oil	97	1 590, 1 700, 3 160	4.55 (d, 1 H, ² J _{PH} 19.7 Hz, =CH), 6.83 (s, 1 H, NH), 9.87 (d, 1 H, ² J _{PH} 7.9 Hz, NH)	57.2 (d, ¹ J _{PC} 116.5 Hz, C-1), 153.0 (CO), 165.2 (C-2)	+21.3
[6a]	4-MeC ₆ H ₄		Me	138—139 ^a	90 (87) ^b				
(6b)	c-C ₆ H ₁₁		Me	152—153	86 (83) ^b	1 620, 3 320, 3 400, 3 460	1.39 (d, 3 H, ³ J _{PH} 15.7 Hz, Me), 4.0 (s, 1 H, NH)	13.5 (d, ² J _{PC} 15.7 Hz, Me), 73.9 (d, ¹ J _{PC} 119.7 Hz, C-1), 164.4 (d, ² J _{PC} 3.9 Hz, C-2)	+15.4
(6c)	Ph		Me	102—103 ^a	85 (79) ^b				
(6d)	c-C ₆ H ₁₁		CH ₂ Ph	105—106	90 (83) ^b	1 610, 3 480	3.28 (d, 2 H, ³ J _{PH} 18.9 Hz, CH ₂)	32.6 (d, ² J _{PC} 15.6 Hz, C-11), 74.4 (d, ¹ J _{PC} 123.8 Hz, C-1), 166.9 (d, ² J _{PC} 3.2 Hz, C-2)	+15.7
(6e)	4-MeC ₆ H ₄		CH ₂ Ph	165—166	87 (80) ^b	1 610, 3 440	3.22 (d, 2 H, ³ J _{PH} 18.9 Hz, CH ₂)	34.9 (d, ² J _{PC} 14.0 Hz, C-11), 83.0 (d, ¹ J _{PC} 116.6 Hz, C-1), 162.1 (d, ² J _{PC} 5.4 Hz, C-2)	+14.5
(6f)	4-MeC ₆ H ₄		CH ₂ =CHCH ₂	Oil	92 (87) ^b	1 600, 3 300, 3 460	2.47 (dd, 2 H, ³ J _{PH} 18.9, ³ J _{HH} 6.3 Hz, CH ₂), 4.0 (s, 1 H, NH), 4.28 (m, 2 H, =CH ₂), 4.95 (m, 1 H, =CH)	32.4 (d, ² J _{PC} 18.9 Hz, C-11), 81.3 (d, ¹ J _{PC} 118.1 Hz, C-1), 112.9 (C-11), 137.2 (d, ³ J _{PC} 9.0 Hz, C-12), 161.2 (d, ² J _{PC} 5.2 Hz, C-2)	+14.5
(6g)	c-C ₆ H ₁₁		CH ₂ =CHCH ₂	Oil	88 (75) ^b	1 640, 3 320, 3 480	2.57 (dd, 2 H, ³ J _{PH} 18.9, ³ J _{HH} 5.5 Hz, CH ₂), 4.16 (s, 1 H, NH), 4.76 (m, 2 H, =CH ₂), 5.63 (m, 1 H, =CH)	30.6 (d, ² J _{PC} 15.2 Hz, C-1), 75.5 (d, ¹ J _{PC} 121.7 Hz, C-1), 114.2 (C-13), 136.8 (d, ³ J _{PC} 7.1 Hz, C-12), 166.2 (d, ² J _{PC} 3.1 Hz, C-2)	+15.5

+ 13.5 p.p.m.) by treatment with triethylamine. Compound (8) could be synthesized in one step, without affecting the overall yield, by running the bromination reaction of (2) in the presence of triethylamine.

In conclusion, we have shown that primary *Z*- β -enamino- λ^5 -phosphazenes (2) react at three centres when treated with different electrophiles. Thus, protonation and alkylation occur in the same way as that observed for simple λ^5 -phosphazenes (position 1) whilst with halogenating agents, e.g., bromine, typical enamine behaviour (position 3) is shown. However, the ambident character of the metallated enamine moiety of (2) leads to regioselective C-alkylation and N-acylation in the reaction with alkyl and acyl halides, respectively (positions 3 and 5).

Experimental

General.—M.p.s were taken on samples in open capillary tubes using a Büchi melting-point apparatus and are uncorrected. N.m.r. spectra were obtained using a Varian FT-80 n.m.r. spectrometer with deuteriated chloroform as solvent; chemical shifts are reported in p.p.m. downfield from an internal SiMe₄ (TMS) for ¹H- and ¹³C-n.m.r. or from H₃PO₄ 85% in the case of the ³¹P n.m.r. I.r. spectra were recorded in Nujol on a Perkin-Elmer 298 spectrophotometer. Microanalyses were performed on a Perkin-Elmer Model 240 instrument and mass spectra were obtained using a Hewlett-Packard 5930A spectrometer. Compounds (2) were obtained according to the literature methods⁶ and the same process was applied in the synthesis of (2) in which R¹ = c-C₆H₁₁.

Synthesis of (Z)-(β-Amino-β-p-tolylvinyl)diphenyl(phenyl-amino)phosphonium Iodide (3).—A stoichiometric amount of HI was bubbled, under an argon atmosphere through a solution of compound (2a) (2.04 g, 5 mmol). The precipitate of (3) which formed immediately was filtered off and recrystallised from a mixture of toluene–chloroform to give pure (3) (2.6 g, 98%); ν_{\max} . 1 640, 3 200, 3 280, and 3 440 cm⁻¹; δ_{H} 2.35 (s, 3 H, Me), 4.53 (d, 1 H, ²J_{PH} 22.1 Hz, =CH), 6.16 (s, 1 H, NH), and 6.57–8.35 (m, 14 H, ArH, NH₂); δ_{C} 20.9 (Me), 56.9 (d, ¹J_{PC} 112.2 Hz, C-1), 119.2–133.9 (21-C, ArC), 138.9 (C-7), 141.1 (C-6), and 162.3 (d, ²J_{PC} 1.1 Hz, C-2); δ_{P} + 21.2 p.p.m.

Synthesis of Enaminophosphonium Halides (4): General Procedure.—(Z)-(β-Amino-β-p-tolylvinyl)(methylphenyl-amino)diphenylphosphonium iodide (4a). Methyl iodide (5 mmol) was added dropwise to a solution of compound (2a) in dry THF (30 ml) and the solution stirred for 2 h. The solvent was evaporated off to produce compound (4a) quantitatively; ν_{\max} . 1 630, 3 160, 3 300, and 3 440 cm⁻¹; δ_{H} 2.31 (s, 3 H, Me), 3.39 (d, 3 H, ³J_{PH} 9.4 Hz, Me), 4.2 (d, 1 H, ²J_{PH} 17.3 Hz, =CH), 6.06 (s, 1 H, NH), and 7.0–7.91 (m, 19 H ArH, NH); δ_{C} 19.7 (Me), 39.3 (d, ²J_{PC} 5.9 Hz, Me), 60.7 (d, ¹J_{PC} 119.6 Hz, C-1), 118.6–132.8 (21-C, ArC), 140.2 (C-6), 140.5 (C-7), and 163.8 (C-2); δ_{P} + 36.8 p.p.m.

Synthesis of (Z)-(β-Ethoxycarbonylamino-β-p-tolylvinyl)diphenyl(phenylamino)phosphonium Chloride (5).—This was prepared by the same method as compound (4). For (5) ν_{\max} . 1 700 and 3 160 cm⁻¹; δ_{H} 1.31 (t, 3 H, ³J_{HH} 6.3 Hz, Me), 2.4 (s, 3 H, Me), 4.2 (q, 2 H, ³J_{HH} 6.3 Hz, CH₂), 4.55 (d, 1 H, ²J_{PH} 19.7 Hz, =CH), 6.83 (s, 1 H, NH), 6.95–8.10 (m, 19 ArH), and 9.87 (d, 1 H, ²J_{PH} 7.9 Hz, NH); δ_{C} 13.9 (Me), 20.0 (Me), 57.2 (d, ¹J_{PC} 116.5 Hz, C-1), 59.0 (CH₂), 117.6–130.5 (21 C, ArC), 138.0 (C-6), 140.1 (C-3), 151.6 (C-7), 153.0 (CO), and 165.2 (C-2); δ_{P} + 21.3 p.p.m.

Table 2. Final atomic co-ordinates

Atom	x/a	y/b	z/c
I	0.094 98(2)	0.130 24(6)	0.180 04(2)
P	0.184 4(1)	0.358 7(3)	0.082 4(1)
N(1)	0.199 8(3)	0.254 9(8)	0.139 2(3)
C(2)	0.243 3(3)	0.420 0(8)	0.076 7(3)
C(3)	0.290 5(3)	0.483 1(8)	0.121 9(3)
N(4)	0.301 3(3)	0.472 7(9)	0.178 6(3)
C(11)	0.144 9(4)	0.507 3(9)	0.097 2(4)
C(12)	0.170 3(4)	0.641 9(9)	0.115 4(5)
C(13)	0.140 6(5)	0.754 1(10)	0.118 9(5)
C(14)	0.085 0(5)	0.738 5(12)	0.106 4(7)
C(15)	0.058 8(5)	0.606 9(13)	0.089 1(8)
C(16)	0.088 1(4)	0.490 6(9)	0.085 4(5)
C(21)	0.137 6(4)	0.271 1(10)	0.014 5(4)
C(22)	0.104 0(4)	0.157 9(11)	0.016 3(5)
C(23)	0.064 1(4)	0.099 1(12)	-0.035 5(5)
C(24)	0.056 5(4)	0.151 6(13)	-0.088 9(5)
C(25)	0.089 1(5)	0.260 9(16)	-0.091 5(5)
C(26)	0.130 1(5)	0.323 4(14)	-0.039 7(4)
C(31)	0.236 2(3)	0.134 6(9)	0.150 3(5)
C(32)	0.250 3(5)	0.065 9(12)	0.110 4(5)
C(33)	0.287 4(6)	-0.051 7(13)	0.129 1(6)
C(34)	0.307 0(5)	-0.099 7(12)	0.185 4(6)
C(35)	0.291 9(6)	-0.032 4(15)	0.223 6(6)
C(36)	0.257 2(5)	0.083 7(13)	0.206 9(5)
C(41)	0.330 3(3)	0.567 5(8)	0.107 9(3)
C(42)	0.385 6(3)	0.595 3(9)	0.151 5(4)
C(43)	0.421 3(4)	0.680 1(11)	0.133 4(5)
C(44)	0.404 8(4)	0.737 4(10)	0.082 1(5)
C(45)	0.350 6(4)	0.709 9(12)	0.040 0(5)
C(46)	0.313 4(4)	0.627 4(11)	0.052 0(4)
C(47)	0.445 3(6)	0.824 7(16)	0.089 2(8)
Cl(1)*	0.500 0	0.282 0(29)	0.250 0
Cl(2)*	0.524 8(10)	0.021 1(29)	0.247 5(12)
C(50)*	0.540 2(14)	0.175 9(36)	0.242 4(14)

* Means population parameters = 0.50

Synthesis of α-Alkyl-β-enamino-λ⁵-phosphazenes (6): General Procedure.—(Z)-4-Cyclohexyl-3-methyl-1,2,2-triphenyl-1,5-diaza-2λ⁵-phosphapenta-1,3-diene (6b). Method A. Compound (2b) (5 mmol) dry THF (40 ml) was added to BuLi (5 mmol) at -20 °C under argon and the mixture was stirred for 0.5 h during which time the temperature decreased to -70 °C. Methyl iodide (5 mmol) was added dropwise and the mixture was left to reach room temperature and then hydrolysed with ice-water. Aqueous work-up afforded an oil that was recrystallised from hexane–dichloromethane to give (6b) (1.8 g, 86%).

Method B. A solution of *N*-phenyl methyl diphenyl-λ⁵-phosphazene (5 mmol) in THF was added to BuLi (5 mmol) at -20 °C and the mixture stirred for 0.5 h after which cyclohexanecarbonitrile (5 mmol) at -70 °C was added. Once room temperature had been reached methyl iodide again at -70 °C was added. Aqueous work-up and purification as indicated in method A yielded (6b) (1.7 g, 83%); ν_{\max} . 1 620, 3 320, 3 400, and 3 460 cm⁻¹; δ_{H} 0.55–1.87 (m, 11 H, c-C₆H₁₁), 1.39 (d, 3 H, ³J_{PH} 15.7 Hz, Me), 4.0 (s, 1 H, NH), and 6.2–7.83 (m, 15 H ArH, NH); δ_{C} 13.55 (d, ²J_{PC} 15.7 Hz, Me), 25.9 (C-5, C-6), 29.9 (C-4), 41.2 (d, ³J_{PC} 12.6 Hz, C-3), 73.9 (d, ¹J_{PC} 119.7 Hz, C-1), 116.5–133.2 (14 C, ArC), 150.34 (d, ²J_{PC} 3.1 Hz, C-7), and 164.4 (d, ²J_{PC} 3.9 Hz, C-2); δ_{P} + 15.4 p.p.m.

Synthesis of (Z)-(β-Amino-α-bromo-β-p-tolylvinyl)diphenyl(phenylamino)phosphonium Bromide (7).—Bromine (5 mmol) in benzene (10 ml) was added dropwise to a solution of (2a) (5 mmol) in dry benzene (40 ml) over a period of 0.5 h. The mixture was stirred for 6 h and then evaporated to afford a solid which

Table 3. Selected bond distances (Å) and bond angles (°) for compound (3)

P-N(1)	1.622(8)
P-C(2)	1.724(10)
P-C(11)	1.870(10)
P-C(21)	1.792(8)
N(1)-C(31)	1.421(12)
N(4)-C(3)	1.331(12)
C(2)-C(3)	1.384(9)
C(3)-C(41)	1.476(13)
N(1)-P-C(2)	113.3(5)
N(1)-P-C(11)	101.8(4)
N(1)-P-C(21)	111.3(4)
C(11)-P-C(2)	112.2(4)
C(21)-P-C(2)	109.3(4)
C(11)-P-C(21)	108.8(5)
P-N(1)-C(31)	121.4(7)
P-C(2)-C(3)	125.7(7)
N(4)-C(3)-C(2)	122.0(8)
N(4)-C(3)-C(41)	117.9(7)
C(2)-C(3)-C(41)	120.2(7)

was recrystallised from toluene-chloroform to give (7) (2.7 g, 97%); ν_{\max} 1 620, 3 240, and 3 400 cm^{-1} ; δ_{H} 2.0 (s, 3 H, Me), 6.2–7.97 (m, 19 H ArH, NH_2), and 9.0 (d, 1 H, $^2J_{\text{PH}}$ 7.9 Hz); δ_{C} 21.1 (Me), 88.4 (d, $^1J_{\text{PC}}$ 119.7 Hz, C-1), 121.0–133.4 (21 C, ArC), 138.9 (C-7), 140.2 (C-6), and 164.4 (d, $^2J_{\text{PC}}$ 22.1 Hz, C-2); δ_{P} +28.4 p.p.m.; m/z 566–568 (M^+).

Synthesis of (Z)-3-Bromo-1,2,2-triphenyl-4-p-tolyl-1,5-diazapenta-2,5-diene (8).—Method A. Bromine (5 mmol) was added to a mixture of (7) (5 mmol) and triethylamine (5 mmol) in toluene. After 8 h of vigorous stirring at room temperature the triethylamine bromohydrate was filtered off and the mother liquor was evaporated at reduced pressure, to yield a solid which was recrystallised from hexane-dichloromethane (2.3 g, 95%).

Method B. The procedure was as indicated for method A, using compound (2a) instead of the brominated derivative (7), in a one-pot reaction with bromine and triethylamine to give the products (8) (2.2 g, 90%); ν_{\max} 1 590 and 3 440 cm^{-1} ; δ_{H} 2.31 (s, 3 H, Me) and 6.35–8.08 (m, 14 H ArH, NH_2); δ_{C} 21.3 (Me), 63.6 (d, $^1J_{\text{PC}}$ 119.7 Hz, C-1), 117.9–133.5 (21 C, ArC), 136.8 (d, $^3J_{\text{PC}}$ 12.6 Hz, C-3), 139.6 (C-6), 150.7 (C-7), and 163.4 (d, $^2J_{\text{PC}}$ 8.3 Hz, C-2); δ_{P} +13.5 p.p.m.; m/z 486–488 (M^+).

Crystal Data for Compound (3).— $[\text{C}_{27}\text{H}_{26}\text{N}_2\text{P}]^+ \text{I}^- \cdot \frac{1}{2}\text{Cl}_2\text{CH}_2$. Space group $C2/c$, $Z = 8$, $D_x = 1.381 \text{ g cm}^{-3}$, $a = 24.415 \text{ (7) Å}$, $b = 9.318 \text{ (0) Å}$, $c = 25.343 \text{ (11) Å}$, $\beta = 116.893 \text{ (3) }^\circ$ (from a least-squares fit to the h , k , l and 2θ values of 83 reflexions of θ up to 45° with $\text{Cu-K}\alpha$ radiation), $\mu = 107.55 \text{ cm}^{-1}$ (min. and max. transmission factors were 0.762–1.334).¹¹ A pale yellow rhombic prism of $0.17 \times 0.17 \times 0.27 \text{ mm}$ was used in the analysis.

Data Collection and Processing.—Philips PW1100 diffractometer, $\omega/2\theta$ scans, width 1.5° , graphite monochromated $\text{Cu-K}\alpha$ radiation, θ up to 65° , 1 min/reflex. Stability checked every 90 min, using two standard reflexions, with no variation detected. Usual Lorentz and polarization corrections were applied. The number of total independent [and observed, with $3\sigma(I)$, $3\sigma(I)$, $3.5\sigma(I)$ criteria] were 4 277 (3 068), 4 631 (3 823), and 4 069 (2 420) respectively.

Structure Solution and Refinement.—Patterson and/or Direct Methods¹² were used for the solution and weighted full matrix

Table 4. Selected torsion angles (°)

C(2)-P-N(1)-C(31)	-51.7(9)
C(11)-P-N(1)-C(31)	-172.4(8)
C(11)-P-C(2)-C(3)	64.5(9)
C(11)-P-C(21)-C(26)	84.9(9)
P-C(2)-C(3)-N(4)	16.3(12)
P-C(2)-C(3)-C(41)	-162.4(6)
P-N(1)-C(31)-C(32)	-19.1(15)
C(26)-C(21)-P-C(2)	-37.9(10)
C(22)-C(21)-P-N(1)	23.0(10)
C(16)-C(11)-P-N(1)	-78.5(9)
C(12)-C(11)-P-C(2)	-14.3(10)
C(2)-C(3)-C(41)-C(42)	-160.6(8)
N(4)-C(3)-C(41)-C(42)	20.6(12)
C(2)-C(3)-N(4)-H(4B)	13(7)

Table 5. Hydrogen interactions (Å, °). Italic numbering indicates the symmetry operation

Compound ($i = 1/2 - x, 1/2 + y, 1/2 - z$)				
X-H...Y	X-H	X...Y	H...Y	X-H...Y
N(1)-H(1)...I	1.02(16)	3.558(20)	2.67(15)	146(9)
N(4)-H(4A)...I; i	0.78(8)	3.681(7)	2.96(8)	161(11)
N(4)-H(4B)...N(1)	0.92(11)	3.144(12)	2.38(9)	140(7)

least-squares for the refinement, working on F_{obs} with one block full matrix.¹³ After the isotropic cycles an empirical absorption correction was applied in the iodide-containing salts. The thermal models were anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, which were sought from difference synthesis. Weights were chosen through empirical functions on F_{obs} and $\sin \theta/\lambda$ so as to give no trends in $\langle w\Delta^2 F \rangle$, versus F_{obs} and/or $\sin \theta/\lambda$. Scattering factors were taken from the International Tables for X-Ray Crystallography.¹⁴ 394 Parameters; final R and R_w indices were 0.071 and 0.078; the final residual density was within $\pm 2.2 \text{ e}\text{Å}^{-3}$, the maximum being near the P and N(1) atoms; the maximum thermal value was $U_{33}(\text{C}15)$, $0.16(1) \text{ Å}^2$. The disordered Cl_2CH_2 molecule of crystallization was kept with the fixed population in the last cycles of refinement, isotropically. Its H-atoms could not be located.

Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2, with numbering given in the Figure.⁵ Tables 3 and 4 give the main geometrical features. Table 5 shows the H-bonding network. Thermal parameters and H-atom co-ordinates are available on request from The Cambridge Crystallographic Data Centre.*

* See 'Instructions for Authors (1988)', *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1.

References

- P. M. Hickmott, *Tetrahedron*, 1982, **38**, 1975.
- B. F. Feriuga, *J. Chem. Soc., Chem. Commun.*, 1985, 466.
- I. Tokumitsu and T. Hayashi, *J. Org. Chem.*, 1985, **50**, 1547.
- (a) J. Barluenga, B. Olano, and S. Fustero, *J. Org. Chem.*, 1983, **48**, 2255. (b) J. Barluenga, J. Jardón, V. Rubio, and V. Gotor, *J. Org. Chem.*, 1983, **48**, 1379.
- A. Corsaro, U. Chiachio, A. Compagnini, and G. Purrello, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1635.
- J. Barluenga, F. López, and F. Palacios, *J. Chem. Res.* 1985, (S), 211; (M), 2541.
- (a) J. Barluenga, F. López, and F. Palacios, *J. Chem. Soc., Chem. Commun.*, 1985, 1681. (b) J. Barluenga, F. López, and F. Palacios, *Tetrahedron Lett.*, 1987, 2875.

- 8 E. V. Abel and S. A. Mucklejohn, *Phosphorus Sulfur*, 1981, **9**, 235.
- 9 (a) M. I. Kabachnik, *Phosphorus*, 1971, **1**, 117. (b) R. A. Shaw, *Phosphorus Sulfur*, 1979, **5**, 363.
- 10 J. Barluenga, J. Jardón, and V. Gotor, *J. Org. Chem.*, 1985, **50**, 802.
- 11 N. Walker and D. Stuart, 'Difabs,' *Acta Crystallogr., Sect. A*, 1983, **39**, 158—166.
- 12 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson. 'Multan 80 System,' University of York, 1980.
- 13 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack. 'The X-Ray System' Technical report TR-446, Computer Science Center, University of Maryland, 1976.
- 14 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974, vol. IV.
- 15 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A., 1965.

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