Tritylamine (triphenylmethylamine) in organic synthesis; III. The synthesis of 1-aminoalkylphosphonic acids in the reaction of *N*-(triphenylmethyl)alkanimines with phosphorus trichloride in acetic acid or with phosphonic (phosphorous) acid in acetic anhydride

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Abstract
The reaction of phosphorus trichloride in acetic acid or phosphonic (phosphorous) acid in acetic anhydride, with *N*-(triphenylmethyl)alkanimines gives 1-acetylaminoalkylphosphonic acids **1a-j**, which after hydrolysis give 1-aminoalkylphosphonic acids **2a-j** in good yields.

Keywords: Ammonia equivalent, aminophosphonic acids, aminoalkylation, amidoalkylation, alkanimines, Schiff bases, acyliminium ions

Introduction

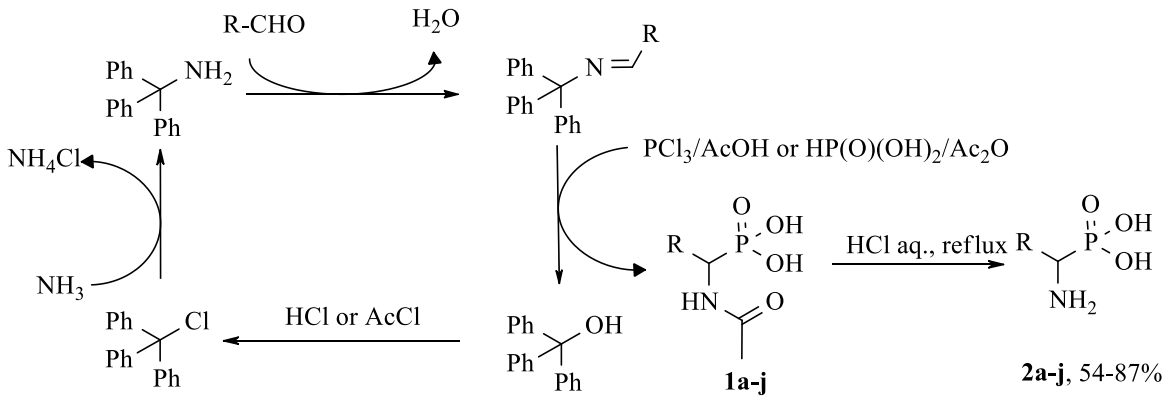
In 1988 we published a paper[1] concerning the application of tritylamine (triphenylmethylamine) as an ammonia equivalent in the synthesis of *N*-(triphenylmethyl)alkanimines and 1-(triphenylmethylamino)alkylphosphonates. Our method is especially useful when orthogonally protected derivatives of 1-aminoalkylphosphonic acids are needed. Moreover, the trityl group can be easily removed or replaced, and then reused again for the synthesis, what makes the tritylamine an excellent ammonia equivalent.[2]

Unfortunately, this method of synthesis of 1-aminoalkylphosphonates has some limitations. The first is that the *N*-(triphenylmethyl)arylmethanimines derived from aromatic aldehydes do not react with dialkyl or diaryl phosphonates.[1a] For example, *N*-(triphenylmethyl) phenylmethanimine does not react with dimethyl phosphonate, even when heated for 2 hrs at 100 ^{o}C. This method is also rather inconvenient when one wishes to prepare just free 1-aminoalkylphosphonic acid. In this case using the dialkyl phosphonate (prepared in a separate

reaction from phosphorus trichloride and alkanol) for the synthesis, and then removing the alkyl groups by hydrolysis in the next step, makes no sense.

Results and Discussion

To avoid these unnecessary steps, we decided to use directly phosphorus trichloride[3] or phosphonic acid (phosphorous acid)[4] (two basic industrial phosphorus compounds), respectively in acetic acid or in acetic anhydride, for the reaction with *N*-(triphenylmethyl)alkanimines (Scheme 1).



Scheme 1

We found that in most cases these reactions gave corresponding 1-aminoalkylphosphonic acids with good yields (Table). Furthermore, also *N*-(triphenylmethyl)arylmethanimines (derived from aromatic aldehydes) gave excellent yields of the desired amino(aryl)methylphosphonic acids. The only side products we found in these reactions were iminobis(alkyl-1-yl-phosphonic) acids - $NH[CH(R)\text{-}P(O)(OH)_2]_2$.

Table. Yield[a] [%] of isolated crystalline 1-aminoalkylphosphonic acids **2a-j**

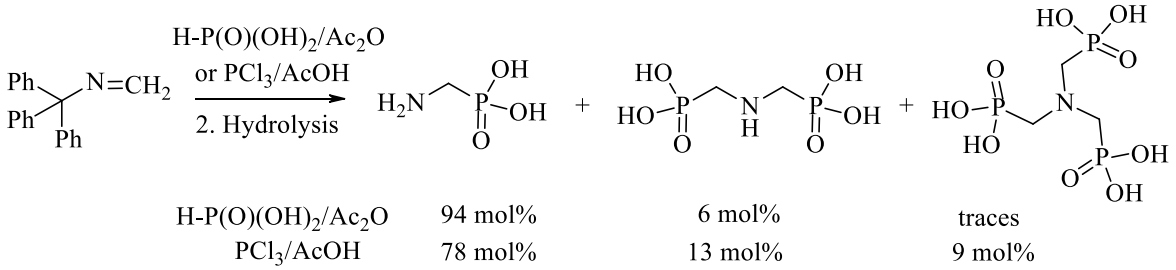
No	R	Method A [PCl_3/AcOH]	Method B [$HP(O)(OH)_2/Ac_2O$]	Ref.
2a	H	54	74	1a, 5a, 5b
2b	Me	64	81	1a, 5c, 5b
2c	Et	66	61	1a, 5c, 5d
2d	Pr	87	71	5c, 5d
2e	i-Pr	66	71	1a, 5d
2f	Bu	81	67	5c, 5d
2g	Et_2CH	60	59	5e
2h	Ph	65	66	5f, 5c, 5d

Table. Continued

No	R	Method A [PCl3/AcOH]	Method B [HP(O)(OH)2/Ac2O]	Ref.
2i	4-MeOC6H4	76	84	5f
2j	2-HOC_6H_4	80	71	5f

[a] The yield assayed by ^{31}P NMR was always much higher, usually more than 90%.

The reaction of *N*-(triphenylmethyl)alkanimines with phosphonic acid in acetic anhydride proceeds slightly more selective than when phosphorus trichloride in acetic acid was used. In the first case, we observed only a few percent of disubstituted products (iminobisphosphonic acids)[6] assayed by means of ^{31}P NMR; whereas, in the second case, when a mixture of phosphorus trichloride and acetic acid was applied, which is obviously much "harder" phosphonylating reagent, we observed as much as 8-12%[7] of disubstituted products. Nonetheless, after hydrolysis and typical workup procedure pure crystalline 1-aminoalkylphosphonic acids were isolated in good yields. Interestingly, when we applied the same reaction to the simplest *N*-tritylated alkanimine - *N*-(triphenylmethyl)methanimine, we found by means of ^{1}H and ^{31}P NMR that the crude reaction mixtures contain all possible aminoalkylated products, namely: aminomethylphosphonic acid (main product), iminobis(methylphosphonic) acid and nitrilotris(methylphosphonic) acid, but mainly aminomethylphosphonic acid (Scheme 2.).



Scheme 2

It is worthy of note, that according to the literature data, aminoalkylation or amidoalkylation reactions of tervalent phosphorus compound by any kind of Mannich base derived from formaldehyde, give only perphosphonomethylated products.[8] For example, an ammonia gives only the nitrilotris(methylphosphonic) acid. Once again, a reaction of *N*-(triphenylmethyl)methanimine with a mixture of phosphonic acid and acetic anhydride gave more selective results – the main product was aminomethylphosphonic acid.[9] After short hydrolysis we were able to isolate pure crystalline aminomethylphosphonic acid by simple crystallization (Table).

These results clearly indicate that nucleophilic attack of phosphonylating agent (we believe that it is "acetyl phosphite"[10]) on acyliminium ions generated "in situ" by detritylation of *N*-

(triphenylmethyl)alkanimine is faster than any side reactions, for example self-condensation, polymerization or decomposition of iminium salts.

Redmore[4a, 4b] investigated the reaction of some *N*-alkylalkanimines with phosphonic (phosphorous) acid, and found that reasonable results could be obtained only for imines prepared from aromatic aldehydes, which give rather stable iminium ions, because of their benzylic character. However, when he tried to use imines prepared from aliphatic aldehydes, he obtained only secondary amines – products of reduction of imines, where the phosphonic acid serves as hydride ion source.

Under such circumstances we tried to apply Redmore's protocol in the reaction of phosphonic acid with *N*-(triphenylmethyl)alkanimine, what in fact could simplify the whole procedure. Unfortunately, when we mixed phosphonic acid with the simplest *N*-trityl alkanimine, namely *N*-(triphenylmethyl)methanimine in aprotic solvents under anhydrous conditions, we neither isolate aminomethylphosphonic acid nor any product of the reduction of *N*-(triphenylmethyl)methanimine. The only product was a salt of *N*-(triphenylmethyl)methanimine with phosphonic acid, which was isolated with nearly quantitative yield.[11] Our experiments also confirmed the known fact, that the so-called "phosphorous acid" exists only as a non-nucleophilic phosphonic acid,[12] which contains the H-P bond. Thereafter, this reagent must be always activated to more nucleophilic form by addition of some Brönsted acid, acetic anhydride or acetyl chloride, as we have done in this work.

Conclusions

In summary, the reaction of phosphorus trichloride in acetic acid or phosphonic acid in acetic anhydride with N-(triphenylmethyl)alkanimines is a very useful method of preparation of 1-aminoalkylphosphonic acids, as well as their N-acetyl derivatives. The starting N-(triphenylmethyl)alkanimines are easy available[1a] from inexpensive triphenylmethylamine (tritylamine).[13] Moreover, the trityl group could be easily re-circulated. We produced large amounts of 1-aminoalkylphosphonic acids and circulated many kilograms of the trityl group without perceptible loss of it. In our hands it was the most economical method of preparation of 1-aminoalkylphosphonic acids, therefore it is in part a subject of our Polish patent.[14]

Experimental Section

General. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer locked on deuterium from solvent (D_2O was used). Chemical shifts (δ [ppm]) were calculated from chemical shift of deuterium lock and were not calibrated. All reagents and solvents were of commercial quality. The *N*-(triphenylmethyl)alkanimines were prepared essentially as described in our first paper[1a]. The triphenylmethylamine was prepared as described in the reference 13. The

1-aminoalkylphosphonic acids used as standards were from our collection. Most of them are also available from the Acros Catalogue [www.acros.com] (see for example: 29164, 29165, 34477, 34478, 34481, 34479, 34491).

Preparation of triphenylmethylamine[13]

Finely powdered solid chlorotriphenylmethane (trityl chloride) (28 g, 0.10 mole) was introduced in small portions to a vigorously stirred solution of ammonium chloride (10.8 g, 0.20 mol) in 25% of aqueous ammonia (100 cm^3) at the temperature about 0 ^oC (ice-water bath). Then, the reaction mixture was stirred 12-24 hrs, white precipitate was removed by suction, washed with water (5 x 20 cm^3), and dried "on air" to give a crude Ph_3CNH_2 which contains about 10-15% of Ph_3COH. If a practically pure Ph_3CNH_2 is needed, the following procedure is recommended: A solution of chlorotriphenylmethane (278.5 g, 1.00 mol) in toluene (1000 cm^3) was introduced dropwise to a vigorously stirred solution of ammonium chloride (saturated, but at least 53.5 g, 1.0 mol) in 25% of aqueous ammonia (1000 cm^3) at temperature about 0 ^oC (ice-water bath). Then, the reaction mixture was stirred vigorously for about 24 hrs at the temperature about 20 ^oC, organic phase was separated, dried over Na_2SO_4, then after removing of inorganic salt by suction, a solvent was evaporated under "vacuo" from water bath at the temperature below 70 ^oC. The warm oily residue was stirred in the same flask on rotavap, and hexane (about 800 cm^3) was introduced portion-wise to cause a crystallization of Ph_3CNH_2. The crystallizing mixture was stirred additionally for about 30 minutes, then the crystalline precipitate was removed by suction, washed with a cold hexane (3 x 100 cm^3), dried "on air" to give 233-246 g (90-95% of yield) of triphenylmethylamine with purity between 95-98% (assayed by ^1H NMR or by titration with $HClO_4$ in water/acetone). Pure triphenylmethylamine could be obtained by precipitation of its hydrochloride.

Synthesis of 1 aminoalkylphosphonic acids. General procedure A

Phosphorus trichloride (8.8 cm^3, 0.10 mol) was added drop-wise to acetic acid (50 cm^3) at temperature below 20 ^oC (a cold water bath was used), then the solution was stirred additionally for about 30 minutes, cooled to about 0 ^oC (ice-water bath) and finely powdered N-(triphenylmethyl)alkanimine (0.10 mol) was added portion-wise with vigorous stirring (PTFE stirring shaft with blade was used). The reaction mixture was stirred additionally for about 30 minutes at the same temperature, then it was gradually heated to about 100 ^oC (water bath) under reflux condenser connected to the HCl absorber. After about 1 hr of heating, the volatile material was removed by evaporation, and oily residue was treated with water (100 cm^3) and stirred for about 15 minutes. The precipitated triphenylmethanol was separated by suction and washed with water (4 x 10 cm^3). Collected filtrates were evaporated to give crude oily 1-acetylaminoalkylphosphonic acids **1a-j** (identified by means of ^1H and ^{31}P NMR). Oily residue was treated with 6M of hydrochloric acid (200 cm^3), and refluxed gently for about 8 hrs. The hydrolysate was evaporated, residue was dissolved in methanol (50 cm^3) and the 1-aminoalkylphosphonic acid was precipitated by drop-wise addition of methyloxirane (propylene

oxide) (about 7 cm^3). The crystallizing mixture was kept overnight at the temperature about -20 ^oC, then precipitated product was separated by suction, washed with methanol (5 x 10 cm^3) and dried "on air" to give the corresponding 1-aminoalkylphosphonic acid.

Synthesis of 1 aminoalkylphosphonic acids. General procedure B

Phosphonic acid (8.2 g, 0.10 mol) was dissolved in acetic anhydride (50 cm^3) at the temperature about 20 ^oC, then the solution was cooled to about 0 ^oC (ice-water bath) and N-(triphenylmethyl)alkanimine was added portion-wise with vigorous stirring. After analogous procedure as it was described in the procedure A, the corresponding 1-aminoalkylphosphonic acid was isolated.

Aminomethylphosphonic acid (2a). In the procedure A ($HP(O)(OH)_2$/ Ac_2O) the hydrolysate contained a mixture of $H_2NCH_2PO_3H_2$, and $HN(CH_2PO_3H_2)_2$ in molar ratio: 94:6 assayed by ^{31}P NMR (121 MHz, D_2O): δ = 13.3 and 10.7 respectively. In the procedure B (PCl_3/AcOH) the hydrolysate contained a mixture of $H_2NCH_2PO_3H_2$, $HN(CH_2PO_3H_2)_2$ and $N(CH_2PO_3H_2)_3$ in molar ratio: 78:13:9 assayed by ^{31}P NMR (121 MHz, D_2O): δ = 13.3, 10.7, and 9.0 respectively; and by ^1H NMR (300 MHz, D_2O): δ = 2.97 (d, *J* = 13.1 Hz, 2H, CH_2), 3.19 (d, *J* = 12.7 Hz, 4H, CH_2), and 3.61 (d, *J* = 12.9 Hz, 6H, CH_2) respectively. After precipitation and recrystallization as it was described before, a pure aminomethylphosphonic acid was isolated.

1-Acetylaminoethylphosphonic acid (1b). ^1H NMR (300 MHz, D_2O): δ = 1.1 (dd, *J* = 7.4 Hz, *J* = 16.5 Hz, 3H, CH_3), 1.8 (s, 3H, CH_3CO), 4.0 (dq, *J* = 7.4 Hz, *J* = 14.7 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 24.2.

1-Aminoethylphosphonic acid (2b). ^1H NMR (300 MHz, D_2O): δ = 1.16 (dd, *J* = 7.3 Hz, *J* = 15.8 Hz, 3H, CH_3), 3.22 (dq, *J* = 7.2 Hz, *J* = 14.3 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 17.7.

1-Acetylaminopropylphosphonic acid (1c). ^1H NMR (300 MHz, D_2O): δ = 0.70 (t, *J* = 7.3 Hz, 3H, CH_3), 1.25-1.44 (m, 1H, $\underline{CH_a}H_b$), 1.57-1.71 (m, 1H, $CH_a\underline{H_b}$), 1.8 (s, 3H, CH_3CO), 3.80 (ddd, *J* = 3.3 Hz, *J* = 11.4 Hz, *J* = 14,9 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 23.6.

1-Aminopropylphosphonic acid (2c). ^1H NMR (300 MHz, D_2O): δ = 0.95 (t, *J* = 7.5 Hz, 3H, CH_3), 1.55-1.69 (m, 1H, $\underline{CH_a}H_b$), 1.72-1.90 (m, 1H, $CH_a\underline{H_b}$), 3.04 (ddd, *J* = 5.2 Hz, *J* = 8.8 Hz, *J* = 13.9 Hz 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 14.7.

1-Acetylaminobutylphosphonic acid (1d). ^1H NMR (300 MHz, D_2O): δ = 0.74 (t, *J* = 7.3 Hz, 3H, CH_3), 1.15 (m, 1H, $\underline{CH_a}H_bCH_2CHP$), 1.29 (m, 1H, $CH_a\underline{H_b}CH_2CHP$), 1.46 (m, 1H, $\underline{CH_a}H_bCHP$), 1.61 (m, 1H, $CH_a\underline{H_b}CHP$), 1.89 (s, 3H, CH_3CO), 3.96 (ddd, *J*=2.5 Hz, *J*=12.0 Hz, *J*=14.7 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 23.1.

1-Aminobutylphosphonic acid (2d). ^{1}H NMR (300 MHz, D_2O+D_2SO_4): δ = 0.49 (t, *J* = 7.3 Hz, 3H, CH_3), 1.03 (m, 2H, $\underline{CH_2}CH_2CHP$), 1.4-1.5 (m, 2H, $\underline{CH_2}CHP$), 3.00 (ddd, *J* = 5.7 Hz, *J*=8.6 Hz, *J* = 13.7 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O+D_2SO_4): δ = 17.6.

1-Acetylamino-2-methylpropylphosphonic acid (1e). ^{1}H NMR (300 MHz, D_2O): δ = 0.79 (d, *J* = 6.6 Hz, 3H, CH_3), 0.87 (d, *J* = 5.9 Hz, 3H, CH_3), 1.88 (s, 3H, CH_3CO), 1.91-2.03 (m, 1H, CH), 3.87 (dd, *J* = 5.5 Hz, *J* = 17.5 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 23.1.

1-Amino-2-methylpropylphosphonic acid (2e) .^{1}H NMR (300 MHz, D_2O): δ = 0.95 (d, *J* = 6.9, 3H, CH_3), 0.99 (d, *J* = 6.9, 3H, CH_3), 2.11 (m, 1H, CH), 2.96 (dd, *J* = 6.3 Hz, *J*=14.1 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 14.0.

1-Acetylaminopentylphosphonic acid (1f). ^{1}H NMR (300 MHz, D_2O): δ = 0.69 (t, *J* = 6.4 Hz, 3H, CH_3), 1.0-1.3 (m, 4H, $\underline{CH_2}\underline{CH_2}CH_2CHP$), 1.42 (m, 1H, $\underline{CH_a}H_bCHP$), 1.65 (m, 1H, $CH_a\underline{H_b}CHP$), 1.86 (s, 3H, CH_3CO), 3.91 (ddd, *J* = 2.8 Hz, *J*=11.8 Hz, *J* = 14.9 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 23.2.

1-Aminopentylphosphonic acid (2f). ^{1}H NMR (300 MHz, D_2O): δ = 0.47 (t, *J* = 7.2 Hz, 3H, CH_3), 0.7-1.2 (m, 4H, $\underline{CH_2}\underline{CH_2}CH_2CHP$), 1.4-1.6 (m, 2H, $\underline{CH_2}CHP$), 3.00 (ddd, *J* = 8.1 Hz, *J* = 5.8 Hz, *J* = 14.0 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 17.7.

1-Acetylamino-2-ethylbutylphosphonic acid (1g). ^{1}H NMR (300 MHz, D_2O): δ = 0.74 (t, *J*=7.1 Hz, 6H, CH_3), 1.0-1.2 (m, 2H, CH_2), 1.37 (m, 1H, $\underline{CH_a}H_b$), 1.52 (m, 2H, $CH_a\underline{H_b}$+CH), 1.90 (s, 3H, CH_3CO), 4.15 (dd, *J*=4.1 Hz, *J*=18.2 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 23.7.

1-Amino-2-ethylbutylphosphonic acid (2g). ^{1}H NMR (300 MHz, D_2O): δ = 0.51 (t, *J* = 7.6 Hz, 3H, CH_3), 0.54 (t, *J* = 8.0 Hz, 3H, CH_3), 0.90 (m, 1H, $\underline{CH_a}H_b$), 1.10 (m, 1H, $CH_a\underline{H_b}$), 1.12-1.4 (m, 3H, CH+CH_2), 3.15 (dd, *J*=4.0 Hz, *J*=16.0 Hz, 1H, CH-P).
^{31}P NMR (121 MHz, D_2O): δ = 17.6.

1-Acetylamino-1-phenylmethylphosphonic acid (1h). ^{1}H NMR (300 MHz, D_2O): δ = 1.85 (s, 3H, CH_3CO), 5.02 (d, *J* = 20.9 Hz, 1H, CH-P), 7.2 (m, 5H, ArH).
^{31}P NMR (121 MHz, D_2O): δ = 18.7.

1-Amino-1-phenylmethylphosphonic acid (2h). ^{1}H NMR (300 MHz, D_2O+D_2SO_4): δ = 4.12 (d, *J* = 16.7 Hz, 1H, CH-P), 6.98 (m, 5H, ArH).
^{31}P NMR (121 MHz, D_2O+D_2SO_4): δ = 13.5.

1-Acetylamino-1-(4-methoxyphenyl)methylphosphonic acid (1i). ^{1}H NMR (300 MHz, D_2O): δ = 1.76 (s, 3H, CH_3CO), 3.57 (s, 3H, CH_3O), 5.01 (d, *J* = 20.5 Hz, 1H, CH-P), 6.73 (d, *J* = 8.5 Hz, 2H, o-ArH), 7.14 (d, *J* = 8.5 Hz, 2H, m-ArH).

^{31}P NMR (121 MHz, D_2O): δ = 19.0.

1-Amino-1-(4-methoxyphenyl)methylphosphonic acid (2i). ^{1}H NMR (300 MHz, D_2O+D_2SO_4): δ = 3.31 (s, 3H, CH_3), 4.00 (d, *J* = 16.7 Hz, 1H, CH-P), 6.51 (d, *J* = 8.4 Hz, 2H, o-ArH,), 6.9 (d, *J* = 8.4 Hz, 2H, m-ArH).
^{31}P NMR (121 MHz, D_2O+D_2SO_4): δ = 14.0.

1-Acetylamino-1-(2-acetoxyphenyl)methylphosphonic acid (1j). ^{1}H NMR (300 MHz, D_2O): δ = 1.94 (s, 3H, CH_3CON), 1.97 (s, 3H, CH_3COO), 5.5 (d, *J* = 15.8 Hz, 1H, CH-P), 6.82 (d, *J* = 7.6 Hz, 1H, H-6), 6.86 (t, *J* = 7.6 Hz, 1H, H-5), 7.13 (t, *J* = 7.6 Hz, 1H, H-4), 7.26 (d, *J* = 7.6 Hz, 1H, H-3).
^{31}P NMR (121 MHz, D_2O): δ = 19.9.

1-Amino-1-(2-hydroxyphenyl)methylphosphonic acid (2j). ^{1}H NMR (300 MHz, D_2O+D_2SO_4): δ = 4.4 (d, *J*=17.6 Hz, 1H, CH-P), 6.48 (d, *J* = 7.7 Hz, 1H, H-6), 6.52 (t, *J* = 7.7 Hz 1H, H-5), 6.83 (t, *J* = 7.7 Hz, 1H, H-4), 6.89 (d, *J* = 7.7 Hz, 1H, H-3).
^{31}P NMR (121 MHz, D_2O+D_2SO_4): δ = 14.4.

Acknowledgements

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6. Iminobisphosphonic acids were observed only for R=H (see ref. 9), and R=Me (4-13% in few experiments). Other N-(triphenylmethyl)alkanimines gave only 1-aminoalkylphosphonic acids (more than 90% yields, assayed by ^{31}P NMR), phosphonic acid and traces of phosphorus acid.
7. About 8% for R=Me, Et and Ph, and about 12% for R=4-$MeOC_6H_4$. In the case of R=Ph the structure of side product (iminobisphosphonic acid)was confirmed additionally by comparison with authentic sample prepared as in: Soroka, M.; Kołodziejczyk, K. *Pat.* PL187457, **2004**; *Chem. Abstr*. **2006**, *144*, 51712.
8. Moedritzer, K.; Irani, R. R. *J. Org. Chem.* **1966**, *31*, 1603.
9. Crude hydrolysate contains $H_2NCH_2PO_3H_2$, $NH(CH_2PO_3H_2)_2$ and $N(CH_2PO_3H_2)_3$ in a molar ratio: 78:13:9, in the case of PCl_3/AcOH, and respectively 94:6:traces, in the case of $HP(O)(OH)_2/Ac_2O$.
10. Acyl phosphites are described in the literature. See for example: (a) Cade, J. A.; Gerrard, W. *J. Chem. Soc.* **1954**, 2030. (b) Nerdell, F.; Burghardt, W. *Naturwissenschaften* **1960**, *47*, 178. (c) Petrov, K. A.; Nifant'ev, E. E.; Sopikova, I. I. *Dokl. Akad. Nauk SSSR* **1963**, *151*, 859; *Chem. Abstr.* **1963**, *59*, 68654. (d) Munoz, A.; Boisdon, M.-T.; Beazier, J.-F.; Wolf, R. *Bull. Soc. Chim. Fr.* **1971**, *4*, 1424. (e) Stawinski, J.; Thelin, M. *J. Chem. Soc. Perkin Trans.2* **1990**, 849.
11. This salt was characterized by FTIR and NMR. IR (1/200 in KBr): 3500-2400 with max. 3464 (NH, OH), 2367 (H-P), 1629 (C=N), 1251 (P=O), 1153, 1035 (P-O) cm^{-1}. ^{31}P NMR (121 MHz, CH_3OH, external lock DMSO-d_6: δ = 2.6 (d, *J*=615Hz); ^{31}P NMR {^{1}H}: δ = 2.6.
12. Phosphonic acid (sometimes called "phosphorous acid") has tetrahedral structure with one hydrogen atom directly bound to the phosphorus, as was demonstrated by means of IR and

Raman spectroscopy: (a) Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1574; and later by ^{1}H and ^{31}P NMR, see for example: (b) Moedritzer, K. *Inorg. Chem.* **1967**, *6*, 936. (c) Sheldrick, G. M. *J. Chem. Soc. Faraday Trans.* **1967**, 1077. (d) Haas, T. E.; Gillman, H. D. *Inorg. Chem.* **1968**, *7*, 2051.

13. Soroka, M.; Iwańczyk, D. *Pat* PL195536, **2007**; *Chem. Abstr.* **2008**, *149*, 176009.
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