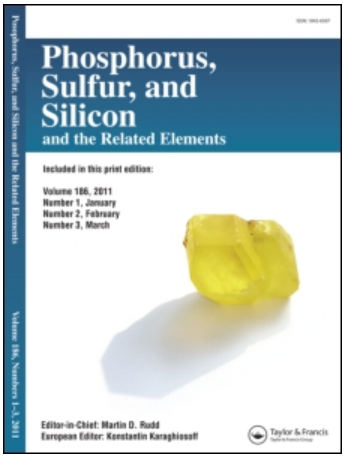

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ORGANIC PHOSPHORUS COMPOUNDS 88[1] SULFONIC- AND SULFINIC ACID ANALOGUES OF GLYPHOSATE

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Under alkaline conditions aminomethylphosphonic acid reacts with hydroxymethylsulfonic- and hydroxymethylsulfinic acid to give N-phosphonylmethyl-amino-methylsulfonic-, **1**, $Na_2O_3PCH_2NHCH_2SO_3Na$, and N-phosphonylmethyl-aminomethylsulfinic acid trisodium salt, **2**, $Na_2O_3PCH_2NHCH_2SO_2Na$, respectively. Glyphosate also interacts with the sulfur compounds and yields N-hydroxysulfonylmethyl- and N-hydroxysulfinylmethyl-glyphosate, **3**, $Na_2O_3PCH_2N(CH_2SO_3Na)CH_2CO_2Na$ and **4**, $Na_2O_3PCH_2N(CH_2SO_2Na)CH_2CO_2Na$, respectively. Whereas **1** and **2** are biologically not active, **3** and **4** show herbicidal activity in post-application which is by a factor of 2 weaker than that of glyphosate.

Key words: N-Phosphonylmethyl-aminomethylsulfonic acid; N-phosphonylmethyl-aminomethyl-sulfinic acid; N-hydroxysulfonylmethyl-glyphosate; N-hydroxysulfinylmethyl-glyphosate.

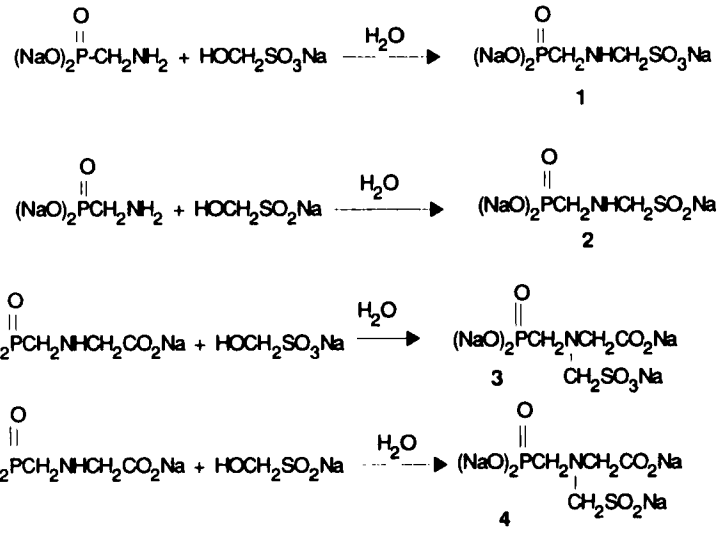
INTRODUCTION

The class of N-phosphonomethyl-[2,3,4] and N-alkylphosphinylmethyl-glycines[4,5,6,7] has been studied intensively during the past 15 years because several of these compounds show herbicidal and plant growth regulating properties. In more recent studies we have synthesized aza- and aminoglyphosate[8] and also N-phosphonylmethyl- and N-phosphinylmethyl-aminomalonic acids and derivatives[9] and have shown that several of those compounds also possess plant growth regulating and herbicidal properties. Continuing these studies we have now synthesized glyphosate analogous compounds which bear in place of the carboxylic acid group a sulfonic or sulfinic acid group or in which the hydrogen atom on nitrogen is replaced by a hydroxysulfonylmethyl- or a hydroxysulfinyl-methyl group.

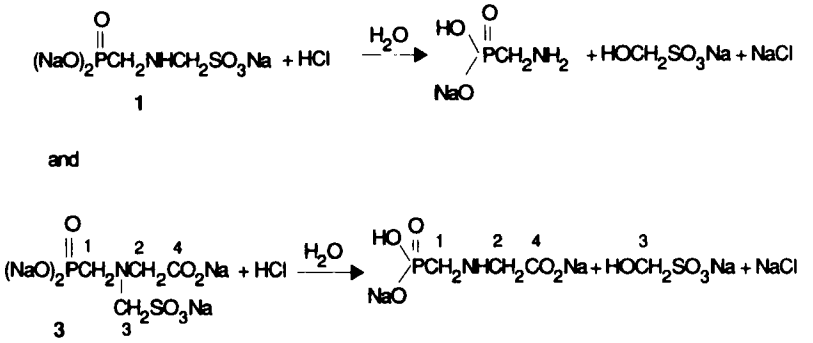
RESULTS AND DISCUSSION

Whereas glycine and hydroxymethylsulfonic acid condense only under acidic conditions and form N-hydroxysulfonylmethyl-glycine which is unstable in alkaline solution,[10] aminomethylphosphonic acid or glyphosate interact with hydroxymethyl-sulfonic or-sulfinic acid only under alkaline conditions at around pH 11 and produce the compounds **1** to **4**.

Attempts to prepare the free acids were unsuccessful. Even the addition of only one equivalent acid to each of the compounds **1** to **4** caused complete



decomposition to the starting materials as indicated by ^{13}C-NMR spectroscopy e.g.:



^{13}C-NMR (in D_2O, ppm)

1: 54.15 (d, J_{PC1} 145 Hz)	1: 46.9 (d, J_{PC1} 128 Hz)
2: 59.20 (d, J_{PC2} 5.67 Hz)	2: 51.7 (d, J_{PC2} ~6 Hz)
3: 72.30 (d, J_{PC3} 8.25 Hz)	3: 74.4 (s)
4: 180.3 (s)	4: 180.0 (s)

In **3** the carbon atom of the sulfonylmethyl group (CH_2SO_3Na) is split into a doublet due to long range coupling with phosphorus; in the decomposition products this signal becomes a singlet indicating that free hydroxymethylsulfonic acid (sodium salt) is present. However, the trisodium salt of **1** and **2** and the tetrasodium salts of **3** and **4** are stable, also in aqueous solution, for several months. In the ^{13}C-NMR spectra no decomposition could be detected when an aqueous solution of **1** or **4** was kept for 4 months at 20°C. The herbicidal activity of **3** and **4** is very similar to that of glyphosate. Both compounds are translocated

like glyphosate and are only effective in post application. However, the activity of **3** and **4** is by a factor of two weaker than that of glyphosate. Compounds **1** and **2** were biologically not active.

ACKNOWLEDGEMENT

We wish to thank CIBA-GEIGY's central function research for combustion analysis and for the ^{31}P- and ^{31}C-NMR spectra and Mr. M. Walti for experimentlal help.

EXPERIMENTAL

Phosphorus NMR-spectra were recorded using a Bruker WP 80 spectrometer at 32.28 MHz (Reference 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 (Reference $(CH_3)_4Si$). The chemical shifts are reported in ppm, with negative values being upfield of the standard, and positive downfield.

1. *N-Phosphonylmethyl-aminomethylsulfonic acid-trisodium salt*, **1**. To a solution of 5.55 g (0.05 mol) of aminomethylphosphonic acid in 20 ml H_2O is added slowly 4 g (0.1 mol) of NaOH dissolved in 20 ml H_2O. Then 6.7 g (0.05 mol) of $HOCH_2SO_3Na$ are added and the mixture stirred for 4 h at 20°C. The clear solution is evaporated on a rotavapor and the residue dried in the vacuum at 80°C. There is obtained 13.43 g(=99.1%) **1**, a crystalline white solid, m.p. 256°C (dec.).

^{1}H-NMR (in D_2O) δ = 2.9 (d, J_{PCH} 12.8, CH_2P, 2H); 4.0 (s, CH_2S, 2H): 4.95 (s,OH, NH_2) [ppm]
^{31}P-NMR (in D_2O) 16.09 ppm
^{13}C-NMR (in D_2O) δ = 48.26 (d, J_{PC} 138.7 Hz, CH_2P); 67.9 (d, J_{PCNC} 13.7 Hz) [ppm]
$C_2H_5NO_6PSNa_3 \times 0.16\ H_2O$ (273.95). Calc: C, 8.77; H, 1.99; N, 5.11; P, 11.31; H_2O, 1.02%. Found: C, 8.6; H, 2.1; N, 5.2; P, 11.2; H_2O, 1.0%

2. *N-Phosphonylmethyl-aminomethylsulfinic acid trisodium salt*, **2**. To a solution of 5.55 g (0.05 mol) of $H_2NCH_2PO_3H_2$ and 4 g NaOH in 40 ml of H_2O is added 7.77 g (0.55 mol) of rongalit ($HOCH_2SO_2Na$) and the mixture stirred at room temperature for 4 h. Then the clear solution is evaporated and the residue dried in the vacuum at 90°C. There is obtained 12.7 g (~90%) of **2**, a white, crystalline, hygroscopic solid, m.p. 258°C (dec.)
^{1}H-NMR (in D_2O) δ = 2.73 (d, J_{PCH} 13, CH_2P, 2H): 3.23 (s, CH_2S, 2H); 4.8 (s, OH, NH) [ppm]
^{31}P-NMR (in D_2O) 16.09 ppm
^{13}C-NMR (in D_2O) δ = 48.6 (d, J_{PC} 137.7 Hz, CH_2P); 78.34 (d, J_{PCNC} 12.7 Hz) [ppm]
$C_2H_5NO_5PSNa_3 \times 1.7\ H_2O$ (285.7. Calc: C, 8.41; H, 2.97; N, 4.9; P, 10.84%. Found: C, 8.9; H, 3.0; N, 5.0; P, 10.8%

3. *N-Phosphonylmethyl-N-hydroxysulfonylmethyl-glycine tetrasodium salt*, **3**. To a solution of 8.45 g (0.05 mol) of $H_2O_3PCH_2NHCH_2CO_2H$ and 6.0 g (0.15 mol) of NaOH in 40 ml of H_2O is added 6.7 g (0.05 mol) of $HOCH_2SO_3Na$. Then the mixture is stirred for 4 h at 20°C and the clear solution evaporated on a rotavapor. The crystalline, white residue is dried at 80°C in the vacuum. There is obtained 17.3 g (98.68%) **3**, a crystalline white solid, m.p. 241°C (dec.)
^{1}H-NMR (in D_2O) δ = 3.07 (d, J_{PCH} 11.6 Hz, CH_2P, 2H); 3.8 (s, CH_2S, 2H); 4.23 (s, CH_2CO, 2H); 5.05 (s, H_2O [ppm]
^{31}P-NMR (in D_2O) 16.53 ppm
^{13}C-NMR (in D_2O) δ = 54.15 (d, J_{PC} 145 Hz); 59.2 (d, J_{PCNC} 5.67, CH_2CO); 72.3 (d, J_{PCNC} 8.25 Hz, CH_2S); 180.3 (s, CO) [ppm]
$C_4H_6NO_8PSNa_4 \times 0.15\ H_2O$ (353.70). Calc: C, 13.58; H, 1.83; N, 3.96; P, 8.76; H_2O, 0.76%. Found: C, 13.3; H, 2.0; N, 3.9; P, 8.7; H_2O, 0.8%

4. *N-Phosphonylmethyl-N-hydroxysulfinylmethyl-glycine tetrasodium salt*, **4**. To a solution of 8.4 g (0.05 mol) of $H_2O_3PCH_2NHCH_2CO_2H$ and 6.0 g (0.15 mol) of NaOH in 40 ml of H_2O is added 7.77 g of $HOCH_2SO_2Na \times 2H_2O$ (0.05 mol). The mixture is stirred for 4 h at 20°C and the clear solution evaporated on a rotavapor. The solid residue is dried at 80°C in the vacuum. There is obtained 16.4 g (97.97%) **4**, a hygroscopic solid, m.p. 250°C (dec.)
^{1}H-NMR (in D_2O) δ = 3.0 (d, J_{PC} 11 Hz, CH_2P, 2H); 3.57 (s, CH_2S, 2H); 3.7 (s, CH_2CO, 2H); 5.1 (s, H_2O) [ppm]
^{31}P-NMR (in D_2O) 16.34 ppm

^{13}C-NMR (in D_2O) δ = 55.33 (d, J_{PC} 144 Hz, CH_2P); 60.8 (d, J_{PCNC} 5.6 Hz, CH_2CO); 85.74 (d, J_{PCNC} 8 Hz, CH_2S); 180.38 (s, CO) [ppm]
$C_4H_6NO_7PSNa_4 \times 1.9\,H_2O$ (369.29) Calc: C, 13.01; H, 2.65; N, 3.79; P, 8.39%. Found: C, 13.5, H, 2.1; N, 3.7; P, 8.4%.

REFERENCES

1. Part 87: L. Maier and P. J. Diel, *Phosphorus and Sulfur*, in press.
2. Monsanto, Co., U.S. Pat. 3'799'758 (1974); inv. J. E. Franz.
3. Monsanto, Co., U.S. Pat. 3'556'762 (1971); inv. P. C. Hamm.
4. P. J. Diel and L. Maier, *Phosphorus and Sulfur*, **20**, 313 (1984).
5. L. Maier, *Phosphorus and Sulfur*, **8**, 67 (1980).
6. L. Maier, *Phosphorus and Sulfur*, **11**, 139 (1981).
7. L. Maier, *Phosphorus and Sulfur*, **11**, 149 (1981).
8. P. J., Diel and L. Maier, *Phosphorus and Sulfur*, **39**, 159 (1988).
9. L. Maier, *Phosphorus and Sulfur*, **36**, 1 (1988).
10. D. L. Ingles, *Chem. & Ind.* 1492 (1967).