

Journal of Organometallic Chemistry, 382 (1990) 61–67
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20369

Reactions of *N*-alkoxycarbonyl alkylidiphenyl- λ^5 -phosphazenes with acetylene esters. Synthesis of 1-aza-2-oxo-4 λ^5 -phosphinines *

José Barluenga, Fernando López and Francisco Palacios

Departamento de Química Organometálica. Universidad de Oviedo. 33071 Oviedo (Spain)

(Received June 7th, 1989)

Abstract

N-Alkoxycarbonyl alkylidiphenyl- λ^5 -phosphazenes react with acetylene esters yielding stabilized phosphonium ylides. Subsequent metalation with KH leads to azaphosphinines.

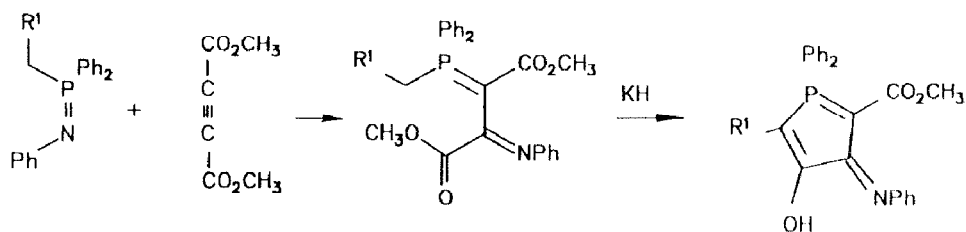
Introduction

It is well known that λ^5 -phosphazenes were first synthesised as early as the beginning of this century [1]. However, only recently has a real interest been shown in this type of compounds owing to their widespread application in the preparation of organic semiconductors [2], backbone polymer precursors [3] and as ligands in transition metal complexes [4]. Moreover, they are versatile key intermediates in the synthesis of natural products [5] and in the preparation of acyclic [6] and heterocyclic nitrogen derivatives [7] by means of the aza-Wittig reaction. However, applications of these species for synthesis of phosphorus containing heterocycles has hitherto hardly been explored [8–10], in spite of their usefulness in the preparation of the potentially biological active six-membered heterocycles containing both phosphorus and nitrogen atoms [11,12].

We recently reported [9] that the reaction of *N*-arylalkylidiphenyl- λ^5 -phosphazenes with dimethyl acetylenedicarboxylate (DMAD) yields conjugated phosphonium ylides. Subsequent treatment of the adduct with potassium hydride leads to phosphole derivatives (Scheme 1).

On the other hand, although a new synthetic method for *N*-functionalised λ^5 -phosphazenes was recently reported [13], very little is known about their reactivity. In fact, the reactivity of the P=N double bond is considerably reduced when

* Dedicated to Prof. G. Wilke on the occasion of his 65th birthday.



Scheme 1

electron-withdrawing groups are attached to the nitrogen atom of λ^5 -phosphazenes [14].

Continuing our interest in the chemistry of phosphorus containing heterocycles, we report here the reaction of N -functionalized λ^5 -phosphazenes with dialkyl acetylenedicarboxylates as well as the first synthesis of 1-aza-2-oxo-4 λ^5 -phosphinines.

Results

Reaction of conjugated phosphonium ylides [15] with acetylene esters proceeds via [2 + 2] cyclization leading to stabilised phosphonium ylides, in a similar way to that outlined in Scheme 1. However, the related isoelectronic N -ethoxycarbonyl- λ^5 -phosphazenes derived from triphenylphosphine do not react with acetylene esters [14].

This limitation can be overcome by increasing the reactivity of the λ^5 -phosphazenes through replacement of the phenyl group attached to the phosphorus atom by an alkyl group. This effect has been observed on the isoelectronic phosphonium ylides [16].

Thus, when N -alkoxycarbonylalkyldiphenyl- λ^5 -phosphazenes (**1**) react with dimethyl (DMAD) and diethyl acetylenedicarboxylate (DEAD) (**2**) in methylene chloride at room temperature, stabilized phosphonium ylides (**3**) are formed in excellent yields (see Table 1). Formation of these compounds, by analogy with simple λ^5 -phosphazenes [9] and phosphonium ylides [15], could be explained through [2 + 2] cyclization of the P=N linkage of **1** to the carbon-carbon triple bond of acetylene esters followed by an electrocyclic ring opening. Compounds **3** were characterised on the basis of their spectroscopic data and mass spectrometry (Table 2). The proposed structure was confirmed by hydrolytic cleavage of **3** with 1.5 *M* sulfuric acid, leading to methyldiphenylphosphine oxide and enamide **4** (see Scheme 2). On the other hand, derivatives **3** were alternatively prepared by a similar reaction starting from N -trimethylsilyl- λ^5 -phosphazenes (**5**) and DMAD giving rise to the corresponding N -silylated 1/1 adduct **6**. Subsequent reaction of these compounds with alkyl chloroformate yields the target derivatives **3**.

Metallation of **3e–3i** ($R^2 = R^3$) with potassium hydride in tetrahydrofuran at 70 °C followed by aqueous work-up affords the 1-aza-2-oxo-4 λ^5 -phosphinines (**7**) with excellent yields (see Table 1). Spectroscopic data support the proposed structure. On the other hand, the metallation of **3a–3c**, where $R^2 = R^3$, gives rise to a mixture of heterocycles. These compounds were probably formed from the transesterification processes between the potassium ethoxide produced in the cyclocon-

Table 1

Some physical data for the compounds prepared.

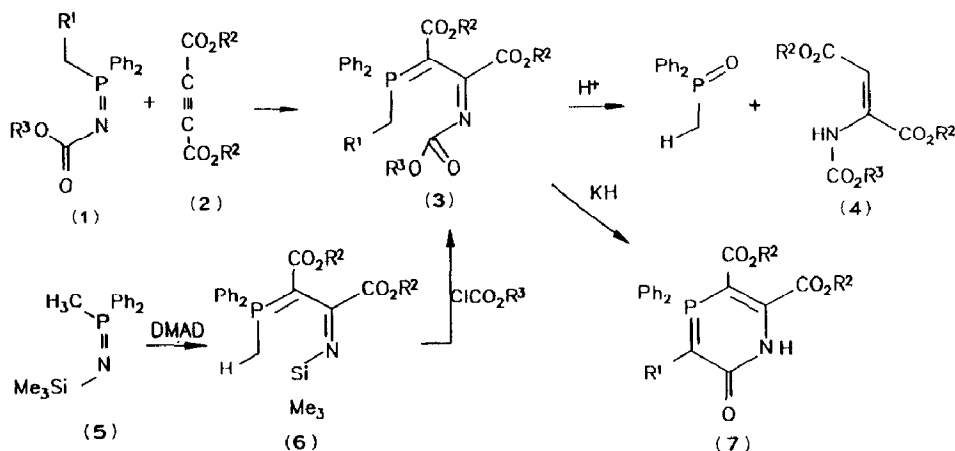
Compound ^a	R ¹	R ²	R ³	M.p. (°C)	Yield (%)
3a	H	CH ₃	C ₂ H ₅	138–139	85
3b	CH ₃	CH ₃	C ₂ H ₅	115–116	89
3c	CH ₂ =CH	CH ₃	C ₂ H ₅	125–126	86
3d	C ₆ H ₅	CH ₃	C ₂ H ₅	114–115	84
3e	H	CH ₃	CH ₃	182–183	87
3f	CH ₃	CH ₃	CH ₃	155–156	88
3g	CH ₂ =CH	CH ₃	CH ₃	158–159	85
3h	H	C ₂ H ₅	C ₂ H ₅	130–131	84
3i	CH ₃	C ₂ H ₅	C ₂ H ₅	109–110	88
7a	H	CH ₃		230–231	86
7b	CH ₃	CH ₃		208–209	88
7c	CH ₂ =CH	CH ₃		211–212	84
7d	H	C ₂ H ₅		209–210	85
7e	CH ₃	C ₂ H ₅		198–199	89

^a All new compounds reported gave satisfactory elemental analysis.

densation reaction and the methoxycarbonyl substituents. In the case of *P*-benzyl-λ⁵-phosphazenes (3d), however, no reaction products were observed, probably due to the lower reactivity of the corresponding anion.

In conclusion, substitution of phenyl substituents by alkyl groups at the phosphorus atom of *N*-alkoxycarbonyl-λ⁵-phosphazenes increases their reactivity and enables these systems to react with acetylene esters thus, yielding stabilized phosphonium ylides 3. These compounds 3 are starting materials for the synthesis of a new type of phosphorus and nitrogen containing heterocycles, 1-aza-2-oxo-4λ⁵-phosphazenes (3), through metalation with KH followed by a cyclocondensation reaction.

(continued on p. 66)



Scheme 2

Table 2

Selected spectral data for the compounds prepared

Compound	IR (KBr) (cm ⁻¹)	MS (<i>m/z</i>) (<i>M</i> ⁺)	¹ H NMR (CDCl ₃) (ppm)	¹³ C NMR (CDCl ₃) (ppm)	³¹ P NMR (CDCl ₃) (ppm)
3a	1730(C=O) 1670(C=O)	429	1.08(t, 3H, ³ J(HH) 7.6 Hz, CH ₃), 2.39(d, 3H, ² J(PH) 13.7 Hz, CH ₃ -P), 3.39 and 3.83(s, 3H, OCH ₃), 3.95(q, 2H, ³ J(HH) 7.6 Hz, OCH ₂)	13.8(CH ₃), 13.9(CH ₃ -P, ¹ J(PC) 63.3 Hz), 50.0 and 51.4(OCH ₃), 60.4(OCH ₂), 68.3(d, C=P, ¹ J(PC) 108.4 Hz)	15.4
3b	1740(C=O) 1660(C=O)	443	1.12(t, 3H, ³ J(HH) 7.0 Hz, CH ₃), 1.12(dt, 3H, ³ J(HH) 7.6 Hz, ³ J(PH) 17.3 Hz, CH ₃ CH ₂ -P), 2.87(dq, 2H, ³ J(HH) 7.6 Hz, ² J(PH) 12.6 Hz, CH ₂ -P), 3.43 and 3.83(s, 3H, OCH ₃), 3.91(q, 2H, ³ J(HH) 7.0 Hz, OCH ₂)	4.9(CH ₃ CH ₂ -P, ² J(PC) 2.7 Hz), 12.4(CH ₃), 18.6(CH ₂ -P, ¹ J(PC) 59.0 Hz), 48.6 and 50.0(OCH ₃), 58.9(OCH ₂), 67.1(C=P, ¹ J(PC) 108.4 Hz)	21.8
3c	1730(C=O) 1660(C=O)	455	1.12(t, 3H, ³ J(HH) 7.6 Hz, CH ₃), 3.41 and 3.85(s, 3H, OCH ₃), 3.7(m, 2H, CH ₂ -P), 3.94(q, 2H, ³ J(HH) 7.6 Hz, OCH ₂), 5.21(m, 2H, =CH ₂), 5.86(m, 1H, =CH)	12.4(CH ₃), 32.1(CH ₂ -P, ¹ J(PC) 55.9 Hz), 47.9 and 49.1(OCH ₃), 59.8(OCH ₂), 67.5(C=P, ¹ J(PC) 108.7 Hz)	16.5
3d	1740(C=O) 1680(C=O)	505	1.2(t, 3H, ³ J(HH) 7.6 Hz, CH ₃), 3.35 and 3.87(s, 3H, OCH ₃), 3.95(q, 2H, ³ J(HH) 7.6 Hz, OCH ₂), 4.43(d, 2H, ² J(PH) 15.7 Hz, CH ₂ -P)	13.9(CH ₃), 32.5(CH ₂ -P, ¹ J(PC) 53.6 Hz), 50.1 and 51.6(OCH ₃), 60.6(OCH ₂), 67.3(C=P, ¹ J(PC) 107.1 Hz)	19.0
3e	1730(C=O) 1670(C=O)	415	2.46(d, 3H, ² J(PH) 14.7 Hz, CH ₃ -P), 3.41, 3.43 and 3.92(s, 3H, OCH ₃)	14.6(CH ₃ -P, ¹ J(PC) 63.5 Hz), 50.6, 52.0 and 52.4(OCH ₃), 67.8(C=P, ¹ J(PC) 107.1 Hz)	15.6
3f	1750(C=O) 1670(C=O)	429	1.08(dt, 3H, ³ J(HH) 7.6 Hz, ³ J(PH) 18.1 Hz, CH ₃ -CH ₂ -P), 2.87(dq, 2H, ³ J(HH) 7.6 Hz, ² J(PH) 12.9 Hz, CH ₂ -P), 3.41, 3.47 and 3.83(s, 3H, OCH ₃)	7.1(CH ₃ CH ₂ -P, ² J(PC) 5.2 Hz), 19.3(CH ₂ -P, ¹ J(PC) 57.7 Hz), 50.5, 51.6 and 52.0(OCH ₃), 67.1(C=P, ¹ J(PC) 103.3 Hz)	21.9

3g	1730(C=O) 1680(C=O)	441	3.40 and 3.83(s, 3H, OCH ₃), 3.68(m, 2H, CH ₂ -P), 5.2(m, 2H, =CH ₂), 5.84(m, 1H, =CH)	32.4(CH ₂ -P, ¹ J(PC) 56.1 Hz), 48.2, 50.1 and 50.4(OCH ₃), 67.6(C=P, ¹ J(PC) 108.4 Hz)	16.6
3h	1740(C=O) 1660(C=O)	443	0.91, 1.05 and 1.28(t, 3H, ³ J(HH) 7.6 Hz, OCH ₂ -CH ₃), 2.41(d, 3H, ² J(PH) 13.8 Hz, CH ₃ -P), 3.85, 3.88 and 4.20(q, 2H, ³ J(HH) 7.6 Hz, OCH ₂)	14.3(CH ₃ -P, ¹ J(PC) 63.5 Hz), 58.9, 60.6 and 60.8(OCH ₂), 66.9(C=P, ¹ J(PC) 108.4 Hz)	15.8
3i	1740(C=O) 1670(C=O)	458	0.91(t, 3H, ³ J(HH) 7.2 Hz, CH ₃), 1.05(m, 12H, CH ₃), 1.28(t, 3H, ³ J(HH) 7.2 Hz, CH ₃), 2.84(dq, 2H, ³ J(HH) 7.4 Hz, ² J(PH) 13.3 Hz, CH ₂ -P), 3.87(m, 4H, OCH ₂), 4.24(q, 2H, ³ J(HH) 7.2 Hz, (OCH ₂))	6.7(CH ₃ CH ₂ -P, ² J(PC) 4.9 Hz), 13.7(CH ₃), 14.2(CH ₃), 20.3(CH ₂ -P, ¹ J(PC) 58.7 Hz), 59.2, 60.8 and 60.9(OCH ₂), 66.4(C=P, ¹ J(PC) 109.0 Hz)	22.3
7a	3310(NH) 1750(C=O)	383	3.35(d, 1H, ² J(PH) 25.2 Hz, =CH-P), 3.40 and 3.95(s, 3H, OCH ₃)	46.3(C-3, ¹ J(PC) 104.3 Hz), 51.4 and 53.5(OCH ₃), 74.7(C-5, ¹ J(PC) 97.9 Hz), 154.1(C-2), 163.5(C-6)	9.1
7b	3310(NH) 1740(C=O)	397	1.48(d, 3H, ³ J(PH) 16.9 Hz, CH ₃), 3.42 and 3.91(s, 3H, OCH ₃)	9.7(CH ₃ , ² J(PC) 8.3 Hz), 49.7(C-3, ¹ J(PC) 106.7 Hz), 51.2 and 53.4(OCH ₃), 74.3(C-5, ¹ J(PC) 100.4 Hz), 153.0(C-2), 162.5(C-6)	11.8
7c	3310(NH) 1740(C=O)	409	3.42 and 3.99(s, 3H, OCH ₃), 4.2(m, 2H, =CH ₂) 6.35(m, 1H, =CH)	51.3 and 53.3(OCH ₃), 59.6(C-3, ¹ J(PC) 105.4 Hz), 78.7(C-5, ¹ J(PC) 99.2 Hz), 107.0(=CH, ² J(PC) 17.1 Hz), 152.5(C-2), 163.2(C-6)	6.7
7d	3320(NH) 1740(C=O)	411	0.88 and 1.36(t, 3H, ³ J(HH) 7.2 Hz, CH ₃), 3.34(d, 1H, ² J(PH) 25.7 Hz, =CH-P) 3.88 and 4.38(q, 2H, ³ J(HH) 7.2 Hz, OCH ₂)	13.6 and 13.9(CH ₃), 46.4(C-3, ¹ J(PC) 104.3 Hz), 60.7 and 62.8(OCH ₃), 74.6(C-5, ¹ J(PC) 98.1 Hz), 153.6(C-2), 163.7(C-6)	9.3
7e	3320(NH) 1750(C=O)	425	0.88 and 1.31(t, 3H, ³ J(HH) 7.2 Hz, CH ₃), 1.50(d, 3H, ³ J(PH) 16.9 Hz, CH ₃) 3.90 and 4.34(q, 2H, ³ J(HH) 7.2 Hz, OCH ₂)	9.6(CH ₃ , ² J(PC) 8.5 Hz), 13.7 and 13.8(CH ₃), 46.4(C-3, ¹ J(PC) 105.8 Hz), 60.7 and 63.0(OCH ₂), 74.4(C-5, ¹ J(PC) 98.9 Hz), 153.1(C-2), 162.6(C-6)	12.3

Experimental

All manipulations were carried out in freshly distilled solvents and under nitrogen. NMR spectra were recorded on a Varian FT-80A or a Bruker 300AC instrument; chemical shifts are reported in ppm downfield from internal SiMe_4 for ^1H and ^{13}C NMR or from 85% H_3PO_4 in the case of ^{31}P NMR. IR spectra were recorded in KBr on a Perkin–Elmer model 240 instrument and mass spectra were obtained using a Hewlett–Packard 5930A spectrometer.

Reaction of N-alkoxycarbonyl- λ^5 -phosphazenes 1 with dialkyl acetylenedicarboxylate. A general procedure for the synthesis of phosphonium ylides (3). Dimethyl (DMAD) or diethyl acetylenedicarboxylate (DEAD) (5.0 mmol) was added to a solution of the λ^5 -phosphazenes (1) (5 mmol) in dry dichloromethane (20 ml) at room temperature and the mixture was stirred for 6 h. The solvent was removed by evaporation. The residue was taken up in ether (10 ml) until a crystalline solid formed, which was recrystallised from hexane/dichloromethane to give compounds 3 (see Table 1). Analytical data of 3a are as follows:

1-Aza-4-phospha-1-ethoxycarbonyl-4,4-diphenyl-2,3-dimethoxycarbonyl-1-penta-1,3-diene (3a). (m.p. 138–139°C). Anal. Found: C, 61.34; H, 5.63; N, 3.26. $\text{C}_{22}\text{H}_{29}\text{NO}_6\text{P}$ calcd.: C, 61.34; H, 5.56; N, 3.45%. Spectroscopic data are found in Table 2.

Synthesis of phosphonium ylides 3a from N-trimethylsilyl-P-methyldiphenyl- λ^5 -phosphazenes (5). To a solution of N-trimethylsilyl-P-methyldiphenyl- λ^5 -phosphazene (5) [18] (1.45 g, 5 mmol) in tetrahydrofuran (20 ml) was added DMAD (0.7 g, 6 mmol) with stirring at room temperature. After 5 h the reaction is complete as indicated by ^{31}P NMR. Evaporation of the solvent leads to the N-silylated phosphonium ylides 6. Acylation of the crude product without further purification with ethyl and methyl chloroformate (5.5 mmol) in tetrahydrofuran (10 ml) and work-up as described above yields 3a (1.76 g, 82%) and 3e (1.86 g, 84%), respectively. Spectroscopic data for compound 6. ^1H NMR (δ , 80 MHz, CDCl_3): 0.21(s, 9H, CH_3Si), 2.38(d, 3H, $J(\text{HH})$ 12.7 Hz., CH_3P), 3.48(s, 3H, OCH_3), 3.71(s, 3H, OCH_3), 7.5–8.1(m, 10H, ArH) ppm. ^{31}P NMR (δ , 32.3, MHz, CDCl_3): +15.0 ppm.

Hydrolysis of phosphonium ylide 3a. Fragmentation products. A solution of 3a (2.1 g, 5 mmol) in a mixture of tetrahydrofuran (40 ml) and 1.5 M sulfuric acid (20 ml) was stirred at room temperature 3h. After aqueous work-up and extraction with methylene chloride, the organic phase afforded methyldiphenylphosphine oxide (0.8 g) m.p. 111–112°C (Lit. [17] 111–112°C) and dimethyl ethoxycarbonyl fumarate (4) (0.8 g) isolated by vacuum distillation b.p. 130–131°C/0.1 Torr. Anal. Found: C, 46.57; H, 5.60; N, 4.34. $\text{C}_9\text{H}_{13}\text{NO}_6$ calcd.: C, 46.57; H, 5.67; N, 4.15. MS (60 eV) m/z 213 (M^+ , 3%), 154 (100). IR ν (neat) 3320, 1760, 1700, 1640, 1300, 1110, 700 cm^{-1} . ^1H NMR (δ , 80 MHz, CDCl_3): 1.28(t, 3H, CH_3), 3.71(s, 3H, OCH_3), 3.83(s, 3H, OCH_3), 5.39(s, 1H, =CH), 9.51(s, 1H, NH) ppm. ^{13}C NMR (δ , 20 MHz, CDCl_3): 11.8(CH_3), 49.4(OCH_3), 50.5(OCH_3), 60.2(OCH_2), 97.4(=CH), 142.1(=C), 150.8(NCO), 161.6(CO), 165.8(CO) ppm.

Metalation of phosphonium ylides (3) with KH. Synthesis of 1-aza-2-oxo-4 λ^5 -phosphinines (7). General procedure. To a suspension of KH (240 mg, 6 mmol) in tetrahydrofuran (30 ml) was added dropwise compounds 3 (5 mmol) in THF (10 ml) at room temperature. When no more gas evolution was observed, the mixture was heated for 6 h at 70°C. After aqueous work-up and extraction with methylene

chloride (100 ml), the extract was evaporated to give crystalline compounds **7**, that were recrystallized from hexane/methylene chloride.

Analytical data of 1-aza-4,4-diphenyl-5,6-dimethoxycarbonyl-2-oxo-4 λ^5 -phosphinine (**7a**) (m.p. 231–232°C). Anal. Found: C, 62.48; H, 4.62; N, 3.81. C₂₀H₁₈NO₅P calcd.: C, 62.66; H, 4.73; N, 3.65%. Selected spectroscopic data are given in Table 2.

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica (Spain) for financial support.

References

- 1 H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2** (1919) 2635.
- 2 M.R. Bryce, A.J. Moore, Y.H. Kim, Z.X. Liu and M.J. Nowak, *Tetrahedron Lett.*, **28** (1987) 4465.
- 3 H.R. Allcock, *Chem. Eng. News*, **63** (1985) 22.
- 4 W. Keim, A. Behr, B. Gruber, B. Hoffmann, F.H. Kowaldt, U. Kurschner, B. Limbäker and F.P. Sistig, *Organometallics*, **5** (1986) 2356; R.E. Cramer, F. Edelman, A.L. Mori, S. Roth, J.W. Gilge, K. Tatsumi and A. Nakamura, *ibid.*, **7** (1988) 841; M.J. Fernández, J.J. Del Val, L.A. Oro, F. Palacios and J. Barluenga, *Polyhedron*, **29** (1987) 1999.
- 5 B.T. Golding, H.C. O'Sullivan and L.L. Smith, *Tetrahedron Lett.*, **29** (1988) 6651.
- 6 J. Barluenga, M. Ferrero and F. Palacios, *Tetrahedron Lett.*, **29** (1988) 4863.
- 7 H. Takeuchi, S. Yanagida, T. Ozaki, S. Hagiwara, S. Eguchi, *J. Org. Chem.*, **54** (1989) 431; M. Khoukhi, M. Vaultier, R. Carrié, *Tetrahedron Lett.*, **27** (1986) 1031.
- 8 J. Barluenga, F. López and F. Palacios, *J. Chem. Soc. Chem. Commun.*, (1985) 1681.
- 9 J. Barluenga, F. López and F. Palacios, *J. Chem. Soc. Chem. Commun.*, (1986) 1574.
- 10 J. Barluenga, F. López and F. Palacios, *Tetrahedron Lett.*, **28** (1987) 2875.
- 11 J.F. Labarre *Top. Curr. Chem.* **102** (1982) 1. L.A. Cates and V.S. Li, *J. Pharm. Sci.*, **71** (1982) 308.
- 12 K. Dimroth, in A.R. Katritzky and C.W. Rees (Eds.), *Comprehensive Heterocyclic Chemistry*, Pergamon Press, London, 1984, Vol. 1, p. 493.
- 13 S. Bittner, M. Pomerantz, Y. Assaff, P. Krief, S. Xi and M.K. Witczak, *J. Org. Chem.*, **53** (1988) 1.
- 14 G.W. Brown, R.C. Cookson I.D.R. Stevens, *Tetrahedron Lett.*, (1964) 1263; G. Brown, *J. Chem. Soc. C*, (1967) 2018.
- 15 J. Barluenga, F. López, F. Palacios and F. Sanchez, *Tetrahedron Lett.*, **29** (1988) 381.
- 16 S. Triplett and P.M. Walker, *J. Chem. Soc.*, (1961) 1267; E. Vedejs, C.F. Marth and R. Ruggeri, *J. Am. Chem. Soc.*, **110** (1988) 3940; E. Vedejs and C.F. Marth, *J. Am. Chem. Soc.*, **110** (1988) 3958.
- 17 H.R. Hays and D.J. Peterson, in G.M. Kosolapoff and L. Maier (Eds.), *Organic Phosphorus Compounds*, J. Wiley, New York, 1972, Vol. 3, p. 343.
- 18 K. Itoh, M. Okamura and Y. Ishii, *J. Organomet. Chem.*, **65** (1974) 327.