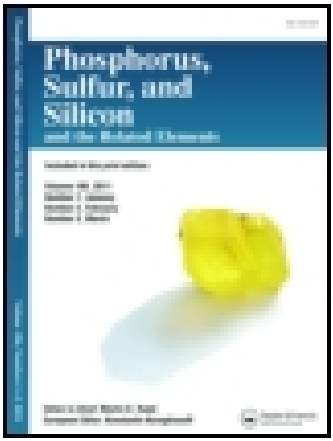


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

N-Acyl-α-triphenylphosphonio-α-amino Acids: Synthesis and Decarboxylation to α-(N-Acylamino)alkyltriphenylphosphon Salts

Roman Mazurkiewicz [a], Agnieszka Październiok-Holewa [a] & Mirosława Grymel [a]
[a] Department of Organic Chemistry, Biochemistry and Biotechnology, Silesian University of Technology, Gliwice, Poland
Published online: 26 Mar 2009.

To cite this article: Roman Mazurkiewicz, Agnieszka Październiok-Holewa & Mirosława Grymel (2009) N-Acyl-α-triphenylphosphonio-α-amino Acids: Synthesis and Decarboxylation to α-(N-Acylamino)alkyltriphenylphosphonium Salts, Phosphorus, Sulfur, and Silicon and the Related Elements, 184:4, 1017-1027, DOI: 10.1080/10426500902720204

To link to this article: http://dx.doi.org/10.1080/10426500902720204

Phosphorus, Sulfur, and Silicon, 184:1017–1027, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902720204

N-Acyl-α-triphenylphosphonio-α-amino Acids: Synthesis and Decarboxylation to α-(*N*-Acylamino)alkyltriphenylphosphonium Salts

Roman Mazurkiewicz, Agnieszka Październiorok-Holewa, and Mirosława Grymel
Department of Organic Chemistry, Biochemistry and Biotechnology, Silesian University of Technology, Gliwice, Poland

4-Phosphoranylidene-5(4H)-oxazolones **1** *undergo hydrolysis in THF in the presence of* HBF_4 *at room temperature to give* N*-acyl-α-triphenyphosphonioglycines* **3** (R^2 = *H) in very good yields. 4-Alkyl-4-triphenylphosphonio-5(4*H*)-oxazolones* **2** *react with water in* CH_2Cl_2*/THF solution without any acidic catalyst at 0–5°C in a few days yielding N-acyl-α-triphenylphosphonio-α-amino acids* **3** (R^2 = *Me) or α-(N-acylamino)alkyltriphenylphosphonium salts* **4** (R^2 = *alkyl, other then Me). α-Triphenylphosphonio-α-amino acids* **3** *upon heating to 105–115°C under reduced pressure (5 mm Hg) or upon treatment with a Hünig base in* CH_2Cl_2 *at 20°C undergo decarboxylation to give the corresponding α-(N-acylamino)-alkyltriphenylphosphonium salts* **4***, usually in very good yields.*

Keywords 4-Alkyl-4-triphenylphosphonio-5(4*H*)-oxazolone hydrolysis; 4-triphenylphosphoranylidene-5(4*H*)-oxazolone hydrolysis; α-(*N*-acylamino)alkyltriphenylphosphonium salts; decarboxylation; *N*-acyl-α-triphenyphosphonio-α-amino acids

INTRODUCTION

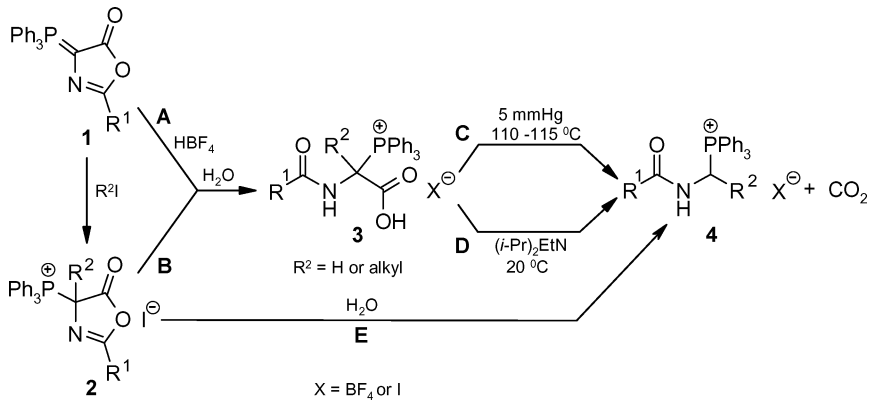
A few known types of α-amino acid derivatives with a C_α-P bond have attracted significant attention of organic chemists due to several important applications in organic synthesis.[1] A few years ago, we described a simple synthesis of 4-triphenylphosphoranylidene-5(4*H*)-oxazolones (TPO) **1** from *N*-acylglycines[2] and effective methods for their 4-*C* alkylation to 4-alkyl-4-triphenylphosphonio-5(4*H*)-oxazolones (ATPO) **2**[3]

Received 28 December 2007; accepted 7 February 2008.

Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

The financial help of the Ministry of Science and Higher Education of Poland (Grant No. N N204 238334) is gratefully acknowledged.

Address correspondence to Professor Roman Mazurkiewicz, Department of Organic Chemistry, Biochemistry and Biotechnology, Silesian University of Technology, Krzywoustego 4, PL 44-100 Gliwice, Poland. E-mail: roman.mazurkiewicz@polsl.pl



SCHEME 1

(Scheme 1). Both 4-phosphoranylidene-5(4*H*)-oxazolones **1** and their alkylation products **2** are quite stable, crystalline compounds, the elaborated procedures being useful for their synthesis even on a kilogram scale.

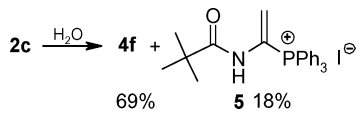
In this article, we describe simple and effective methods for the hydrolysis of 4-phosphoranylidene-5(4*H*)-oxazolones **1** and 4-alkyl-4-triphenylphosphonio-5(4*H*)-oxazolones **2** to hitherto unknown *N*-acyl-α-triphenylphosphonio-α-amino acids (PAA) **3**, as well as the reaction of their decarboxylation to α-(*N*-acylamino)alkyltriphenylphosphonium salts (APS) **4** (Scheme 1).

α-(*N*-Acylamino)alkyltriphenylphosphonium salts **4** are valuable difunctional organic reagents used for syntheses of heterocyclic systems, including oxazole,[4–6] thiazole,[5–7] imidazole,[7,8] tetrazole,[9,10] and quinazoline derivatives.[10] They have also been applied as α-amidoalkylating agents.[11,12] The most frequently used method for the synthesis of α-(*N*-acylamino)alkyltriphenylphosphonium salts consists of the alkylation of triphenylphosphine with *N*-(α-chloroalkyl)amides,[4,9–11,13,14] *N*-(α-hydroxyalkyl)amides,[7,14,15] or *N*-(α-alkoxyalkyl)amides.[15] Synthetic equivalents of *N*-(α-haloalkyl) amides, such as trimethylsilylmethyl isocyanide,[16] chloromethylisocyanate,[12] and bromomethylisocyanate[17] were also used for the alkylation of triphenylphosphine; the isocyanide or isocyanate groups in the alkylation products were hydrolyzed or alcoholized to formylamino or alkoxycarbonylamino groups, respectively. Unfortunately, these methods are applicable mainly for the synthesis of *N*-acylaminomethyltriphenylphosphonium salts (**4**, $R^2 = H$).

RESULTS AND DISCUSSION

Phosphoranylidene-5(4*H*)-oxazolones **1**, dissolved in CH_2Cl_2, react smoothly with an equimolar amount of water in the presence of tetrafluoroboric acid at room temperature to give *N*-acyl-α-triphenylphosphonioglycine tetrafluoroborates **3** in excellent yields within 10 min (Table I, Procedure A). The obtained α-triphenylphosphonioglycine derivatives **3a**–**c** are stable, crystalline compounds; they can be stored at 0°C for a few months without decomposition.

Phosphonium salts **2** undergo hydrolysis in CH_2Cl_2/THF solution without any acidic catalyst at 0–5°C in a few days; however, only in the case of phosphonium salts **2a** and **2b** we were able to isolate relatively stable α-triphenylphosphonio-α-amino acids **3d** and **3e** (Table I, Procedure B). When stored at 0°C, they undergo a very slow decarboxylation to the corresponding α-(*N*-acylamino)alkyltriphenylphosphonium salts. In the case of other phosphonium salts (**2c**–**d**), we obtained directly the corresponding α-(*N*-acylamino)alkyltriphenylphosphonium salts **4f**–**g** as the main reaction products (Table II, Procedure E). It seems that, in this case, the primarily formed α-triphenylphosphonio-α-amino acids undergo consecutive decarboxylation to α-(*N*-acylamino)alkyltriphenylphosphonium salts **4f**–**g**, the decarboxylation being probably faster than hydrolysis (Table II). In the case of phosphonium salt **2c**, we have also obtained α-(*N*-pivaloylamino)vinyltriphenylphosphonium iodide **5** in a yield of 18%, apart from the expected hydrolysis product **4f** (Scheme 2). The phosphonium salt **5** is evidently formed as a result of the elimination of methanol from the starting phosphonium salt **2c**, or the corresponding α-triphenylphosphonio-α-amino acid **3** or the primary decarboxylation product **4f**.



SCHEME 2

The α-triphenylphosphonio-α-amino acids **3a–d**, when heated to 105–115°C under reduced pressure (5 mm Hg) underwent decarboxylation to the corresponding α-(*N*-acylamino)alkyltriphenylphosphonium salts **4a**–**d**, usually in very good yields; only in the case of compound **4d** was the yield of decarboxylation poor (Table II, Procedure C). In the latter case, we also identified *N*-pivaloyl-β-triphenylphosphonioalanine iodide **6** in the reaction mixture (yield 59 % by ^{1}H NMR). The formation of this compound can be explained as a result of the thermal elimination of

TABLE I Synthesis of *N*-Acyl-α-triphenylophosphonio-α-amino Acids 3

TPO **1** or ATPO **2**			Reaction conditions				PAA **3**				Elemental analysis [%] (calcd./found) [%]			
	R^1	R^2	Procedure	Solvent	Temp. [°C]	Time	No.	Yield [%]	m p [°C]	IR [cm^{-1}]	C	H	N	P
1a	*t*-Bu	—	A	CH_2Cl_2	20	10 min	**3a**	99	114.0–115.0	3350br, 1764vs, 1732vs, 1672vs, 1516s[b]	59.19/59.07	5.36/5.78	—	6.11/5.80
1b	Ph	—	A	CH_2Cl_2	20	10 min	**3b**	93	144.0–145.0	3320br, 1768vs, 1740vs, 1676vs, 1526s[b]	61.51/61.58	4.40/4.29	—	5.87/5.57
1c	Me	—	A	CH_2Cl_2	20	10 min	**3c**[a]	97	95.0–97.0	3324br, 1760vs, 1744vs, 1700vs 1520s[b]	58.12/58.52	5.44/5.53	—	5.76/5.65
2a	*t*-Bu	Me	B	CH_2Cl_2/THF	0–5	7 d	**3d**	71	117.5–118.0	3340br, 1740vs, br, 1672vs, 1516s[c]	55.63/55.52	5.21/5.30	2.50/2.52	5.52/5.17
2b	Ph	Me	B	CH_2Cl_2/THF	0–5	6 d	**3e**	65	122.0–123.0	3336br, 1728vs, br, 1660vs, 1520s[c]	57.84/57.67	4.33/4.39	2.41/2.45	5.33/5.43

[a]For the formula $C_{26}H_{29}BF_4NO_4P$ (crystals contains 1 mol of THF per 1 mol of compound **3c**).
[b]In CH_3CN.
[c]In Nujol.

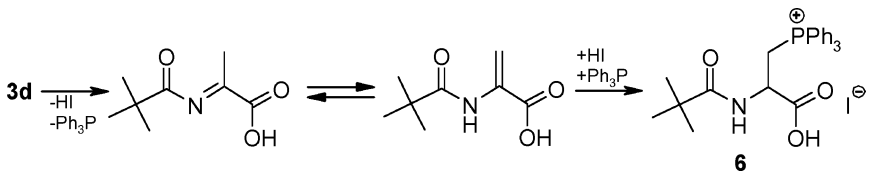
TABLE II Synthesis of α-(*N*-Acylamino)alkyltriphenylphosphonium Salts 4

ATPO **2** or PAA **3**				Reaction conditions			APS **4**				Elemental analysis (calcd./found) [%]			
	R^1	R^2	X	Procedure	Temp. [°C]	Time	No.	Yield [%]	mp [°C]	IR [CH_2Cl_2,cm^{-1}]	C	H	N	P
3a	*t*-Bu	H	BF_4	C	105	4.5 h	**4a**	99	183.0–183.5	3384br, 1668vs, 1520vs	62.22/61.83	5.87/5.77	—	6.69/6.42
3a	*t*-Bu	H	BF_4	D	20	24 h	**4a**	99						
3b	Ph	H	BF_4	C	105	2.5 h	**4b**	94	192.0–192.5	3368br, 1664vs, 1528vs	64.62/64.25	4.80/4.72	—	6.41/6.52
3b	Ph	H	BF_4	D	20	24 h	**4b**	98						
3c	Me	H	BF_4	C	105	1 h	**4c**	99	168.5–169.0	3364br, 1688vs, 1524vs	59.89/59.86	5.03/4.76	—	7.35/7.46
3c	Me	H	BF_4	D	20	12 d	**4c**	89						
3d	*t*-Bu	Me	I	C	115	1 h	**4d**	36[a]						
3d	*t*-Bu	Me	I	D	20	19 h	**4d**	72	178.5–179.5	3230br, 1652vs, 1512vs	58.04/58.04	5.65/5.64	2.71/2.73	5.99/5.86
3e	Ph	Me	I	D	20	18 h	**4e**	90	166.5–167.0	3210br, 1656vs, 1528vs	60.35/60.25	4.69/4.59	2.61/2.59	5.76/5.92
2c	*t*-Bu	$MeOCH_2$	—	E	0–5	8 d	**4f**	69[b]	146.5–148.0	3220br, 1656vs, 1512vs	57.05/57.09	5.71/5.56	2.56/2.51	5.66/5.46
2d	*t*-Bu	$N{\equiv}CCH_2$	—	E	0–5	5 d	**4g**	60	187.0–187.5	3205br, 1656vs, 1512vs	57.57/57.55	5.20/4.97	5.16/5.01	5.71/6.16

[a] *N*-pivaloyl-β-triphenylphosphonioalanine iodide **6** was also identified in the reaction mixture (yield 59 %). ^{1}H NMR [CD_3CN, δ (ppm)]: 7.90–7.67 (m, 15H, Ph), 7.23 (d, br, J = 8.4 Hz, 1H, NH), 4.74–4.63 (m, 1H, $Ph_3P^+CH_2C\underline{H}$), 4.31 (ddd, J_{PH} = 10.8 Hz, J_{HH} = 16.0 Hz, J_{HH} = 10.8 Hz, 1H, $Ph_3P^+C\underline{H}_2$—one of two diastereotopic protons), 3.95 (ddd, J_{PH} = 14.1 Hz, J_{HH} = 16.2 Hz, J_{HH} = 3.3 Hz, 1H, $Ph_3P^+C\underline{H}_2$—one of two diastereotopic protons), 0.90 (s, 9H, *t*-Bu). ^{13}C NMR [CD_3CN, δ (ppm)/J_{PC}(Hz)]: 180.2 (HNC=O), 171.1/15.6 (HOC=O), 136.1/3.0 (Ph_3P^+, C^4), 134.8/10.0 (Ph_3P^+, C^2), 131.2/13.1 (Ph_3P^+, C^3), 118.8/91.1 (Ph_3P^+, C^1), 48.2/3.0 ($Ph_3P^+CH_2\underline{C}H$), 39.1 ($\underline{C}Me_3$), 27.3 ($C\underline{Me}_3$), 25.5/54.8 ($Ph_3P^+\underline{C}H_2$).

[b] α-(N-Pivaloylamino)vinyltriphenylphosphonium iodide **5** was also isolated from the reaction mixture in 18% yield (see the Experimental section).

[c] One of two diastereotopic protons of the methylene group.



SCHEME 3

triphenylphosphine and hydrogen iodide from the starting *N*-pivaloyl-α-triphenylphosphonioalanine iodide **3d** followed by an imine–enamine type tautomerization of the elimination product, the nucleophilic attack of triphenylphosphine at the β-position of the α-aminoacrylic acid derivative, and the consecutive addition of hydrogen iodide (Scheme 3). A similar synthesis of β-triphenylphosphoniocarboxylic acids by the addition of triphenylphosphine and hydrogen bromide or hydrogen iodide to α,β-usaturated carboxylic acids was described by Hoffmann.[18]

Another elaborated, milder, and, in some cases, more efficient procedure for decarboxylation of α-triphenylphosphonio-α-amino acids **3** involves their decarboxylation in CH_2Cl_2 at 20°C, in the presence of a catalytic amount of diisopropylethylamine (Hünig base) (Table II, Procedure D).

The structures of *N*-acyl-α-triphenylphosphonio-α-amino acids **3a–e** and α-(*N*-acylaminomethyl)triphenylphosphonium salts **4a–g** were confirmed by their spectroscopic properties (IR, ^{1}H, and ^{13}C NMR); in the case of all new compounds satisfactory elemental analyses were obtained (Tables I–IV).

CONCLUSION

The hydrolysis of 4-triphenylphosphoranylidene-5(4*H*)-oxazolones **1** and 4-alkyl-4-triphenylphosphonio-5(4*H*)-oxazolones **2** provides the hitherto unknown *N*-acyl-α-triphenylphosphonio-α-amino acids **3**. Their decarboxylation offers an effective and convenient way for the synthesis of α-(*N*-acylamino)alkyltriphenylphosphonium salts **4**, including α-substituted derivatives ($R^2 \neq H$), which are difficult to obtain by other synthetic methods.

EXPERIMENTAL

Melting points were determined in capillary tubes in a Stuart Scientific SMP3 melting point apparatus and are uncorrected. IR spectra were recorded on a Zeiss Specord M 80 spectrophotometer.

TABLE III ^{1}H and ^{13}C-NMR Spectroscopic Data of *N*-Acyl-α-triphenylophosphonio-α-amino Acids 3

No.	^{1}H NMR [CD_3CN/TMS, δ (ppm)]	^{13}C NMR [CD_3CN/TMS, δ (ppm)/J_{PC}(Hz)]							
					Ph_3P^+				
		O=C–NH	P^+–C	>C=O	C^1	C^2	C^3	C^4	Other carbon atoms
3a	7.89–7.65 (m, 15H, Ph), 7.45 (dd, J_{PH} = 2.7 Hz, J_{HH} = 7.5 Hz, 1H, NH), 6.35 (dd, J_{PH} = 14.7 Hz, J_{HH} = 8.1 Hz, 1H, CH), 0.88 (s, 9H, *t*-Bu)	179.6/2.0	54.0/62.4	166.4/7.0	119.2/85.5	135.8/10.0	130.9/13.0	136.1/3.0	39.1 ($\underline{C}Me_3$), 26.9 ($C\underline{Me}_3$)
3b	8.11 (d, br, J = 7.8 Hz, 1H, NH), 7.88–7.40 (m, 20H, Ph), 6.74 (dd, J_{PH} = 14.7 Hz, J_{HH} = 8.7 Hz, 1H, CH)	168.5/2.6	54.0/61.0	166.2/7.0	118.5/85.1	135.7/10.0	131.0/12.6	136.3/3.0	133.8, 132.7, 129.6 128.4 (Ph)
3c	7.92–7.67 (m, 15H, Ph), 7.63 (d, br, J = 8.7 Hz, 1H, NH), 6.63 (dd, J_{PH} = 14.7 Hz, J_{HH} = 9.0 Hz, 1H, CH), 1.76 (s, 3H, Me)	171.4/2.6	52.9/60.4	166.3/7.1	118.0/85.6	135.6/9.6	131.0/12.5	136.4/3.0	26.2 (Me)
3d	7.84–7.60 (m, 15H, Ph), 7.52 (d, br, J = 7.5 Hz, 1H, NH), 1.91 (d, J = 18.9 Hz, 3H, Me), 0.80 (s, 9H, *t*-Bu)	179.4	64.5/61.0	169.8/11.1	120.5/83.1	135.7/9.1	129.6/12.6	134.6/3.0	38.0 ($\underline{C}Me_3$), 26.5 ($C\underline{Me}_3$), 26.0 (Me)
3e	8.23 (d, br, J = 5.4 Hz, 1H, NH), 7.86–7.34 (m, 20H, Ph), 2.00 (d, J = 18.3 Hz, 3H, Me)	168.8	65.8/59.8	170.3/10.6	120.7/82.1	136.5/9.1	130.4/12.8	135.5/3.1	133.8, 132.7, 129.4, 128.5 (Ph), 26.4 (Me)

TABLE IV ^{1}H and ^{13}C-NMR Spectroscopic Data of α-(*N*-Acylamino)alkyltriphenylphosphonium Salts 4

No.	^{1}H NMR [$CDCl_3$/TMS, δ (ppm)]	^{13}C NMR [$CDCl_3$/TMS, δ (ppm)/J_{PC}(Hz)]						
				Ph_3P^+				
		O=C–NH	P^+–CH	C^1	C^2	C^3	C^4	Other carbons
4a	7.82–7.65 (m, 16H, Ph, NH), 5.08 (dd, J_{PH} = 3.3 Hz, J_{HH} = 6.0 Hz, 2H, CH_2), 0.92 (s, 9H, *t*-Bu)	180.3	37.6/56.9	117.7/84.1	134.2/9.6	130.1/12.6	135.0/3.0	38.5 ($\underline{C}Me_3$), 26.8 ($C\underline{Me}_3$)
4b	8.30 (dd, br, J_{PH} = 5.8 Hz, J_{HH} = 5.8 Hz, 1H, NH), 7.80–7.31 (m, 20H, Ph), 5.30 (dd, J_{PH} = 3.1 Hz, J_{HH} = 6.1 Hz, 2H, CH_2)	168.3	37.8/56.9	117.1/84.1	134.1/10.0	130.1/12.6	135.2/3.0	132.2, 131.6, 128.5, 127.2 (Ph)
4c	7.86–7.68 (m, 16H, Ph, NH), 5.06 (dd, J_{PH} = 3.4 Hz, J_{HH} = 6.4 Hz, 2H, CH_2), 1.81 (d, J_{PH} = 1.2 Hz, 3H, Me)	171.9	37.1/57.9	117.0/84.1	134.0/10.1	130.3/12.5	135.3/3.0	21.9 (Me)
4d	8.72 (dd, J_{PH} = 6.7 Hz, J_{HH} = 6.7 Hz, 1H, NH), 7.89–7.62 (m,15H, Ph), 6.24–6.11 (m, 1H, CH); 1.76 (dd, J_{PH} = 17.4 Hz, J_{HH} = 7.3 Hz, 3H, Me), 0.94 (s, 9H, *t*-Bu)	179.3/2.2	44.6/51.9	118.8/82.4	134.7/9.4	129.8/12.2	134.4/3.0	38.5 ($\underline{C}Me_3$), 27.3 ($C\underline{Me}_3$), 17.4/4.8 (Me)
4e	9.53 (dd, J_{PH} = 4.3 Hz, J_{HH} = 7.6 Hz, 1H, NH), 7.93–7.32 (m, 20H, Ph), 6.39–6.27 (m, 1H, CH); 1.93 (dd, J_{PH} = 17.5 Hz, J_{HH} = 7.3 Hz, 3H, Me)	167.8/2.2	45.8/51.3	118.4/82.1	134.6/9.5	129.9/12.4	134.6/3.5	132.2, 131.5, 128.3, 127.8 (Ph), 17.6/4.9 (Me)
4f	8.75 (dd, J_{PH} = 4.8 Hz, J_{HH} = 7.5 Hz, 1H, NH), 7.95–7.59 (m, 15H, Ph), 6.32–6.22 (m, 1H, CH), 4.12 (ddd, J_{PH} = 9.6 Hz, J_{HH} = 9.6 Hz, J_{HH} = 9.6 Hz, 1H, $C\underline{H}_2OMe^a$), 3.77 (ddd, J_{PH} = 31.8 Hz, J_{HH} = 9.0 Hz, J_{HH} = 5.1 Hz, 1H, $C\underline{H}_2OMe^a$), 2.67 (s, 3H, OMe), 0.91 (s, 9H, *t*-Bu)	179.9/1.8	49.3/51.2	119.1/83.0	135.2/9.7	129.4/12.7	134.0/3.0	67.8/2.5 ($\underline{C}H_2OMe$), 57.8 ($CH_2O\underline{Me}$), 38.6 ($\underline{C}Me_3$), 27.3 ($C\underline{Me}_3$)
4g	9.08 (dd, J_{PH} = 4.3 Hz, J_{HH} = 7.3 Hz, 1H, NH), 7.99–7.67 (m, 15H, Ph), 6.59–6.50 (m, 1H, CH), 3.44 (ddd, J_{PH} = 9.3 Hz, J_{HH} = 16.9 Hz, J_{HH} = 7.5 Hz, 1H, $C\underline{H}_2CN^a$), 3.20 (ddd, J_{PH} = 22.9 Hz, J_{HH} = 16.5 Hz, J_{HH} = 6.0 Hz, 1H, $C\underline{H}_2CN^a$), 0.92 (s, 9H, *t*-Bu)	180.0/2.0	44.6/54.4	117.2/83.1	135.2/10.0	130.0/13.1	135.1/4.5	115.2/7.0 ($CH_2\underline{C}N$), 38.6 ($\underline{C}Me_3$), 27.1 ($C\underline{Me}_3$), 20.1/8.6 ($\underline{C}H_2CN$)

[a]One of two diastereotopic protons of the methylene group.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3CN with a Varian UNITY INOVA-300 spectrometer operating at 300 and 75.5 MHz, respectively, in the FT mode using TMS as an internal standard. Kieselgel 60 (Merck, 0.063–0.200 mm) was used for column chromatography.

Starting Materials

Commercial grade acetonitrile, acetone, ethyl acetate, chloroform, CH_2Cl_2, and THF were distilled and dried over molecular sieves (4 Å). The following reagents were of commercial quality (Aldrich or Across): HBF_4 (ethereal solution, 54%), iodomethane, iodoacetonitrile, iodomethyl methyl ether. 4-Triphenylphosphoranylidene-5(4*H*)-oxazolones **1a–c** and 4-alkyl-4-triphenyl-phosphonio-5(4*H*)-oxazolones **2a–d** were synthesized as described in the literature.[2,3]

Synthesis of *N*-Acyl-α-triphenylphosphonio-α-amino Acids 3a–c from 4-Triphenylphosphoranylidene-5(4*H*)-oxazolones 1 (Procedure A)

To a stirred solution of 4-triphenylphosphoranylidene-5(4*H*)-oxazolone **1** (5 mmol) in CH_2Cl_2 (7.5 mL), water (0.09 mL, 5 mmol) and an ethereal solution of tetrafluoroboric acid (54%, 0.70 mL, 5.1 mmol) were added. After 10 min, the solvent was evaporated under reduced pressure, and the residue was crystallized from THF (**3a** and **3c**) or chloroform (**3b**).

Synthesis of *N*-Acyl-α-triphenylphosphonio-α-amino Acids 3d–e from 4-Methyl-4-triphenylphosphonio-5(4*H*)-oxazolones 2a–b (Procedure B)

To a suspension of 4-alkyl-4triphenylphosphonio-5(4*H*)-oxazolone **2** (5 mmol) in CH_2Cl_2 (6.75 mL for **2a** or 13.5 mL for **2b**), a solution of water (0.22 mL, 12.5 mmol) in THF (6.75 mL) was added, and the mixture was stirred at 0–5°C for the time given in Table I. The reaction mixture was diluted with CH_2Cl_2 (25 mL) dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Crude acids **3d–e** were purified by dissolving in CH_2Cl_2 and precipitating by addition of diethyl ether.

Synthesis of α-(*N*-Acylamino)alkyltriphenylphosphonium Salts 4a–e from *N*-Acyl-α-triphenylphosphonio-α-amino Acids 3a–e

Procedure C

N-Acyl-α-triphenylphosphonio-α-amino acid **3** was heated at 105–115°C under reduced pressure (5 mm Hg) for the time given in Table II. The residue was purified by dissolving in CH_2Cl_2 and precipitating by addition of diethyl ether (**4a**,**b)** or by crystallization from ethyl acetate (**4c**).

Procedure D

To a stirred suspension of *N*-acyl-α-triphenylphosphonio-α-amino acid **3** (4 mmol) in CH_2Cl_2 (32 mL), diisopropylethylamine (0.14 mL, 0.8 mmol) was added. The reaction mixture was left for the time given in Table II at room temperature, and then the solvent was evaporated under reduced pressure. The residue was purified by crystallization from a mixture of toluene and methanol (6:1, v/v; **4a–c**) or ethyl acetate (**4d**) or by dissolving in CH_2Cl_2 and precipitating by addition of diethyl ether (**4e**).

Synthesis of α-(*N*-Acylamino)alkyltriphenylphosphonium Salts 4f–g from 4-Alkyl-4-triphenylphosphonio-5(4*H*)-oxazolones 2c–d (Procedure E)

To a stirred suspension of 4-alkyl-4-triphenylphosphonio-5(4*H*)-oxazolone **2** (5 mmol) in CH_2Cl_2 (6.75 mL), a solution of water (0.22 mL, 12.5 mmol for **2c** or 0.13 mL, 7.5 mmol for **2d**) in THF (6.75 mL) was added, and the mixture was stirred at 0–5°C for the time given in Table II. The reaction mixture was diluted with CH_2Cl_2 (30 mL), dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude phosphonium salt **4f** was dissolved in CH_2Cl_2, and the pure product was precipitated by addition of diethyl ether. In the case of compound **4g**, the crude product was isolated by column chromatography, eluted with a mixture of acetone and CH_2Cl_2 (1:3, v/v), and finally purified by crystallization as described above.

Isolation of α-(*N*-Pivaloylamino)vinyltriphenylphosphonium Iodide 5

Phosphonium salt **5** was isolated from the residue after crystallization of compound **4f** (see Procedure E) by column chromatography, and

eluting with a mixture of ethyl acetate and CH_2Cl_2 (1:1, v/v). The crystallization of the crude chromatography product from ethyl acetate gave the pure phosphonium salt **5** in a yield of 18%, mp 168.0–169.0°C.

Spectral and analytical data for compound **5:** IR (CH_2Cl_2, cm^{-1}): 3144br, 1660vs, 1512s. ^1H NMR ($CDCl_3$): $\delta =$ 10.17 (d, br, $J =$ 12.0 Hz, 1H, NH), 7.84–7.61 (m, 15H, Ph), 7.21 (dd, $J_{PH} =$ 41.7 Hz, $J_{HH} =$ 2.4 Hz, 1H, C=C$\underline{H}_2$), 5.64 (dd, $J_{PH} =$ 15.6 Hz, $J_{HH} =$ 1.8 Hz, 1H, C=C$\underline{H}_2$), 1.01 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, δ / J_{PC} (Hz)): 179.0 (C=O), 134.2/3.0 (Ph_3P^+, C^4), 134.1/10.0 (Ph_3P^+, C^2), 133.8/17.1 (C=$\underline{C}H_2$), 129.6/13.1 (Ph_3P^+, C^3), 126.7/100.6 ($Ph_3P^+\underline{C}$), 120.4/92.4 (Ph_3P^+, C^1), 38.5 ($\underline{C}Me_3$), 27.2 ($C\underline{Me}_3$). Elemental analysis: Calcd. for $C_{25}H_{27}INOP$: C, 58.26; H, 5.28; N, 2.72; P, 6.01; Found: C, 58.21; H, 5.19; N, 2.68; P, 6.04%.

REFERENCES

[1] R. Mazurkiewicz, A. Kuźnik, M. Grymel, and A. Październiok-Holewa, *Arkivoc*, **VI,** 193 (2007).
[2] R. Mazurkiewicz and A. Pierwocha, *Monatsh. Chem.*, **127,** 219 (1996).
[3] R. Mazurkiewicz and A. Pierwocha, *Monatsh. Chem.*, **128,** 893 (1997).
[4] B. S. Drach, I. Yu. Dolgushina, and A. D. Sinitsa, *Zh. Obsch. Khim.*, **45,** 1251 (1975).
[5] V. S. Brovarets, O. P. Lobanov, and B. S. Drach, *Zh. Obsch. Khim.*, **53,** 660 (1983).
[6] V. S. Brovarets, O. P. Lobanov, A. A. Kisilenko, V. N. Kalinin, and B. S. Drach, *Zh. Obsch. Khim.*, **56,** 1492 (1986).
[7] V. S. Brovarets, O. P. Lobanov, T. K. Vinogradova, and B. S. Drach, *Zh. Obsch. Khim.*, **54,** 288 (1984).
[8] O. B. Smolii, V. S. Brovarets, V. V. Pirozhenko, and B. S. Drach, *Zh. Obsch. Khim.*, **58,** 2635 (1988).
[9] O. B. Smolii, V. S. Brovarets, B. S. Drach, *Zh. Obsch. Khim.*, **56,** 2802 (1986).
[10] O. B. Smolii, V. S. Brovarets, V. V. Pirozhenko, and B. S. Drach, *Zh. Obsch. Khim.*, **58,** 2465 (1988).
[11] B. S. Drach, E. P. Sviridov, and A. V. Kirsanov, *Zh. Obsch. Khim.*, **42,** 953 (1972).
[12] B. N. Kozhushko, A. V. Gumenyuk, Yu. A. Palichuk, and V. A. Shokol, *Zh. Obsch. Khim.*, **47,** 333 (1977).
[13] V. A. Shokol, B. N. Kozushko, and A. V. Gumenyuk, *Zh. Obsch. Khim.*, **47,** 1110 (1977).
[14] L. F. Kasukhin, V. S. Brovarets, O. B. Smolii, V. V. Kurg, L. V. Budnik, and B. S. Drach, *Zh. Obsch. Khim.*, **61,** 2679 (1991).
[15] H. Petersen and W. Reuther, *Liebigs Ann. Chem.*, **766,** 58 (1972).
[16] G. Zinner and W. P. Fehlhammer, *Angew. Chem. Int. Ed. Engl.*, **24,** 979 (1985).
[17] V. A. Shokol, E. B. Silina, B. N. Kozushko, and G. A. Golik, *Zh. Obsch. Khim.*, **49,** 312 (1979).
[18] H. Hoffmann, *Chem. Ber.*, **94,** 1331 (1961).