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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

A NEW SYNTHESIS OF α-AMINO ACID DERIVATIVES BY REACTION OF N-ACYL-α-TRIPHENYLPHOSPHOSPHONIO-GLYCINATES WITH CARBON NUCLEOPHILES

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Version of record first published: 27 Oct 2006.

To cite this article: Roman Mazurkiewicz & Miroslawa Grymel (2000): A NEW SYNTHESIS OF α -AMINO ACID DERIVATIVES BY REACTION OF N-ACYL- α -TRIPHENYLPHOSPHOSPHONIO-GLYCINATES WITH CARBON NUCLEOPHILES, Phosphorus, Sulfur, and Silicon and the Related Elements, 164:1, 33-43

To link to this article: http://dx.doi.org/10.1080/10426500008045231

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A NEW SYNTHESIS OF α-AMINO ACID DERIVATIVES BY REACTION OF N-ACYL-α-TRIPHENYLPHOSPHONIO-GLYCINATES WITH CARBON NUCLEOPHILES

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(Received December 16, 1999)

Recently described¹, easily accessible N-acyl- α -triphenylphosphonioglycinates react smoothly with activated carbonyl compounds or enamines in the presence of a base (DBU or Et₃N) yielding the corresponding α -functionalized glycine derivatives.

Keywords: α -Triphenylphosphonioglycinates; cationic glycine equivalent; carbon nucleophiles; nucleophilic substitution; glycine α -functionalization

INTRODUCTION

Since the pioneering investigations of Ben-Ishai *et. al.*² on the first glycine electrophilic equivalents (N-acyl- α -hydroxy- and N-acyl- α -methoxyglycinates), the important problem of synthesising α -amino acids by a new carbon-carbon bond formation between the glycine-cation equivalents and carbon nucleophiles has been attempted by many authors³⁻⁵. The most common way to carry out such a transformation consists in photochemical bromination of N-acylglycinates with bromine or NBS to α -bromoglycinates, followed by the nucleophilic substitution of bromide by carbon nucleophiles⁴⁻⁷. Many other electrophilic glycine equivalents have been introduced for the synthesis of α -amino acids in the course of the last 25 years, *e.g.* N-acyl- α -chloroglycinates⁶, unstable N-acyliminoacetates^{4,5,7}, N-acyl- α -acetoxyglycinates⁸, iminoacetates and iminoacetamides (esters

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and amides of Shiff bases derived from glycine)⁹, α -acetoxy-, α -phenylthio-, α -dimethylamino- and α -methoxy-N-diphenylmethyleneglycinates¹⁰, N-acyliminomalonates¹¹, chlorinated "bis-lactim ethers"¹² and 2,3,5,6-tetrahydro-4*H*-1,4-oxazin-2-one^{13,14} or its 3-chloro- or 3-bromo- derivatives^{14,15}. With the advent of peptide-derived chemotherapeutics, the synthesis, both, natural non-proteinogenic and unnatural α -amino acids by the functionalization of the glycine α -position with carbon nucleophiles attracts significant attention of organic chemists³.

In our previous paper¹ we described a convenient and effective synthesis of crystalline, stable N-acyl- α -triphenylphosphonioglycinates 1 from 4-triphenylphosphoranylidene-5(4*H*)-oxazolones. We also described a simple method of the substitution of their triphenylphosphonium group by a variety of oxygen, sulphur and nitrogen nucleophiles, demonstrating in this way, that N-acyl- α -triphenylphosphonioglycinates may be considered as a new, interesting cationic glycine equivalent¹. The described transformations enable an easy functionalization of the glycine α -position with heteroatom nucleophiles. In the present paper we want to report the application of N-acyl- α -triphenylphosphonioglycinates for the functionalization of glycine with two kinds of carbon nucleophiles: enolates of activated carbonyl compounds and enamines.

RESULTS AND DISCUSSION

N-Acyl- α -triphenylphosphonioglycinates 1 react easily with β -dicarbonyl compounds 2 in the presence of 1,8-diazabicyclo[5.4.0]undecene (DBU) in acetonitrile at room temperature giving the corresponding α -functionalized glycine derivatives in 53 – 77 % yield (Scheme 1 and Table I).

In the case of ethyl cyanoacetate we obtained the expected mixture of two diastereoisomeric substitution products **4e** merely in 40 % yield; apart from that we isolated a mixture of all the four possible diastereoisomeric by-products **5** (58 %) which are formed probably in result of the reaction of the primary substitution products **4e** with a second molecule of N-acyl- α -triphenylphosphonioglycinate (Scheme 2). It seems, that in this particular case the proton at the α -position in the substrate **2e** is less acidic than the corresponding proton of the product **4e**, due to the electron-withdrawing inductive effect of the acylamino and ethoxycarbonyl groups in **4e**. In consequence, the primary reaction product **4e** is more reactive towards triphenylphosphonioglycinate than the substrate **2e**.





Our attempts to extend the scope of this reaction into simple ketones, e.g. acetone, acetophenone or cyclohexanone, failed; no reaction was observed, probably because of the too low acidity of the protons at the α -position. If, however, a ketone is transformed into the corresponding enamine **3**, the substitution reaction becomes again possible (Scheme 1, Table I). Reactions with enamines run smoothly in the presence of triethylamine at room temperature. After hydrolysis of the primary reaction products with aqueous citric acid we obtained final products, which correspond to the compounds that should be formed in the reaction of N-acyl- α -triphenylphosphonioglycinates with the respective simple ketones.



SCHEME 2

<u> </u>											
ung Salt 1	-	Carbonyl Nucleophile 2 or 3				Reaction product 4		Diastereo-	Elemental analyses (calcd./four		
	No.		R ³	A	time [h]	No.	Yield [%]	isomers ratio	C	Н	
1 <u>0</u>	2a	Ac	Me	_	1.5	4 a	62 ^a	_	61.85/61.82	5.88/5.91	4.8
	2ъ	Ac	Me	-	24	4 b	77	-	52.40/52.45	6.60/6.55	6.
I at	2c	Ac	OEt	-	2.5	4c	53	54:46	59.81/59.64	5.96/5.84	4.3
BF4	2d	EtOCO	OEt	-	1.0	4d	63 ^b	-	58.11/58.32	6.02/6.21	3.9
	2e	CN	OEt	-	1.0	4e	40	52:48	54.92/54.55	7.09/7.27	9.8
I ^{Sity}	3a	-(CH ₂	2)3-	-(CH ₂) ₂ O(CH ₂) ₂ -	1.5	4f	78	65 : 35	61.16/60.74	8.29/8.43	5.4
I Ker	3b	-(CH ₂	2)3-	-(CH ₂) ₄ -	1.5	4f	57	53:47 ^c			
I <u>Ö</u>	3c	-(CH ₂	2)4-	-(CH ₂) ₂ O(CH ₂) ₂ -	1.5	4g	71	90:10	62.43/62.07	8.61/8.74	5.2
A BF₄	3d	-(CH ₂)5-	-(CH ₂) ₂ O(CH ₂) ₂ -	2.0	4h	61	82 : 18	59.73/59.88	7.94/8.21	5.8

 \square ABLE I Reactions of N-acyl- α -triphenylphosphonioglycinates (1) with enolates of carbonyl compounds (2) or enamines (3)

B² –120°C; –<u>6</u>4.5°C; d by comparison with the product obtained from **3a** (IR, ¹H and ¹³C NMR).

The structure of the obtained products was confirmed by their spectral properties (IR, ¹H and ¹³C NMR; cf. Table II and III) as well as by satisfactory results of elemental analyses. In the case of prochiral ethyl acetylacetate, ethyl cyanoacetate and enamines the obtained products **4** were mixtures of two possible diastereoisomers, the ratio of which was determined using ¹H NMR spectroscopy (Table II).

An alternative way of synthesis of N-acyl- α -triphenylphosphonioglycinates by reaction of unstable N-acyl- α -bromoglycinates with triphenylphosphine was mentioned in the paper of Kober and Steglich in 1983¹⁶, however, the authors did not examine the reaction of the obtained compounds with nucleophiles. They proposed an equilibrium between N-acyl- α -triphenylphosphonioglycinate and the corresponding N-acyliminoacetate **6** in the presence of triethylamine¹⁶. In the later works Steglich and co-workers^{4,7} and other authors^{5,6} postulated that the reactions of N-acyl- α -halogenoglycinates with nucleophiles in the presence of triethylamine proceeds *via* the analogous N-acyliminoacetates as intermediates. Therefore, the nucleophilic substitution of the triphenylphosphonium group described here occurs probably *via* the N-acyliminoacetate intermediate **6** (Scheme 3), however further investigations on the mechanism of this reaction seem to be necessary.



SCHEME 3

Summing up, the recently reported easily accessible, stable N-acyl- α -triphenylphosphonioglycinates¹ enable an easy functionalization of the glycine α -position with carbon nucleophiles derived from activated carbonyl compounds or enamines.

n product				
<i>∂R</i> ²	R ³	- 'H-NMR (CDCl y 1MS, δ (ppm))	IR ^a [cm ⁻¹]	
6 Mark	Me	2.22 (s, 3H, COMe ^b), 2.31 (s, 3H, COMe ^b), 3.68 (s, 3H, OMe), 4.55 (d, 1H, $J = 3.9$ Hz, NHCHC <u>H</u>), 5.47 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 3.9$ Hz, NHC <u>H</u>), 7.24 (d, 1H, $J = 9.0$ Hz, NH), 7.30–7.55 (m, 3H, Ph), 7.65–7.75 (m, 2H, Ph)	3442m, 1723vs, 171 1665vs	
22:4 3 2	Me	2.00 (s, 3H, Me), 2.24 (s, 3H, COMe ^b), 2.34 (s, 3H, COMe ^b), 3.72 (s, 3H, OMe), 4.49 (d, 1H, $J = 4.2$ Hz, NHCHC <u>H</u>), 5.33 (dd, 1H, $J_1 = 9.2$ Hz, $J_2 = 4.2$ Hz, NHC <u>H</u>), 6.63 (d, 1H, $J = 9.0$ Hz, NH)	3430m, 1726vs, 171 1678vs	
f York]åt	OEt	1.18–1.33 (m, 3H, CH ₂ CH ₃), 2.34 (s, 3H, COMe ^c), 2.36 (s, 3H, COMe ^d), 3.73 (s, 3H, OMe ^c), 3.74 (s, 3H, OMe ^d), 4.13–4.29 (m, 2H, CH ₂), 4.43 (d, 1H, $J = 4.5$ Hz, NHCHC <u>H</u>), 5.50 (dd, 1H, $J_I = 8.7$ Hz, $J_2 = 4.5$ Hz, NHC <u>H^d</u>), 5.51 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 3.9$ Hz, NHC <u>H^c</u>), 7.38–7.58 (m, 4H, Ph and NH), 7.74–7.83 (m, 2H, Ph)	3439m, 1736vs, 172 1664s	
niversity 0000	OEt	1.22 (t, 3H, $J = 7.1$ Hz, $CH_2CH_3^{e}$), 1.31 (t, 3H, $J = 7.1$ Hz, $CH_2CH_3^{b}$), 3.78 (s, 3H, OMe), 4.18 (q, 2H, $J = 7.1$ Hz, $CH_2CH_3^{e}$), 4.24–4.38 (m, 2H, $CH_2CH_3^{e}$), 4.28 (d, 1H, $J = 4.2$ Hz, NHCHC <u>H</u>), 5.55 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 4.0$ Hz, NHC <u>H</u>), 7.35–7.57 (m, 4H, Ph and NH), 7.77–7.83 (m, 2H, Ph)	3440m, 1739vs, 166 1512s	
ded by 😰	OEt	1.23 (s, 9H, CMe ₃ ^{df}), 1.26 (s, 9H, CMe ₃ ^{cf}), 1.32–1.42 (m, 3H, OCH ₂ CH ₃ ^g), 3.82 (s, 3H, OMe ^c), 3.85 (s, OMe ^d), 4.19–4.40 (m, 3H, NHCHCH+ OCH ₂ CH ₃ ^g), 5.13 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 3.9$ Hz, NHCH ^d), 5.29 (dd, 1H, $J_1 = 7.5$ Hz, $J_2 = 3.9$ Hz, NHCH ^c), 6.59 (d, br, 1H, $J = 8.4$ Hz, NH ^d), 6.63 (d, br, 1H, $J = 7.5$ Hz, NH ^c)	3439m, 3319m, 1750 1681s	
(CH ₂)3-		1.14 (s, 9H, <i>t</i> -Bu ^d), 1.15 (s, 9H, <i>t</i> -Bu ^c), 1.50–2.40 (m, 6H, C ₄ H ₇ CO), 2.48–3.24 (m, 1H, NHCHC <u>H</u> ^c), 2.85 (ddd, 1H, $J_1 = 11.3$ Hz, $J_2 = 8.4$ Hz, $J_3 = 4.5$ Hz, NHCHC <u>H</u> ^d), 3.65 (s, 3H, OMe ^c), 3.70 (s, 3H, OMe ^d), 4.74 (dd, 1H, $J_1 = 7.5$ Hz, $J_2 = 4.2$ Hz, NHC <u>H</u> ^d), 4.80 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, NHC <u>H</u> ^c), 6.32 (d, 1H, $J = 7.5$ Hz, NH ^d), 7.00 (d, 1H, $J = 8.1$ Hz, NH ^c)	3440m, 1751vs, 173 1665vs	

TABLE II ¹H NMR and IR spectral data of the N-acyl-α-aminoacid methyl esters synthesised

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n groduct	R ³	¹ H-NMR (CDCl ₃ /TMS, δ (ppm))	IR ^a [cm ⁻¹]
at 22:43 2 -		1.20 (s, 9H, <i>t</i> -Bu ^c), 1.22 (s, 9H, <i>t</i> -Bu ^d), 1.40–2.40 (m, 8H, C ₅ H ₉ CO), 2.78 (m, 1H, NHCH-CH ^c), 3.32 (ddd, 1H, $J_I = 13.2$ Hz, $J_2 = 5.1$ Hz, $J_3 = 3.1$ Hz, NHCHCH ^d), 3.70 (s, 3H, OMe ^d), 3.72 (s, 3H, OMe ^c), 4.53 (dd, 1H, $J_I = 8.1$ Hz, $J_2 = 3.8$ Hz, NHCH ^e), 4.74 (dd, 1H, $J_I = 9.6$ Hz, $J_2 = 3.0$ Hz, NHCH ^d), 6.55 (d, 1H, $J = 9.3$ Hz, NH ^d), 6.67 (d, 1H, $J = 8.1$ Hz, NH ^c)	3460m, 1744s, 1732 1706vs, 1660vs
CH2)5-		1.13–2.02 (m, 8H, $C_7H_{10}CO$), 2.02 (s, 3H, Me ^c), 2.05 (s, 3H, Me ^d), 2.30–2.66 (m, 2H, $C_7H_{10}CO$), 2.92–3.02 (m, 1H, NHCHC <u>H</u> ^c), 3.45–3.56 (m, 1H, NHCHC <u>H</u> ^d), 3.69 (s, 3H, OMe ^d), 3.72 (s, 3H, OMe ^c), 4.64 (dd, 1H, $J_I = 8.1$ Hz, $J_2 = 4.2$ Hz, NHC <u>H</u> ^c), 4.90 (dd, 1H, $J_I = 9.8$ Hz, $J_2 = 3.9$ Hz, NHC <u>H</u> ^d), 6.03 (d, 1H, $J = 8.4$ Hz, NH ^c), 6.54 (d, 1H, $J = 9.7$ Hz, NH ^d)	3439m, 1750vs, 173 1680vs
ACHCla inSchereoizo astereoizo toppic CH assignmer magpuolumo nagpuolumo	; omer; omer; 2 gro nt als s of b	ups; o possible; oth diastereoizomers.	

\mathbf{c}					
Product 201				¹³ C-NMR (CDCl ₃ /TMS, δ (ppm)) ^a	
HURCHR ² R ³	<u>С</u> ООМе	ОМе	NHCH <u>C</u>	R ¹	Other carbons
50.9 50.9	170.4	53.2	66.7	127.2, 128.7, 132.2, 133.1 (Ph: C_3, C_2, C_4, C_1)	30.2, 30.4 (CO <u>Me^b</u>); 203.3, 205.0 (<u>C</u> OMe ^d)
⁷ .50.3	170.4	53.1	66.7	23.0 (Me)	30.2, 30.1 (CO <u>Me^b</u>); 203.3, 204.7 (<u>C</u> OMe ^d)
² 3:14 ^e	170.4 ^e	53.1 ^e	59.5 ^e	127.18, 128.8, 128.9, 132.0 (Ph: C ₄ , C ₂ , C ₃ , C ₁ ^e); 127.21, 128.6, 128.3, 132.1 (Ph:	13.94 ^e , 13.99 ^f (OCH ₂ CH ₃); 29.79 ^f , 29.97 ^e (C 62.0 ^f , 62.2 ^e
¹⁰ 51.1 ^f	170.3 ^f	53.2 ^f	59.7 ^f	$C_2, C_3, C_4, C_1^{(1)}$	(OCH ₂ CH ₃); 167.5 ^e , 168.5 ^f (COOEt ⁸); 201.4 203.4 ^e (COMe)
⁰ A 151.4	170.1	53.1 ⁱ	53.1 ⁱ	127.2, 128.7, 132.0, 133.6 (Ph: C_3, C_2, C_4, C_1)	13.95, 13.99 (OCH ₂ CH ₃ ^b); 62.16, 62 26 (OCH ₂ CH ₃ ^c); 166.9, 168.3 (COOEt ^{dh})
°.⊒50.5°	167.5 ^e	52.5 ^{ej}	63.2 ^e	26.25 (<u>Me₃C^e); 39.0 (Me₃C^e)</u>	12.8 ^f , 12.9 ^e (OCH ₂ CH ₃); 62.48 ^e , 62 55 ^f
∑50.6 ^f	167.6 ^f	52.5 ^{fj}	63.1 ^f	26.21 (<u>Me₃C^f</u>); 39.2 (Me ₃ <u>C^f</u>)	$(OCH_2CH_3); 112.8 (C=N^2); 163.0 (COOEt^2)$
ຊີ ຊີ 50.8 °	170.4 ^e	51.5 ^e	49.5 ^e	26.33 (<u>Me₃C^e);</u> 37.7 (Me ₃ <u>C^e)</u>	21.2, 25.46, 37.2, 219.6 (C ₄ H ₇ CO: C ₅ , C ₄ , C
900 49.9 ^f	170.6 ^f	51.6 ^f	50.4 ^f	26.39 (<u>Me₃C^f);</u> 37.8 (Me ₃ C ^f)	20.9, 25.42, 36.9, 218.1, (C ₄ H ₇ CO: C ₅ , C ₄ , C
¹ ¹ ¹ ¹ ¹ ¹ ¹ ¹	170.7 ^{ie}	51.5 ^e	53.3 ^e	26.35 (<u>Me₃C^e);</u> 37.5 (Me ₃ <u>C^e)</u>	25.7, 30.2, 37.5, 40.7, 211.2 (C ₅ H ₉ CO: C ₅ , C C ₃ , C ₂ ^e)

TABLE III ^{13}C NMR spectral data of the N-acyl- $\alpha\text{-aminoacid}$ methyl esters synthesised

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Product				¹³ C-NMR (CDCl ₃ /TMS, δ (ppm)) ^a		
	<u>Ç</u> OOMe	e OMe NHCH <u>C</u>		R ¹	- Other carbons	
€ 50.4 ^f 7 7 7 7 7 7 7 7 7 7 7 7 7	170.7 ^{if}	51.2 ^f	51.9 ^f	26.32 ($\underline{Me_3C^f}$); 37.7 ($Me_3\underline{C^f}$)	23.7, 26.5, 30.0, 41.0, 211.2 (C ₅ H ₉ CO: C ₅ , C ₇ , C ₃ , C ₂ ^f)	
ਟੂ ਸ਼ੂ53.7 ^f ਤ੍ਰਿ	170.6 ^f	52.7 ^{fk}	52.6 ^{fk}	23.2 (Me ^f)	23.4, 28.3, 29.3, 29.4, 43.5, 216.1 (C ₇ H ₁₀ CO: C ₆ , C ₅ , C ₄ , C ₃ , C ₂ ^f)	
topic Me gro topic CH ₂ g topic CH ₂ g topic carbon stereoizome stereoizone stereoizome	r; r; r; so possibl so possibl s; both diaste lso possibl	e; e; reoizon e.	ieris;			

EXPERIMENTAL

General

M. p.'s, determined in capillary tubes, are uncorrected. IR spectra were recorded on a Zeiss Specord M 80 spectrophotometer; the measurements were carried out in CHCl₃ (0.2 *M*) using cells of 0.075 mm. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Varian UNITY INOVA-300 spectrometer at operating frequencies of 300 and 75.5 MHz, respectively, in the FT mode using TMS as an internal standard. The yields of isolated products given were not optimised.

Starting materials

N-Acyl- α -triphenylphosphonioglycinates were synthesised as previously described¹. Commercial grade acetonitrile was distilled and dried over molecular sieves 4A. Kieselgel 60 Merck (0.063–0.200 mm) was used for column chromatography. The other reagents were of commercial quality.

Reaction of N-acyl- α -triphenylphosphonioglycinates (1) with carbonyl compounds (2); General procedure

A solution of carbonyl compound 2 (20 mmol) and DBU (1.78 ml, 12 mmol) in acetonitrile (16.0 ml) was added dropwise to a stirred solution or suspension of N-acyl- α -triphenylphosphonioglycinate 1 (10 mmol) in acetonitrile (24.0 ml). The mixture was stirred at room temperature for the time given in Table I and the solvent was removed under reduced pressure. The pure product was isolated by column chromatography on silica gel (90 ml) eluting with a mixture of ethyl acetate and benzene in a volume ratio of 1:10 or 1:5. Crystalline products 4 were recrystallised from a mixture of benzene and hexane.

Reaction of N-acyl- α -triphenylphosphonioglycinates (1) with enamines (3); General procedure

A solution of enamine 3 (20 mmol) and triethylamine (1.67 ml, 12 mmol) in acetonitrile (16.0 ml) was added dropwise to a stirred solution or suspension of N-acyl- α -triphenylphosphonioglycinate 1 (10 mmol) in acetonitrile (24.0 ml). The mixture was stirred at room temperature for the

time given in Table I, after that aqueous citric acid (45 ml, 20%) was added, the mixture was stirred at room temperature for 1 h and then neutralised with saturated aqueous sodium hydrogen carbonate. The product was extracted with CH_2Cl_2 (4 × 25 ml), the organic phase was dried with MgSO₄ and evaporated under reduced pressure. The pure product **4** was isolated by column chromatography on silica gel (90 ml) eluting with ethyl acetate or a mixture of ethyl acetate and benzene in a volume ratio of 1:2.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (Grant No 3T09A 114 16). The financial help is gratefully acknowledged.

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