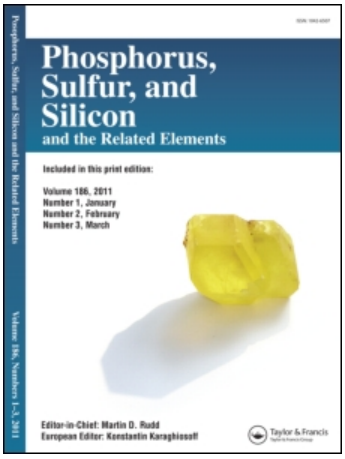

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ORGANIC PHOSPHORUS COMPOUNDS 77[1] SYNTHESIS AND PROPERTIES OF PHOSPHINOTHRICIN HOMOLOGS AND ANALOGS

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ORGANIC PHOSPHORUS COMPOUNDS 77[1] SYNTHESIS AND PROPERTIES OF PHOSPHINOTHRICIN HOMOLOGS AND ANALOGS

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(*Received May 2, 1983*)

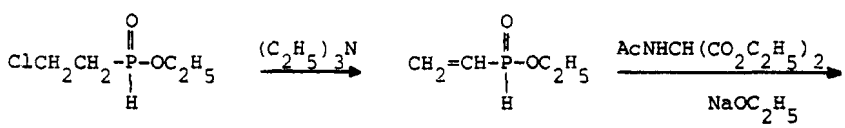
The synthesis, chemical, and spectral properties of (3-amino-3-hydroxycarbonyl-propyl)phosphonous acid (**2**), bis(3-amino-3-hydroxycarbonylpropyl)phosphinic acid (**5**), (2-amino-2-hydroxycarbonylethyl)-methylphosphinic acid (**6**), (1-amino-2-hydroxycarbonylethyl)methylphosphinic acid (**10**), and of a structural isomer of phosphinothricin, (3-amino-2-hydroxycarbonylpropyl)-methylphosphinic acid (**12**) are described. While the phosphonous acid derivative **2** exhibited weak herbicidal activity, the acids **4**, **5**, **8**, **10**, and **12**, showed no activity as herbicides. The phosphinic acid **12** showed weak plant growth regulator properties.

INTRODUCTION

In a preceding paper[1] we described the synthesis of phosphinic acids which differed from phosphinothricin by having a different substituent either on phosphorus or on nitrogen. In the present paper we shall describe the synthesis of a phosphonous acid derivative **2**, of bis(3-amino-3-hydroxycarbonylpropyl)phosphinic acid, of a homolog, and of a structural isomer of phosphinothricin.

RESULTS AND DISCUSSION

The phosphonous acid derivative **2** of phosphinothricin was synthesized by the following reaction sequence:



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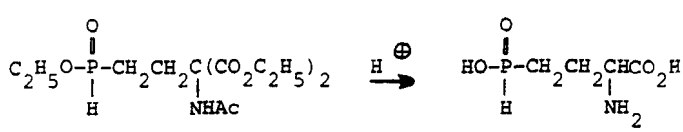
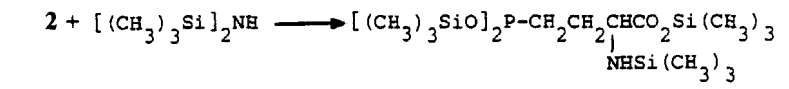


1a **2**

O-Ethyl-2-chloroethylphosphonite was prepared as described previously.[2] The vinylphosphonite **1** must be stabilized by the addition of small amounts of hydroquinone, otherwise the product polymerizes on standing at room temperature.

Like the phosphonic and phosphinic acid derivatives[1] the phosphonous acid **2** also yielded a distillable silyl derivative **3** on refluxing with excess hexamethyldisilazane. The ^{31}P chemical shift of 114.9 ppm proves the phosphonite structure of this silylester **3**. On hydrolysis with alcohol or water the pure acid **2** was obtained in quantitative yield. The phosphonite half-ester **1a** shows the typical reactions of P—H containing compounds; thus it added easily to *N*, *N'*, *N''*-tribenzylhexahydrotriazine and yielded after hydrolysis and debenzylation 3-amino-3-hydroxycarbonylpropylaminomethylphosphinic acid **4** in high yield.



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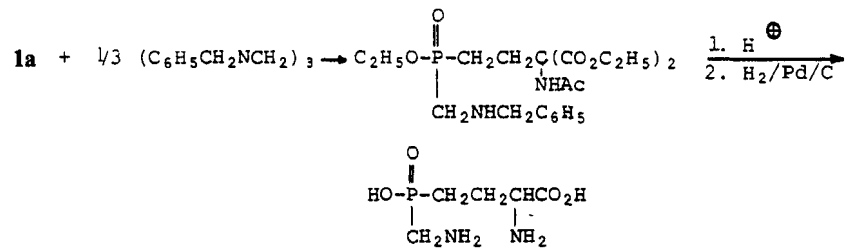

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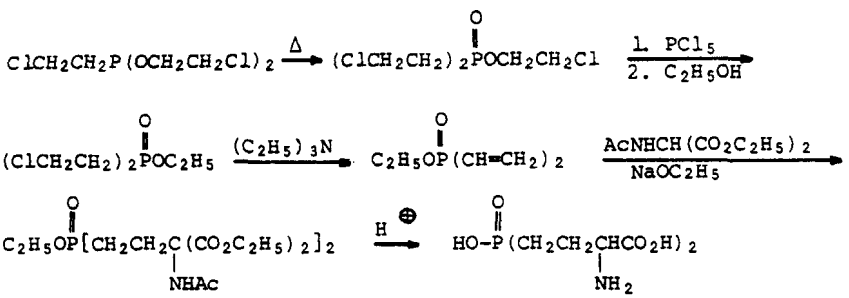
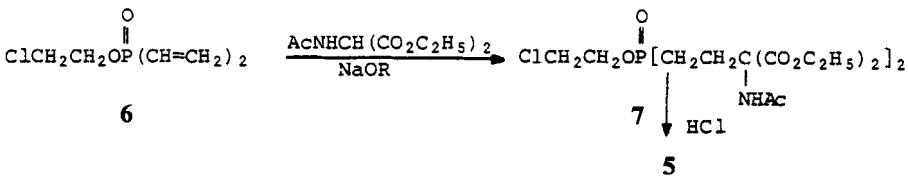
Bis(3-amino-3-hydroxycarbonylpropyl)phosphinic acid (**5**) was obtained from *O*-ethyl-bis(vinyl)phosphinate[3] and acetaminomalonate as shown below:



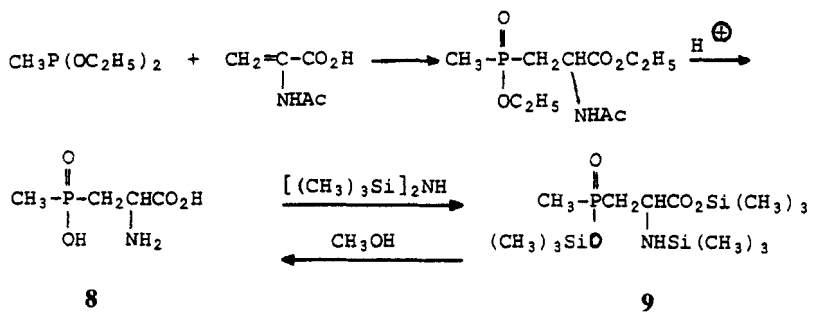
5

All steps proceeded in better than 80% yield. Subsequently it was found that **5** is also formed by the interaction of *O*-2-chloroethyl-bis(vinyl)phosphinate (**6**) and acetaminomalonate followed by hydrolysis, thus making conversion of the chloroethyl ester to the ethyl ester unnecessary.



6 7 5

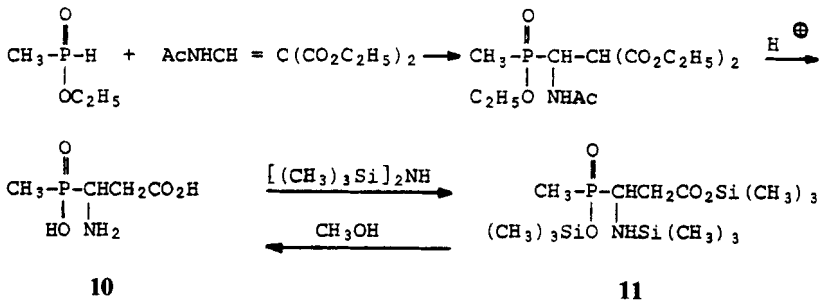
The homolog **8** of phosphinothricin was prepared by a procedure which was used previously for the preparation of phosphonic and phosphinic acid derivatives:[4,5]



8 9

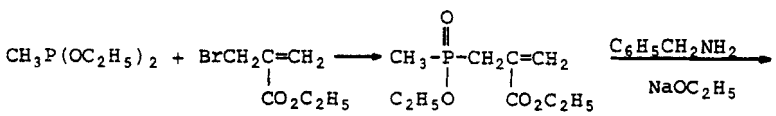
Purification was again achieved by conversion to the trisilylderivative **9** and hydrolysis with methanol. In this way **8** was obtained as a crystalline solid, m.p. 215–216°C (dec.) (lit.[5] m.p. 218–224°C) in 94% yield.

The structural isomer **10** of **8** was obtained by the addition of *O*-ethyl-methylphosphonite to diethylacetamidomethylenemalonate as described in the literature.[6] The crude acid was purified by conversion to the trisilyl derivative **11** and hydrolysis



10 11

with methanol. It had a m.p. of 205–206°C (dec.) and thus differed substantially from the one reported in the literature,[6] m.p. 275–278°C. However, the ^{1}H-NMR spectrum at 250 MHz (Table I), the ^{31}P chemical shift of 33.03 ppm and the combustion analysis are in agreement with structure **10**. It thus would seem that the m.p. of 275–278° reported in the literature[6] is in error. The structural isomer **12** of phosphinothricin was prepared in the following way:



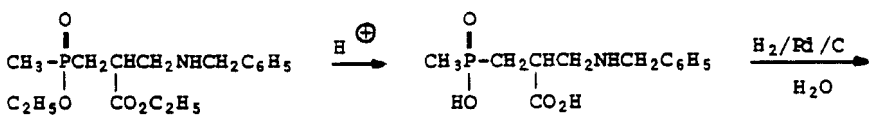
13

TABLE I

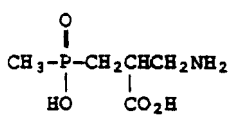
Phosphorus–proton and proton–proton coupling constants of compounds **2**, **8** and **10**[a]

Compound **2**	Compound **8**	Compound **10**
$J(P,H_{\gamma a})$ } = 15–16 $J(P,H_{\gamma b})$ }	$J(P,H_{\beta a}) = 12.6$ $J(P,H_{\beta b}) = 13.3$	$J(P,H_{\beta}) = 9.9$
$J(P,H_{\beta a})$ } = 14 $J(P,H_{\beta b})$ }	$J(P,H_{\alpha}) = 14.8$	$J(P,H_{\alpha a}) = 8.0$ $J(P,H_{\alpha b}) = 6.6$
$J(P,H_P) = 519.3$	$J(P,CH_3) = 14.5$	$J(P,CH_3) = 14.0$
$J(H_{\gamma a},H_{\beta b}) =$ $J(H_{\beta a},H_{\gamma b}) = 10–11$	$J(H_{\beta a},H_{\alpha}) = 4.7$ $J(H_{\beta b},H_{\alpha}) = 9.1$	$J(H_{\beta},H_{\alpha a}) = 3.9$ $J(H_{\beta},H_{\alpha b}) = 10.1$
$J(H_{\gamma a},H_{\beta a}) =$ $J(H_{\gamma b},H_{\beta b}) = 5.5–6$	$J(H_{\beta a},H_{\beta b}) = 15.6$	$J(H_{\alpha a},H_{\alpha b}) = 18$
$J(H_{\gamma a},H_{\gamma b}) = 15–16$		
$J(H_{\beta a},H_{\beta b}) = 18$		
$J(H_{\gamma a},H_P) =$ $J(H_{\gamma b},H_P) = 1.4$		
$J(H_{\beta a},H_{\alpha}) =$ $J(H_{\beta b},H_{\alpha}) = 6.0$		

[a] In D_2O solution (pH 1–2), coupling constants in Hz, recorded on a Bruker WM 250 spectrometer.



14 **15**



12

With the exception of the Michaelis–Arbuzov reaction (first step) which gave only a 23% yield of the phosphinate **13**, all the other steps proceeded in good yield (47 to 98 per cent).

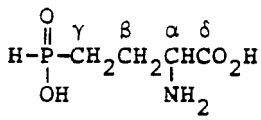
Spectroscopie Studies

Confirmation of the structures of **2**, **8**, and **10** was also obtained from the ^{1}H-NMR and ^{31}P-NMR spectra.

Phosphorus substituted aminoacids of Structure **2** have not been characterized so far. In Table I we have collected therefore proton–proton and proton–phosphorus

TABLE II

^{13}C-parameters of compound **2**,



Carbon	Chemical Shift[a]	J_{PC} (Hz)[b]
C_γ	27.2	78.8
C_β	23.1	
C_α	54.4	7.7
C_δ	172.7	

[a] In ppm versus TMS, solvent D_2O (pH = 1–2).
[b] Cycles/sec.

coupling constants of this compound. For comparison purposes coupling constants of the aminoacids **8** and **10** are included. Parameters of compound **10** have already been discussed in ref. 7. Rotamer populations of these aminoacids and three bond coupling constants are linked by Karplus's rule. If we consider only gauche conformations, rotamer populations for the rotation C_β—C_γ (**2**) and C_α—C_β (**8**, **10**) can be readily estimated from the appropriate coupling constants in Table I. Assuming values for ^3J (H, H gauche) = 2.3 Hz and ^3J (H, H trans) = 13.9 Hz[7] one obtains a population of approximately 0.6 for the main rotamer of compound **2** at low pH value. The phosphonous group and the C_α carbon are in a trans position. The main rotamers of compounds **8** and **10** have the phosphinic group and the carboxylic acid group in a trans arrangement.

In Table II we have listed the ^{13}C-parameters of Compound **2**.

Biological Activity

While the phosphonous acid derivative **2** exhibited weak herbicidal activity,[1] the phosphinic acid derivatives **4**, **5**, **8**, **10**, and **12** showed no activity as herbicides. Compound **12** exhibited weak plant growth regulator properties.

EXPERIMENTAL

Phosphorus NMR-spectra were recorded using a Bruker WP 80 spectrometer at 32.28 MHz (ref. 85% H_3PO_4), and ^{1}H-NMR-spectra were recorded with a Varian EM 360 spectrometer at 60 MHz or a Bruker WM 250/250 MHz spectrometer (ref. $(CH_3)_4Si$). The chemical shifts are reported in ppm, with negative values being upfield of the standard, and positive downfield. The reactions with trivalent phosphorus compounds were run under argon.

1. *O-Ethyl-vinylphosphonite*, $CH_2{=}CH{-}\underset{\displaystyle H}{\overset{\displaystyle |}{P}}(O)OC_2H_5$, (**1**). A mixture of 62.7 g (0.4 mol) of *O*-ethyl-2-chloroethylphosphonite[2], 62 ml of $(C_2H_5)_3N$ and 200 ml of benzene is refluxed for 5 h. Then the precipitated amine hydrochloride is filtered, and the filtrate fractionated. There is obtained 36.2 g (= 75%) of **1**, a colorless liquid, b.p. 75–78°C/14 torr; 81–85°C/20 torr; n_D^{20} 1.4465. The compound polymerizes on standing at room temperature. It can be stabilized by addition of small amounts of hydroquinone. ^{1}H-NMR (in $CDCl_3$) δ: CH_3 1.4 (t); OCH_2 4.2 (2 qu); $CH_2{=}CH$ 5.8–6.8 (m); P—H 7.27 (d, J_{PH} 560 Hz) (ppm). ^{31}P 23.81 ppm (d, J_{PH} 560 Hz; in $CDCl_3$). $C_4H_9O_2P$ (120.09): Calc'd: C, 40.01; H, 7.56; P, 25.79%. Found: C, 39.75; H, 7.59; P, 24.74%.

2. *3-Amino-3-hydroxycarbonyl-propylphosphonous acid*, $H-\underset{HO}{\overset{|}{P}}(O)CH_2CH_2\underset{NH_2}{\overset{|}{C}}HCO_2H$, (**2**). A mixture of 24 g (0.2 mol) of **1** and 43.4 g of acetaminodiethylmalonate is heated with stirring to 80°C and then 4 ml of a 6% solution of $NaOC_2H_5$ in C_2H_5OH is added. An exothermic reaction ensues and the temperature rises to 120°C. After further heating at 95°C for 8 h the crude triester **1a** (^{31}P 37.21 ppm, d, J_{PH} 537 Hz) is hydrolyzed with 200 ml conc. HCl by refluxing for 5 h. Evaporation of the clear, slightly yellow colored solution on a rotavapor, dissolution of the residue in 100 ml dest. H_2O and addition of 800 ml acetone precipitates an oily mass which on treatment with methanol yields 10 g (30%) crystalline **2**, m.p. 193–197°C (dec.). ^{1}H-NMR (in D_2O): CH_2CH_2P 1.9 (m, 4 H); CH 4.07 (t, 1 H); OH, NH_2 4.77 (s); P—H 7.01 (d, J_{PH} 534 Hz, 1 H). ^{31}P 32.75 ppm (d, J_{PH} 527.8 Hz, in D_2O, pH = 1). $C_4H_{10}NO_4P$ (167.10): Calc'd: C, 28.75; H, 6.03; N, 8.38; P, 18.54%. Found: C, 28.41; H, 6.15; N, 8.22; P, 18.38%.

3. *Bis(trimethylsilyloxy)(3-trimethylsilylamino-3-trimethylsilyloxycarbonyl-propyl)phosphonite* (**3**). A mixture of 20.3 g of **2** and 200 ml of $[(CH_3)_3Si]_2NH$ is refluxed for 12 h and then fractionally distilled. There is obtained 11.1 g (24.3%) of **3**, a colorless liquid, b.p. 73–79°C/0.15 torr. Hydrolysis by refluxing in methanol for 2 h gave pure **2**. ^{1}H-NMR (in CCl_4): $(CH_3)_3Si$ 0.35 and 0.45 (36 H); NH 1.2 (d, 1 H); CH_2CH_2P 2.27 (m, 4 H); CH 4.17 (m, 1 H). ^{31}P + 114.9 ppm (in $CDCl_3$).

4. *3-Amino-3-hydroxycarbonylpropyl-aminomethylphosphinic acid*, $H_2NCH_2-\overset{\overset{O}{\|}}{P}(HO)CH_2CH_2\underset{NH_2}{\overset{|}{C}}HCO_2H$,

(**4**). A mixture of 13.5 g of **1a** and 4.75 g of tribenzylhexahydrotriazine is heated to 110–120°C for 4 h and then hydrolyzed with conc. HCl and refluxing for 12 h. The solution is evaporated on a rotavapor and the residue dissolved in 100 ml water and 150 ml acetic acid and debenzylated with hydrogen using 5% Pd/C as a catalyst (9 g over a period of 60 h, H_2-uptake 120% of theory). The catalyst is filtered and the filtrate evaporated to give **4**, a white solid in quantitative yield. ^{1}H-NMR (in D_2O): CH_2CH_2P 2.05 (m, 4 H); NCH_2P 3.2 (d, J 9 Hz, 2 H); CH 4.1 (t, 1 H); OH, NH 4.77 (s).

5. *Bis(3-amino-3-hydroxycarbonylpropyl)phosphinic acid*, $HO-\overset{\overset{O}{\|}}{P}(CH_2CH_2\underset{NH_2}{\overset{|}{C}}HCO_2H)_2$, (**5**). To 4.4 g (0.03 mol) of *O*-ethyl-bis(vinyl)phosphinate[3] and 13 g of acetaminomalonate is added with stirring and heating to 90°C 6 ml of a 6% solution of $NaOC_2H_5$ in ethanol. Then the mixture is stirred at 100°C for 12 h, and hydrolyzed by adding 50 ml conc. HCl and refluxing for 12 h. Evaporation of the clear solution yields 9 g (= 100%) of **5**, a beige resin, which did not crystallize. **5** is obtained as the hydrochloride. ^{1}H-NMR (in D_2O): CH_2CH_2 2.55 (m, 4 H); CH 4.7 (complex t, 1 H); OH, NH_2 5.25 (s) (ppm). ^{31}P 49.40 ppm (in D_2O, pH = 1).

6. *O-Chloroethyl-bis(vinyl)phosphinate* (**6**). A mixture of 63.4 g (0.25 mol) of $(ClCH_2CH_2)_2P(O)OCH_2CH_2Cl$[3] and 84 ml of Et_3N in 500 ml of toluene was refluxed for 5 h, filtered, and the filtrate distilled. There was obtained 20.4 g (= 45.2%) of **6**, a colorless liquid b.p. 63–65°/0.08 torr. ^{1}H-NMR (in $CDCl_3$): $ClCH_2$ 3.7 (m, 2 H); OCH_2 4.2 (m, 2 H); CH_2=CH 5.7–6.7 (m, 6 H). ^{31}P 29.96 ppm (in $CDCl_3$).

7. *O-Chloroethyl-bis[3-di(ethoxycarbonyl)-3-acetylaminopropyl]phosphinate* (**7**). From 13.9 g (77 mmol) of **6**, 30.4 g (70 mmol) of acetylaminomalonate and NaOEt as described in 5. Yield 36.6 g (= 85%) **7**, waxy material. ^{1}H-NMR (in $CDCl_3$): CH_3 1.22 (t, 12 H); CH_3CO 2.05 (s, 6 H); CH_2CH_2P 2.45 (m, 8 H) CH_2Cl 3.62 (t, 2 H); OCH_2 4.2 (m, 10 H); NH 6.9 (s, 2 H). ^{31}P 57.03 ppm (in $CDCl_3$). Hydrolysis of **7** with conc. HCl under reflux gave **5** in over 90% yield.

8. *2-Amino-3-(methyl-hydroxyphosphinyl)propanoic acid*, $CH_3-\underset{OH}{\overset{|}{P}}(O)CH_2\underset{NH_2}{\overset{|}{C}}HCO_2H$, (**8**). A mixture of 27.2 g (0.2 mol) of *O*, *O*-diethyl-methylphosphonite and 26 g of α-acetaminoacrylic acid is heated with stirring. At 70°C a strong exothermic reaction ensued and the temperature rose to 150°C in spite of cooling with ice. The mixture is stirred at 130°C for 1 h, then hydrolyzed by adding 500 ml of a 20% solution of HCl in water and refluxing for 5 h. The brown solution is evaporated and the residue treated with 84 ml of $(Me_3Si)_2NH$ and refluxed for 2 h. Fractional distillation gave 17.7 g (57.7%) of **9**, b.p.

102–108°C/0.12 torr. ^{31}P + 42.89 ppm (in $CDCl_3$). These on treating with 90 ml of CH_3OH gave a white suspension. After 2 h stirring the solid was filtered and washed with methanol. There was obtained 7.10 g (94.4%) of **8**, a white solid, m.p. 215–216°C (dec). (lit.[5] m.p. 218–224°C). ^{1}H-NMR (in D_2O): CH_3P 1.33 (d, J_{PCH} 14 Hz, 3 H); CH_2P 2.2 (complex d, J_{PCH} 13 Hz, 2 H); CH 4.1 (m, 1 H); OH, NH_2 4.87. ^{31}P 42.52 ppm (in D_2O, pH = 1). $C_4H_{10}NO_4P$ (167.10): Calc'd: C, 28.75; H, 6.03; N, 8.38; P, 18.54%. Found: C, 28.73; H, 6.04; N, 8.39; P, 18.45%. Titration in H_2O with 0.1 N NaOH gave 2 breaks, equiv. weight found 174 (cal'd 167.1) pK_1 = 2.76; pK_2 = 9.61.

10. *3-Amino-3-(methyl-hydroxyphosphinyl)propanoic acid*, $CH_3P(O)CHCH_2CO_2H$ (**10**). From
OH NH$_2$

16.0 g of *O*-ethyl-methylphosphonite, 7.57 g of diethyl-acetamidomethylenemalonate and NaOEt, then hydrolysis with conc. HCl according to Ref. 6. The crude acid **10** was treated with 65 ml of $(Me_3Si)_2NH$ and refluxed for 5 h. Fractional distillation gave 7.5 g (= 31.5%) of **11**, a colorless liquid, b.p. 103–104°C/0.12 torr. Hydrolysis of **11** with methanol at 20°C gave 3.2 g (= 98.2%) of **10**, a white crystalline solid, m.p. 205–206°C (dec.) (lit.[6] m.p. 275–278°C). ^{1}H-NMR (in D_2O/DCl): CH_3P 1.33 (d, J_{PCH} 15 Hz, 3 H); CH_2 2.65 (m, 2 H); CHP 3.6 (m, 1 H); OH, NH 5.0 (s) ^{31}P 33.03 ppm (in D_2O; pH = 2). $C_4H_{10}NO_4P$(167.10): Calc'd: C, 28.75; H, 6.03; N, 8.38; P, 18.54%. Found: C, 28.46; H, 5.98; N, 8.26; P, 18.49%. Titration in H_2O with 0.1 N NaOH gave two inflection points, equiv. weight found 172 (calc'd 167.1); pK_1 = 3.58; pK_2 = 8.32.

12. *Preparation of 2-aminomethyl-3-(methyl-hydroxyphosphinyl)-propanoic acid*,
$CH_3-P(O)CH_2CHCO_2H$, (**12**).
OH CH$_2$NH$_2$

(a) $CH_3-P(O)CH_2C=CH_2$ (**13**). To 81.7 g (0.5 mol) of *O,O*-diethylmethylphosphonite is added
OC$_2$H$_5$ CO$_2$C$_2$H$_5$

with stirring and heating to 80°C 96.5 g of α-bromomethylacrylic acid ethyl ester at a rate which keeps the temperature below 90°C. After 2 h stirring at room temperature the product is molecularly distilled and then fractionated in the vacuum. There is obtained 25.4 g (= 23%) of **13**, a colorless liquid, b.p. 101–104°C/0.015 torr. ^{1}H-NMR (in $CDCl_3$): CH_3 1.33 (t, 6 H); CH_3P 1.5 (d, J_{PCH} 15 Hz, 3 H); CH_2P 2.95 (d, J_{PCH} 18.4 Hz, 2 H); OCH_2 4.2 (qui, 4 H); CH_2=C 5.9 (d, J_{HH} 5 Hz, 1 H) and 6.4 (d, J_{HH} 5 Hz, 1 H) (ppm). ^{31}P 50.05 ppm (in $CDCl_3$).

(b) $CH_3-P(O)CH_2CHCH_2NHCH_2C_6H_5$ (**14**). To 6.6 ml of benzylamine, 9 ml of ethanol,
OC$_2$H$_5$ CO$_2$C$_2$H$_5$

and 13.2 g (0.06 mol) of **13** is added 0.6 ml of a 6% $NaOC_2H_5$ solution in ethanol. A slight exothermic reaction ensues and the temperature increases from 28° to 38°C. After 50 h standing at 20°C the mixture is molecularly distilled. There is obtained 14.8 g (= 75%) of **14**, a colorless oil, b.p. 160°C/0.1 torr. ^{1}H-NMR (in $CDCl_3$): CH_3 1.3 (t); CH_3P 1.5 (d, J_{PCH} 14 Hz); NH 1.6 (s); CH_2P 2.1 (2 d, J_{PCH} 15 Hz); $CHCH_2N$ 2.9 (m); $PhCH_2$ 3.8 (s); OCH_2 4.13 (qui); C_6H_5 7.3 (br.s) (ppm). ^{31}P 52.94 ppm (in $CDCl_3$).

(c) $CH_3-P(O)CH_2CHCH_2NHCH_2C_6H_5$ (**15**). A mixture of 14.4 g (0.044 mol) of **14** and 50
OH CO$_2$H

ml of conc. HCl is refluxed for 14 h. The clear solution is evaporated on a rotavapor, the residue dissolved in ethanol and propylene oxide added. **15** crystallizes out (5.6 g = 47%). ^{1}H-NMR (in D_2O): CH_3P 1.3 (d, J_{PCH} 13.5 Hz); CH_2P 1.8 (m); NCH_2CH 2.8–3.4 (m); $PhCH_2$ 4.2 (s); OH, NH 4.67 (s); C_6H_5 7.4 (br.s).

^{31}P 42.33 ppm (in D_2O, pH = 2). $C_{12}H_{18}NO_4P \times 0.2H_2O$ (274.8): Calc'd: C, 52.43; H, 6.77; N, 5.09; P, 11.27; H_2O, 1.33%. Found: C 52.24; H, 6.77; N, 4.91; P, 11.08; H_2O, 1.33%.

(d) $CH_3-P(O)CH_2CHCH_2NH_2$ (**12**). To 4.9 g (0.018 mol) of **15**, dissolved in 50 ml of H_2O,
OH CO$_2$H

is added 0.5 g catalyst (5% Pd on C) and the mixture hydrogenated at 25°C. After 15% hydrogen uptake, another 1 g catalyst is added. After 29 h hydrogen uptake stopped (uptake 110% of theory). The catalyst is filtered and the filtrate evaporated on a rotavapor. As a residue is obtained 3.2 g (= 98%) of **12**, a white crystalline solid. ^{1}H-NMR (in D_2O): CH_3P 1.5 (d, J_{PCH} 14 Hz, 3 H): CH_2P 2.2 (m, 2 H); NCH_2CH 3.4 (m, 3 H); OH, NH_2 4.8 (s) ^{31}P 42.24 ppm (in D_2O, pH = 3).

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