Pergamon

Tetrahedron, Vol. 53, No. 40, pp. 13603-13608, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00880-6

Synthesis of α-Aminoalkylphosphonates from Vinylphosphonates *via* Aziridinylphosphonates

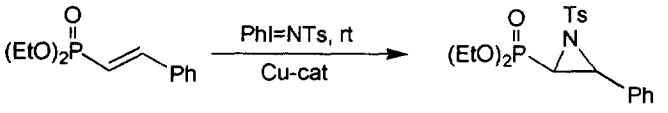
Dae Young Kim* and Dae Yong Rhie

Department of Chemistry, Soonchunhyang University,
Asan P. O. Box 97, Chungnam 336-600, Korea

Abstract : A new synthesis of α-aminoalkylphosphonates from vinylphosphonates is described. The synthetic method involves the aziridination of vinylphosphonates using PhI=NTs in the presence of copper catalyst. Aziridinylphosphonates thus obtained furnish the corresponding α-amino-alkylphosphonates in good overall yields after catalytic hydrogenation.

α-Aminoalkylphosphonates have received an increasing amount of attention since they are key substrates in the synthesis of phosphonopeptide.[1] In these connections, the utilities α-aminoalkylphosphonates as enzyme inhibitors,[2] antibiotics and pharmacological agents,[3] herbicides,[4] and heptens of catalytic antibodies[5] are well documented. A number of synthetic methods for the preparation of α-aminoalkylphosphonates have been available.[6] The most commonly employed method is nucleophilic addition of phosphite to imine derivatives.[7] Other miscellaneous methods include alkylation of anionic or cationic phosphonoglycine equivalents,[8] electrophilic amination of anions of alkylphosphonates,[9] hydrogenation of dehydroaminophosphonate devivatives,[10] amination of α-hydroxyalkylphosphonates,[11] and aldol reaction of (isocyanomethyl)phosphonate with aldehydes.[12]

In this paper, we wish to report a new synthesis of α-aminoalkylphosphonates **3** from vinyl phosphonates **1**. It was performed by the aziridination[13] of vinylphosphonates **1** with [*N*-(*p*-toluenesulfonyl)imino]-phenyliodonane(PhI=NTs)[14] in the presence of copper catalyst and followed by the reductive ring opening of aziridinylphosphonates **2**.[15] The copper catalyzed aziridination of vinylphosphonates **1** employing PhI=NTs, as the nitrene precursor, affords *N*-tosyl aziridinylphosphonates **2** in good yields. The optimized reaction conditions are summarized in Table 1 for representative substrate(**1a**). Aziridination of vinylphosphonate **1a** may be achieved with PhI=NTs in the presence of copper catalyst in either nonpolar or polar solvents in good yields.



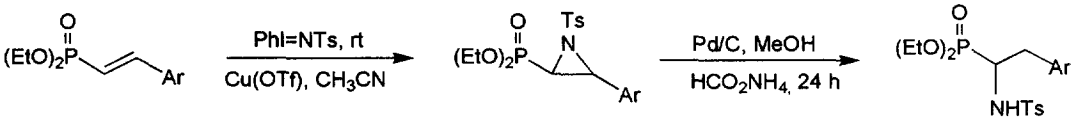
1a **2a**

Table 1. Aziridination of Vinylphosphonate(1a).

Entry	Solvent	equiv of		catalyst	Time	Yield[a] (%)
		1a	PhINTs	(10 mol%)		
1	CH_3CN	1	1.2	$Cu(OTf)_2$	10 min	21
2	CH_3CN	5	1	$Cu(OTf)_2$	10 min	80
3	CH_3CN	5	1	Cu(OTf)	10 min	82
4	CH_2Cl_2	1	1.2	$Cu(OTf)_2$	1 h	35
5	CH_2Cl_2	5	1	$Cu(OTf)_2$	3 h	69
6	C_6H_6	1	1.2	$Cu(OTf)_2$	91 h	53
7	C_6H_6	1	3	$Cu(OTf)_2$	84 h	78
8	C_6H_6	5	1	$Cu(OTf)_2$	76 h	82
9	C_6H_6	5	1	Cu(OTf)	91 h	83

[a] Yields are based on limiting reagent.

The influence of solvent polarity on the reaction rate is striking. In nonpolar solvent such as benzene, the reaction are substantially slower(entries 6-9). In contrast, this same reaction when carried out acetonitrile at room temperature proceeded to completion within 10 min(entries 1-3). The preceding results show that, with Cu(I) and Cu(II) salts, acetonitrile is the optimal solvent for the aziridination of vinylphosphonate **1a** with PhI=NTs. With (phenylsubstituted)vinylphosphonate(**1a**), both CuOTf and $Cu(OTf)_2$ afford high yield of aziridinylphosphonate **2a**. The low yields that were obtained from the reactions in excess PhI=NTs with vinylphosphonate as the limiting reactant. The yields increase when reactions were carried out employing the PhI=NTs as the limiting reagent in the presence of 5 equiv of vinylphosphonates and CuOTf in acetonitrile at room temperature. Under optimal conditions(10 mol% of CuOTf, 1 equiv of PhI=NTs, 5 equiv of vinylphosphonate, acetonitrile, room temperature), the aziridination proceeds in good yields (Table 2).[16] Recently, regiospecific cleavages of aziridine-2-carboxylic acid derivatives by the catalytic hydrogenation were reported.[17] The C-N bond of the aziridine ring of aziridinylphosphonates **2** was also regioselectively reduce by catalytic transfer hydrogenation in the presence of 10% Pd(0)/C and ammonium formate to afford α-aminoalkyl phosphonates in quantitative yields(Table 2).



1 2 3

Table 2. Syntheses of aziridinylphosphonates(2) and α-aminoalkylphosphonates(3).

No	R	Yield (%) of **2**	Yield (%) of **3**
a	C_6H_5	82	86
b	*p*-Cl,C_6H_4	95	89
c	1-Naphthyl	87	83
d	2-Naphthyl	85	81

In summary, we have found a new synthetic route for the preparation of α-aminoalkylphosphonates **3** from vinylphosphonates **1** in good yields. Present procedure involve the aziridination of vinylphosphonate using PhI=NTs and hydrogenolytic cleavage of aziridinylphosphonate **2** with site-selective manner.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Buruker AC 200 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are measured in part per million(δ) and coupling constants , *J*, are reported in Hz. Multiplicity was simplified such as s=singlet, bs=broad singlet, d=doublet, t=triplet, dq=double quartet, and m=multiplet. Infrared spectra were measured on a Perkin-Elmer 283B. Mass spectra were determined with a Hewlett-Packard 5985A or Jeol HX 100/110 through EI or FAB method. Methylene chloride was refluxed and distilled from phosphorus pentoxide. Bezene and acetonitrile were distilled from calsium hydride and stored over 4A° molecular sieves. Column chromatography was performed on Merck silica gel 60(230-400mesh). The vinylphosphonates **1**[18] and PhI=NTs[14a] prepared as reported previously.

Representative procedure of aziridination of vinylphosphonate. Preparation of diethyl 2-phenyl-1-*N*-tosylaziridinylphosphonate(2a). To stirred solution of vinylphosphonate (**1a**, 360.4 mg, 1.5 mmol) and Cu(OTf) (6.4 mg, 10 mol%) in acetonitrile (5 mL) was added PhI=NTs (0.112 g, 0.3 mmol) at room temperature under N_2. When the reaction mixture had turned homogeneous it was filtered through a plug of silica with ethyl acetate (30 mL) as eluent and concentrated *in vacuo*. Purification by flash column chromatography(2:1, ethyl acetate/*n*-hexane) afforded 101mg(82%) of **2a**. R_f: 0.4(ethyl acetate : *n*-hexane = 2 : 1); ^{1}H NMR($CDCl_3$, 200MHz) δ 1.22-1.35(m, 6H), 2.41(s, 3H), 3.52(dd, 1H, J_{PH}=15, J_{HH}=5.1), 3.94-

4.21(m, 1H, 4H), 7.23-7.7(m, 9H); ^{13}C NMR($CDCl_3$, 50MHz) δ 16.4, 21.6, 38.1(d, J=198.3), 48.4, 63.3(d, J=20.8), 128, 128.1, 128.3, 129.2, 129.4; IR (neat, cm^{-1}) 3005, 2970, 1330, 1250, 1120, 980; HRMS: calcd for $C_{19}H_{24}NO_5PS$ 409.1113, found 409.1120.

Diethyl 2-(4-chlorophenyl)-1-*N*-tosylaziridinylphosphonate(2b). R_f : 0.32(methylene chloride : ethyl acetate = 10 : 1); ^{1}H NMR($CDCl_3$, 200MHz) δ 1.14-1.39(m, 6H), 2.42(s, 3H), 3.47(dd, 1H, J_{PH}=14.7, J_{HH}=5), 3.95-4.2(m, 1H, 4H), 7.16-7.72(m, 8H); ^{13}C NMR($CDCl_3$, 50MHz) δ 16.3, 21.6, 38.4(d, J=198.7), 47.7, 63.5(d, J=22), 127.5, 128, 128.3, 128.6, 129.1, 129.5, 130.2, 130.7; IR (neat, cm^{-1}) 3010, 2980, 1260, 1050, 1020, 975; HRMS: calcd for $C_{19}H_{23}ClNO_5PS$ 443.0723, found 443.0778.

Diethyl 2-(1-naphthyl)-1-*N*-tosylaziridinylphosphonate(2c). R_f : 0.35(methylene chloride : ethyl acetate = 10 : 1); mp 88-91 °C; ^{1}H NMR($CDCl_3$, 200MHz) δ 1.26-1.43(m, 6H), 2.32(s, 3H), 3.7(dd, 1H, J_{PH}=14.8, J_{HH}=5.2), 4.15-4.31(m, 4H), 4.62(dd, 1H, J_{PH}=9.1, J_{HH}=5.2), 7-7.95(m, 11H); ^{13}C NMR($CDCl_3$, 50MHz) δ 16.4, 21.5, 36.7(d, J=198.8), 47.2, 63.5(d, J=30.3), 123.8, 124.8, 125.9, 126.4, 126.5, 128.1, 128.3, 129.1, 129.9; IR (neat, cm^{-1}) 3045, 2985, 1258, 1105, 1021; HRMS: calcd for $C_{26}H_{17}NO_4PS$ 459.1269, found 459.1242.

Diethyl 2-(2-naphthyl)-1-*N*-tosylaziridinylphosphonate(2d). R_f : 0.31(methylene chloride : ethyl acetate = 10 : 1); mp 85-86 °C; ^{1}H NMR : ($CDCl_3$, 200MHz) δ 1.23-1.37(m, 6H), 2.37(s, 3H), 3.63(dd, 1H, J_{PH}=14.9, J_{HH}=4.8), 4.04-4.21(m, 4H), 4.32(dd, 1H, J_{PH}=4.5, J_{HH}=4.9), 7.15-7.85(m, 11H); ^{13}C NMR ($CDCl_3$, 50MHz) δ 16.4, 21.5, 38.4(d, J=197.8), 48.6, 63.4(d, J=21.4), 126.1, 126.5, 126.8, 127.7, 128, 128.1, 129.2, 129.3; IR (neat, cm^{-1}) 3046, 2987, 1593, 1323, 1262, 1102, 1023; HRMS: calcd for $C_{26}H_{17}NO_4PS$ 459.1269, found 459.1259.

Representative procedure of reductive cleavage of aziridinylphosphonates 2. Preparation of diethyl 2-phenyl-1-*N*-tosylaminoethylphosphonate(3a). To a stirred suspension of aziridinylphosphonate **2a** (81.8 mg, 0.2 mmol) and Pd/C (80 mg) in dry methanol (2 mL), anhydrous ammonium formate(63 mg, 1 mmol) was added in a single portion. The resultion mixture was stirred at room temperature for 24 h under N_2, the catalyst was removed by filteration through a celite pad and washed with ethyl ether and methanol. The filterate was evaporated under reduced pressure. The resulting residue was triturated with water and extracted with ethyl acetate and the combined organic extracts were dried, filtered, and concentrated *in vacuo*. Purification by silica gel flash chromatography provided 70.7 mg, of **3a** (86 %) as white solid. R_f : 0.3(ethyl acetate : *n*-hexane = 2 : 1); mp 104-105 °C; ^{1}H NMR($CDCl_3$, 200MHz) δ 1.22(t, 6H, J=6.9), 2.39(s, 3H), 2.76-3.18(m, 2H), 3.88-4.17(m, 1H, 4H), 5.28(brdd, NH), 7.06-7.67(m, 9H); ^{13}C NMR ($CDCl_3$, 50MHz) δ 16.2, 21.5, 36.7, 51.7(d, J=156.1), 62.9(d, J=39.2), 126.7, 126.8, 128.3, 128.5, 129.5, 129.7; IR (neat, cm^{-1}) 3070, 2965, 1256, 1120, 1043, 1023, 995; HRMS: calcd for $C_{19}H_{21}NO_5PS$ 411.1269, found 411.1258.

Diethyl 2-(4-chlorophenyl)-1-*N*-tosylaminoethylphosphonate(3b). R_f : 0.23(ethyl acetate : *n*-hexane = 1 : 1); mp 116.2-116.5 °C; ^{1}H NMR ($CDCl_3$, 200MHz) δ 1.21(t, 6H, J=7), 2.38(s, 3H), 2.76-3.18(m, 2H), 3.88-4.18(m, 1H, 4H), 5.41(brd, NH), 6.92-7.56(m, 8H); ^{13}C NMR ($CDCl_3$, 50MHz) δ 16.3, 21.4, 36.6, 51.7(d,

J=156.2), 62.9(d, *J*=43), 126.7, 126.8, 128.3, 129.5, 129.7; IR (neat, cm^{-1}) 3060, 2963, 1251, 1062, 1020, 982; HRMS: calcd for $C_{19}H_{25}NO_5PS$ 445.0880, found 445.0871.

Diethyl 2-(1-naphthyl)-1-*N*-tosylaminoethylphosphonate(3c). R_f: 0.18(ethyl acetate : *n*-hexane = 1 : 1); mp 144-145 °C; ^1H NMR ($CDCl_3$, 200MHz) δ 1.22-1.38(m, 6H), 2.27(s, 3H), 3.15-3.28(m, 1H), 3.6-3.7(m, 1H), 4.03-4.32(m, 1H, 4H), 5.84(brd, NH), 6.75-7.88(m, 11H); ^{13}C NMR ($CDCl_3$, 50MHz) δ 16.4, 21.4, 34.0, 51.4(d, *J*=157.7), 63.2(d, *J*=72.5), 123.3, 125.2, 125.5, 126.1, 127.5, 128.4, 128.7, 129; IR (neat, cm^{-1}) 3080, 2983, 1218, 1160, 1058, 1015; HRMS: calcd for $C_{23}H_{28}NO_5PS$ 461.1408, found 461.1408.

Diethyl 2-(2-naphthyl)-1-*N*-tosylaminoethylphosphonate(3d). R_f: 0.15(ethyl acetate : *n*-hexane = 1 : 1); mp 137-138 °C; ^1H NMR($CDCl_3$, 200MHz) δ 1.22-1.34(m, 6H), 2.09(s, 3H), 2.93-3.05(m, 1H), 3.2-3.34(m, 1H), 4.05-4.33(m, 1H, 4H), 6.04(brd, NH), 6.65-7.88(m, 11H); ^{13}C NMR($CDCl_3$, 50MHz) δ 16.3, 21.4, 36.7, 52(d, *J*=155.5), 63(d, *J*=40.1), 125.6, 125.9, 126.3, 127.4, 127.5, 128, 128.5, 129; IR (neat, cm^{-1}) 3114, 2981, 1334, 1210, 1161, 1063, 1018, 946; HRMS: calcd for $C_{23}H_{28}NO_5PS$ 461.1408, found 461.1421.

Acknowledgement: This research was supported by research grants from the KOSEF(961-0302-012-1) and Ministry of Education, Korea(BSRI-96-3447).

References and Notes

1. (a) Hilderbrand, R. L. In *The Role of Phosphonates in Living Systems, CRC Press: Boca Raton, Fl.* **1983**. (b) Kafarski, P.; Lejczak, B. *Phosphorus Sulfur Silicon Relat. Elem.* **1991**, 63, 193. (c) Boutin, J. A.; Cudennec, C. A.; Hautefaye, P.; Lavielle, G.; Pierre, A.; Schaeffer, C. *J. Med. Chem.* **1991**, 34, 1998.(d) Bartlett, P. A.; Kezer, W. B. *J. Am. Chem. Soc.* **1984**, 106, 4282. (e) Bartlett, P. A.; Giannousis, P. P. *J. Med. Chem.* **1987**, 30, 1603.
2. (a) Allen, M. C.; Fuhrer, W.; Tuck, B.; Wade, R.; Wood, J. M. *J. Med. Chem.* **1989**, 32, 1652. (b) Logusch, E. W.; Walker, D. M.; McDonald, J. F.; Leo, G. C.; Grang, J. E. *J. Org. Chem.* **1988**, 53, 4069. (c) Giannousis, P. P.; Bartlett, P. A. *J. Med. Chem.* **1987**, 30, 1603.
3. (a) Atherton, F. R.; Hassel, C. H.; Lambert, R. W. *J. Med. Chem.* **1986**, 29, 29. (b) Allen, J. G.; Atherton, F. R.; Hassel, C. H.; Holmes, S. W.; Lambert, R. W.; Nisbet, L. J.; Ringrose, P. S. *Nature* **1978**, 272, 56. (c) Allen, J. G.; Atherton, F. R.; Hall, M. J.; Hassel, C. H.; Lambert, R. W.; Nisbet, L. J.; Ringrose, P. S. *Antimicrob. Agents Chemother.* **1979**, 15, 684. (d) Atherton, F. R.; Hall, M. J.; Hassel, C. H.; Lambert, R. W.; Ringrose, P. S. *Antimicrob. Agents Chemother.* **1979**, 15, 677. (e) Atherton, F. R.; Hall, M. J.; Hassel, C. H.; Lambert, R. W.; Lloyd, W. J.; Ringrose, P. S. *Antimicrob. Agents Chemother.* **1979**, 15, 696.
4. (a) Stauffer Co. U.S.Pat 4 170 463, 1979. (b) Emsley, J.; Hall, E. D. *The Chemistry of Phosphorus*, Harper and Row, London, 1976. (c) Barder, A. *Aldrichim. Acta.* 1988, 21, 15.
5. (a) Hirschmann, R.; Smith, A. B. III; Taylor, C. M.; Benkovic, P. A.; Taylor, S. D.; Yager, K. M.; Sprengler, P. A.; Venkovic, S. J. *Science* **1994**, 265, 234. (b) Napper, A. D.; Benkovic, S. J.; Tramontano, A.; Lerner, R. A. *Science* **1987**, 237, 1041. (c) Smith, A. B. III; Taylor, C. M.; Venkovic, S. J.; Hirschmann, R. *Tetrahedron Lett.* **1994**, 37, 6854.
6. (a) Maier, L. *Phosphorus Sulfur* **1983**, 14, 295. (b) Yokomatsu, T,; Yamagishi, T.; Shibuya, S. *J. Synth. Org. Chem. Jpn.* **1995**, 53, 881. (c) Dhawan, B.; Resmore, D. *Phosphorus Sulfur* **1987**, 32, 119.
7. (a) Sardarian, A. R.; Kaboudins, B. *Tetrahedron Lett.* **1997**, 38, 2543. (b) Smith, III. A. B.; Yager, K. M.; Taylor, C. M. *J. Am. Chem. Soc.* **1995**, 117, 10874. (c) Smith, A. B. III; Yager, K. M.; Taylor, C. M. *J.*

Am. Chem. Soc. **1994**, 116, 9377. (d) Chung, S. K.; Kang, D. H. *Tetrahedron Asymmetry* **1996**, 7, 21. (e) Ha, H. J.; Nam, G. S. *Synth. Commun.* **1992**, 22, 1143. (f) Afarinkia, K.; Rees, C. W.; Cadogan, J. I. G. *Tetrahedron* **1990**, 46, 7175. (g) Maury, C.; Gharbaoui, T.; Royer, J.; Husson, H-P. *J. Org. Chem.* **1996**, 61, 3687. (h) Huber, R.; Vesella, A. *Helv. Chim. Acta* **1987**, 70, 1461. (i) Sasai, H.; Arai, S.; Tahara, Y.; Shibasaki, M. *J. Org. Chem.* **1995**, 60, 6656. (j) Hamilton, R.; Walker, B.; Walker, B. J. *Tetrahedron Lett.* **1995**, 36, 4451. (k) Oshikawa, T.; Yamashita, M. *Bull. Chem. Soc. Jpn.* **1989**, 62, 3177. (l) Laschat, S.; Kunz, H. *Synthesis* **1992**, 90. (m) Hoppe, I.; Schollkorpf, U.; Nieger, M.; Egert, E. *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 1067. (n) Shatzmiller, S.; Dolitzky, B. Z.; Meirovich, R.; Neidlein, R.; Weik, C. *Liebig Ann. Chem.* **1991**, 161.

8. (a) Ryglowski, A.; Lazaro, R.; Roumestant, M. L.; Viallefont, P. *Synth. Commun.* **1996**, 26, 1739. (b) Groth, U.; Richter, L.; Schollkorpf, U. *Liebig Ann. Chem.* **1992**, 903. (c) Cabella, G.; Jommi, G.; Paglianrin, R.; Sello, G.; Sisti, M. *Tetrahedron Lett.* **1995**, 36, 1917. (d) Hanessian, S.; Bennani, Y. L. *Tetrahedron Lett.* **1990**, 31, 6465. (e) Hanessian, S.; Bennani, Y. L. *Tetrahedron Lett.* **1990**, 31, 6461.
9. (a) Hanessian, S.; Bennani, Y. L. *Synthesis* **1994**, 1272. (b) Denmark, S. E.; Chatani, N.; Pansare, S. V. *Tetrahedron* **1992**, 48, 2191.
10. (a) Schmidt, U.; Oehme, G.; Kraus, H. *Synth. Commun.* **1996**, 26, 777. (b) Schollkorpf, U.; Hoppe, I.; Thiele, A. *Liebig Ann. Chem.* **1985**, 555.
11. (a) Chakraborty, S.; Engel, R. *Synth Commun.* **1991**, 21, 1093. (b) Gajda, T.; Matsiak, M. *Synth. Commun.* **1992**, 22, 2193. (c) Yokomatsu, T.; Yoshida, Y.; Shibuya, S. *J. Org. Chem.* **1994**, 59, 7930. (d) Yokomatsu, T.; Shibuya, S. *Tetrahedron : Asymmetry* **1992**, 3, 377.
12. Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, 30, 2247.
13. (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, 113, 726. (b) Lowenthal, R. E.; Masamune, S. *Tetrahedron Lett.* **1991**, 32, 7373. (c) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, 117, 5889. (d) Evans, D. A.; Faul, M. M.; Biolodeau, M. T. *J. Am. Chem. Soc.* **1994**, 116, 2742. (e) Perez, P. J.; Brookhart, M.; Tempton, J. L. *Organometallics.* **1993**, 12, 2742. (f) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, 115, 5326. (g) Evans, D. A.; Faul, M. M.; Biolodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, 115, 5328. (h) Noda, K.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T. *Synlett.* **1993**, 469. (i) Evans, D. A.; Faul, M. M.; Biolodeau, M. T. *J. Org. Chem.* **1991**, 56, 6744. (j) For a review, see: Tanner, D. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 599.
14. (a) Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361. (b) Besenyei, G.; Nemeth, S.; Simandis, L. I. *Tetrahedron Lett.* **1993**, 34, 6105. (c) Takaya, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S. *J. Chem. Soc. Chem. Commun.* **1996**, 931. (d) Suzuki, A.; Ikegami, T. *J. Chem. Research(S)* **1996**, 24.
15. (a) Hanessian, S.; Bennani, Y. L.; Herve, Y. *Synlett.* **1993**, 35. (b) Coutrot, P.; Elgadi, A.; Grison, C. *Heterocycles* **1989**, 28, 1179.
16. Aziridination of β–alkylsubstituted vinylphosphonates afforded corresponding aziridinylphosphonates with trace amounts under the same reaction conditions.
17. (a) Satake, A.; Shimizu, I.; Yamamoto, A. *Synlett.* 1995, 64. (b) Lim, Y.; Lee, W. K. *Tetrahedron Lett.* **1995**, 46, 8431. (c) ElAmin, B.; Anantharamaiah, G. M.; Royer, G. P.; Means, G. E. *J. Org. Chem.* **1979**, 44, 3442. (d) Kowalik, J.; Mastalerz, J. *Phosphorus and Sulfur* **1983**, 18, 393
18. (a) Aboujaoude, E. E.; Lietje, S.; Collignon, N.; Teulade, M. P.; Savignac, P. *Tetrahedron Lett.* **1985**, 26, 4435. (b) Savignac, P.; Teulade, M. P.; Cdllignon, N. *J. Organometal. Chem.* **1987**, 323, 135. (c) For a review, see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 33.

(*Received in Japan* 30 *June* 1997; *accepted* 29 *July* 1997)