Reactivity and Selectivity of *N*-Vinylic λ^5-Phosphazenes towards Electrophiles. Synthesis of 2-Aza-1,3-dienes

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The reactivity of the P=N double bond of the *N*-vinylic λ^5-phosphazene (**1**) towards several electrophiles is reported. Intermolecular aza-Wittig reaction of λ^5-phosphazene (**1**) with aldehydes, phenyl isocyanate, and acid anhydrides leads to ethoxycarbonyl 2-aza-1,3-dienes (**3**), conjugated carbodi-imides (**4**), and *N*-protected amino acrylic acid derivatives (**5**), respectively, while the 2-azahexa-1,3,5-triene (**8**) and also the pyridine (**7**) are obtained when dienyl λ^5-phosphazenes (**6**) are used. Reaction of λ^5-phosphazene (**1**) with methyl iodide and acetyl chloride leads to *N*-alkylated (**10**) and *N*-acylated derivatives (**11**), respectively. Treatment of compound (**11**) in the presence of amino derivatives affords 1-amino-2-azabuta-1,3-dienes (**14**).

There has been increasing interest in the chemistry of λ^5-phosphazenes in recent years owing to their applications as starting materials in the synthesis of a wide range of simple organic derivatives such as amines,[1] amides,[2] and nitro compounds[3] as well as in the preparation of natural products[4] and phosphorus-containing heterocycles.[5] Moreover, λ^5-phosphazene derivatives have also been used as organic semiconductors,[6] backbone polymer precusors,[7] and as ligands in transition-metal complexes.[8]

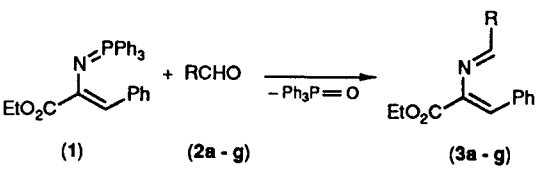
Regarding their reactivity, λ^5-phosphazenes undergo reactions with carbonyl compounds in a similar way to phosphonium ylides, leading to an excellent method for the reaction of iminic double bonds (>C=N–) through intermolecular[9,10] and intramolecular[11,12] aza-Wittig reactions. However, the use of λ^5-phosphazenes in organic synthesis remains much less explored compared with that of the isoelectronic phosphonium ylides.

Previously, we have reported on the synthesis and reactivity of *C*-functionalized λ^5-phosphazenes,[13,14] as well as on the use of *N*-acyl λ^5-phosphazenes as valuable intermediates in the preparation of acyclic[15] and heterocyclic[16] derivatives. Here, we report on the reactivity of *N*-functionalized λ^5-phosphazenes derived from dehydroamino acid esters towards several electrophiles, and their utility in the synthesis of iminic compounds such as 2-aza-1,3-dienes. These compounds have acquired, in recent years, great relevance as building blocks in organic synthesis.[17,18]

Results and Discussion

Reactions of N-*Vinylic* λ^5-*Phosphazenes* (**1**) *with Carbonyl Compounds.*—The preparation of the λ^5-phosphazene (**1**) was accomplished through the classical Staudinger reaction[19] of azidoacrylates[20] and triphenylphosphine after nitrogen evolution. Treatment of compound (**1**) with aromatic, heteroaromatic, and aliphatic aldehydes (**2**) in methylene dichloride or acetonitrile at 60 °C resulted in the formation of 3-ethoxycarbonyl-2-aza-1,3-dienes (**3**) in excellent yield (Scheme 1), through aza-Wittig reaction of the phosphazene (**1**) with the corresponding aldehyde. The end of the reaction can be easily detected by quantitative formation of triphenylphosphine oxide, which was separated from the iminic derivatives (**3**) by means of short-column chromatography with diethyl ether as eluant. Yields are given in the Table.

This reaction can be extended to other carbonyl compounds such as phenyl isocyanate[21] and acid anhydrides.[22] Thus, when



(**1**) (**2a - g**) (**3a - g**)

(2), (3) R		(2), (3) R	
a;	Ph	**e**;	PhCH=CH
b;	4-ClC_6H_4	**f**;	MeCH=CH
c;	2-Thienyl	**g**;	$MeCH_2C(Me)H$
d;	2-Furyl		

Scheme 1.

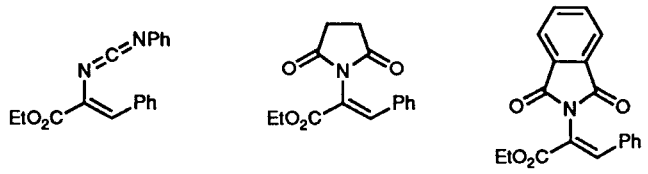
Table. Substituted 2-aza-1,3-dienes (**3**) and (**14**).

Compound[a]	Reaction time (h)	Yield (%)[b]	M.p. (°C)
(**3a**)	18	92	oil
(**3b**)	18	91	oil
(**3c**)	24	90	oil
(**3d**)	30	90	67–68
(**3e**)	20	89	76–77
(**3f**)	28	86	oil
(**3g**)	40	86	oil
(**14a**)	72	80	oil
(**14b**)	72	80	oil
(**14c**)	72	83	76–77

[a] Microanalytical data correlate well with the proposed structures; solids: C ± 0.25%; H ± 0.20%; N ± 0.22%; oils: C ± 0.40%; H ± 0.28%; N ± 0.31%. [b] Isolated yield.

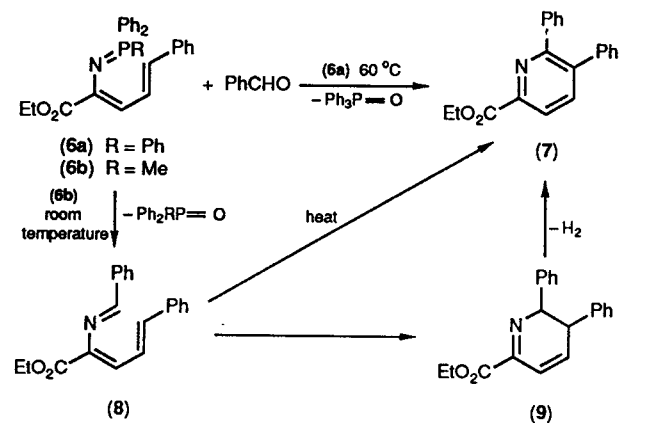
compound (**1**) was treated with phenyl isocyanate in methylene dichloride at room temperature,α,β-unsaturated carbodi-imide (**4**) was obtained, while the reaction of λ^5-phosphazene (**1**) with succinic and phthalic anhydrides afforded the *N*-protected amino acid derivatives (**5**), in a similar way to that reported for simple λ^5-phosphazenes.[22]

With these results in mind, we tried to apply this methodology to the synthesis of 2-aza-1,3,5-trienes. The required *N*-functionalized λ^5-phosphazenes (**6**) were prepared using the corresponding azido ester[23] and phosphines in diethyl ether. However, when compound (**6a**) was allowed to react with



(4) (5a) (5b)

benzaldehyde in acetonitrile at 60 °C and after triphenylphosphine oxide had separated out, the acyclic iminic compound (**8**) was not obtained, but instead the substituted pyridine (**7**) was isolated in very high yield. The spectral data are in agreement with the cyclic compound (**7**) (Scheme 2). Thus, the mass spectrum of compound (**7**) showed the pyridine molecular ion peak, while the pyridine proton signals appear at δ 7.77 and 8.05 as well resolved doublet ($^3J_{HH}$ 8.0 Hz). This result suggests that the process is initiated by an aza-Wittig reaction, giving rise to the 2-azahexa-1,3,5-triene (**8**), which subsequently undergoes electrocyclic ring closure; further dehydrogenation of heterocycle (**9**) under the reaction conditions yields the pyridine (**7**).



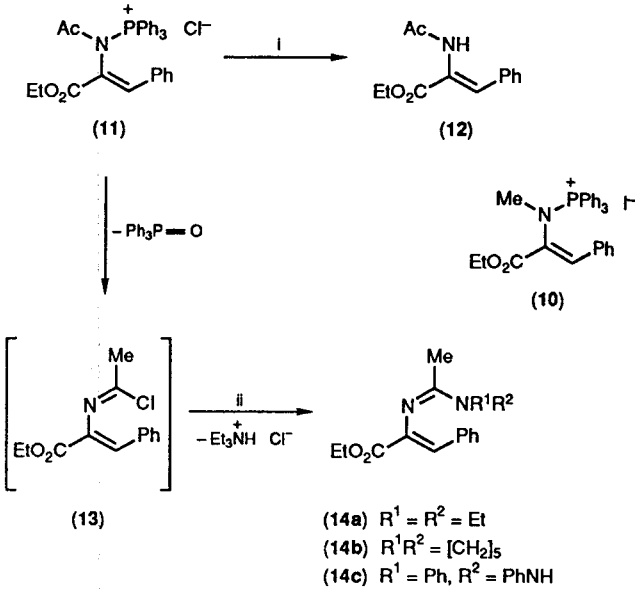
(6a) R = Ph
(6b) R = Me

Scheme 2.

Taking into account this result we then used a more reactive λ^5-phosphazene (**6b**), and worked at lower temperature to accomplish the synthesis of conjugated imine compound (**8**). Thus, *N*-functionalized λ^5-phosphazene (**6b**) was allowed to react with benzaldehyde at room temperature, affording the 2-azahexa-1,3,5-triene (**8**) and methyldiphenylphosphine oxide in excellent yield. Heating of compound (**8**) at 60 °C led to the pyridine (**7**) (Scheme 2). Therefore, 2-aza-1λ^5-phosphahexa-1,3,5-trienes (**6**) were revealed as key intermediates in the synthesis of 2-azahexa-1,3,5-trienes (**8**) and highly substituted pyridines[24] (**7**) under mild reaction conditions and in high yields.

Alkylation and Acylation of N-*Vinylic* λ^5-*Phosphazenes* (**1**).—In a previous paper we have reported the reactivity and chemoselectivity of *C*-functionalized λ^5-phosphazenes.[14] Continuing with our interest in the chemistry of λ^5-phosphazenes we have explored the behaviour of *N*-(1-ethoxycarbonyl-2-phenylvinyl)-*P*,*P*,*P*-triphenyl-λ^5-phosphazene (**1**) towards alkylating and acylating agents. Moreover, an adjacent double bond in conjugation with the λ^5-phosphazene moiety introduces the interesting problem of site selectivity; *i.e.*, reaction at the nitrogen or at the γ-*C*-atom. In this context, alkylation at the γ-*C*-atom of *N*-(1-phenylvinyl)-λ^5-phosphazenes with α-bromo ketones has been reported,[25] in a similar reaction to that described for allylidenephosphorane with halogeno esters[26] and acyl halides.[27]

However, when λ^5-phosphazene (**1**) reacted with methyl iodide at room temperature in chloroform, the crystalline *N*-methylaminophosphonium iodide (**10**) was obtained in a regioselective fashion. The high shift-value of the ^{31}P NMR signal (δ_P 46.6) and the P–H (^3J 8.8 Hz) and P–C (^2J 3.4 Hz) coupling constants observed in the ^{1}H and ^{13}C NMR spectra, respectively, for the methyl group are fully consistent[14] with the phosphonium salt structure (**10**).



(11) (12) (10) (13)

(14a) $R^1 = R^2 = Et$
(14b) $R^1R^2 = [CH_2]_5$
(14c) R^1 = Ph, R^2 = PhNH

Scheme 3. *Reagents:* i, water; ii, HNR^1R^2, Et_3N.

Likewise, reaction of acetyl chloride with *N*-vinylic λ^5-phosphazene (**1**) led to the hygroscopic *N*-acetylated aminophosphonium salt (**11**) (δ_P 32.0). Hydrolysis of compound (**11**) give the acyl α,β-dehydroamino acid derivative (**12**). This reaction can also be used for the one-pot synthesis of the not readily available[17] 1-amino-2-azabuta-1,3-dienes (**14**). Thus, reaction of compound (**1**) with acetyl chloride followed by addition of diethylamine, piperidine, or *N*,*N*′-diphenylhydrazine in the presence of triethylamine afforded 2-azabuta-1,3-dienes (**14a–c**). The formation of these derivatives can be assumed to proceed *via* the salt (**11**), leading to the halogeno imine (**13**) and subsequent reaction with the amino compounds (Scheme 3). Yields are given in the Table.

In this context, it is noteworthy that organophosphorus reagents have found useful applications in the protection of amino proteins in peptide synthesis, due to the readily occurring acid hydrolysis of the phosphorus–nitrogen single bond.[28] However, suitable crystalline *N*-monomethylamino acid derivatives (**10**) incorporating acid-labile protecting groups are not readily available.[29] On the other hand, although some procedures for the preparation of 2-azadienes derived from dehydroamino acid derivatives have been reported,[30] the use of *N*-vinylic λ^5-phosphazenes provides an easy, high-yield and, apparently general entry to 3-substituted electron-poor heterodienes (**3**) and mixed 2-azabuta-1,3-dienes (**14**), with both electron-donating and electron-withdrawing groups, from readily available starting materials and under mild reaction conditions. Simultaneously with our work[9] in this field, a new strategy for the preparation of 2-azadienes from phosphonium ylides and t-butoxyallyl imidates[31] or t-butyl *N*-(diphenylmethylene)oxamates was described.[32] It is noteworthy that 2-aza-1,3-dienes (**3**) and (**14**) could be valuable intermediates in the synthesis of new amino acid derivatives,[32,33] as well as in the preparation of heterocycles.[17,34]

In conclusion, we have shown that reactions of the *N*-vinylic

λ^5-phosphazene (1) with aldehydes, phenyl isocyanate, acid anhydrides, methyl iodide, and acetyl chloride involve the phosphorus–nitrogen double bond in a regioselective fashion, giving protected α,β-dehydro α-amino acid derivatives (5), (10), and (11), conjugated carbodi-imides (4), and 2-azadienes (3) and (14) under mild reaction conditions. Moreover, λ^5-phosphazenes (6) can be used in the synthesis of a 2-azahexa-1,3,5-triene (8) and the highly substituted pyridine (7).

Experimental

General.—M.p.s were taken on samples in open capillary tubes using a Büchi melting-point apparatus and are uncorrected. NMR spectra were obtained using a Bruker AC300 spectrometer with deuteriated chloroform as solvent; chemical shifts are reported downfield from internal $SiMe_4$ for ^1H and ^{13}C NMR, or from H_3PO_4 85% in the case of ^{31}P NMR spectra. IR spectra were recorded on a Philips PU 9716 or a Perkin-Elmer 1720-X FT spectrophotometer. Microanalyses were performed on a Perkin-Elmer model 240 instrument, and mass spectra were obtained using a Hewlett-Packard 5987 A spectrometer. Starting material (1) was obtained by the method reported in the literature [35] (m.p. 141–142 °C).

Synthesis of 3-*Ethoxycarbonyl*-2-*aza*-1,3-*dienes* (3). *General Procedure.*—3-*Ethoxycarbonyl*-1,4-*diphenyl*-2-*azabuta*-1,3-*diene* (3a).* In a dried, argon-filled Schlenck tube a mixture of the *N*-vinylphosphazene (1) (2.3 g, 5 mmol), benzaldehyde (5 mmol), and chloroform (10 ml) was heated for 18 h at 60 °C. The solvent was evaporated off and the resulting oil was purified by means of short silica-gel column chromatography in diethyl ether to give *compound* (3a) (1.3 g, 92%) as an oil (R_f 0.8) (Found: C, 77.5; H, 6.1; N, 5.0. $C_{18}H_{17}NO_2$ requires C, 77.42; H, 6.09; N, 5.02%); ν_{max}(NaCl) 1 710 (C=O) and 1 630 cm^{-1} (C=N); δ_H($CDCl_3$) 1.42 (3 H, t, Me), 4.42 (2 H, q, OCH_2), 7.25–8.09 (11 H, m, Ph + HC=), and 8.56 (1 H, s, HC=N); δ_C($CDCl_3$) 14.1 (Me), 61.2 (OCH_2), 126.7–137.7 (C_{arom} + C_{olef}), 164.2 (C=N), and 164.5 (C=O); *m/z* 279 (M^+, 45%), 206 (70), 178 (63), and 89 (100).

1-(p-*Chlorophenyl*)-3-*ethoxycarbonyl*-4-*phenyl*-2-*azabuta*-1,3-*diene* (3b). This *oil* had R_f 0.7 (Found: C, 68.9; H, 5.0; N, 4.3. $C_{18}H_{16}ClNO_2$ requires C, 69.01; H, 5.11; N, 4.47%); ν_{max}(NaCl) 1 710 (C=O) and 1 625 cm^{-1} (C=N); δ_H($CDCl_3$) 1.30 (3 H, t, Me), 4.25 (2 H, q, OCH_2), 7.25–7.82 (10 H, m, ArH + HC=), and 8.52 (1 H, s, HC=N); δ_C($CDCl_3$) 14.3 (Me), 61.4 (OCH_2), 127.5–137.8 (C_{arom} + C_{olef}), 162.8 (C=N), and 164.6 (C=O); *m/z* 315 (M^+ + 2, 5%), 313 (M^+, 13), 278 (44), and 277 (100).

3-*Ethoxycarbonyl*-4-*phenyl*-1-(2-*thienyl*)-2-*azabuta*-1,3-*diene* (3c). This was prepared by the same method as for compound (3a) on using acetonitrile as solvent; *oil* (R_f 0.8) (Found: C, 67.7; H, 5.1; N, 5.0. $C_{16}H_{15}NO_2S$ requires C, 67.37; H, 5.26; N, 4.91%); ν_{max}(Nujol) 1 720 (C=O) and 1 610 cm^{-1} (C=N); δ_H($CDCl_3$) 1.35 (3 H, t, Me), 4.31 (2 H, q, OCH_2), 7.10–7.82 (9 H, m, ArH + HC=), and 8.78 (1 H, s, HC=N); δ_C($CDCl_3$) 14.2 (Me), 61.2 (OCH_2), 127.8–143.3 (C_{arom} + C_{olef}), 156.1 (C=N), and 164.5 (C=O); *m/z* 285 (M^+, 5%), 203 (30), and 92 (100).

3-*Ethoxycarbonyl*-1-(2-*furyl*)-4-*phenyl*-2-*azabuta*-1,3-*diene* (3d). This *compound* had m.p. 67–68 °C (from hexane–CH_2Cl_2) (Found: C, 71.4; H, 5.6; N, 5.2. $C_{16}H_{15}NO_3$ requires C, 71.38; H, 5.58; N, 5.20%); ν_{max}(KBr) 1 703 (C=O) and 1 631 cm^{-1} (C=N); δ_H($CDCl_3$) 1.42 (3 H, t, Me), 4.37 (2 H, q, OCH_2), 6.60–7.80 (9 H, m, ArH + HC=), and 8.50 (1 H, s, HC=N); δ_C($CDCl_3$) 14.2 (Me), 61.3 (OCH_2), 112.2–151.9 (C_{arom} + C_{olef}), 152.2 (C=N), and 164.5 (C=O); *m/z* 269 (M^+, 47%), 268 (27), and 196 (100).

2-*Ethoxycarbonyl*-1,6-*diphenyl*-3-*azahexa*-1,3,5-*triene* (3e). This *compound* had m.p. 76–77 °C (from hexane–CH_2Cl_2) (Found: C, 78.9; H, 6.2; N, 4.0. $C_{20}H_{19}NO_2$ requires C, 78.69; H, 6.23; N, 4.19%); ν_{max}(KBr) 1 710 (C=O) and 1 580 cm^{-1} (C=N); δ_H($CDCl_3$) 1.23 (3 H, t, Me), 4.18 (2 H, q, OCH_2), 7.02–7.61 (13 H, m, Ph + HC=), and 8.19 (1 H, d, $^3J_{HH}$ 7 Hz, HC=N); δ_C($CDCl_3$) 14.2 (Me), 61.2 (OCH_2), 126.5–138.2 (C_{arom} + C_{olef}), 144.7 (HC=), 164.6 (C=O) and 166.1 (C=N); *m/z* 305 (M^+, 15%), 203 (45), and 191 (100).

2-*Ethoxycarbonyl*-1-*phenyl*-3-*azahepta*-1,3,5-*triene* (3f). This *oil* had R_f 0.8 (Found: C, 73.9; H, 6.9; N, 5.9. $C_{15}H_{17}NO_2$ requires C, 74.07; H, 7.00; N, 5.76%); ν_{max}(NaCl) 1 715 (C=O) and 1 600 cm^{-1} (C=N); δ_H($CDCl_3$) 1.36 (3 H, t, Me), 1.98 (3 H, d, $^1J_{HH}$ 5.3 Hz, Me), 4.35 (2 H, q, OCH_2), 6.45 (1 H, dd, $^1J_{HH}$ 7.4, $^1J_{HH}$ 7.2 Hz, HC=), 7.12–7.68 (7 H, m, Ph + HC=), and 8.09 1 H, d, $^1J_{HH}$ 7.2 Hz, HC=N); δ_C($CDCl_3$) 14.2 (Me), 61.3 (OCH_2), 108.8–138.4 (C_{arom} + C_{olef}), 144.6 (HC=), 164.8 (C=O), and 166.5 (C=N); *m/z* 243 (M^+, 6%), 168 (41), 105 (79), and 77 (100).

2-*Ethoxycarbonyl*-5-*methyl*-1-*phenyl*-3-*azahepta*-1,3-*diene* (3g). This *oil* had R_f 0.75 (Found: C, 74.5; H, 7.9; N, 5.2. $C_{16}H_{21}NO_2$ requires C, 74.13; H, 8.11; N, 5.41%); ν_{max}(Nujol) 1 720 (C=O) and 1 600 cm^{-1} (C=N); δ_H($CDCl_3$) 0.96 (3 H, t, Me), 1.11 (3 H, d, Me), 1.35 (3 H, t, Me), 1.40 (2 H, m, CH_2), 2.20 (1 H, m, CH), 4.30 (2 H, q, OCH_2), and 7.05–7.71 (7 H, m, Ph, HC=, and HC=N); δ_C($CDCl_3$) 11.1 (Me), 13.7 (Me), 15.6 (Me), 26.1 (CH_2), 41.4 (CH), 61.1 (OCH_2), 124.2–134.5 (C_{arom} + C_{olef}), 164.1 (C=O), and 174.9 (C=N); *m/z* 259 (M^+, 2%) and 202 (100).

Synthesis of 4-*Ethoxycarbonyl*-1,5-*diphenyl*-1,3-*diazapenta*-1,2,4-*triene* (4). *General Procedure.*—This was prepared in a similar way to that described for the preparation of compounds (3), on using methylene dichloride as solvent at room temperature. The *oil* had R_f 0.8 (Found: C, 74.0; H, 5.5; N, 9.8. $C_{18}H_{16}N_2O_2$ requires C, 73.97; H, 5.48; N, 9.59%); ν_{max}.(Nujol) 2 180 (N=C=N), 1 680 (C=O), and 1 610 cm^{-1} (C=N); δ_H($CDCl_3$) 1.21 (3 H, t, Me), 4.14 (2 H, q, OCH_2), and 6.98–7.92 (11 H, m, Ph + HC=); δ_C($CDCl_3$) 14.1 (Me), 62.2 (OCH_2), 124.2–138.2 (C_{arom} + C_{olef}), and 164.4 (C=O); *m/z* 292 (M^+, 7%), 203 (20), and 91 (100).

N-(1-*Ethoxycarbonyl*-2-*phenylvinyl*)*succinimide* (5a). *General Procedure.*—In a dried, argon-filled Schlenck tube a solution of phosphazene (1) (2.3 g, 5 mmol) in toluene (15 ml) was heated with succinic anhydride (0.6 g, 6 mmol), and the mixture was heated at 110 °C for 3 days, then was cooled, and excess of succinic anhydride was filtered off. Evaporation of the toluene afforded a crude product, which was purified by means of silica gel column chromatography in diethyl ether. The oil obtained was *compound* (5a) (1.0 g, 76%) (R_f 0.8) (Found: C, 66.0; H, 5.3; N, 5.0. $C_{15}H_{15}NO_4$ requires C, 65.93; H, 5.49; N, 5.13%); ν_{max}(NaCl) 1 785 (C=O) and 1 718 cm^{-1} (OC=O); δ_H($CDCl_3$) 1.33 (3 H, t, Me), 2.87 (4 H, m, CH_2), 4.29 (2 H, q, OCH_2), 7.25–7.55 (5 H, m, Ph), and 8.05 (1 H, s, HC=); δ_C($CDCl_3$) 13.8 (Me), 28.4 (CH_2), 61.8 (OCH_2), 120.8–141.8 (C_{arom} + C_{olef}), and 162.4 and 175.4 (C=O); *m/z* 273 (M^+, 35%), 199 (26), 116 (28), 89 (26), and 55 (100).

N-(1-*Ethoxycarbonyl*-2-*phenylvinyl*)*phthalimide* (5b). This *compound* (1.4 g, 87%) prepared similarly, had m.p. 94–95 °C (from hexane–CH_2Cl_2) (Found: C, 71.0; H, 5.0; N, 4.1. $C_{19}H_{15}NO_4$ requires C, 71.03; H, 4.67; N, 4.36%); ν_{max}(KBr) 1 788 (C=O) and 1 708 cm^{-1} (OC=O); δ_H($CDCl_3$) 1.30 (3 H, t, Me), 4.29 (2 H, q, OCH_2), 7.25–8.05 (9 H, m, ArH), and 8.11 (1 H, s, HC=); δ_C($CDCl_3$) 14.0 (Me), 61.9 (OCH_2), 123.4–142.6 (C_{arom} + C_{olef}), and 162.6 and 163.3 (C=O); *m/z* 321 (M^+, 51%), 247 (34), and 104 (100).

Synthesis of 3-*Ethoxycarbonyl*-2-*aza*-1λ^5-*phosphahexa*-1,3,5-*trienes* (6). *General Procedure.*—3-*Ethoxycarbonyl*-1,1,1,6-*tetra*-

* Non-systematic names are used throughout this paper for compounds (1)–(9) and (14).

phenyl-2-aza-1λ⁵-phosphahexa-1,3,5-triene (**6a**). A solution of triphenylphosphine (1.3 g, 5 mmol) in diethyl ether (10 ml) was added dropwise to a solution of ethyl 2-azido-5-phenylpenta-2,4-dienoate[23] (1.2 g, 5 mmol) in diethyl ether (10 ml) at 0 °C and the reaction mixture was then stirred for 12 h at room temperature. Evaporation of solvent afforded a crude solid, which was recrystallized from hexane–methylene dichloride to give *compound* (**6a**) (2.3 g, 95%), m.p. 112–113 °C (Found: C, 78.0; H, 5.7; N, 2.7. $C_{31}H_{28}NO_2P$ requires C, 77.99; H, 5.87; N, 2.94%); ν_{max}(KBr) 1 690 (C=O) and 1 364 cm^{-1} (P=N); $\delta_H(CDCl_3)$ 1.15 (3 H, t, Me), 3.92 (2 H, q, OCH_2), 6.63 (1 H, d, $^1J_{HH}$ 15.9 Hz, HC=), 6.71 (1 H, dd, $^1J_{HH}$ 11.1, $^1J_{HH}$ 4.2 Hz, HC=), and 7.35–7.90 (21 H, m, Ph + HC=); $\delta_C(CDCl_3)$ 13.8 (Me), 60.2 (OCH_2), 120.0–138.4 (C_{arom} + C_{olef}), and 167.1 (C=O); $\delta_P(CDCl_3)$ 4.96; *m/z* 477 (M^+, 8%) and 215 (100).

4-Ethoxycarbonyl-2,2,7-triphenyl-3-aza-2λ⁵-phosphahepta-2,4,6-triene (**6b**). This *compound* had m.p. 118–119 °C (from hexane–CH_2Cl_2) (Found: C, 75.4; H, 6.1; N, 3.2. $C_{26}H_{26}NO_2P$ requires C, 75.18; H, 6.26; N, 3.37%); ν_{max}(KBr) 1 689 (C=O) and 1 362 cm^{-1} (P=N); $\delta_H(CDCl_3)$ 1.14 (3 H, t, Me), 2.25 (3 H, d, $^1J_{PH}$ 13.0 Hz, Me), 4.01 (2 H, q, OCH_2), 6.66 (1 H, dd, $^1J_{HH}$ 10.8, $^1J_{HH}$ 5.5 Hz, HC=), 6.67 (1 H, d, $^1J_{HH}$ 15.1 Hz, HC=), and 7.15–7.95 (16 H, m, Ph + HC=); $\delta_C(CDCl_3)$ 14.1 (Me), 16.5 (d, $^1J_{PC}$ 66.7 Hz, PMe), 60.6 (OCH_2), 120.0–138.7 (C_{arom} + C_{olef}), and 168.5 (C=O); $\delta_P(CDCl_3)$ 5.29; *m/z* 415 (M^+, 10%), 215 (23), and 201 (100).

Synthesis of 6-Ethoxycarbonyl-2,3-diphenylpyridine (**7**).—*Method A.* Benzaldehyde (0.5 g, 5 mmol) was added to a stirred solution of the λ⁵-phosphazene (**6a**) (2.4 g, 5 mmol) in dry acetonitrile (20 ml) and the mixture was heated at 60 °C for 28 h. The solvent was evaporated off and the crude product was passed through a silica gel column with diethyl ether as eluant to afford *compound* (**7**) (1.3 g, 86%) as an oil (R_f 0.7) (Found: C, 79.5; H, 5.5; N, 4.4. $C_{20}H_{17}NO_2$ requires C, 79.21; H, 5.61; N, 4.62%); ν_{max}(NaCl) 1 730 (C=O) and 1 630 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 1.37 (3 H, t, Me), 4.42 (2 H, q, OCH_2), 7.00–7.40 (10 H, m, Ph), 7.77 (1 H, d, $^3J_{HH}$ 8.0 Hz, HC=), and 8.05 (1 H, d, $^3J_{HH}$ 8.0 Hz, HC=); $\delta_C(CDCl_3)$ 14.1 (Me), 61.7 (OCH_2), 123.1–157.2 (C_{arom}), and 165.2 (C=O); *m/z* 303 (M^+, 14%) and 231 (100).

Method B. Preparation of 3-Ethoxycarbonyl-1,6-diphenyl-2-azahexa-1,3,5-triene (**8**). A mixture of benzaldehyde (0.5 g, 5 mmol) and the λ⁵-phosphazene (**6b**) (2.1 g, 5 mmol) in methylene dichloride (15 ml) was stirred for 46 h at room temperature. The reaction mixture was worked up in a similar way to that described for compound (**7**), and this gave *compound* (**8**) (1.3 g, 88%) as an oil (R_f 0.8) (Found: C, 78.7; H, 6.2; N, 4.3. $C_{20}H_{19}NO_2$ requires C, 78.69; H, 6.23; N, 4.59%); ν_{max}(NaCl) 1 725 (C=O) and 1 650 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 1.27 (3 H, t, Me), 4.22 (2 H, q, OCH_2), 6.80–7.90 (13 H, m, Ph + HC=), and 8.58 (1 H, s, HC=N); $\delta_C(CDCl_3)$ 14.2 (Me), 60.9 (OCH_2), 123.6–138.1 (C_{arom} + C_{olef}), 162.9 (C=N), and 164.4 (C=O); *m/z* 305 (M^+, 83%), 276 (6), and 232 (100).

Cyclization of Compound (**8**). A solution of compound (**8**) (0.9 g, 3 mmol) in dry acetonitrile (10 ml) was heated for 4 h at 60 °C. Evaporation of the solvent yielded the pyridine (**7**).

Synthesis of N-(1-Ethoxycarbonyl-2-phenylvinyl)-N-methylamino-P,P,P-triphenylphosphonium Iodide (**10**).—Methyl iodide (0.8 g, 5.5 mmol) was added to a solution of compound (**1**) (2.3 g, 5 mmol) in methylene dichloride under nitrogen. The reaction mixture was stirred for 2 days at room temperature. Evaporation of the solvent at reduced pressure afforded a crude solid, which was recrystallized from hexane–CH_2Cl_2 to yield *compound* (**10**) (2.8 g, 94%), m.p. 139–140 °C (Found: C, 60.4; H, 5.0; N, 2.5. $C_{30}H_{29}INO_2P$ requires C, 60.71; H, 4.89; N, 2.36%); ν_{max}(KBr) 1 680 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.15 (3 H, t, Me), 3.40 (3 H, d, $^3J_{PH}$ 8.8 Hz, Me), 4.01 (2 H, q, OCH_2), and 7.20–8.09 (21 H, m, Ph + HC=); $\delta_C(CDCl_3)$ 13.8 (Me), 40.5 (d, $^2J_{PC}$ 3.4 Hz, NMe), 62.2 (OCH_2), 117.9–142.3 (C_{arom} + C_{olef}), and 164.4 (C=O); $\delta_P(CDCl_3)$ 46.6; *m/z* 593 (M^+, 1%), 262 (42), and 201 (100).

Synthesis of N-Acetyl-N-(1-ethoxycarbonyl-2-phenylvinyl)-amino-P,P,P-triphenylphosphonium Chloride (**11**).—To a solution of the phosphazene (**1**) (2.3 g, 5 mmol) in dry benzene (20 ml) was added dropwise acetyl chloride (0.5 g, 6 mmol). Reaction was complete after 6 h at room temperature and a white crystalline precipitate was formed. Compound (**11**) is very hygroscopic and was used without purification; $\delta_H(CDCl_3)$ 1.30 (3 H, t, Me), 2.62 (3 H, s, Me), 4.29 (2 H, q, OCH_2), and 7.09–8.10 (16 H, m, Ph + HC=); $\delta_P(CDCl_3)$ 32.7.

Hydrolysis of Compound (**11**). *Synthesis of Ethyl* (Z)-*2-Acetylamino-3-phenylpropenoate* (**12**).—Aminophosphonium salt (**11**) was stirred with NaOH (2M; 20 ml) for 4 h at room temperature. The mixture was then extracted with methylene dichloride and the organic layer was dried (Na_2SO_4). Removal of solvent by distillation afforded an oil, which was purified by column chromatography (silica gel; diethyl ether). Recrystallization from hexane–methylene dichloride yielded *title compound* (**12**), m.p. 83–84 °C (Found: C, 67.1; H, 6.2; N, 5.9. $C_{13}H_{15}NO_3$ requires C, 66.95; H, 6.44; N, 6.01%); ν_{max}(KBr) 3 255 (NH), 1 725 (C=O), and 1 661 and 1 525 cm^{-1} (NC=O); $\delta_H(CDCl_3)$ 1.29 (3 H, t, Me), 1.98 (3 H, s, Me), 4.21 (2 H, q, OCH_2), 7.22–7.49 (6 H, m, Ph + HC=), and 7.92 (1 H, s, NH); $\delta_C(CDCl_3)$, 13.7 (Me), 22.3 (OMe), 61.1 (OCH_2), 124.6–133.2 (C_{arom} + C_{olef}), 164.9 (C=O), and 169.6 (NC=O); *m/z* 233 (M^+, 13%), 191 (82), and 117 (100).

Synthesis of 3-Azapenta-1,3-dienes (**14**). *General Procedure.*—*4-Diethylamino-2-ethoxycarbonylphenyl-3-azapenta-1,3-diene* (**14a**). In a dried, argon-filled Schlenck tube a solution of the phosphazene (**1**) (2.3 g, 5 mmol) in tetrahydrofuran (15 ml) was treated with acetyl chloride (0.5 g, 6 mmol). The mixture was stirred for 6 h at room temperature. The solvent was evaporated off and the crude aminophosphonium salt (**11**) was dissolved in acetonitrile (15 ml), and then triethylamine (1 ml) and piperidine (0.5 g, 6 mmol) were added. The reaction mixture was stirred for 2 days at room temperature, and was then worked up as described for derivative (**12**), to give *compound* (**14a**) (1.2 g, 80%) as an oil (R_f 0.8) (Found: C, 71.0; H, 8.1; N, 9.6. $C_{17}H_{24}N_2O_2$ requires C, 70.83; H, 8.33; N, 9.72%); ν_{max}(NaCl) 1 705 (C=O) and 1 590 cm^{-1}); $\delta_H(CDCl_3)$ 1.29 (6 H, t, Me), 1.40 (3 H, t, Me), 1.83 (3 H, s, Me), 3.53 (4 H, q, NCH_2), 4.29 (2 H, q, OCH_2), and 7.01–7.87 (6 H, m, Ph + HC=); $\delta_C(CDCl_3)$ 13.9 (Me), 14.2 (Me), 15.6 (Me), 42.3 (NCH_2), 60.7 (OCH_2), 120.3–136.4 (C_{arom} + C_{olef}) 157.5 (C=N), and 166.6 (C=O); *m/z* 288 (M^+, 16%), 216 (17), and 215 (100).

2-Ethoxycarbonyl-1-phenyl-4-piperidine-3-azapenta-1,3-diene (**14b**). This *oil* (1.2 g, 80%) had R_f 0.8 (Found: C, 71.9; H, 7.8; N, 9.5. $C_{18}H_{24}N_2O_2$ requires C, 72.00; H, 8.00; N, 9.33%); ν_{max}(NaCl) 1 708 (C=O) and 1 615 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 1.32 (3 H, t, Me), 1.60 (4 H, m, CH_2), 1.70 (2 H, m, CH_2), 1.75 (3 H, s, Me), 3.58 (4 H, m, CH_2), 4.25 (2 H, q, OCH_2), 6.99 (1 H, s, HC=), and 7.20–7.65 (5 H, m, Ph); $\delta_C(CDCl_3)$ 15.8 (Me), 24.7 (CH_2), 26.0 (CH_2), 46.1 (CH_2), 60.8 (OCH_2), 120.4–138.2 (C_{arom} + C_{olef}), 157.8 (C=O), and 166.5 (C=N); *m/z* 300 (M^+, 11%) and 227 (100).

4-(N¹,N²-Diphenylhydrazino)-2-ethoxycarbonyl-1-phenyl-3-azapenta-1,3-diene (**14c**). This compound (1.6 g, 83%) had m.p. 76–77 °C (from hexane–methylene dichloride) (Found: C, 75.3; H, 6.3; N, 10.4. $C_{25}H_{25}N_3O_2$ requires C, 75.19; H, 6.27; N, 10.53%); ν_{max}(KBr) 3 320 and 3 270 (NH), 1 680 (C=O), and 1 590 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 1.36 (3 H, t, Me), 1.89 (3 H, s, Me), 4.28 (2 H, q, OCH_2), 5.63 (1 H, s, NH), and 6.80–7.51 (16 H, m

Ph + HC=); $\delta_C(CDCl_3)$ 14.3 (Me), 17.8 (Me), 61.2 (OCH_2), 112.2–148.8 (C_{arom} + C_{olef}), 160.0 (C=N), and 165.4 (C=O); *m/z* 399 (M^+, 4%), 326 (13), 216 (30), 170 (22), 118 (59), and 77 (100).

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