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Thermogravimetrical investigations of the dealkoxycarbonylation of *N*-acyl-α-triphenylphosphonioglycinates

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ABSTRACT

Thermogravimetrical experiments revealed that immediately after the endothermic process of the melting of *N*-acyl-α-triphenylphosphonioglycinates **1**, an exothermic demethoxycarbonylation of phosphonioglycinates commenced, accompanied by the release of CO_2. The residues contained the corresponding *N*-acylaminomethyltriphenylphosphonium salts **2** (18.3–49.5%), methyltriphenylphosphonium salts **7** (21.8–67.9%), and the corresponding 1,2-di(*N*-acylamino)fumaric acid dimethyl ester **6** (2.1–26.0%). When the reaction was carried out in the presence of Ph_3P and the corresponding triphenylphosphine hydrobromide, hydroiodide, or tetrafluoroborate, *N*-acyl-α-triphenylphosphoniumglycinate bromides and iodides **1a–f** underwent demethoxycarbonylation to form the corresponding *N*-acylaminomethyltriphenylphosphonium salts **2a–f** at 95–130 °C in good to excellent yields (79–100%). On the other hand, tetrafluoroborates **1g–i** underwent corresponding reactions at about 170–175 °C to give phosphonium tetrafluoroborates **2g–i** in much lower yields (34–67%). Plausible mechanisms of the investigated reaction are discussed. It was also demonstrated that the obtained crude α-(*N*-acylamino)alkyltriphenylphosphonium salts **2** could be applied as valuable α-amidoalkylating agents in spite of their contamination with inert methyltriphenylphosphonium salts **7**.

1. Introduction

A few years ago, we developed the effective synthesis of a new class of α-amino acid derivatives—*N*-acyl-α-triphenylphosphonioglycinates **1**. These compounds were applied to organic synthesis as new valuable cationic glycine equivalents and precursors of phosphorus ylides which were used in the Wittig reaction to synthesise α,β-dehydro-α-amino acids [1,2]. *N*-Acyl-α-triphenylphosphonioglycinates **1** are crystalline compounds and usually melt with decomposition over 130 °C. Our preliminary investigation on the decomposition of methyl *N*-pivaloyl-α-triphenylphosphoniumglycinate bromide **1** (R^1 = *t*-Bu, R^2 = Me, X = Br) using ^{1}H NMR analysis revealed that the residue following decomposition contained *N*-pivaloylaminomethyltriphenylphosphonium bromide **2** (R^1 = *t*-Bu, X = Br) as the main product, which was formed in a yield of 35% (Scheme 1).

A similar dealkoxycarbonylation of activated esters, for example malonates, β-ketoesters, α-cyanoesters, α-nitroesters or α-sulfonylesters in the presence of water and inorganic salts in DMSO or DMF, are of considerable importance in organic synthesis. This process is known as the Krapcho reaction or Krapcho dealkoxycarbonylation (Scheme 2) [3]. An analogous dealkoxycarbonylation of α-phosphonioesters (**3**, X = PR_3^+ Y^-), including *N*-acyl-α-triphenylphosphonioglycinates **1**, is to date unknown.

The aim of this work was to investigate the nature of this new type of thermal dealkoxycarbonylation of *N*-acyl-α-triphenylphosphonioglycinates **1** by means of thermogravimetry with online analysis of gaseous decomposition products by FTIR spectrometry. Another aim of our work was to apply this method as a new way to synthesise of α-(*N*-acylamino)alkyltriphenylphosphonium salts **2**. Recently, we have demonstrated that *N*-acylaminomethyltriphenylphosphonium salts **2** are novel precursors of *N*-acylimines and reactive amidoalkylating agents that offer numerous applications in organic synthesis [4].

2. Experimental

2.1. General

Melting points are uncorrected and were determined in capillary tubes using a Stuart Scientific SMP3 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian

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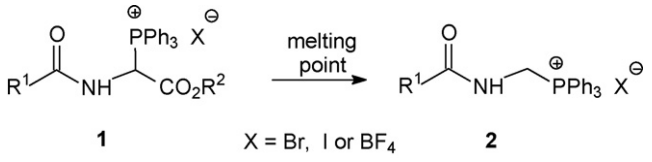
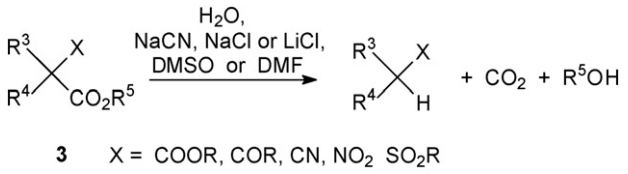


Scheme 1.



Scheme 2.

UNITY INOVA-300 spectrometer at operating frequencies of 300 or 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.

2.2. Thermogravimetric measurements

Thermogravimetric measurements were made with a Mettler Toledo thermobalance (Star 851, LF/1100) using standard platinum crucibles (150 μl) and sample size of 11–18 mg. Samples were heated at a rate of 5 °C min^{-1} from 25 to 200 or 300 °C with a nitrogen flow of 50 ml min^{-1}. Spectra of gaseous products were recorded online in a Thermo Electron Corporation FTIR spectrometer (Nicolet 6700) with external interface module Nicolet X700 connected to the thermobalance by a heated quartz capillary. Homogeneous mixtures of *N*-acyl-α-triphenylphosphonioglycinates, triphenylphosphine and triphenylphosphine hydrohalides or tetrafluoroborates were prepared by the dissolution of *N*-acyltriphenylphosphonioglycinate **1** (0.1 mmol) and other components in a proper ratio (see Table 2) in chloroform (0.7 cm^3). Evaporation of the solvent and the drying of the residue were carried out at 25 °C under reduced pressure (1–2 mm Hg) for 60 min.

2.3. Dealkoxycarbonylations monitored by ^{1}H NMR

N-acyl-α-triphenylphosphonioglycinate **1** (0.05 mmol) or a mixture of *N*-acyl-α-triphenylphosphonioglycinate **1** (0.1 mmol) triphenylphosphine and triphenylphosphine hydrohalides or tetrafluoroborates in a proper ratio (see Table 2) were dissolved in chloroform (0.7 cm^3). The solvent was then evaporated and the residue was dried at 25 °C under reduced pressure (1–2 mm Hg) for 60 min. The dry residue was heated in an oil bath at reduced pressure (see Table 2). The composition of the obtained mixture was monitored using ^{1}H NMR

2.4. Synthesis and purification of α-(N-benzoylamino) methyltriphenylphosphonium bromide **2c**

A mixture of methyl *N*-benzoyl-α-triphenylphosphoniumglycinate bromide **1c** (0.418 g, 0.781 mmol), triphenyphosphine (0.102 g, 0.389 mmol) and triphenylphosphine hydrobromide (0.295 g, 0.859 mmol) was dissolved in chloroform (1 cm^3). The solvent was evaporated to dryness and the residue was heated at 115 °C under reduced pressure (1–2 mm Hg) for 1.5 h. After crystallisation using CH_2Cl_2/Et_2O (1:2, v/v), a crystalline substance containing 0.266 g of the expected product (71.5%) and about 0.030 g of methyltriphenylphosphonium bromide (estimated by ^{1}H NMR) was obtained. After purification by column chromatography and recrystallisation from CH_2Cl_2/Et_2O (1:1, v/v) the pure product was obtained.

2c: yield 71.5%, m.p. 227–229 °C, (lit. [5]: 234–236 °C). ^{1}H NMR (δ, ppm): 10.0 (t, 1H, *J* = 5.4 Hz, N**H**), 7.92–7.30 (m, 20H, arom.), 5.41 (dd, 2H, J_1 = 5.8 Hz, J_2 = 2.5 Hz, C**H$_2$**P$^+$Ph$_3$); ^{13}C NMR (δ, ppm): 168.1 (**C**ONH), 134.9 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 10.0 Hz), 129.9, 117.5 (d, *J* = 83.9 Hz) (Ph$_3$P$^+$), 38.2 (d, *J* = 55.5 Hz, P$^+$**C**H$_2$), 132.0, 130.0, 128.3, 127.7 (Ph) lit. [5]: ^{1}H NMR (δ, ppm): 9.96 (t, 1H), 8.0–7.5 (m, 17H), 7.40–7.28 (m, 3H), 5.41 (dd, 2H, J_1 = 6.0 Hz, J_2 = 3.0 Hz, C**H$_2$**P$^+$Ph$_3$).

2.5. Synthesis of α-(N-acetylamino)methyltriphenylphosphonium iodide **2d** and its transformation to dimethyl α-(N-acetylamino)methylphosphonate **9**

A mixture of methyl *N*-acetyl-α-triphenylphosphoniumglycinate iodide **1d** (0.407 g, 0.783 mmol), triphenylphosphine (0.102 g, 0.389 mmol) and triphenylphosphine hydroiodide (0.337 g, 0.863 mmol) was dissolved in chloroform (1 cm^3). The solvent was then evaporated to dryness and the residue was heated at 110 °C under reduced pressure (1–2 mm Hg) for 2 h. After recrystallisation of the residue using CH_2Cl_2/Et_2O (1:2, v/v), a crystalline substance (0.707 g) containing the expected product **2d** (0.322 g, 89%), methyltriphenylphosphonium iodide (0.348 g) and only 0.037 g of triphenylphosphine (estimated by ^{1}H NMR) was obtained. Synthesis of dimethyl α-(*N*-acetylamino)methylphosphonate **9** was carried out in a glass vial sealed with a screw-cap. Trimethylphosphite (0.061 cm^3, 64.2 mg, 0.52 mmol) and (*i*-Pr)$_2$EtN (0.006 cm^3, 4.4 mg, 0.034 mmol) were added to a solution of the crystalline substance obtained as described above (0.349 g) in CH_2Cl_2 (0.6 cm^3), contained α-(*N*-acetylamino)methyltriphenylphosphonium iodide **2d** (0.159 g, 0.345 mmol). The mixture was heated at 60 °C for 28 h, and the solvent was then evaporated under reduced pressure. The residue was extracted with toluene, and the toluene was subsequently evaporated. The crude product (50 mg) was purified by column chromatography (CH_2Cl_2/MeOH, 20:1) to obtain the pure product as a thick oil (34.5 mg).

9: yield 55%, oil. ^{1}H NMR (δ, ppm): 6.71 (br, 1H, N**H**), 3.79 (d, 6H, *J* = 5.4 Hz, OC**H$_3$**), 3.74 (dd, 2H, J_1 = 11.7 Hz, J_2 = 5.7 Hz, C**H$_2$**P), 2.04 (d, 3H, *J* = 0.9 Hz, C**H$_3$**C=O); ^{13}C NMR (δ, ppm): 170.1 (**C**ONH), 53.0 (O**C**H$_3$), 33.7 (d, *J* = 157 Hz, P**C**H$_2$), 22.8 (**C**H$_3$C=O) lit. [6]: ^{1}H NMR (δ, ppm): 7.60 (br, 1H, N**H**), 3.78 (d, 6H, *J* = 11.0 Hz, OC**H$_3$**), 3.65 (d, 2H, *J* = 12.0 Hz, C**H$_2$**P), 2.02 (s, 3H, C**H$_3$**C=O).

3. Results and discussion

Fig. 1 shows TG, DTG and SDTA curves for demethoxycarbonylation of methyl *N*-acetyl-α-triphenylphosphoniumglycinate bromide **1a**, methyl *N*-acetyl-α-triphenylphosphoniumglycinate iodide **1d** and methyl *N*-acetyl-α-triphenylphosphoniumglycinate tetrafluoroborate **1g**.

Thermogravimetrical experiments revealed that immediately after the endothermic process of the melting of phosphonium salts, an exothermic demethoxycarbonylation of phosphonioglycinates started, which was accompanied by the release of CO_2 and a loss of 9.5, 9.5, and 12.5% mass, respectively. The calculated values corresponding to the loss of one CO_2 molecule are equal to 9.3, 8.5 and 9.2%, respectively (see Fig. 1). The highest concentration of CO_2 in a nitrogen stream was detected almost exactly at the same time as the DTG curves achieved the minimum value. The experiments were repeated on a larger scale (0.1 mmol of salts **1a**, **1d** and **1 g**) in a glass flask. Samples of phosphonium salts were heated in an oil bath at the temperature that produced the most rapid weight-loss (145, 135 and 215 °C, respectively) under reduced pressure (1 mm Hg) for

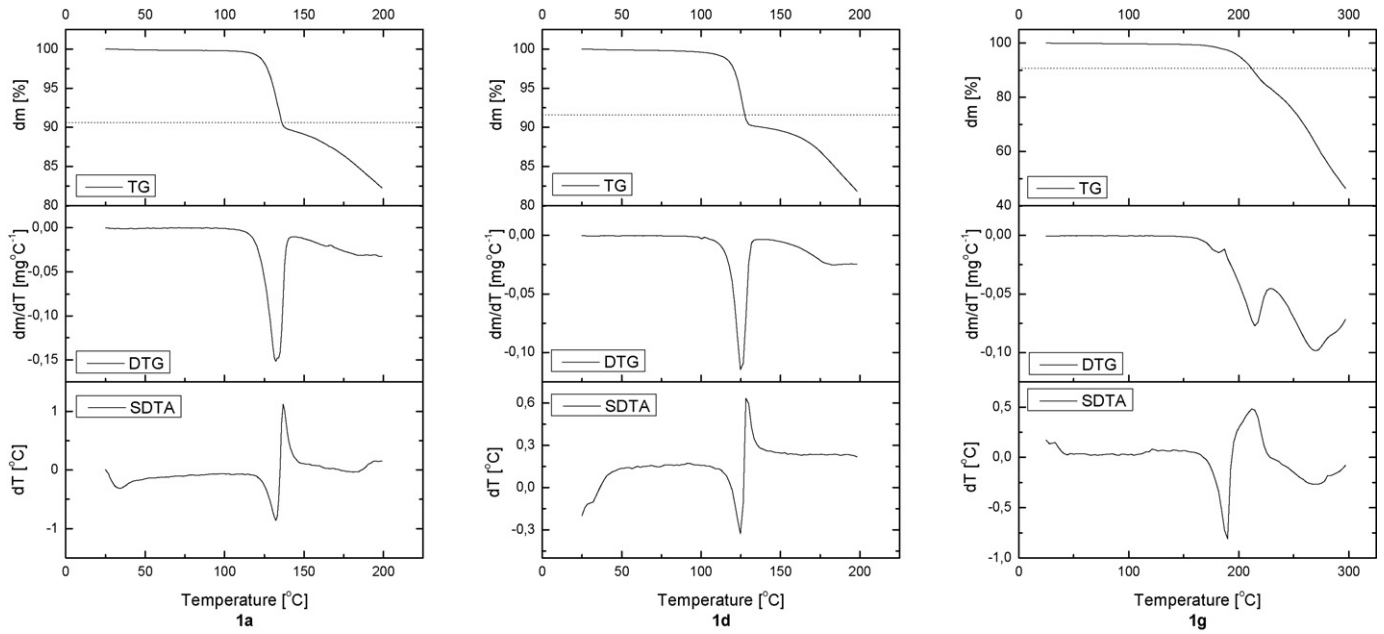
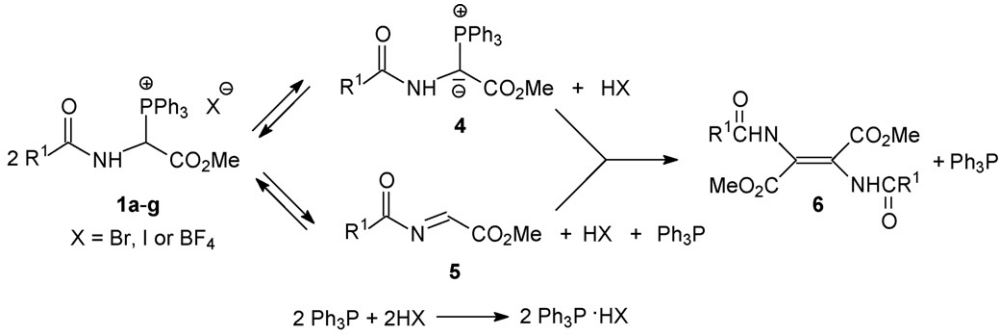


Fig. 1. TG, DTG and SDTA curves for demethoxycarbonylation of methyl *N*-acetyl-α-triphenylphosphoniumglycinate bromide **1a** (17.6 mg), iodide **1d** (11.2 mg) and tetrafluoroborate **1g** (14.2 mg). The theoretical loss of mass corresponding to the loss of one CO_2 molecule (dotted lines on TG-curves) 9.3, 8.5 and 9.2%, respectively.

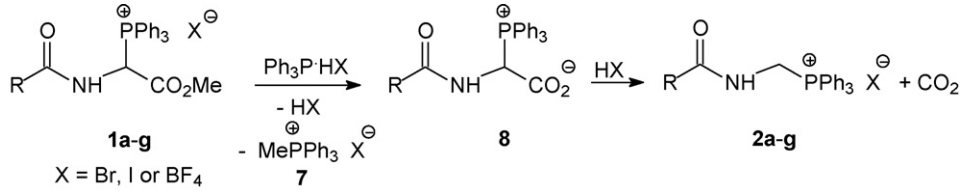
Table 1
Results of demethoxycarbonylation of *N*-acyl-α-triphenylphosphonioglycinates.

Phosphonium salt **1**						Dealkoxycarbonylation conditions and results					
Entry	No	R^1	R^2	X	M.p.[a] (°C)	Dec. temp.[b] (°C)	Time (h)	Temp. (°C)	Yields of reaction products (%)		
									2	**6**	**7**
1	**1a**	Me	Me	Br	132	135	0.5	140–150	49.5	19.4	37.2
2	**1b**	*t*-Bu	Me	Br	115–116	–	0.5	120	34.5	22.9	21.8
3	**1c**	Ph	Me	Br	152–154	–	0.5	155	27.0	2.9	55.4
4	**1d**	Me	Me	I	126–127	125	0.5	135	44.7	26.0	40.9
5	**1e**	*t*-Bu	Me	I	138–139	140	0.5	145–150	38.1	–	52.0
6	**1f**	Ph	Me	I	137–138	135	0.5	130–150	28.2	4.9	67.9
7	**1g**	Me	Me	BF_4	193–194	215	0.5	215	18.3	2.1	59.8

[a] Determined using Bibby Stiriling type SMP 3 apparatus.
[b] Temperature of the minimum of a DTG curve.



Scheme 3.



Scheme 4.

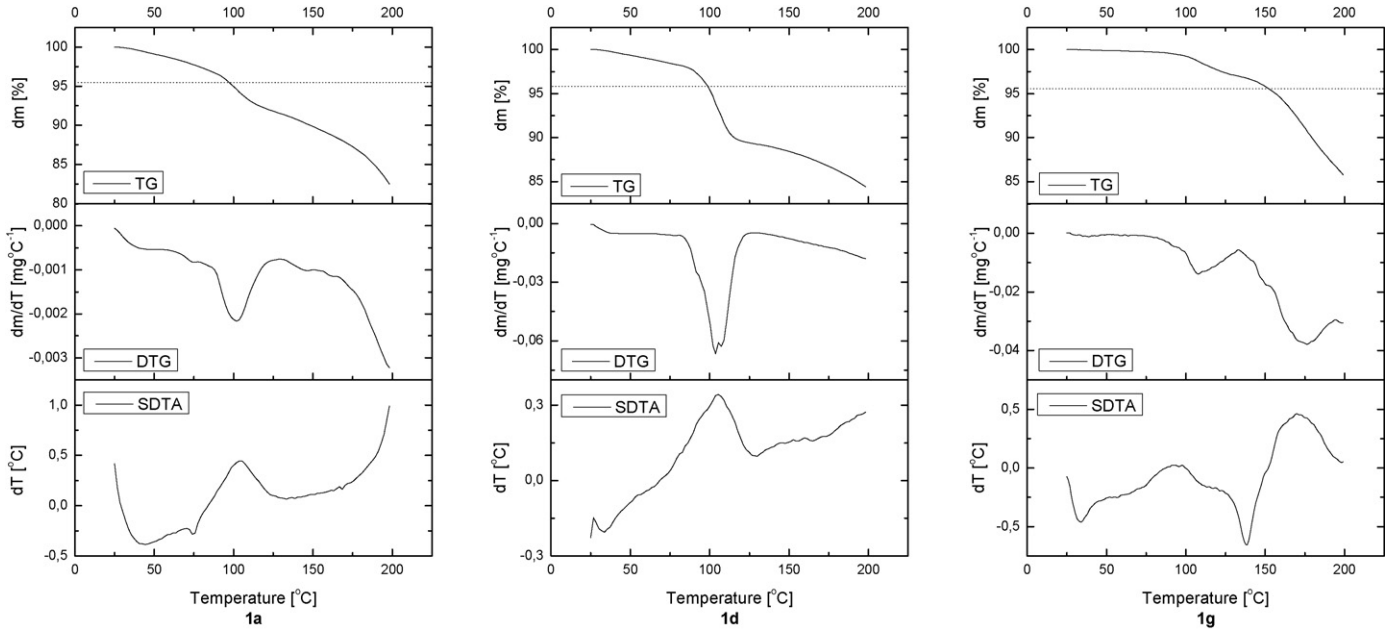


Fig. 2. TG, DTG and SDTA curves for demethoxycarbonylation of methyl *N*-acetyl-α-triphenylphosphoniumglycinate bromide **1a**, iodide **1d** and tetrafluoroborate **1g** in the presence of the corresponding triphenylphosphine hydrohalide or tetrafluoroborate and triphenylphosphine. Samples weight: 13.4, 14.9 and 15.1 mg, respectively. The theoretical loss of mass corresponding to the loss of one CO_2 molecule (dotted lines on TG-curves) 4.5, 4.1 and 4.4%, respectively.

30 min (Table 1). The composition of the residues were determined by means of ^{1}H and ^{13}C NMR and were found to contain the corresponding *N*-acylaminomethyltriphenylphosphonium salts **2a**, **2d** or **2g** obtained in yields of 49.5, 44.7 and 18.3%, respectively, methyltriphenylphosphonium bromide, iodide or tetrafluoroborate **7** (37.2, 40.9 and 59.8%) and, unexpectedly, the corresponding 1,2-di(*N*-acylamino)fumaric acid dimethyl ester **6** (19.4, 26.0 and 2.1%). Very similar results were obtained for other methyl *N*-acyl-α-triphenylphosphoniumglycinate bromides and iodides **1b**–**f** (Table 1). The structure of the obtained compounds **(2a**–**b**, **2d**–**i** and **7a**–**c)** was determined by comparison of ^{1}H and ^{13}C NMR spectra with the spectra of authentic samples of these compounds that were previously described (see Supplementary data) [5,7–13]. It seems that the stoichiometry of the investigated process can be formulated as shown in Schemes 3 and 4.

A few years ago, we described the formation of 1,2-diaminofumaric acid derivatives **6** by condensation of two molecules of methyl *N*-acyl-α-triphenylphosphonioglycinates **1** in the presence of a basic catalyst (Et_3N or DBU) at room temperature in CH_2Cl_2 [14]. We have proven that this reaction consists in the condensation of two intermediates: nucleophilic ylide **4** and electrophilic iminoacetic acid derivative **5** [14]. Here, we first report the thermal condensation of triphenylphosphonioglycinates **1** to form fumaric acid derivatives **6** (Scheme 3). Interestingly, that two molecules of triphenylphosphine and two molecules of hydrogen halide, formed in this reaction as by-products, (Scheme 3) effect demethylation and consecutive decarboxylation of two molecules of triphenylphosphonioglycinate **1**, eventually providing *N*-acylaminomethyltriphenylphosphonium halides **2**, methyltriphenylphosphonium halides **7**, and CO_2 (Scheme 4). Some other transformations of reactive ylide **4** and iminoacetic acid derivative **5** are also possible, as yields of fumaric acid derivatives **6** are too low as compared to yields of phosphonium salts **2**. According to the suggested stoichiometry of this reaction (Schemes 3 and 4), the yield of *N*-acylaminomethyltriphenylphosphonium halides **2** cannot exceed 50%.

To support the proposed mechanism of the investigated reactions and to improve their yields, a similar set of thermogravimetric demethoxycarbonylation experiments were carried out in the presence of the corresponding triphenylphosphine hydrohalide or tetrafluoroborate ($Ph_3P{\cdot}HX$) and triphenylphosphine (Ph_3P) at the molar ratio of the methyl *N*-acyl-α-triphenylphosphoniumglycinate salt **1**:$Ph_3P{\cdot}HX$:Ph_3P = 1:1.1:0.5. The stoichiometry of the reaction shown in Scheme 4 requires solely one molecule of $Ph_3P{\cdot}HX$ per molecule of methyl triphenylphosphonioglycinate **1**. Nevertheless, free triphenylphosphine was used in this reaction as an active nucleophile, which can be considered as a catalyst for the demethylation reaction. The reaction mixtures were made homogeneous by dissolution of the all substrates in chloroform, and the subsequent evaporation of the solvent. The endothermic melting process of these prepared reaction mixtures was only noticeable on the SDTA curves for tetrafluoroborates **1g** and **1h**, at about 140 and 130 °C, respectively. That is, the other reaction mixtures had no sharp, specific melting points (cf. Fig. 2). Contrastingly, the exothermic demethoxycarbonylation reaction effect was clearly visible on the SDTA curves for all methyl *N*-acyl-α-triphenylphosphonioglycinates **1a**–**i** (cf. Fig. 2). The highest intensity of CO_2 release was again detected when DTG curves achieved their minimum value. The temperatures, at which the decarboxylation of glycinates **1a**–**i** achieved the highest intensity was not related to the melting points of these compounds, but depended strongly on the type of the counterion of the phosphonium salts. Phosphonium bromides and iodides **1a**–**f** underwent demethylation and decarboxylation in the temperature range of 95–130 °C, whereas tetrafluoroborates underwent these reactions at much higher temperatures (170–175 °C).

^{1}H NMR analyses of the residues after demethoxycarbonylation reactions that were carried out on a larger scale (0.1 mmol of **1**) revealed that phosphonium bromides and iodides **1a**–**f** were transformed into the corresponding *N*-acylaminomethyltriphenylphosphonium salts **2a**–**f** in good to excellent yield in these conditions (79–100%). The residues also contained the corresponding methyltriphenylphosphonium halides **7**, formed in 45–100% yield, whereas the formation of 1,2-di(*N*-acylamino)fumaric acid dimethyl esters **6** did not exceed a few percent yield (Table 2). The yields of *N*-acylaminomethyltriphenylphosphonium tetrafluoroborates **2g**–**i**

Table 2
Results of demethoxycarbonylation of *N*-acyl-α-triphenylphosphonioglycinates in the presence of the corresponding triphenylphosphine hydrohalide or tetrafluoroborate and triphenylphosphine.

Phosphonium salt **1**						Dealkoxycarbonylation conditions and results[c]					
Entry	No	R^1	R^2	X	M.p.[a] (°C)	Dec. temp.[b] (°C)	Time (h)	Temp. (°C)	Yields of reaction products (%)		
									2	**6**	**7**
8	**1a**	Me	Me	Br	132	95	1	100–115	98.6	–	87.0
9	**1b**	*t*-Bu	Me	Br	115–116	120	1.5	120	78.7	4.4	44.5
10	**1c**	Ph	Me	Br	152–154	110	1	110–120	89.1	6.2	81.0
11	**1d**	Me	Me	I	126–127	105	1.5	110	100	–	100
12	**1e**	*t*-Bu	Me	I	138–139	125	1.5	120–130	100	–	80.2
13	**1f**	Ph	Me	I	137–138	130	1.5	120–130	100	–	79.9
14	**1g**	Me	Me	BF_4	193–194	170	1.5	175	64.6	–	69.9
15	**1h**	*t*-Bu	Me	BF_4	172–173	170	1	175–180	34.2	–	91.8
16	**1i**	Ph	Me	BF_4	176–178	175	1	175–180	67.3	5.4	99.4
17	**1j**	Me	Et	BF_4	196–200	221	1.5	225	5.6	–	25.1[d]

[a] Determined using Bibby Stiriling type SMP 3 apparatus.
[b] Temperature of the minimum of a DTG curve.
[c] Molar ratio of **1**:$Ph_3P{\cdot}HX$:Ph_3P = 1:1.1:0.5.
[d] Ethyltriphenylphosphonium salt.

obtained from the corresponding phosphonium tetrafluoroborates **1g–i** at 175 °C were much lower (34–67%, Table 2).

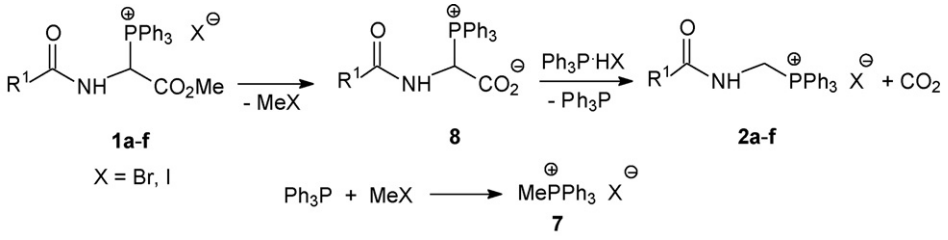
The differing behaviour between phosphonium bromides and iodides **1a–f** in comparison with phosphonium tetrafluoroborates **1g–i** in the investigated reactions can be explained if in the first case, the demethylation of methyl glycinates consists of attack of nucleophilic bromide or iodide anions on the methyl group via a S_N2 reaction, followed by methylation of triphenylphosphine with methyl bromide or methyl iodide (Scheme 5). Therefore, bromide or iodide anions may act as nucleophilic catalysts in this reaction.

On the other hand, the non-nucleophilic tetrafluoroborate anion cannot be involved in demethylation of triphenylphosphonioglycinates **1g–i**. Thus, in this case, the demethoxycarbonylation is probably initiated by direct attack of triphenylphosphine on the methyl group, which requires a much higher temperature due to steric bulk of a triphenylphosphine molecule (Scheme 6).

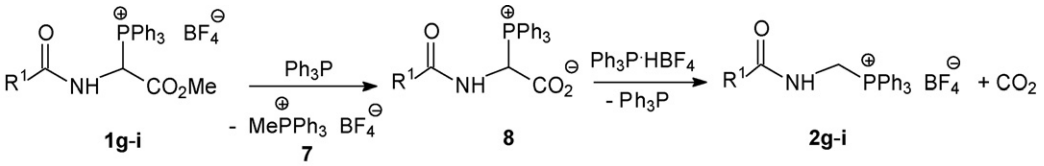
The significant impact of steric effects on the dealkylation step of the investigated reaction was demonstrated by thermogravimetrical experiments with participation of the ethyl *N*-acetyl-α-triphenylphosphoniumglycinate tetrafluoroborate **1j** (R^1 = Me, R^2 = Et, X = BF_4). According to resulting DTG curves, the decomposition of the ethyl triphenylphosphonioglycinates **1j** achieved their maximum intensity at ca. 220 °C, which are much higher temperatures as compared to the analogous methyl ester (175 °C). Therefore, branching at the α carbon of the alkoxy group hinders a triphenylphosphine molecule from the approach to this carbon atom, increasing the decomposition temperature of the investigated compounds.

In accordance with thermogravimetrical data, the best results of syntheses of α-(*N*-acylamino)alkyltriphenylphosphonium salts **2** by the dealkoxycarbonylation of *N*-acyl-α-triphenylphosphonioglycinates **1** could be effected starting with methyl *N*-acyl-α-triphenylphosphoniumglycinate bromides or iodides.

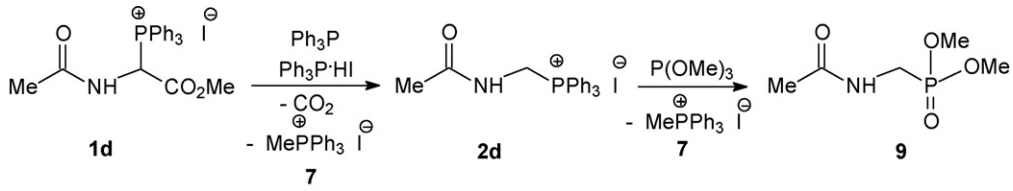
To demonstrate a practical usefulness of this reaction, we carried out the synthesis of α-(*N*-benzoylamino)methyltriphenylphosphonium bromide **2c** on a larger scale (0.8 mmol of **1c**) and isolated this compound in high purity and good yield (71.5%). We have also synthesised α-(*N*-acetylamino)methyltriphenylphosphonium iodide **2d** and, after preliminary crystallisation, we used the crude product for the synthesis of dimethyl α-(*N*-acetylamino)methylphosphonate **9** to obtain the final product in 55% yield (Scheme 7). Therefore, it was demonstrated that for practical purposes, the accurate purification of α-(*N*-acylamino)methyltriphenylphosphonium salts **2** is not necessary because the main by-product of this reaction,



Scheme 5.



Scheme 6.



Scheme 7.

methyltriphenylphosphonium salt **7**, can be considered, as an inert contaminant.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.08.017.

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