Reaction of (Z)-β-Enamino λ⁵-Phosphazenes and Dimethyl Acetylenedicarboxylate

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N-Phenyl-β-enamino λ⁵-phosphazenes (1) react with dimethyl acetylendicarboxylate to give stable 1 : 1 adducts (2). The enamine moiety of the functionalised phosphonium ylides (2) displays ambident nucleophility; thus, heating of compounds (2) results in N-cyclocondensation, affording 1-aza-4λ⁵-phosphinines (3), while 1-aza-2-oxo-4λ⁵-phosphinines (5) and enamino λ⁵-phosphole derivatives (4) are obtained when adducts (2) are treated with KH and BuLi, respectively. The reaction of N-ethoxycarbonyl- and N-benzoyl-β-enamino λ⁵-phosphazenes (6) and (7) with the dicarboxylate, however, involves the C_β–H enamino bond, affording phosphorylated 2-pyridones (10) and (11).

Primary enamines are very useful reagents in organic synthesis; in the last few years, new types with an electron-withdrawing group at the β-position have been described, as well as their applications in the synthesis of heterocycles[1] and enamides.[2] Likewise, we have shown the utility of β-enamino imines in the preparation of a broad group of cyclic compounds with different ring sizes and heteroatoms.[3]
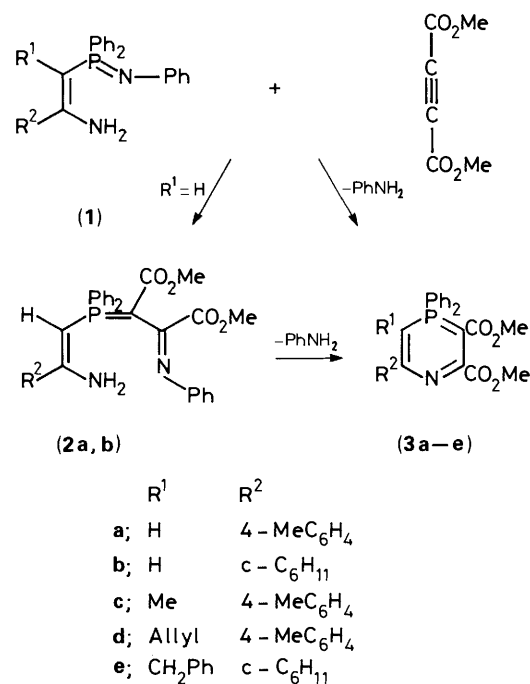
Previously we reported the first synthesis of primary (Z)-β-enamino λ⁵-phosphazenes[4] (1), which offers an easy route to phosphorus-containing heterocycles[5,6] because of their multifunctional character.[7] Continuing our study on the reactivity of these systems, we now report the results of the reaction of β-enamino λ⁵-phosphanes (1), (6), and (7) with dimethyl acetylendicarboxylate (DMAD) and we also show the ambident nucleophilicity of the enamino moiety of stable β-enamino phosphonium ylides (2).
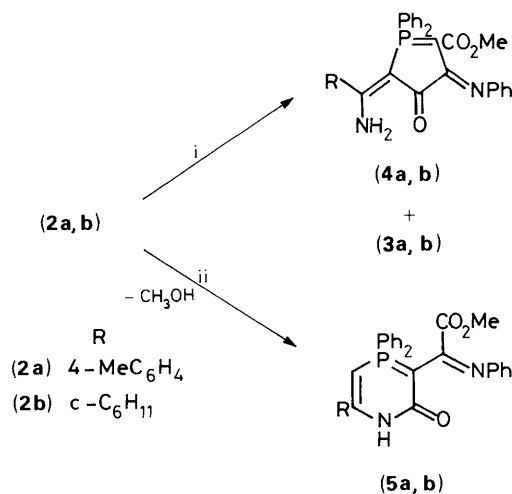
Results and Discussion

(Z)-N-*Phenyl-β-enamino λ⁵-Phosphazenes and DMAD.*— Treatment of β-enamino derivatives (1) with DMAD in acetonitrile leads to 1-aza-4λ⁵-phosphinines (3) in excellent yields.[5] While the reaction occurs at room temperature when α-alkylated β-enamino λ⁵-phosphazenes (1) (R¹ ≠ H) are employed as starting material, in the case of R¹ = H the process requires the use of acetonitrile at reflux. The lower reactivity of enamines (1a and b) allowed us to isolate at room temperature the primary β-enamino phosphonium ylide derivatives (2). The formation of compounds (2) can be explained through a (2 + 2) cyclisation followed by a ring-opening reaction, in a similar way to that reported for non-functionalised λ⁵-phosphazenes.[8–10] Heating of β-enamines (2) at 80 °C results in cyclocondensation and loss of aniline to afford products (3) (Scheme 1).

Primary β-enamino λ⁵-phosphazenes (1) exhibit marked ambident nucleophilicity[7] in a similar way to that recently reported in the case of other β-enamines such as primary aminoketene dithioacetals.[11] Then, it could be that expected the related functionalised phosphonium ylides (2), in which the enamino moeity still remains, would display similar behaviour; therefore, the N- and/or C-cyclocondensation reactions with the electrophilic centres of the molecule would lead to new phosphorus-containing heterocycles.

Thus, when β-enamino compounds (2a and b) were treated with butyl-lithium at room temperature a mixture of two derivatives in the approximate ratio 40:60 (detected by ³¹P n.m.r. spectroscopy) was obtained after stirring for 12 h and aqueous work-up (Scheme 2). Fractional recrystallisation allowed us to identify the minor components as the above mentioned compounds (3a and b), which are formed by

(1)

(2a, b)   −PhNH₂   (3a—e)

	R¹	R²
a;	H	4 – MeC₆H₄
b;	H	c – C₆H₁₁
c;	Me	4 – MeC₆H₄
d;	Allyl	4 – MeC₆H₄
e;	CH₂Ph	c – C₆H₁₁

Scheme 1.

(2a, b)

(4a, b)

+

(3a, b)

− CH₃OH

R	
(2a)	4 – MeC₆H₄
(2b)	c – C₆H₁₁

(5a, b)

Scheme 2. *Reagents and conditions:* i, BuLi–THF, 25 °C; ii, KH–THF, 60 °C

Table 1. 1-Aza-4λ⁵-phosphinines (3), λ⁵-phosphole derivatives (4), and 1-aza-2-oxo-4λ⁵-phosphinines (5)

Compound	R^1	R^2	Yield (%)^a	M.p. (°C)
(3a)	H	4-MeC₆H₄	80 (90) ^{b}	228—229
(3b)	H	c-C₆H₁₁	77 (88) ^{b}	186—187
(3c)	Me	4-MeC₆H₄	76	209—210
(3d)	Allyl	4-MeC₆H₄	79	210—211
(3e)	CH₂Ph	c-C₆H₁₁	78	215—216
(4a)		4-MeC₆H₄	51	188—189
(4b)		c-C₆H₁₁	55	193—194
(5a)		4-MeC₆H₄	78	230—231
(5b)		c-C₆H₁₁	73	235—236

^{a} Isolated yields. ^{b} Yield from (2).

intramolecular condensation of the amino group with the imine C=N double bond.
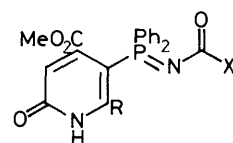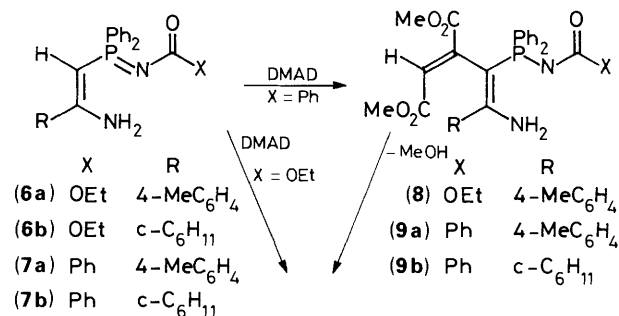
Mass spectrometry of the other products (4a and b) showed the loss of methanol from (2), so the cyclocondensation involved the enamine moiety and a methoxycarbonyl group. The observed i.r. absorptions in the 3 150—3 450 and 1 550—1 700 cm⁻¹ regions suggested the presence of the primary enaminone.[12] Also, the absence, in the ¹H n.m.r. spectra, of absorptions corresponding to the C$_β$-enamino hydrogen of the starting compound (2), as well as the shielding of the remaining methoxy signals and the downfield shift of the phosphorus absorption (δ_P 23.6—25.6 p.p.m.) in compounds (4) relative to (2), supported the condensation between the C$_β$-H enamino and the α-imine ester group[10] leading to the cyclic phosphonium ylide derivatives (4). The intramolecular hydrogen bonding between NH and the carbonyl group of the thus formed enaminone system hence allowed us to isolate the stable functionalised λ⁵-phosphole compounds (4). It is noteworthy that primary β-enamino carbonyl derivatives are potential intermediates in the synthesis of natural and synthetic compounds possessing biological activity.[13]

Nevertheless, the action of an excess of potassium hydride on ylides (2) resulted in the N-cyclocondensation of the enamine moiety with the α-phosphonium ylide methoxycarbonyl group, yielding the hitherto unknown 1-aza-2-oxo-4λ⁵-phosphinines[14] (5). Compounds (5) were characterised on the basis of their spectroscopy and mass spectrometry data. Thus, the deshielding of the proton bonded to C-5 of (5a) (δ_H 4.8), the lower value of the phosphorus–hydrogen coupling constant ($^2J_{PH}$ 9.8 Hz), as well as the upfield shift of the phosphorus absorption (δ_P—1.0 p.p.m.) relative to those of the acyclic starting compound (2a) (δ_H 4.57; $^2J_{PH}$ 14.2 Hz; and δ_P 3.9 p.p.m.), modifications that were also observed in the azaphosphine rings (3), are consistent with the proposed structure (5). Yields of compounds (3)—(4) are given in Table 1.

N-*Ethoxycarbonyl-* and N-*Benzoyl-β-enamino-λ⁵-Phosphazenes and DMAD.*—The conjugation of λ⁵-phosphazenes with electron-withdrawing groups reduces their reactivity through the P=N double bond. For instance, while N-phenyl triphenyl-λ⁵-phosphazenes react easily with DMAD, the presence of electron-attracting substituents at the nitrogen atom, such as benzoyl or ethoxycarbonyl groups, suppresses the addition of the P=N linkage to the acetylenic ester.[8] Therefore, if β-enamino derivatives (6) and (7) show similar chemical behaviour we would be able to direct the addition to the enamino group in the same way to that reported for β-imino enamines.[15]

Thus, when N-ethoxycarbonyl derivatives (6) reacted with DMAD in methylene dichloride at room temperature phosphorylated 2-pyridones (10) are formed in excellent yield. Formation of products (10) could be explained by addition of

the C$_β$-H enamine bond to the carbon–carbon triple bond of the DMAD affording the non-isolated 1:1 adducts (8); subsequent cyclocondensation, in a similar way to that proposed for β-imino enamines[15] and primary β-enamino ketones[16] with acetylenic esters, leads to heterocycles (10).

	X	R
(6a)	OEt	4-MeC₆H₄
(6b)	OEt	c-C₆H₁₁
(7a)	Ph	4-MeC₆H₄
(7b)	Ph	c-C₆H₁₁

	X	R
(8)	OEt	4-MeC₆H₄
(9a)	Ph	4-MeC₆H₄
(9b)	Ph	c-C₆H₁₁

	X	R
(10a)	OEt	4-MeC₆H₄
(10b)	OEt	c-C₆H₁₁
(11a)	Ph	4-MeC₆H₄
(11b)	Ph	c-C₆H₁₁

Scheme 3.

However, the use of N-benzoyl-β-enamino λ⁵-phosphazenes (7) under the same reaction conditions as given for (6) (25 °C; CH₂Cl₂) gave the 1:1 adducts (9), isolated in excellent yield (Scheme 3). Thus, the ¹H n.m.r. spectrum of (9a) shows a downfield shift absorption for the methine proton (δ_H 5.71) and a greatly reduced phosphorus–hydrogen coupling constant ($^4J_{PH}$ 4.0 Hz) relative to those observed for the starting compound (7a) (δ_H 4.31; and $^2J_{PH}$ 17.3 Hz). Heating of compound (9) for 30 min at 50 °C afforded 2-pyridone derivatives (11). Yields of compounds (9)—(11) are given in Table 2.

In conclusion, we have shown the multifunctional character of the β-enamino phosphonium ylides (2), obtained by reaction of functionalised N-aryl-λ⁵-phosphazenes (1) with DMAD; the ambident nucleophilicity of the enamine moiety can be exploited in the preparation of six- (3), (5) and five-membered (4) phosphorus-containing heterocycles from N- and C-cyclocondensation reactions, respectively. However, the less reactive λ⁵-phosphazene derivatives (6) and (7) do not react with DMAD through the P=N double bond, but instead the C$_β$-H enamino bond is involved leading to phosphorylated 2-pyridones (10) and (11).

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 internal SiMe₄ for ¹H and ¹³C n.m.r. or from H₃PO₄ (85%) in the case of ³¹P n.m.r. spectra. I.r. spectra were recorded in KBr on a Perkin-Elmer 298 spectrometer. Microanalyses were performed on a Perkin-Elmer model 240 instrument and mass spectra were obtained using a Hewlett-Packard 5930A spectrometer.

Table 2. M.p.s. and yields of derivatives (9) and 2-pyridones (10) and (11)

Compound	X	R^2	Yield (%)^a	M.p. (°C)
(9a)		4-MeC$_6$H$_4$	85	168—169
(9b)		c-C$_6$H$_{11}$	82	165—166
(10a)	OEt	4-MeC$_6$H$_4$	87	190—191
(10b)	OEt	c-C$_6$H$_{11}$	92	164—165
(11a)	C$_6$H$_5$	4-MeC$_6$H$_4$	93	201—202
(11b)	C$_6$H$_5$	c-C$_6$H$_{11}$	91	164—165

Compounds (1), (6), and (7) were obtained according to the literature methods.[4,6,7]

Synthesis of β-Enamino Phosphonium Ylides (2). *General Procedure.*—2,3-Bis(methoxycarbonyl)-1,4,4-triphenyl-6-(p-tolyl)-1, 7-diaza-4λ^5-phosphahepta-1,3,5-triene (2a). In a dried, argon-filled round-bottomed flask DMAD (0.78 g, 5 mmol) was added to a solution of compound (1a) (2.04g, 5 mmol) in acetonitrile (20 ml). After being stirred for 6 h at room temperature, the mixture was evaporated and the resulting oil was taken up in a mixture of ether–chloroform until formation of a crystalline solid, which was recrystallised from hexane–methylene dichloride to give *compound* (2a) (2.36 g, 86%), m.p. 166—167 °C (Found: C, 72.2; H, 5.5; N, 5.2. C$_{33}$H$_{31}$N$_2$O$_4$P requires C, 71.98; H, 5.67; N, 5.09%) ν$_{max.}$ 3 420, 3 360 (NH), 1 720, 1 680, 1 660, 1 580, and 1 550 cm^{-1}, (C=C, C=O, C=N); δ$_H$ 2.26 (3 H, s, Me), 3.16 (3 H, s, OMe), 3.39 (3 H, s, OMe), 4.57 (1 H, d, $^2J_{PH}$ 14.2 Hz, CH=), and 6.16—7.93 (21 H, m, ArH + NH$_2$); δ$_C$ 21.0 (p-Me), 49.6 (OMe), 51.2 (OMe), 60.8 (C-3, $^1J_{PC}$ 109.7 Hz), 67.7 (C-5, $^1J_{PC}$ 102.8 Hz), 120.4—149.6 (Ph), 161.7 (C-2, $^2J_{PC}$ 3 Hz), 161.9 (C-6, $^2J_{PC}$ 1.9 Hz), 166.9 (CO, $^2J_{PC}$ 12.6 Hz), and 168.6 (CO, $^3J_{PC}$ 12.6 Hz); δ$_P$ 3.9; m/z 550 (M^+, 2%), 457 (5), and 442 (100).

6-Cyclohexyl-2,3-Bis(methoxycarbonyl)-1,4,4-triphenyl-1,7-diaza-4λ^5-phosphahepta-1,3,5-triene (2b). This had m.p. 179—180 °C (from hexane–methylene dichloride) (Found: C, 71.0; H, 6.5; N, 5.0. C$_{32}$H$_{35}$N$_2$O$_4$P requires C, 70.83; H, 6.45; N, 5.16%); ν$_{max.}$ 3 420, 3 360 (NH), 1 770, 1 730, 1 640, 1 550, and 1 530 cm^{-1} (C=C, C=O, C=N); δ$_H$ 1.06—2.37 (11 H, m, C$_6$H$_{11}$), 3.28 (3 H, s, Me), 3.47 (3 H, s, Me), 4.24 (1 H, d, $^2J_{PH}$ 15.5 Hz, CH=), and 6.00—7.95 (17 H, m, ArH + NH$_2$); δ$_C$ 25.7 (CH$_2$), 26.1 (CH$_2$), 32.0 (CH$_2$), 47.4 (CH, $^3J_{PC}$ 12.8 Hz), 49.4 (OMe), 51.1 (OMe), 61.0 (C-3 $^1J_{PC}$ 119.7 Hz), 63.5 (C-5, $^1J_{PC}$ 103.5 Hz), 120.3—149.9 (Ph), 161.5 (C-2, $^2J_{PC}$ 7.2 Hz), 166.9 (CO, $^2J_{PC}$ 12.3 Hz), 169.1 (CO, $^3J_{PC}$ 11.5 Hz), and 169.4 (C-6); δ$_P$ 3.4; m/z 542 (M^+, 1%), 483 (3), and 93 (100).

Synthesis of 1-Aza-4λ^5-phosphinines (3). 2,3-Bis(methoxycarbonyl)-4,4-diphenyl-6-(p-tolyl)-1-aza-4λ^5-phosphinine (3a).—*Method A.* DMAD (5 mmol) was added to a solution of compound (1a)[4] (5 mmol) in dry acetonitrile (20 ml) and the reaction mixture was heated 4 h at reflux. The solvent was evaporated off and the crude product was passed through a silica gel column with ethyl acetate as eluant. Recrystallisation from hexane–methylene dichloride afforded *compound* (3a) (1.82 g, 80%), m.p. 228—229 °C.

Method B. Compound (2a) (2.75 g, 5 mmol) was dissolved in dry acetonitrile (20 ml) and the solution was heated for 3 h at reflux. After evaporation of the solvent, recrystallisation from hexane–methylene dichloride gave compound (3a) (2.46 g, 90%) (Found: C, 71.2; H, 5.3; N, 3.0. C$_{27}$H$_{24}$NO$_4$P requires C, 70.89; H, 5.28; N, 3.06%); ν$_{max.}$ 1 770, 1 720, 1 690, 1 620, and 1 550 cm^{-1} (C=C, C=O, C=N); δ$_H$ 2.31 (3 H, s, Me), 3.49 (3 H, s, OMe), 3.87 (3 H, s, OMe), 5.33 (1 H, d, $^2J_{PH}$ 11.0 Hz, CH=), and 6.63—7.95 (14 H, m, ArH); δ$_C$ 20.8 (p-Me), 50.6 (OMe), 52.1 (OMe), 67.0 (C-3, $^1J_{PC}$ 107.1 Hz), 76.5 (C-5, $^1J_{PC}$ 90.6 Hz), 126.5—139.4 (Ph), 160.5 (C-2, $^2J_{PC}$ 3.6 Hz), 161.8 (C-6), 166.7 (CO, $^2J_{PC}$ 10.7

Hz), and 168.7 (CO, $^2J_{PC}$ 14.5 Hz); δ$_P$ 1.2; m/z 457 (M^+, 6%) and 442 (100).

6-Cyclohexyl-2,3-bis(methoxycarbonyl)-4,4-diphenyl-1-aza-4λ^5-phosphinine (3b). This was prepared by the same methods (A and B) as was compound (3a). *Compound* (3b) showed m.p. 186—187 °C (Found: C, 69.2; H, 6.2; N, 3.3. C$_{26}$H$_{28}$NO$_4$P requires C, 69.47; H, 6.28; N, 3.12%); ν$_{max.}$ 1 740, 1 690, and 1 550 cm^{-1} (C=C, C=O, C=N); δ$_H$ 1.00—2.71 (11 H, m, C$_6$H$_{11}$), 3.45 (3 H, s, OMe), 3.87 (3 H, s, OMe), 4.81 (1 H, d, $^2J_{PH}$ 11.0 Hz, CH=), and 7.00—7.91 (10 H, m, ArH); δ$_C$ 26.0 (CH$_2$), 26.2 (CH$_2$), 31.9 (CH$_2$), 48.3 (CH, $^3J_{PC}$ 11.4 Hz), 50.5 (OMe), 52.4 (OMe), 66.2 (C-3, $^1J_{PC}$ 100.8 Hz), 76.2 (C-5, $^1J_{PC}$ 94.4 Hz), 128.0—132.8 (Ph), 162.6 (C-2), 166.3 (CO, $^2J_{PC}$ 6.4 Hz), 168.0 (CO, $^3J_{PC}$ 14.4 Hz), and 172.1 (C-6); δ$_P$ 0.2 m/z 449 (M^+, 41%), 417 (52), and 394 (100).

2,3-Bis(methoxycarbonyl)-5-methyl-4,4-diphenyl-6-(p-tolyl)-1-aza-4λ^5-phosphinine (3c). A solution of the λ^5-phosphazene (1c)[7] (2.11 g, 5 mmol) in dry acetonitrile (20 ml) and DMAD (5 mmol) was stirred for 6 h at room temperature. The reaction mixture was worked up in a similar way to that described for preparation of (3a). Recrystallisation from hexane–methylene dichloride led to *compound* (3c), m.p. 209—210 °C (Found: C, 71.1; H, 5.7; N, 3.2. C$_{28}$H$_{26}$NO$_4$P requires C, 71.33; H, 5.56; N, 2.97%); ν$_{max.}$ 1 750, 1 700, and 1 540 cm^{-1}; δ$_H$ 1.61 (3 H, d, $^2J_{PH}$ 13.9 Hz, Me), 2.24 (3 H, s, Me), 3.35 (3 H, s, OMe), 3.75 (3 H, s, OMe), and 6.85—7.83 (14 H, m, ArH); δ$_C$ 16.1 (Me, $^2J_{PC}$ 15.9 Hz), 21.0 (p-Me), 50.7 (OMe), 52.2 (OMe), 66.9 (C-3, $^1J_{PC}$ 88.2 Hz), 86.5 (C-5, $^1J_{PC}$ 86.7 Hz), 128.2—138.6 (Ph), 162.8 (C-2), 163.0 (C-6), 167.7 (CO, $^2J_{PC}$ 10 Hz), and 168.9 (CO, $^3J_{PC}$ 12.6 Hz); δ$_P$ 6.3; m/z 471 (M^+, 7%), 457 (33), and 456 (100).

5-Allyl-2,3-bis(methoxycarbonyl)-4,4-diphenyl-6-(p-tolyl)-1-aza-4λ^5-phosphinine (3d). This had m.p. 210—211 °C (from hexane–methylene dichloride) (Found: C, 72.2; H, 5.5; N, 3.1. C$_{30}$H$_{28}$NO$_4$P requires C, 72.42; H, 5.67; N, 2.81%); ν$_{max.}$ 1 750, 1 700, and 1 530 cm^{-1}; δ$_H$ 2.28 (3 H, s, Me), 2.89 (2 H, m, CH$_2$), 3.43 (3 H, s, OMe), 3.81 (3 H, s, OMe), 4.20 (2 H, m, CH$_2$=), 4.81 (1 H, m, CH=), and 6.45—7.93 (14 H, m, ArH); δ$_C$ 21.0 (p-Me), 33.0 (CH$_2$, $^2J_{PC}$ 8.7 Hz), 50.7 (OMe), 52.2 (OMe), 67.6 (C-3, $^2J_{PC}$ 89.5 Hz), 87.5 (C-5, $^1J_{PC}$ 84.5 Hz), 115.2 (CH$_2$=), 127.9—137.4 (Ph), 137.5 (CH=, $^3J_{PC}$ 2.2 Hz), 162.6 (C-2), 164.2 (C-6), 166.1 (CO, $^2J_{PC}$ 12.6 Hz), and 168.6 (CO, $^3J_{PC}$ 12.6 Hz); δ$_P$ 5.6; m/z 497 (M^+, 16%), 483 (38), and 482 (100).

5-Benzyl-6-cyclohexyl-2,3-bis(methoxycarbonyl)-4,4-diphenyl-1-aza-4λ^5-phosphinine (3e). This had m.p. 215—216 °C (from hexane–methylene dichloride) (Found: C, 73.1; H, 6.6; N, 2.7. C$_{33}$H$_{34}$NO$_4$P requires C, 73.45; H, 6.35; N, 2.60%); ν$_{max.}$ 1 740, 1 660, and 1 540 cm^{-1}; δ$_H$ 0.7—2.5 (11 H, m, C$_6$H$_{11}$), 3.35 (3 H, s, OMe), 3.61 (2 H, d, $^2J_{PH}$ 15.8 Hz, CH$_2$), 3.87 (3 H, s, OMe), and 6.22—7.71 (15 H, m, ArH); δ$_C$ 25.6 (CH$_2$), 26.2 (CH$_2$), 30.4 (CH$_2$), 33.5 (CH$_2$Ph, $^2J_{PC}$ 9.6 Hz), 43.5 (CH, $^3J_{PC}$ 9.4 Hz), 50.7 (OMe), 52.3 (OMe), 63.4 (C-3, $^1J_{PC}$ 88.2 Hz), 85.1 (C-5, $^1J_{PC}$ 84.9 Hz), 124.0—138.8 (Ph), 162.0 (C-2), 166.7 (CO, $^2J_{PC}$ 12.6 Hz), 168.9 (CO, $^3J_{PC}$ 12.6 Hz), and 170.7 (C-6, $^2J_{PC}$ 2.7 Hz); δ$_P$ 6.2; m/z 539 (M^+, 100), 525 (18), and 498 (21).

Reaction of β-Enamino Phosphonium Ylides (2) *with Bases. Synthesis of* 2H-3,4-Dihydro-λ^5-phospholes (4).—2-(α-Amino-p-methylbenzylidene)-5-methoxycarbonyl-3-oxo-1,1-diphenyl-phenylimino-2H-3,4-dihydro-λ^5-phosphole (4a). In a dried, argon- filled round-bottomed flask, BuLi (5 mmol) in dry tetra-hydrofuran (THF) (10 ml) was added dropwise to a solution of compound (2a) (5 mmol) in dry THF (20 ml) at room temperature; the mixture was stirred for 12 h and then poured into ice–water, extracted with methylene dichloride (100 ml), and the extract was dried (Na$_2$SO$_4$). Evaporation of the solvent afforded a 40:60 mixture of compounds (3a) and (4a) as determined by ^{31}P n.m.r. spectroscopy. Fractional recrystallisation from hexane–methylene dichloride gave *compound*

(4a) (1.32 g, 51%), m.p. 188—189 °C (Found: C, 74.3; H, 5.1; N, 5.7. $C_{32}H_{27}N_2O_3P$ requires C, 74.12; H, 5.25; N, 5.40%); $v_{max.}$ 3 400, 3 200 (NH), 1 680, 1 600, 1 640, and 1 560 cm^{-1} (C=C, C=O, C=N); δ_H 2.31 (3 H, s, Me), 3.1 (3 H, s, OMe), and 6.71—8.0 (21 H, m, ArH + NH$_2$); δ_C 21.1 (p-Me), 50.5 (OMe), 75.81 (C-5, $^1J_{PC}$ 100.8 Hz), 81.7 (C-2, $^1J_{PC}$ 90.1 Hz), 120.9—139.1 (Ph), 157.0 (C-4, $^2J_{PC}$ 26.5 Hz), 163.3 (CO, $^2J_{PC}$ 13.2 Hz), 167.5 (C-3, $^2J_{PC}$ 31.5 Hz), and 173.0 (C=, $^2J_{PC}$ 10.1 Hz); δ_P 25.6; m/z 518 (M^+, 3%), 487 (2), 399 (5), 293 (61), and 77 (100).

2-[Amino(cyclohexyl)methylene]-5-methoxycarbonyl-3-oxo-1,1-diphenyl-phenylimino-2H-3,4-dihydro-λ^5-phosphole (4b). This was prepared by the same method as for compound (4a) and a 36:64 mixture of derivatives (3b) and (4b) was obtained. Fractional recrystallisation from hexane–methylene dichlorate afforded compound (4b) (1.4 g, 55%), m.p. 193—194 °C (Found: C, 72.7; H, 6.3; N, 5.6. $C_{31}H_{31}N_2O_3P$ requires C, 72.92; H, 6.12; N, 5.49%); $v_{max.}$ 3 410, 3 200 (NH), 1 680, 1 660, 1 640, and 1 570 cm^{-1} (C=C, C=O, C=N); δ_H 1.01—2.36 (11 H, m, C_6H_{11}), 3.04 (3 H, s, OMe), and 6.95—7.93 (17 H, m, ArH + NH$_2$); δ_C 25.4 (CH$_2$), 25.8 (CH$_2$), 29.7 (CH$_2$), 44.8 (CH, $^3J_{PC}$ 5.3 Hz), 50.3 (OMe), 74.5 (C-5, $^1J_{PC}$ 97.6 Hz), 82.3 (C-2, $^1J_{PC}$ 112.7 Hz), 112.4-141.5 (Ph), 154.1 (C-4, $^2J_{PC}$ 25.2 Hz), 163.5 (CO, $^2J_{PC}$ 9.4 Hz), 176.3 (C-3, $^2J_{PC}$ 25.2 Hz), and 178.1 (C=, $^2J_{PC}$ 10.1 Hz); δ_P 23.6; m/z 510 (M^+, 10%), 477 (16), 391 (47), and 336 (100).

Synthesis of 2-oxo-1-aza-4λ^5-phosphinines (5). General Procedure.—3(α-Methoxycarbonyl-α-phenylimino methyl)-2-oxo-4,4-diphenyl-6-p-tolyl-1-aza-4λ^5-phosphinine (5a). To a suspension of KH (6 mmol) in dry THF (15 ml) was added dropwise a solution of compound (2a) (5 mmol) in dry THF (20 ml), under argon, and the mixture stirred for 1 h. The mixture was heated at 60 °C and after being vigorously stirred for 6 h, it was quenched with methanol (10 ml)–water (10 ml) and extracted with methylene dichloride. The organic phase was separated and dried (Na$_2$SO$_4$). The solvent was evaporated off and the crude solid was recrystallised from hexane–methylene dichloride to afford compound (5a) (2.02 g, 78%), m.p. 230—231 °C (Found: C, 74.3; H, 5.1; N, 5.6. $C_{32}H_{27}N_2O_3P$ requires C, 74.12; H, 5.25; N, 5.40%); $v_{max.}$ 3 400 (NH), 1 750, 1 720, and 1 610 cm^{-1} (C=O, C=N); δ_H 2.33 (3 H, s, Me), 3.45 (3 H, s, OMe), 4.79 (1 H, d, $^2J_{PH}$ 9.8 Hz, CH=), 4.79 (s, NH), and 6.24—7.95 (19 H, m, ArH); δ_C 21.2 (OMe), 51.0 (OMe), 63.0 (C-3, $^1J_{PC}$ 104.0 Hz), 75.8 (C-5, $^1J_{PC}$ 91.6 Hz), 120.4—149.8 (Ph), 153.2 (C-6, $^2J_{PC}$ 1.8 Hz), 159.2 (C=N, $^3J_{PC}$ 4.4 Hz), 159.5 (C-2, $^2J_{PC}$ 13.9 Hz), and 165.1 (CO, $^3J_{PC}$ 12.6 Hz); δ_P -1.0; m/z 518 (M^+, 9%), 460 (35), and 459 (100).

6-Cyclohexyl-3-(α-methoxycarbonyl-α-phenylimino methyl)-2-oxo-4,4-diphenyl-1-aza-4λ^5-phosphine (5b). This had m.p. 235—236 °C (from hexane–methylene dichloride) (Found: C, 72.7; H, 6.2; N, 5.3. $C_{31}H_{31}N_2O_3P$ requires C, 72.92; H, 6.12; N, 5.49%); $v_{max.}$ 3 400 (NH), 1 740, 1 710, and 1 600 cm^{-1} (C=O, C=N); δ_H 0.90—2.50 (11 H, m, C_6H_{11}), 3.75 (3 H, s, OMe), 4.70 (1 H, d, $^2J_{PC}$ 9.9 Hz, CH=), 6.62—8.30 (15 H, m, ArH), and 10.87 (s, NH); δ_C 25.5 (CH$_2$), 25.7 (CH$_2$), 31.2 (CH$_2$), 44.0 (CH, $^2J_{PC}$ 9.5 Hz) 51.0 (OMe), 62.6 (C-3, $^1J_{PC}$ 102.0 Hz), 72.0 (C-5, $^1J_{PC}$ 91.3 Hz), 119.8—149.3 (Ph), 151.1 (C-6), 157.2 (CN, $^2J_{PC}$ 5.1 Hz), 164.0 (C-2, $^2J_{PC}$ 13.0 Hz), and 165.3 (CO, $^3J_{PC}$ 11.9 Hz); δ_P -0.6; m/z 510 (M^+, 12%) and 451 (100).

Reaction of N-Benzoyl-β-enamino λ^5-Phosphazenes (7) with DMAD.—Synthesis of 1:1 adducts (9). These products were prepared by the same method as compounds (2), using methylene dichloride as solvent at room temperature.

1-Benzoyl-3-[1,2-bis(methoxycarbonyl)vinyl]-2,2-diphenyl-4-(p-tolyl)-1,5-diaza-2λ^5-phosphapenta-1,3-diene (9a) had m.p. 168—169 °C (from hexane–methylene dichloride) (Found: C, 70.4; H, 5.6; N, 4.7. $C_{34}H_{31}N_2O_5P$ requires C, 70.58; H, 5.40; N, 4.84%); $v_{max.}$ 3 320, 3 140 (NH), 1 720, 1 670 (C=C, C=O), and

1 360 cm^{-1} (P=N); δ_H 2.31 (3 H, s, Me), 3.06 (3 H, s, OMe), 3.39 (3 H, s, OMe), 5.71 (1 H, d, $^4J_{PH}$ 4.0 Hz, CH=), 6.71 (s, NH), and 7.00—8.31 (20 H, m, ArH + NH); δ_C 21.1 (p-Me), 51.1 (OMe), 51.6 (OMe), 85.14 (C-3, $^1J_{PC}$ 100.8 Hz), 125.9—142.4 (Ph + CH= + C=), 164.3 (CO, $^3J_{PC}$ 10.0 Hz), 164.8 (C-4), 168.2 (CO, $^4J_{PC}$ 3.1 Hz), and 175.5 (CON, $^2J_{PC}$ 8.0 Hz); δ_P 18.6; m/z 546 (M^+ − 32, 16%), 443 (18), 384 (32), and 103 (100).

1-Benzoyl-3-[1,2-bis(methoxycarbonyl)vinyl]-4-cyclohexyl-2,2-diphenyl-1,5-diaza-2λ^5-phosphapenta-1,3-diene (9b) had m.p. 165—166 °C (Found: C, 69.7; H, 6.0; N, 4.8. $C_{33}H_{35}N_2O_5P$ requires C, 69.46; H, 6.18; N, 4.91%); $v_{max.}$ 3 350, 3 240 (NH), 1 730, 1 650, 1 600 (C=C, C=O), and 1 350 cm^{-1} (P=N); δ_H 0.71—2.02 (11 H, m, C_6H_{11}), 3.49 (3 H, s, OMe), 3.56 (3 H, s, OMe), 5.83 (1 H, d, $^4J_{PH}$ 3.1 Hz, CH=), 6.51 (s, NH), and 7.20—8.39 (16 H, m, ArH + NH); δ_C 25.2 (CH$_2$), 25.5 (CH$_2$), 30.9 (CH$_2$), 42.4 (CH, $^3J_{PC}$ 3.1 Hz), 51.3 (OMe), 51.8 (OMe), 85.8 (C-3, $^1J_{PC}$ 100.8 Hz), 127.3—141.1 (Ph + CH= + C=), 165.5 (CO, $^3J_{PC}$ 4.2 Hz), 166.5 (C-4), 168.3 (CO, $^4J_{PC}$ 3.7 Hz), and 175.5 (NCO); δ_P 18.4; m/z 570 (M^+, 1%), 511 (26), 408 (22), 376 (56), 201 (97), and 105 (100).

Synthesis of 2-Pyridones (10) and (11).—5-[Ethoxycarbonyl-imino(diphenyl)-λ^5-phosphanyl]-4-methoxycarbonyl-2-oxo-6-(p-tolyl)-1,2-dihydropyridine (10a). To a solution of compound (6a)[6] (2.18 g, 5 mmol) in methylene dichloride (20 ml) was added DMAD (5 mmol), and the reaction mixture was stirred for 6 h at room temperature. Evaporation afforded a crude solid, which was recrystallised from hexane–methylene dichloride to give compound (10a) (2.37 g, 87%), m.p. 190—191 °C (Found: C, 67.8; H, 5.3; N, 5.3. $C_{29}H_{27}N_2O_5P$ requires C, 67.69; H, 5.29; N, 5.45%); $v_{max.}$ 3 320 (NH), 1 740, 1 620 (C=O), and 1 300 cm^{-1} (P=N); δ_H 1.22 (3 H, t, $^3J_{HH}$ 6.9 Hz, Me), 2.16 (3 H, s, Me), 3.63 (3 H, s, OMe), 4.0 (2 H, q, OCH$_2$), 6.04 (1 H, s, CH=), 6.59—7.83 (14 H, m, ArH), and 8.71 (s, NH); δ_C 14.8 (Me), 21.3 (p-Me), 52.2 (OMe), 61.3 (OCH$_2$, $^4J_{PC}$, 3.8 Hz), 94.9 (C-5, $^1J_{PC}$ 106.1 Hz), 125.7—141.4 (Ph + C-3 + C-4), 158.5 (C-2, $^4J_{PC}$ 12.8 Hz), 162.2 (CON), 166.3 (C-6), and 166.7 (COO, $^3J_{PC}$ 11.6 Hz); δ_P 14.1; m/z 514 (M^+, 10%) 469 (20), and 441 (100).

6-Cyclohexyl-5-[Ethoxycarbonylimino(diphenyl)-λ^5-phospha nyl]-4-methoxycarbonyl-2-oxo-1,2-dihydropyridine (10b) had m.p. 164—165 °C (from hexane–methylene dichloride) (Found: C, 66.5; H, 6.0; N, 5.4. $C_{28}H_{31}N_2O_5P$ requires C, 66.39; H, 6.17; N, 5.53%); $v_{max.}$ 3 260 (NH), 1 730, 1 700 (C=O), and 1 310 cm^{-1} (P=N); δ_H 0.71—2.68 (11 H, m, C_6H_{11}), 1.31 (3 H, t, $^3J_{PH}$ 6.3 Hz, Me), 3.43 (3 H, s, OMe), 4.12 (2 H, q, OCH$_2$), 7.08—8.08 (10 H, m, ArH), and 9.59 (s, NH); δ_C 14.8 (Me), 25.8 (CH$_2$), 26.2 (CH$_2$), 28.0 (CH$_2$), 33.2 (CH, $^3J_{PC}$ 6.1 Hz), 51.7 (OMe), 61.4 (OCH$_2$, $^4J_{PC}$ 3.8 Hz), 94.9 (C-5, $^1J_{PC}$ 106.1 Hz), 126.8—143.9 (Ph + C-3 + C-4), 158.5 (C-2, $^4J_{PC}$ 12.8 Hz), 162.1 (CON), 168.1 (COO, $^3J_{PC}$ 17.1 Hz), and 169.7 (C-6); δ_P 14.0; m/z 506 (M^+, 36%), 461 (32), 433 (98), 362 (60), and 183 (100).

5-[Benzoylimino(diphenyl)-λ^5-phosphanyl]-4-methoxy-carbonyl-2-oxo-6-(p-tolyl)-1,2-dihydropyridine (11a). A solution of compound (9a) (2.73 g, 5 mmol) in dry acetonitrile (20 ml) was heated for 30 min at 50 °C. Evaporation of the solvent afforded a crude solid, which was recrystallised from hexane–methylene dichloride to give compound (11a) (2.53 g, 98%), m.p. 201–202 °C (Found: C, 72.4; H, 5.1; N, 4.9. $C_{33}H_{27}N_2O_4P$ requires C, 72.52; H, 4.98; N, 5.12%); $v_{max.}$ 3 330 (NH), 1 740, 1 720 (C=O), and 1 360 cm^{-1} (P=N); δ_H 2.28 (3 H, s, p-Me), 3.67 (3 H, s, OMe), 6.17 (1 H, s, CH=), and 6.67—8.31 (20 H, m, ArH + NH); δ_C 21.0 (p-Me), 52.0 (OMe), 93.0 (C-5, $^1J_{PC}$ 107.1 Hz), 125.8—140.7 (Ph + C-3 + C-4), 160.6 (C-2, $^4J_{PC}$ 6.3 Hz), 166.2 (C-6), 167.0 (COO, $^3J_{PC}$ 12.6 Hz), and 174.6 (CON, $^2J_{PC}$ 6.3 Hz); δ_P 11.3; m/z 546 (M^+, 18%), 443 (18), 185 (94), and 103 (100).

5-[Benzoylimino(diphenyl)-λ^5-phosphanyl]-6-cyclohexyl-4-methoxycarbonyl-2-oxo-1,2-dihydropyridine (11b) had m.p. 164—165 °C (from hexane–methylene dichloride) (Found: C,

71.2; H, 5.7; N, 5.4. $C_{32}H_{31}N_2O_4P$ requires C, 71.36; H, 5.80; N, 5.20%); $\nu_{max.}$ 3 310 (NH), 1 740, 1 640, 1 600 (C=O), and 1 350 cm^{-1} (P=N); δ_H 0.70—2.68 (11 H, m, C_6H_{11}), 3.59 (3 H, s, OMe), 6.08 (1 H, s, CH=), 7.12—8.20 (15 H, m, ArH), and 9.22 (s, NH); δ_C 24.8 (CH$_2$), 25.2 (CH$_2$), 29.3 (CH$_2$), 37.3 (CH), 51.66 (OMe), 93.4 (C-5, $^1J_{PC}$ 122.6 Hz), 126.2—138.4 (Ph + C-3 + C-4), 165.7 (COO, $^3J_{PC}$ 15.7 Hz), 166.3 (C-6), 168.3 (C-2, $^4J_{PC}$ 11.5 Hz), and 175.7 (CON, $^2J_{PC}$ 8.3 Hz); δ_P 11.2.

Acknowledgements

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