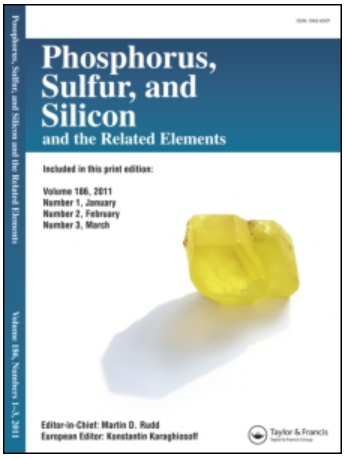

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A CONVENIENT SYNTHESIS OF O-ETHYL-1-AMINOALKYLPHOSPHINATES

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To cite this Article Gajda, Tadeusz(1993) 'A CONVENIENT SYNTHESIS OF O-ETHYL-1-AMINOALKYLPHOSPHINATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 85: 1, 59 — 64
To link to this Article: DOI: 10.1080/10426509308038182
URL: http://dx.doi.org/10.1080/10426509308038182

Phosphorus, Sulfur, and Silicon, 1993, Vol. 85, pp. 59–64
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A CONVENIENT SYNTHESIS OF O-ETHYL-1-AMINOALKYLPHOSPHINATES†

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(Received November 9, 1993)

1-Aminoalkylphosphinates **4** have been obtained in good yields in a one-step transformation by the Mitsunobu reaction of 1-hydroxyalkylphosphinates **1** with hydrazoic acid, and subsequent treatment of the intermediate azides **2**, with triphenylphosphine, followed by hydrolysis of the iminophosphoranes **3** with water.

Key words: 1-Aminoalkylphosphinates; 1-hydroxyalkylphosphinates; Mitsunobu reaction; Staudinger reaction; azidation.

INTRODUCTION

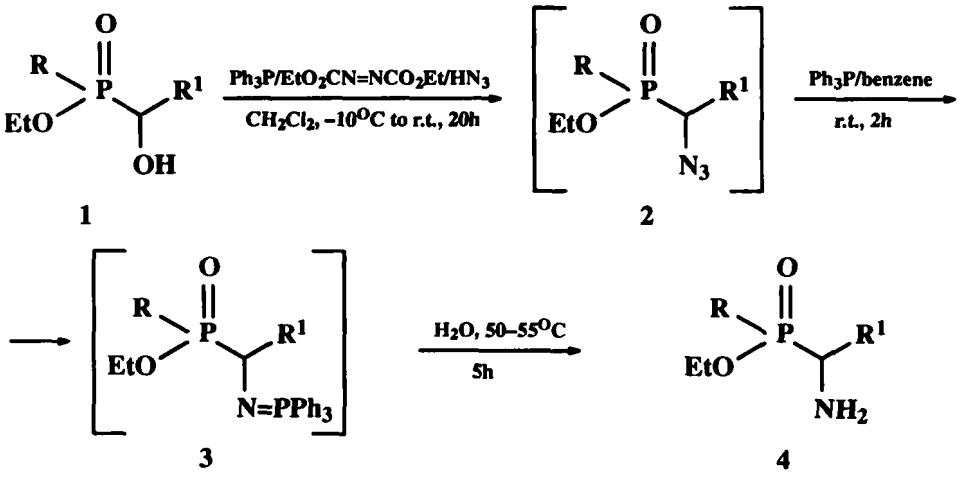
During the last twenty five years, a substantial effort has been devoted to the synthesis and investigation of biological activity of phosphorous analogues of natural α-amino acids.[1–3] Knowledge of the synthesis and chemistry of 1-aminoalkylphosphinic acids and their derivatives has been summarized recently in a review article.[4] Since that time, several works on this subject have been published.[5–19] Most of them have focused on the preparation of 1-aminoalkylphosphinic acid derivatives via the addition of phosphonites to imines,[5,6,15,17–19] or by the alkylation of aminomethylphosphinic acid derivatives with primary alkyl halides.[14,16]

RESULTS AND DISCUSSION

The Mitsunobu reaction[20,21] is an exceptionally useful and general method for replacement of hydroxyl groups by a variety of nucleophiles, e.g., the azide group—a convenient precursor of primary amine function.[22] Recently, the azidation of 1-hydroxyalkylphosphonates under the Mitsunobu conditions has been proved to be a key step in the preparation of aminophosphonates.[23–28] Moreover, it has been shown by us[24,25] in the above mentioned approach to the synthesis of 1-aminoalkylphosphonates, and earlier by Golding *et al.*[29] in the preparation of amines and amino acids from alcohols, that isolation of the intermediate azides is not even necessary.

In continuation of these studies, herein we report a general protocol for a one-pot transformation of O-ethyl-1-hydroxyalkylphosphinates **1**, into O-ethyl-1-ami-

†Presented in part at the XIIth ICPC, Toulouse, France, July 6–10, 1992.



1–4	a	b	c	d	e	f	g	h	i
R	Ph	Ph	Ph	Ph	Ph	Ph	Ph	$(EtO)_2CH$	$(EtO)_2CH$
R^1	H	Me	Et	i-Pr	i-Bu	Ph	4-MeO-C_6H_4	Me	Ph

SCHEME 1

TABLE I

O-Ethyl-1-aminoalkylphosphinates **4a–i** prepared

Product	R	R^1	Yield[a] (%)	b.p.(°C)/Torr and n_D^{20} or m.p.(°C)[b]	Molecular Formula[c]
4a	Ph	H	70[d]	122-123/0.3 1.5377	$C_9H_{14}NO_2P$ (199.2)
4b	Ph	Me	89	oil	$C_{10}H_{16}NO_2P$ (213.2)
4c	Ph	Et	75	oil	$C_{11}H_{18}NO_2P$ (227.2)
4d	Ph	i-Pr	62[e]	oil	$C_{12}H_{20}NO_2P$ (241.2)
4e	Ph	i-Bu	69	oil	$C_{13}H_{22}NO_2P$ (255.3)
4f	Ph	Ph	93	39-41[f] (hygr.)	$C_{15}H_{18}NO_2P$ (275.3)
4g	Ph	4-MeO-C_6H_4	84	oil	$C_{16}H_{20}NO_3P$ (305.3)
4h	$(EtO)_2CH$	Me	59	oil	$C_9H_{22}NO_4P$ (239.3)
4i	$(EtO)_2CH$	Ph	60	oil	$C_{14}H_{24}NO_4P$ (301.3)

[a] Yield of isolated pure product, based on **1**. [b] Due to the liquid state or hygroscopicity and confusing discrepancy in the m.p. of the compound **4f** reported, all aminophosphinates were additionally characterized as oxalates: **4a** m.p. 137-138.5°C (dec.), **4b** m.p. 135-137°C (dec.), Lit.[10] m.p. 136-138°C, **4c** m.p. 137-139°C (dec.), **4d** m.p. 129-131°C (dec.), **4e** m.p. 127-129°C (dec.), **4f** m.p. 147-148°C (dec.), **4g** m.p. 155-156°C (dec.), **4h** m.p. 103-106°C (dec.), **4i** m.p. 136-138°C (dec.). [c] Satisfactory microanalyses obtained: C±0.22, H±0.16, N±0.19, P±0.17. [d] Iminophosphorane **3a** was hydrolysed with water at r.t. for 6h. [e] Azidation was performed in toluene instead of CH_2Cl_2. [f] Lit.[11] m.p. 237.6-238.3°C (EtOH).

TABLE II

Spectroscopic data of O-ethyl-1-aminoalkylphosphinates **4a–i**

Compound	^{1}H-NMR ($CDCl_3$/TMS)[a] δ (ppm), J (Hz)	^{31}P-NMR (C_6D_6, H_3PO_4 ext.)[b] δ (ppm)
4a	1.3 (t, 3H, J=7.06, CH_3), 1.69 (bs, 2H, NH_2), 3.02-3.22 (m, 2H, CH_2), 3.81-4.18 (m, 2H, CH_2), 7.42-7.85 (m, $5H_{arom}$)	39.36
4b	1.17 (dd, 3H, J=7.25, 17.25, CH_3), 1.30* (dd, 1.8H, J=7.18, 16.32, CH_3), 1.31 (t, 1.2H, J=7.1, CH_3), 1.79 (bs, 2H, NH_2), 3.09-3.25 (m, 1H, CH), 3.81-4.22 (m, 2H, CH_2), 7.43-7.86 (m, $5H_{arom}$)	42.85, 42.72 (60 : 40)
4c	0.97, 1.04 (2t, 3H, J=7.35, CH_3), 1.31 (t, 3H, J=7.05, CH_3), 1.39-1.99 (m, 4H, CH_2, NH_2), 2.87-3.01 (m, 1H, CH), 3.79-4.23 (m, 2H, CH_2), 7.42-7.86 (m, $5H_{arom}$)	43.90, 43.55 (60 : 40)
4d	0.94-1.09 (m, 6H, $2CH_3$), 1.30 (t, 3H, J=7.05, CH_3), 1.43 (bs, 2H, NH_2), 1.90-2.24 (m, 1H, CH), 2.87-2.95 (m, 1H, CH), 3.79-4.17 (m, 2H, CH_2), 7.43-7.86 (m, $5H_{arom}$)	42.33, 41.54 (60 : 40)
4e	0.76-0.94 (m, 6H, $2CH_3$), 1.18 (bs, 2H, NH_2), 1.21-1.96 (m, 3H, CH_2, CH), 1.31 (bt, 3H, J=7.05, CH_3), 3.03-3.18 (m, 1H, CH), 3.80-4.23 (m, 2H, CH_2), 7.43-7.86 (m, $5H_{arom}$)	43.05, 42.57 (57 : 43)
4f	1.22, 1.32 (2t, 3H, J=7.02, CH_3), 1.99 (bs, 2H, NH_2), 3.83-4.25 (m, 2H, CH_2), 4.32* (d, 0.5H, J=12.6, CH), 4.35 (d, 0.5H, J=13.6, CH), 7.13-7.69 (m, $10H_{arom}$)	39.84, 38.99 (44 : 56)
4g	1.24, 1.32 (2t, 3H, J=7.04, CH_3), 1.94 (bs, 2H, NH_2), 3.76, 3.79 (2s, 3H, CH_3) 3.83-4.21 (m, 2H, CH_2), 4.28 (d, 0.5H, J=12.0, CH), 4.30* (d, 0.5H, J=12.6, CH), 6.73-7.20 (AA'XX' of p-C_6H_4, 4H), 7.31-7.69 (m, $5H_{arom}$)	40.33, 39.59 (52 : 48)
4h	1.20-1.38 (m, 2H, $4CH_3$), 1.72 (bs, 2H, NH_2), 3.11-3.25 (m, 1H, CH), 3.59-3.95 (m, 4H, $2CH_2$), 4.08-4.30 (m, 2H, CH_2), 4.83 (d, 0.5H, J=7.22, CH), 4.84* (d, 0.5H, J=6.95, CH)	42.82, 42.76 (48 : 52)
4i	1.04-1.32 (m, 9H, $3CH_3$), 1.92 (bs, 2H, NH_2), 3.39-4.22 (m, 6H, $3CH_2$), 4.31* (d, 0.5H, J=11.22, CH), 4.33 (d, 0.5H, J=10.82, CH), 4.55* (d, 0.5H, J=9.95, CH), 4.77 (d, 0.5H, J=8.4, CH), 7.20-7.50 (m, $5H_{arom}$)	39.24, 38.92 (47 : 53)

[a]Recorded at 200 MHz with a Bruker MSL 200 spectrometer. Where possible, signals of the major isomer are assigned by asterisk. (Protons integration partially overlapped). [b] Recorded at 81 MHz with a Bruker MSL 200 spectrometer. Positive chemical shifts are downfield from H_3PO_4 (85%). Ratio of the isomer is given in parentheses.

noalkylphosphinates **4**. The starting materials O-ethyl-1-hydroxyalkylphosphinates[30] **1** are easily obtained by the base catalysed addition of phosphonite mono esters to appropriate aldehydes.

According to Scheme 1, O-ethyl-1-azidoalkylphosphinate **2** is prepared by interaction of O-ethyl-1-hydroxyalkylphosphinate **1** with the preformed betaine-type adduct of triphenylphosphine-diethyl azodicarboxylate-hydrazoic acid under the Mitsunobu conditions. The azide **2** thus formed is converted *in situ* by the Staudinger reaction[31] with triphenylphosphine into iminophosphorane **3**, followed by its water hydrolysis directly to the corresponding 1-aminoalkylphosphinate **4** in good overall yield (59–93%) and purity. The results are summarized in Table I. The structure of O-ethyl-1-aminoalkylphosphinates **4** was confirmed by ^{31}P-NMR and ^{1}H-NMR spectroscopy (Table II). The method presented here is limited to primary and secondary O-ethyl-1-hydroxyalkylphosphinates **1**.

In conclusion, the procedure described here offers a general and efficient approach to 1-aminoalkylphosphinate esters **4**, with a wide range of aliphatic and aromatic substituents at C-1 carbon, as well as the phosphorus moiety. Easily available starting materials are used, reactions take place under mild conditions, and isolation of the intermediate azides **2** is not necessary. Additionally, O-ethyl-1-aminoalkyl-diethoxymethylphosphinates **4h–i**, bearing easily removable 1,1-diethoxymethyl protecting group,[32] could be considered as convenient precursor of 1-aminoalkylphosphonous acids.[14,15,18]

EXPERIMENTAL

^{31}P-NMR spectra were recorded on a Bruker MSL 200 spectrometer operating at 81 MHz. Positive chemical shifts are downfield from ext. H_3PO_4. Ratio of the isomers is given in parentheses. ^{1}H-NMR spectra were recorded on a Bruker MSL 200 operating at 200 MHz. Where possible, signals of the major isomer were assigned by asterisk (Protons integration partially overlapped). Melting points were determined in open capillaries and are uncorrected. Diethyl azodicarboxylate (DEAD) was obtained by the established procedure.[33] O-Ethyl-diethoxymethylphosphonite was prepared according to the described procedure[34] from H_3PO_2 and $CH(OEt)_3$ in the presence of p-TsOH.

O-Ethyl-1-hydroxyalkylphosphinates.[30] **1a–i.** *General procedure. Method A.* Triethylamine (1.01 g. 0.01 mol) is added to a mixture of O-ethyl-phenylphosphonite[35] (3.42 g, 0.02 mol) and appropriate aldehyde (0.022 mol) with a slight exothermic effect. The solution is then stirred for 1 h at 65–70°C. Triethylamine is evaporated under reduced pressure. The oily residue is dissolved in CH_2Cl_2 (60 mL), the solution is successively washed with 5% aq. HCl (2 mL), $NaHCO_3$ aq. (5 mL), water (5 mL), and is then dried over Na_2SO_4. Solvent is evaporated under reduced pressure. The volatile materials are removed at 45°C/0.1. Torr or crude product is distilled in vacuo to give pure **1**.

O-Ethyl-hydroxymethyl-phenylphosphinate **1a**; yield: 63%, colorless liquid, b.p. 150–153°C/0.2 Torr, n_D^{20} = 1.5345 (Lit.[36] b.p. 180°C/0.015 Torr, n_D^{20} = 1.5375).
^{31}P-NMR (C_6D_6): δ = 39.11 ppm.

O-Ethyl-1-hydroxyethyl-phenylphosphinate **1b**; yield: 72%, m.p. 43–45°C

$C_{10}H_{15}O_3P$ (214.2)	calc.:	C56.07	H7.06	P14.46
	found:	56.28	6.92	14.52

^{1}H-NMR ($CDCl_3$): δ = 1.32* (dd, 1.8H, J = 7.07, 17.13 Hz, CH_3), 1.33, 1.34 (2t, 3H, J = 7.0 Hz, CH_3), 1.41 (dd, 1.2H, J = 7.1, 16.55 Hz, CH_3), 2.00 (bs, 1H, OH), 3.92–4.24 (m, 3H, CH, CH_2), 7.43–7.89 (m, $5H_{arom}$).
^{31}P-NMR (C_6D_6): δ = 42.58, 41.99 ppm (58: 42)

O-Ethyl-1-hydroxypropyl-phenylphosphinate **1c**; yield: 85%, oil

$C_{11}H_{17}O_3P$ (228.2)	calc.:	C57.88	H7.51	P13.57
	found:	57.75	7.41	13.58

^{1}H-NMR ($CDCl_3$) δ = 1.02, 1.05 (2t, 3H, J = 7.45 Hz, CH_3), 1.33, 1.34 (2t, 3H, J = 7.06 Hz, CH_3), 1.41–1.91 (m, 2H, CH_2), 2.93 (bs, 1H, OH), 3.83–4.22 (m, 3H, CH_2, CH), 7.45–7.87 (m, $5H_{arom}$).
^{31}P-NMR (C_6D_6) δ = 41.49, 41.22 ppm (62: 38)

O-Ethyl-(1-hydroxy-2-methylpropyl)-phenylphosphinate **1d**; yield: 90%, m.p. 45–48°C
$C_{12}H_{19}O_3P$ (242.3) calc.: C59.49 H7.91 P12.79
found: 59.28 7.84 12.82

^{1}H-NMR ($CDCl_3$) δ = 0.98–1.07 (m, 6H, $2CH_3$), 1.32, 1.33 (2t, 3H, J = 7.05 Hz, CH_3), 1.80–2.15 (m, 1H, CH), 2.52 (bs, 1H, OH), 3.64–3.81 (m, 1H, CH), 3.85–4.26 (m, 2H, CH_2), 7.43–7.97 (m, $5H_{arom}$).
^{31}P-NMR (C_6D_6) δ = 41.21, 40.81 ppm (41: 59)

O-Ethyl-(1-hydroxy-3-methylbutyl)-phenylphosphinate **1e**; yield: 88%, m.p. 76–78°C
$C_{13}H_{21}O_3P$ (256.3) calc.: C60.92 H8.26 P12.09
found: 60.71 8.22 12.17

^{1}H-NMR ($CDCl_3$) δ = 0.85–0.92 (m, 6H, $2CH_3$), 1.33, 1.34 (2t, 3H, J = 7.05 Hz, CH_3), 1.38–1.97 (m, 3H, CH_2, CH), 2.83 (bs, 1H, OH), 3.87–4.27 (m, 3H, CH_2, CH), 7.43–7.89 (m, $5H_{arom}$).
^{31}P-NMR (C_6D_6) δ = 41.99, 41.37 ppm (58: 42)

O-Ethyl-(1-hydroxy-1-phenylmethyl)-phenylphosphinate **1f**; yield: 95%, m.p. 82–84°C, (Lit.[37] m.p. 75°C)
^{31}P-NMR (C_6D_6) δ = 39.48, 38.41 ppm (56: 44).

O-Ethyl-[1-hydroxy-1-(4-methoxyphenyl)methyl]-phenylphosphinate **1g**; yield: 98%, m.p. 103–106°C
$C_{16}H_{19}O_4P$ (306.3) calc.: C62.74 H6.25 P10.01
found: 62.95 6.17 10.13

^{1}H-NMR ($CDCl_3$) δ = 1.27, 1.32 (2t, 3H, J = 7.05 Hz, CH_3), 3.77, 3.78 (2s, 3H, CH_3), 3.84–4.18 (m, 3H, OH, CH_2), 5.04 (d, 0.4H, J = 6.85 Hz, CH), 5.09* (d, 0.6H, J = 9.1 Hz, CH), 6.75–7.69 (m, $9H_{arom}$).
^{31}P-NMR (C_6D_6) δ = 39.55, 38.16 ppm (59: 41)

Method B. A catalytic amount of EtONa/EtOH is added to a solution of O-Ethyl-diethoxymethyl-phosphonite (3.92 g, 0.02 mol) and appropriate aldehyde (0.02 mol) in ethanol (4 mL). A slightly exothermic reaction ensues. The mixture is stirred for 2 h at r.t. The mixture is neutralised with acetic acid, the solvent is removed in vacuo, and the residue is dissolved in CH_2Cl_2 (60 mL). The solution is washed with sat. $NaHCO_3$ aq. (2 mL), water (2 mL), and is then dried over Na_2SO_4. After evaporating the solvent, the volatile materials are removed at 60°C/0.2 Torr or crude product is fractionally distilled to give pure **1**.

O-Ethyl-1-hydroxyethyl-diethoxymethylphosphinate **1h**; yield: 70%, b.p. 115–119°C/0.2 Torr, n_D^{20} = 1.4458 (Lit.[38] b.p. 110°C/0.06 Torr)
^{31}P-NMR (C_6D_6) δ = 40.17, 39.63 ppm (50: 50)

O-Ethyl-(1-hydroxy-1-phenylmethyl)-diethoxymethylphosphinate **1i**; yield: 73%, oil
$C_{14}H_{23}O_5P$ (302.3) calc.: C55.62 H7.67 P10.25
found: 55.35 7.52 10.12

^{1}H-NMR ($C_6D_6/CDCl_3$) δ = 0.91–1.20 (m, 9H, $3CH_3$), 3.29–4.08 (m, 7H, $3CH_2$, OH), 4.60* (d, 0.5H, J = 8.15 Hz, CH), 4.66 (d, 0.5H, J = 9.0 Hz, CH), 5.06* (d, 0.5H, J = 13.72 Hz, CH), 5.08 (d, 0.5H, J = 12.61 Hz, CH), 7.06–7.59 (m, $5H_{arom}$).
^{31}P-NMR (C_6D_6) δ = 35.66, 35.28 ppm (56: 44)

O-Ethyl-1-aminoalkylphosphinates **4a–i**; *General procedure.* A solution of diethyl azodicarboxylate (DEAD) (2.09 g, 0.012 mol) in CH_2Cl_2 (5 mL) is added dropwise with stirring and external cooling (dry ice-acetone bath) to a solution of Ph_3P (3.14 g, 0.012 mol) in CH_2Cl_2 (20 mL) at −5°C. The mixture is cooled to −10°C, and 1.85 molar solution of HN_3 in benzene[39] (0.0125 mol) is slowly added. Stirring is continued for 5 min. at 0°C, and appropriate 1-hydroxyalkylphosphinate **1** (0.01 mol) is then added. The mixture is kept for 30 min. at 0°C, and stirring is then continued for 20 h at r.t. The precipitate of ethyl 3-(ethoxycarbonyl)carbazate is filtered off, and the filtrate is evaporated under reduced pressure. The semisolid residue is dissolved in benzene (10 mL), and Ph_3P (2.75 g, 0.0105 mol) is added in one portion to the solution. Stirring is continued for 2 h at r.t. Water (1.8 mL, 0.1 mol) is then added and the mixture is heated for 5 h at 50–55°C. The mixture is cooled to r.t., and the product is extracted with 5% aq. HCl (3 × 5 mL). The combined acid extracts are then reextracted with CH_2Cl_2 (3 × 20 mL). The acid phase is then cooled to 0°C, and the solution is made alkaline by the addition

of an excess of solid K_2CO_3. The product is extracted with CH_2Cl_2 (5 × 30 mL) and is then dried over Na_2SO_4. Solvent is evaporated under reduced pressure, and the rest of the volatile material is removed at 35°C/0.02 Torr, to give pure 1-aminoalkylphosphinate **4** (Tables I and II).

ACKNOWLEDGEMENT

The author acknowledges financial support for this work by a grant PB-0428/P3/92/03 from the Committee of Scientific Researches.

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