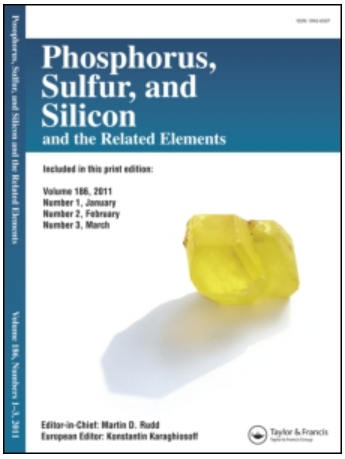

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LONG CHAIN 1-AMINOTHIAALKANE-PHOSPHONATES, THEIR SULPHINYL AND SULPHONYL DERIVATIVES. A NEW TYPE OF COMPLEXANE TYPE SURFACTANTS

Zbigniew H. Kudzin[a]; Jerzy Mokrzan[a]; Romuald Skowroński[a]
[a] Institute of Chemistry, University of Łodź, Łodź, Poland

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LONG CHAIN 1-AMINOTHIAALKANE-PHOSPHONATES, THEIR SULPHINYL AND SULPHONYL DERIVATIVES. A NEW TYPE OF COMPLEXANE TYPE SURFACTANTS

ZBIGNIEW H. KUDZIN,* JERZY MOKRZAN
and ROMUALD SKOWROŃSKI

Institute of Chemistry, University of Łódź, Narutowicza 68, Łódź 90–136, Poland

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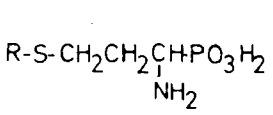
Several long chain 1-aminothiaalkanephosphonic acids **1** were prepared and selectively oxidized to the corresponding sulphinyl **2** and sulphonyl **3** derivatives. For all compounds synthesized surface tension properties were determined. These measurements indicate that the surface activities of compounds **1–3** are comparable with that of typical phosphonate detergents.

Key words: aminoalkanephosphonates, complexane type surfactants.

INTRODUCTION

Phosphonates have been widely used in the detergents industry due to their chemical stability and high surface activity.[1] The chelating properties of amino-alkanephosphonic acids, especially their very high ability to bind Be^{+2} and Pb^{+2} cations, with simultaneous low affinity to alkaline earth metal ions constitute a base for their application in the pharmacology and toxicology.[2,3] The amino-alkanephosphonate complexones have also been used extensively in extractive concentrations and separations of several lanthanides, actinides and transition metal ions.[4,5] Our recent work on the synthesis and chelating properties of low chain 1-aminothiaalkanephosphonates **1** and their sulphinyl **2** and sulphonyl **3** derivatives clearly indicated that this group of amino acids may be considered as compounds possessing chelating activity.[6,7] In this paper we present the synthesis of long chain amino acids **1** ($R \geq n\text{-}C_6H_{13}$) and their sulphoxide **2** and sulphone **3** derivatives, which due to the presence of hydrophobic hydrocarbon chain and hydrophilic, strongly chelating 1-amino-3-thia-alkane-phosphonate or 1-amino-3-(S-oxo)-alkane-phos-phonate groups may be used as a complexane type surfactants.



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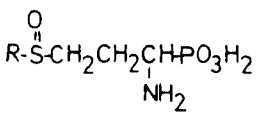

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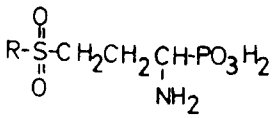
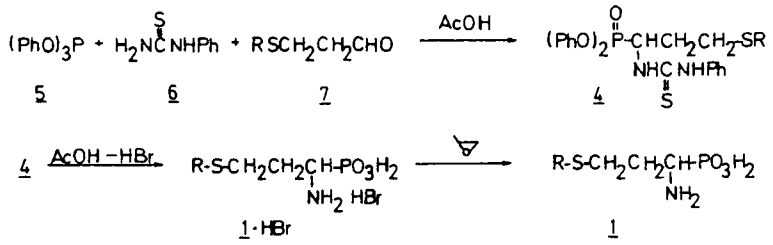


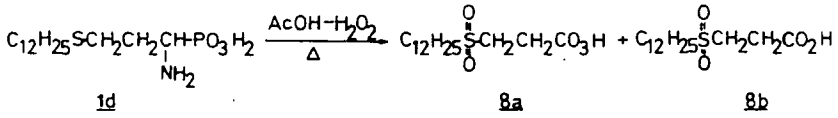
3

Parent amino acids **1** were prepared as reported in Ref. 8, 9 and 10, by hydrolytic degradation of corresponding intermediary thioureido-alkane-phos-

phonates **4**, obtained from triphenyl phosphite (**5**), N-phenylthiourea (**6**) and thiaaldehydes **7**

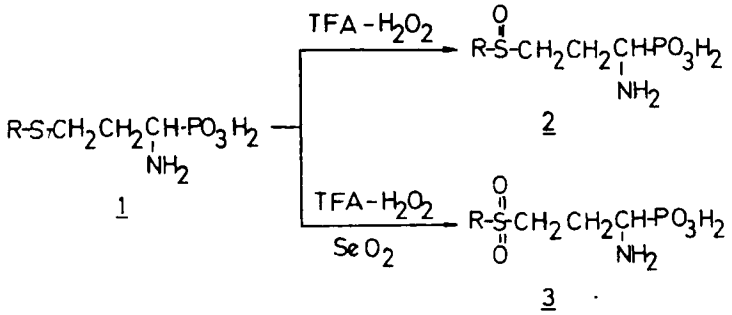


The oxidation of amino acids **1** to their derivatives **2** and **3** were generally performed by means of hydrogen peroxide or hydrogen peroxide in the presence of selenium dioxide, respectively.[6,7] However, the low solubility of long chain amino acids **1** ($R \geq n\text{-}C_6H_{13}$) in most common solvents, limited the number of potential oxidation systems. Thus, the oxidation of **1d** in alkaline solution did not lead to satisfactory yields of **2d** and **3d**, affording multicomponent mixtures, which according to ^{31}P-N.M.R. data contained only low amounts of **2d** and **3d**. Also the conversions **1d**→**2d**→**3d** performed in acetic acid–hydrogen peroxide solutions did not occur at room temperature (due to low solubility of **1d** in the reaction mixture), giving instead upon refluxing the mixture the sulphonyl derivatives **8** as the main product of oxidation.[11]



On the other hand, the excellent solubility of amino acids **1(a–e)** in trifluoroacetic acid, even at low temperatures, has suggested this solvent for the mild conversions of **1** to their sulphinyl **2** and sulphonyl **3** derivatives.

Thus, the oxidation of **1**→**2** and **1**→**3** occurred smoothly, giving selectively the desired products **3** and dilution of reaction mixture with ethyl ether.



The sulphoxides **2** prepared by this procedure were found to be pure according to ^{31}P-N.M.R. and ^{1}H-N.M.R. assays but could be isolated only as the salt with trifluoroacetic acid (**2** · 0.5 TFA). These salts of **2** were dissolved in sodium

TABLE I

Yield and analytical data of amino acids **1** and their sulphinyl **2** and sulphonyl **3** derivatives

Compounds		Yield[a]	M.P.[b]	Molecular formula	Microanalysis data [calc. %/found %]					T.L.C.[c]	^{31}P-N.M.R.[f]
Nr	R-	(%)	(°C)	(weight)	C	H	N	P	S	(R_f)	δ(ppm)
1a	n-C_6H_{13}	70	263–265	$C_9H_{22}NPO_3S$	42.40	8.70	5.50	12.15	12.55	0.72[d]	15.8[g]
				(255.27)	42.50	8.67	5.30	12.19	12.72	0.83[e]	20.3[h]
1b	n-C_8H_{17}	80	262–264	$C_{11}H_{26}NPO_3S$	46.70	9.26	4.94	10.95	11.32	0.56[d]	15.4[g]
				(283.32)	47.20	9.33	4.73	11.00	11.83	0.80[e]	20.2[h]
1c	n-$C_{10}H_{21}$	80	260–262	$C_{13}H_{30}NPO_3S$	50.20	9.74	4.52	9.98	10.30	0.48[d]	15.3[g]
				(311.37)	50.34	9.65	4.26	10.30	10.63	0.79[e]	20.2[h]
1d	n-$C_{12}H_{25}$	80	252–254	$C_{15}H_{34}NPO_3S$	53.20	10.11	4.13	9.14	9.42	0.40[d]	15.4[g]
				(339.42)	53.27	10.12	4.15	9.00	9.57	0.79[e]	20.2[h]
1e	n-$C_{16}H_{33}$	70	207–209	$C_{19}H_{42}NPO_3S$	57.90	10.68	3.54	7.83	8.10		15.0[g]
				(395.53)	57.40	10.72	3.40	7.51	8.14	0.63[e]	20.3[h]
2a	n-C_6H_{13}	83	234–236	$C_9N_{22}NPO_4S$	40.14	8.18	5.16	11.43	11.80		14.5[g]
				(271.27)	39.92	8.25	5.10	11.20	11.50	0.60[e]	19.2[h]
2b	n-C_8H_{17}	86	200–202	$C_{11}H_{26}NPO_4S$	44.12	8.75	4.68	10.35	10.71		14.5[g]
				(299.32)	43.80	8.79	4.40	10.00	10.40	0.58[e]	19.2[h]
2c	n-$C_{10}H_{21}$	81	197–200	$C_{13}H_{30}NPO_4S$	47.73	9.25	4.28	9.48	9.79		14.6[g]
				(327.37)	47.46	9.39	4.00	9.08	9.40	0.56[e]	19.2[h]
2d	n-$C_{12}H_{25}$	85	188–191	$C_{15}H_{34}NPO_4S$	50.75	9.65	3.94	8.73	9.01		14.7[g]
				(355.42)	50.45	9.70	4.04	8.30	8.70	0.54[e]	19.3[h]
2e	n-$C_{16}H_{33}$	83	183–185	$C_{19}H_{42}NPO_4S$	55.44	10.29	3.40	7.53	7.78		14.6[g]
				(411.53)	55.20	10.35	3.02	7.20	7.60	0.52[e]	19.0[h]
3a	n-C_6H_{13}	92	264–266	$C_9H_{22}NPO_5S$	37.70	7.72	4.87	10.87	11.18		14.3[g]
				(287.27)	37.56	7.86	4.41	10.74	11.24	0.66[e]	18.7[h]
3b	n-C_8H_{17}	96	252–254	$C_{11}H_{26}NPO_5S$	42.00	8.31	4.45	9.83	10.15		14.1[g]
				(315.32)	42.25	8.46	4.10	9.88	10.02	0.58[e]	18.8[h]
3c	n-$C_{10}H_{21}$	93	236–238	$C_{13}H_{30}NPO_5S$	45.50	8.81	4.08	9.04	9.33		14.2[g]
				(343.37)	45.20	8.45	4.41	9.24	9.39	0.56[e]	18.9[h]
3d	n-$C_{12}H_{25}$	97	237–239	$C_{15}H_{34}NPO_5S$	48.60	9.24	3.77	8.36	8.63		14.2[g]
				(371.58)	48.50	9.13	3.60	8.27	8.62	0.54[e]	18.9[h]
3e	n-$C_{16}H_{33}$	98	247–249	$C_{19}H_{42}NPO_5S$	53.30	9.89	3.28	7.25	7.47		14.2[g]
				(427.53)	53.01	9.88	2.92	7.08	7.65	0.53[e]	18.9[h]

[a] The yields of obtained **1** were calculated on the base of N-phenylthiourea, the yields of amino acids **2** and **3** were calculated on the base of **1**.

[b] Amino acids **1** were recrystalized from glacial acetic acid solutions, amino acids **2** and **3** were reprecipitated by neutralization of their aqueous alkaline solutions.

[c] Chromatography. Silica-gel 60 silanized, F_{254} plates (E. Merck), indicator—0.5% ninhydrine in ethanol. Solvent systems: [d] DMSO-acetic acid (1:1), [e] DMSO-trifluoroacetic acid (1:1).

[f] 2% solutions of **1**, **2** or **3** in: [g] trifluoroacetic acid, [h] 2N aqueous potassium hydroxide.

hydroxide solutions and reprecipitated by acidification of pH = 6 with diluted hydrochloric acid. The yields, physical and analytical properties of amino acids **1**, **2** and **3** are summarized in Tables I and II, respectively. The results of tensiometric measurements of the compounds **1**, **2** and **3** are represented in Table III.

EXPERIMENTAL

All melting points were measured on a Boetius apparatus and are uncorrected. ^{31}P-N.M.R. spectra were recorded at 24.3 MHz on a Joel-C-60H Spectrometer equipped with Heterospin Decoupler SNH-SD-HC using H_3PO_4 as external chemical shift reference. Negative chemical shift values are reported for compounds absorbing at higher fields than H_3PO_4. ^{1}H-N.M.R. spectra were taken at

TABLE II

Spectral characteristics of amino acids **1**, **2** and **3**

1a	broad 3850–2100, 1690–1565 bs, 1750, 1455, 1320, 1170, 1030, 1000, 920	0.95(t, 3H, CH_3); 1.1–1.9(m, 8H, $CH_3(CH_2)_4$); 2.1–3.5(m, 6H, $CH_2SCH_2CH_2CH$); 3.85–4.75(m, 1H, CH); 7.2–8.1(bs, 3H, NH_3)
1b	broad 3340–2260, 1700–1570 bs, 1540, 1465, 1235, 1170, 1050, 1005, 925	0.9(t, 3H, CH_3); 1.1–1.9(m, 12H, $CH_3(CH_2)_6$); 2.1–3.2(m, 6H, $CH_2SCH_2CH_2CH$); 3.8–4.45(m, 1H, CH); 7.1–8.0(bs, 3H, NH_3)
1c	broad 3700–2000, 1645, 1600, 1465, 1240, 1175, 1070, 1025, 925	1.0(t, 3H, CH_3); 1.2–2.0(m, 16H, $CH_3(CH_2)_8$); 2.35–3.2(m, 6H, $CH_2SCH_2CH_2CH$); 3.9–4.45(m, 1H, CH); 7.4–8.0(m, 3H, NH_3)
1d	broad 3700–2000, 1700–1650 bs, 1530, 1460, 1300–1100 bs, 1060, 1025, 925	0.95(t, 3H, CH_3); 1.1–1.9(m, 20H, $CH_3(CH_2)_{10}$); 2.1–3.2(m, 6H, $CH_2SCH_2CH_2CH$); 3.8–4.5(m, 1H, CH); 7.2–8.2(bs, 3H, NH_3)
1e	broad 3700–2100, 1675, 1640, 1590, 1530, 1460, 1300–1100 bs, 1060, 1030, 925	0.9(t, 3H, CH_3); 1.1–1.85(m, 28H, $CH_3(CH_2)_{14}$); 2.1–3.1(m, 6H, $CH_2SCH_2CH_2CH$); 3.9–4.25(M, 1H, CH); 7.25–7.9(bs, 3H, NH_3)
2a	broad 3700–2100, 1635, 1580, 1530, 1460, 1240, 1190, 1065, 1025, 905	0.89(t, 3H, CH_3); 1.1–1.7(m, 6H, $CH_3(CH_2)_3$); 1.7–2.2(m, 2H, $C_4H_9CH_2$); 2.4–3.8(m, 6H, $CH_2S(O)CH_2CH_2CH$); 2.4–4.6(m, 1H, CH); 7.2–7.9 (bs, 3H, NH_3)
2b	broad 3700–2100, 1635, 1580, 1530, 1465, 1240, 1190, 1130, 1060, 1025, 910	0.9(t, 3H, CH_3); 1.1–1.7(m, 10H, $CH_3(CH_2)_5$); 1.7–2.1(m, 2H, $C_6H_{13}CH_2$); 2.5–3.8(m, 6H, $CH_2S(O)CH_2CH_2CH$); 3.8–4.4(m, 1H, CH); 7.3–8.0 (bs, 3H, NH_3)
2c	broad 3700–2100, 1645, 1585, 1540, 1470, 1190, 1130, 1070, 1030, 910	0.89(t, 3H, CH_3); 1.1–1.7(m, 14H, $CH_3(CH_2)_7$); 1.7–2.2(m, 2H, $C_8H_{17}CH_2$); 2.5–3.8(m, 6H, $CH_2S(O)CH_2CH_2CH$); 3.8–4.5(m, 1H, CH); 7.2–7.9(bs, 3H, NH_3)
2d	broad 3700–2100, 1650, 1640, 1590, 1530, 1465, 1240, 1180, 1130, 1060, 1025, 905	0.9(t, 3H, CH_3); 1.1–1.7(m, 18H, $CH_3(CH_2)_9$); 1.7–2.1(m, 2H, $C_{10}H_{21}CH_2$); 2.5–3.8(m, 6H, $CH_2S(O)CH_2CH_2CH$); 3.8–4.1(m, 1H, CH); 7.4–8.0(bs, 3H, NH_3)
2e	broad 3750–2200, 1645, 1550, 1470, 1190, 1155, 1070, 1030, 910	0.89(t, 3H, CH_3): 1.1–1.8(m, 26H, $CH_3(CH_2)_{13}$); 1.8–2.2(m, 2H, $C_{14}H_{29}CH_2$); 2.4–3.4(m, 6H, $CH_2S(O)CH_2CH_2CH$); 3.75–4.25(m, 1H, CH); 7.3–7.9(bs, 3H, NH_3)
3a	broad 3700–2200, 1650, 1590, 1540, 1470, 1295, 1270, 1240, 1190, 1130, 1070, 1030, 910	0.93(t, 3H, CH_3); 1.1–1.8(m, 6H, $CH_3(CH_2)_3$); 1.8–2.2(m, 2H, $C_4H_9CH_2$); 2.5–3.1(m, 2H, CH_2CH); 3.1–3.95(m, 4H, $CH_2S(O)_2CH_2$); 3.95–4.7(m, 1H, CH); 7.1–7.9(bs, 3H, NH_3)
3b	broad 3700–2000, 1640, 1590, 1540, 1470, 1280, 1250, 1190, 1120, 1060, 905	0.89(t, 3H, CH_3); 1.1–1.7(m, 10H, $CH_3(CH_2)_5$); 1.7–2.2(m, 2H, $C_6H_{13}CH_2$); 2.5–3.1(m, 2H, CH_2CH); 3.1–3.85(m, 4H, $CH_2S(O)_2CH_2$); 3.9–4.5(m, 1H, CH); 7.3–7.9(bs, 3H, NH_3)
3c	broad 3700–2100, 1640, 1590, 1535, 1465, 1280, 1190, 1120 1070, 910	0.9(t, 3H, CH_3); 1.1–1.8(m, 14H, $CH_3(CH_2)_7$); 1.8–2.2(m, 2H, $C_8H_{17}CH_2$); 2.5–3.1(m, 2H, CH_2CH); 3.2–3.9(m, 4H, $CH_2S(O)_2CH_2$); 3.9–4.5(m, 1H, CH); 7.3–7.8(bs, 3H, NH_3)
3d	broad 3700–2100, 1640, 1590, 1540, 1470, 1230–1320 bs, 1190, 1120, 1060, 910	0.91(t, 3H, CH_3); 1.05–1.75(m, 18H, $CH_3(CH_2)_9$); 1.75–2.1(m, 2H, $C_{10}H_{21}CH_2$); 2.5–3.1(m, 2H, CH_2CH); 3.1–3.8(m, 4H, $CH_2S(O)_2CH_2$); 3.9–4.4(m, 1H, CH); 7.1–7.8(bs, 3H, NH_3)
3e	broad 3700–2200, 1645, 1590, 1570, 1470, 1320–1220 bs, 1190, 1120, 1065, 910	0.9(t, 3H, CH_3); 1.1–1.8(m, 26H, $CH_3(CH_2)_{13}$); 1.8–2.2(m, 2H, $C_{14}H_{29}CH_2$); 2.5–3.1(m, 2H, CH_2CH); 3.1–3.8(m, 4H, $CH_2S(O)_2CH_2$); 3.9–4.4(m, 1H, CH); 7.1–7.8(bs, 3H, NH_3)

TABLE III

Tensiometric data of amino acids **1** and their sulphinyl **2** and sulphonyl **3** derivatives

R-	Concentration[a] (mol kg^{-1})	Surface tension[b] (dyne cm^{-1})		
		1	**2**	**3**
n-C_6H_{13}	0.03	62.9	69.2	64.0
	0.015	66.6	71.4	68.3
	0.010	66.7	71.3	69.8
	0.005	67.6	71.7	71.3
n-C_8H_{17}	0.015	57.4	62.0	58.4
	0.010	59.6	64.3	62.9
	0.0050	63.8	66.5	67.4
	0.0025	65.9	67.7	69.6
n-$C_{10}H_{21}$	0.015		46.0	
	0.010	46.0[c]	53.8	52.0
	0.0050	49.7	58.2	57.8
	0.0025	53.6	59.8	61.5
n-$C_{12}H_{25}$	0.0050			44.6
	0.0025			51.5
	0.0015			54.8
	0.0010			55.5
n-$C_{16}H_{33}$	0.0050	55.7	53.7	
	0.0025	56.4	54.7	52.0
	0.0015	57.2	55.2	55.4
	0.0010	57.5	55.4	63.0

[a] Concentration of amino acids **1**, **2** and **3** in 0.42 N aqueous sodium hydroxide solution.

[b] The surface tension of amino acids **1**, **2** and **3** were determined at 25°C using the capillary bubble method. The surface tension of 0.42 N aqueous solution of sodium hydroxide determined under these conditions was 72.7 (dyne cm^{-1}).

[c] Taken at concentration 0.007 (mol kg^{-1}).

80 MHz on a Tesla BS 487 Spectrometer. I.R. spectra (KBr) were measured on a Zeiss–Jena UR-10 instrument. Product purities were determined from integration of ^{31}P-N.M.R. and ^{1}H-N.M.R. spectra.

Thiaaldehydes **9**, were prepared by addition of the corresponding thiols to acrolein according to Reference 13 and purified by distillation or recrystallization before use.

1-Amino-3-alkylthiopropanephosphonic acids **1**. General procedure. Into a solution of triphenyl phosphite (**5**) (0.02 mol) and aldehyde **7** (0.025 mol) in glacial acetic acid (10 ml), powdered N-phenylthiourea (**6**) (0.02 mol) was added in one portion. The reaction mixture was stirred at room temperature for 0.5 h, then for 0.5 h at 80°C (oil bath temperature) and crude **4**, without isolation were treated with 40% hydrobromic acid (d = 1.38 g/ml, 40 ml). The mixture was heated under reflux for 8 h, the solvents were evaporated under reduced pressure and the residue was suspended in ethanol (100 ml). This solution was treated with propylene oxide until the pH of the mixture was 6, then the precipitated amino acids **1** were filtered off and washed with water (2 × 10 ml) and ethanol (2 × 10 ml). The aminoalkanephosphonic acids **1** were recrystallized from glacial acetic acid, washed with ethanol (2 × 10 ml) and dried in a vacuum dessicator over solid potassium hydroxide.

1-Amino-3-alkanesulphinylpropanephosphonic acids **2**. General procedure. To the solution of amino acid **1** (0.01 mol) in trifluoroacetic acid (7.5 ml) stirred and cooled to −20°C, the solution of peroxytrifluoroacetic acid (prepared immediately before use by addition of hydrogen peroxide (30%, d = 1.1 g/ml, 1.1 ml) to trifluoroacetic acid (2.5 ml))[14] was added dropwise. The reaction mixture was stirred for additional 15 min. and was kept at 0°C for 8 h. The amino acids **2** were precipitated by dilution of the reaction mixture with anhydrous ethyl ether (100 ml) and isolated after 3 h by decantation-filtration, washed with ethyl ether (2 × 10 ml) and dried in a vacuum dessicator. Isolated

in this manner the amino acids **2** were homogeneous on T.L.C., and both in ^{1}H-N.M.R. and ^{31}P-N.M.R. but according to elemental analysis data existed in the form of trifluoroacetates (**2** · 0.5 TFA). These salts were dissolved in 1 M aqueous solution of sodium hydroxide and reprecipitated during acidification of pH = 6 by means of 0.25 M aq. solution of hydrochloric acid. Aminoalkanephosphonic acids **2** were isolated by filtration, washed with ethanol (2 × 10 ml) and ethyl ether (2 × 10 ml) and dried in a vacuum dessicator over solid potassium hydroxide.

1-Amino-3-alkanesulphonylpropanephosphonic acids **3**. General procedure. To the stirred mixture cooled to −20°C of trifluoroacetic acid (7.5 ml), amino acids **1** (0.01 mol) and selenium dioxide (0.05 g), a solution of peroxytrifluoroacetic acid (prepared immediately before use by mixing hydrogen peroxide (30%, d = 1.1 g/ml, 2.5 ml) and trifluoroacetic acid (2.5 ml)) was added. The reaction mixture was stirred at −20°C for 5 min., the cooling bath was removed and stirring was continued for an additional 1 h at room temperature. The reaction mixture was diluted with anhydrous ethyl ether (100 ml) and the precipitated amino acids **3** were isolated after 3 h by decantation-filtration, washed with ethanol (2 × 10 ml) and ethyl ether (2 × 10 ml) and dried in a vacuum dessicator over solid potassium hydroxide.

The purity of all amino acids **1**, **2** and **3** was checked by means of ^{1}H-N.M.R. and ^{31}P-N.M.R. spectroscopy.

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