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

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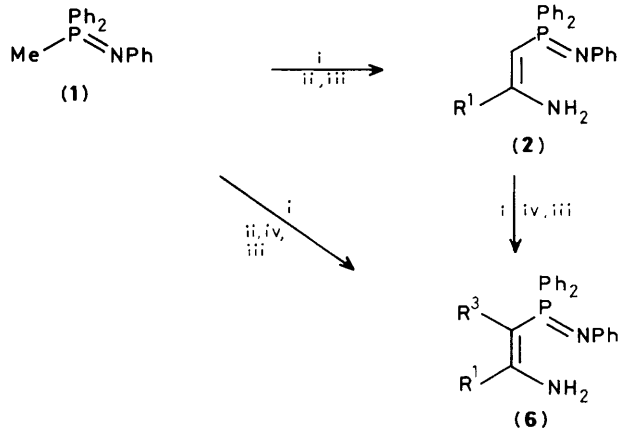
The multifunctional character of *Z*-β-enamino-λ⁵-phosphazenes (**2**) towards several electrophiles is shown. Thus, while hydrogen or alkyl halides react through the P=N double bond, affording β-enaminophosphonium salts (**3**) and (**4**), in the presence of a base, alkylation of the enamine moiety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

Enamines[1] 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[6] (**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-phosphazene[8] 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 paper[6] we reported the reactions of λ⁵-phosphazene derivatives of (**2**) with CO_2, and CS_2. Here, we report our results on the reactivity of (**2**) with other electrophiles (Schemes 1 and 2).



Scheme 1. *Reagents and conditions:* i, BuLi–THF, −70 °C; ii, R^1CN; iii, H_2O; iv, R^3X.

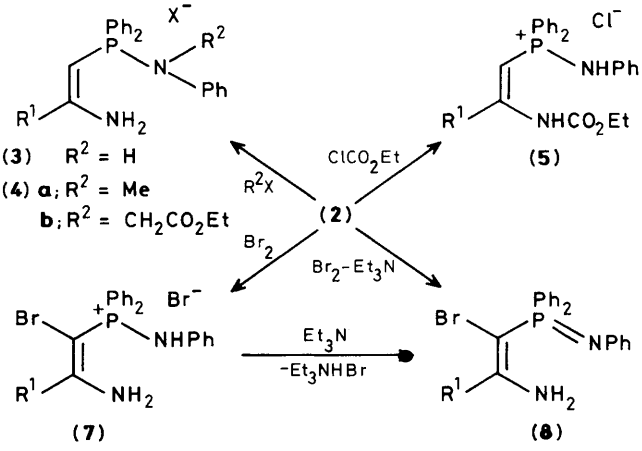
Results and Discussion

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 ^{13}C 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 sp^2 hybridization and *Z*-stereochemistry. The high basicity[9] 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*-alkylarylamino phosphonium salts (**4**) regioselectively in excellent yields. The high shift values of the ^{31}P n.m.r. signals and the P–H (9.4 Hz) and P–C (5.9 Hz) coupling constants observed in ^1H- and ^{13}C-n.m.r., respectively, for the methyl and methylene groups of the alkylating agent are fully consistent with the phosphonium salt structure (**4**).

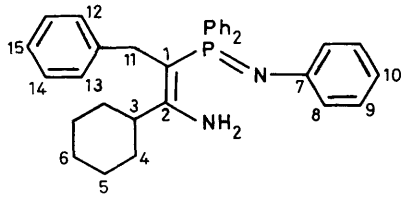
The reaction of compound (**2**) with ethyl chloroformate led, as in the case of β-imino enamines,[10] to exclusive ethoxycarbonylation of the enamino nitrogen and formation of the phosphonium salt (**5**); the chemical shift at 21.3 p.p.m. similar to that found in compound (**3**) was assigned to the 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.



Scheme 2.

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) $\nu_{max.}$ (cm^{-1})	$CDCl_3$ (p.p.m.) δ_H	δ_C	δ_P
(2b)	c-C_6H_{11}			157—158	82	1 650	4.26 (d, $^2J_{PH}$ 22.0 Hz, =CH); 5.93 (s, 1 H, NH)	71.2 (d, $^1J_{PC}$ 115.5 Hz, C-1), 168.4 (C-2)	+4.7
(3)	4-MeC_6H_4	H		164—165	98	1 640, 3 200, 3 280, 3 440	4.53 (d, 1 H, $^2J_{PH}$ 22.1 Hz, =CH), 6.16 (s, 1 H, NH)	56.9 (d, $^1J_{PC}$ 112.2 Hz, C-1), 164.3 (d, $^2J_{PC}$ 1.1 Hz, C-2)	+21.2
(4a)	4-MeC_6H_4	Me		Oil	98	1 630, 3 160, 3 300, 3 440	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)	39.3 (d, $^2J_{PC}$ 5.9 Hz Me), 60.7 (d, $^1J_{PC}$ 119.6 Hz, C-1), 163.8 (C-2)	+36.0
(4b)	4-MeC_6H_4	CH_2CO_2Et		Oil	97	1 600, 1 710, 2 500, 3 300	4.24 (d, 1 H, $^2J_{PH}$ 18.3 Hz, =CH), 4.55 (d, 2 H, $^3J_{PH}$ 12.0 Hz, CH_2), 6.79 (s, 1 H, NH)	52.0 (d, $^2J_{PC}$ 8.8 Hz, CH_2), 58.9 (d, $^1J_{PC}$ 115.9 Hz, C-1), 165.0 (d, $^2J_{PC}$ 0.7 Hz, C-2), 168.9 (d, $^3J_{PC}$ 1.2 Hz, CO)	+37.0
(5)	4-MeC_6H_4			Oil	97	1 590, 1 700, 3 160	4.55 (d, 1 H, $^2J_{PH}$ 19.7 Hz, =CH), 6.83 (s, 1 H, NH), 9.87 (d, 1 H, $^2J_{PH}$ 7.9 Hz, NH)	57.2 (d, $^1J_{PC}$ 116.5 Hz, C-1), 153.0 (CO), 165.2 (C-2)	+21.3
[6a]	4-MeC_6H_4		Me	138—139 [a]	90 (87) [b]				
(6b)	c-C_6H_{11}		Me	152—153	86 (83) [b]	1 620, 3 320, 3 400, 3 460	1.39 (d, 3 H, $^3J_{PH}$ 15.7 Hz, Me), 4.0 (s, 1 H, NH)	13.5 (d, $^2J_{PC}$ 15.7 Hz, Me), 73.9 (d, $^1J_{PC}$ 119.7 Hz, C-1), 164.4 (d, $^2J_{PC}$ 3.9 Hz, C-2)	+15.4
(6c)	Ph		Me	102—103 [a]	85 (79) [b]				
(6d)	c-C_6H_{11}		CH_2Ph	105—106	90 (83) [b]	1 610, 3 480	3.28 (d, 2 H, $^3J_{PH}$ 18.9 Hz, CH_2)	32.6 (d, $^2J_{PC}$ 15.6 Hz, C-11), 74.4 (d, $^1J_{PC}$ 123.8 Hz, C-1), 166.9 (d, $^2J_{PC}$ 3.2 Hz, C-2)	+15.7
(6e)	4-MeC_6H_4		CH_2Ph	165—166	87 (80) [b]	1 610, 3 440	3.22 (d, 2 H, $^3J_{PH}$ 18.9 Hz, CH_2)	34.9 (d, $^2J_{PC}$ 14.0 Hz, C-11), 83.0 (d, $^1J_{PC}$ 116.6 Hz, C-1), 162.1 (d, $^2J_{PC}$ 5.4 Hz, C-2)	+14.5
(6f)	4-MeC_6H_4		CH_2=$CHCH_2$	Oil	92 (87) [b]	1 600, 3 300, 3 460	2.47 (dd, 2 H, $^3J_{PH}$ 18.9, $^3J_{HH}$ 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, $^2J_{PC}$ 18.9 Hz, C-11), 81.3 (d, $^1J_{PC}$ 118.1 Hz, C-1), 112.9 (C-11), 137.2 (d, $^3J_{PC}$ 9.0 Hz, C-12), 161.2 (d, $^2J_{PC}$ 5.2 Hz, C-2)	+14.5
(6g)	c-C_6H_{11}		CH_2=$CHCH_2$	Oil	88 (75) [b]	1 640, 3 320, 3 480	2.57 (dd, 2 H, $^3J_{PH}$ 18.9, $^3J_{HH}$ 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, $^2J_{PC}$ 15.2 Hz, C-1), 75.5 (d, $^1J_{PC}$ 121.7 Hz, C-1), 114.2 (C-13), 136.8 (d, $^3J_{PC}$ 7.1 Hz, C-12), 166.2 (d, $^2J_{PC}$ 3.1 Hz, C-2)	+15.5

Table 1. (*continued*)

Compound	R^1	R^2	R^3	M.p. (°C)	Yield (%)	I.r. (Nujol) $\nu_{max.}$ (cm^{-1})	$CDCl_3$ (p.p.m.) δ_H	δ_C	δ_P
(7)	4-MeC_6H_4			160—161	97	1 620, 3 240, 3 400	9.0 (d, 1 H, $^2J_{PH}$ 7.9 Hz, NH)	88.4 (d, $^1J_{PC}$ 119.7 Hz, C-1), 164.4 (d, $^2J_{PC}$ 22.1 Hz, C-2)	+28.4
(8)	4-MeC_6H_4			123—124	95 (90)[c]	1 590, 3 440	2.31 (s, 3 H, Me)	63.6 (d, $^1J_{PC}$ 119.7 Hz, C-1), 163.4 (d, $^2J_{PC}$ 8.3 Hz, C-2)	+13.5

[a] Lit.,[6] 138—139 °C and 102—103 °C respectively. [b] From method B. [c] From method B. [d] Microanalytical data correlate well with the proposed structures: solids: C ± 0.19%, H ± 0.16%, N ± 0.21%; oils, C ± 0.36%, H ± 0.28%, N ± 0.42%.

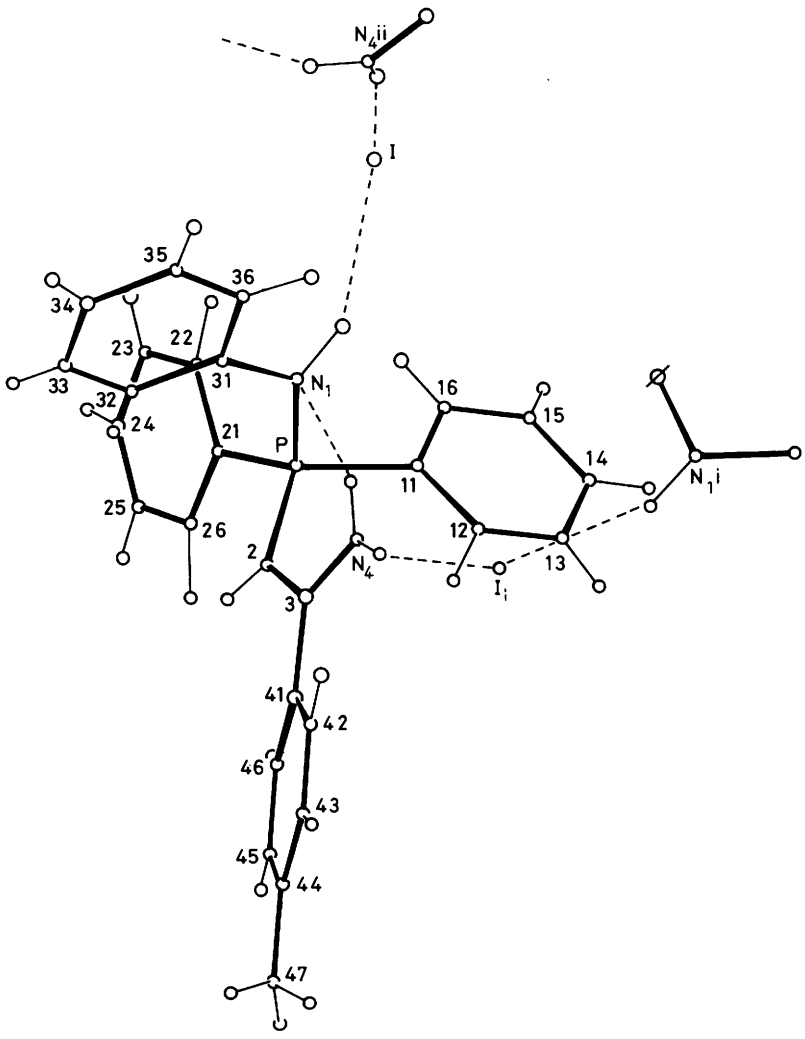


Figure. An ORTEP view of the salt of (**3**), showing the numbering scheme used in the crystallographic work, together with the H-bonding network. i, ii stand for the symmetry operations $(1/2 - x, 1/2 + y, 1/2 - z)$ and $(1/2 - x, -1/2 + y, 1/2 - z)$ respectively

lithium followed by addition of an alkyl halide leads regioselectively to C-alkylation, a result which parallels that reported for β-imino enamines.[10] Compounds (**6**) were formed in high yields and show the ^1H- and ^{13}C-n.m.r. signals expected for the alkyl group attached to the β-enamino carbon; furthermore, (**6a**) and (**6c**) are identical with compounds previously reported from the reaction of ethyldiphenyl-λ^5-phosphazenes.[6] It is worth noting that the conversion of (**1**) into (**6**) can be accomplished in a high yield, one-pot reaction by treatment of the λ^5-phosphazene-derived anion with nitrile and subsequent quenching with the corresponding alkyl halide.

The same regioselectivity was encountered when bromine was employed as the electrophile; thus, the reaction of compound (**2**) with bromine led to α-bromination and hydrobromination of the P=N double bond to afford the phosphonium salt (**7**) (m.p. 160—161 °C, δ_P +28.4 p.p.m.); compound (**7**) was in turn dehydrohalogenated to the β-enamino-λ^5-phosphazene derivative (**8**) (m.p. 123—124 °C, δ_P

+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 $SiMe_4$ (TMS) for ^1H- and ^{13}C-n.m.r. or from H_3PO_4 85% in the case of the ^{31}P 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 methods[6] and the same process was applied in the synthesis of (**2**) in which R^1 = c-C_6H_{11}.

Synthesis of (Z)-(β-*Amino*-β-p-*tolylvinyl*)*diphenyl*(*phenylamino*)*phosphonium Iodide* (**3**).—A stoicheiometric 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%); $\nu_{max.}$ 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, NH_2); 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*)(*methylphenylamino*)*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; $\nu_{max.}$ 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**) $\nu_{max.}$ 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, CH_2), 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 (CH_2), 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*-λ^5-*phosphazenes* (**6**): *General Procedure.*—(Z)-4-*Cyclohexyl*-3-*methyl*-1,2,2-*triphenyl*-1,5-*diaza*-2λ^5-*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 methyldiphenyl-λ^5-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%); $\nu_{max.}$ 1 620, 3 320, 3 400, and 3 460 cm^{-1}; δ_H 0.55—1.87 (m, 11 H, c-C_6H_{11}), 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%); $\nu_{max.}$ 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, $^2J_{PH}$ 7.9 Hz); δ_C 21.1 (Me), 88.4 (d, $^1J_{PC}$ 119.7 Hz, C-1), 121.0—133.4 (21 C, ArC), 138.9 (C-7), 140.2 (C-6), and 164.4 (d, $^2J_{PC}$ 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-*diaza*-2λ^5-*phosphapenta*-1,3-*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%); $\nu_{max.}$ 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, $^1J_{PC}$ 119.7 Hz, C-1), 117.9—133.5 (21 C, ArC), 136.8 (d, $^3J_{PC}$ 12.6 Hz, C-3), 139.6 (C-6), 150.7 (C-7), and 163.4 (d, $^2J_{PC}$ 8.3 Hz, C-2); δ_P +13.5 p.p.m.; *m/z* 486—488 (M^+).

Crystal Data for Compound (**3**).—$\{[C_{27}H_{26}N_2P]^+I^-\}\cdot\frac{1}{2}Cl_2CH_2$. Space group *C*2/*c*, $Z = 8$, $D_x = 1.381$ g cm^{-3}, a = 24.415 7(9), b = 9.318 0(2), c = 25.343 2(11) Å, β = 116.893(3)° (from a least-squares fit to the h, k, l and 2θ values of 83 reflexions of θ up to 45° with Cu-K_α radiation), μ = 107.55 cm^{-1} (min. and max. transmission factors were 0.762—1.334).[11] A pale yellow rhombic prism of 0.17 × 0.17 × 0.27 mm was used in the analysis.

Data Collection and Processing.—Philips PW1100 diffractometer, ω/2θ scans, width 1.5°, graphite monochromated Cu-K_α 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 3σ(I), 3σ(I), 3.5σ(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 Methods[12] were used for the solution and weighted full matrix 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 θ/λ so as to give no trends in $\langle w\Delta^2F\rangle$, *versus* $F_{obs.}$ and/or sin θ/λ. 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 ±2.2 eÅ^{-3}, the maximum being near the P and N(1) atoms; the maximum thermal value was U33(C15), 0.16(1) 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.*

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)

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

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