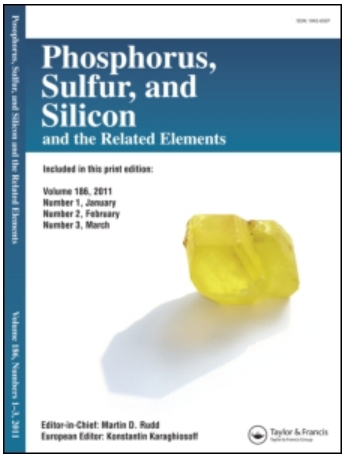


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOSPHONOMETHYLATION OF AMINOALKANOLS PREPARATION OF 4-(PHOSPHONOMETHYL)-2-HYDROXY-2-OXO-1,4,2-OXAZAPHOSPHORINANES[1]

Balram Dhawan[a]; Derek Redmore[a]
[a] Petrolite Corporation, St. Louis, MO.

To cite this Article Dhawan, Balram and Redmore, Derek(1990) 'PHOSPHONOMETHYLATION OF AMINOALKANOLS PREPARATION OF 4-(PHOSPHONOMETHYL)-2-HYDROXY-2-OXO-1,4,2-OXAZAPHOSPHORINANES[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 48: 1, 41 — 47
To link to this Article: DOI: 10.1080/10426509008045880
URL: http://dx.doi.org/10.1080/10426509008045880

Phosphorus, Sulfur, and Silicon, 1990, Vol. 48, pp. 41–47
Reprints available directly from the publisher
Photocopying permitted by license only

PHOSPHONOMETHYLATION OF AMINOALKANOLS PREPARATION OF 4-(PHOSPHONOMETHYL)-2-HYDROXY-2-OXO-1,4,2-OXAZAPHOSPHORINANES[1]

BALRAM DHAWAN* and DEREK REDMORE
Petrolite Corporation, St. Louis, MO. 63119

(Received August 14, 1989; in final form August 20, 1989)

Treatment of aminoalkanols **1** with phosphorous acid and formaldehyde in presence of conc. hydrochloric acid gave mixtures of [(2-hydroxy alkyl)imino] dimethylene diphosphonic acids **3** and 4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinanes **2** from which **2** were isolated as crystalline solids. Similar treatment of 2-amino-2-methyl-1,3-propanediol **8** gave a complex mixture from which dimethylene diphosphonic acid of 5-amino-5-methyl-1,3-dioxane **9** was isolated. 2-Aminoethanethiol, when subjected to phosphonomethylation, gave an unexpected novel quarternary nitrogen product **11**. *N*-Alkylaminoalkanols **4** on phosphonomethylation gave 3:1 mixtures of [*N*-alkyl-*N*-(2-hydroxyalkyl)amino] methane phosphonic acid **6** and *N*-alkyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **5**. Treatment of the crude mixtures of **5** and **6** with aqueous sodium hydroxide gave disodium salts of [*N*-alkyl-*N*-(2-hydroxyalkyl)amino] methanephosphonic acid **7**. The ratio of the cyclic to the open chain structures obtained as well as the formation of any unexpected novel products is dependent on the structure of the aminoalkanol that is phosphonomethylated. The ^{1}H, ^{13}C and ^{31}P spectra are reported for all new compounds.

Key words: Phosphonomethylation; aminoalkanols; 4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinanes; 5-amino-5-methyl-1,3-dioxane.

A variety of amines on treatment with formaldehyde and phosphorous acid in presence of conc. hydrochloric acid undergo Mannich type reaction to yield aminomethylene phosphonic acids.[2,3] Among these are the aminoalkanols, 2-aminoethanol **1a** and 2,2′-iminodiethanol. Moedritzer and Irani[2] reacted **1a** with phosphorous acid and aqueous formaldehyde in presence of conc. hydrochloric acid and isolated a white crystalline solid, mp 255°C, to which they assigned the structure [(2-hydroxyethyl)imino] dimethylene diphosphonic acid **3a**. Later Worms and Wollman[4] reacted **1a** with phosphorous acid, phosphorus trichloride, paraformaldehyde and conc. hydrochloric acid and isolated a white solid (no melting point reported) to which they assigned the structure 4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2a**. It appears that the direct comparison of the products prepared by the above two methods was not made. Similar observations were reported[2,4] for the phosphonomethylation of 2,2′-iminodiethanol. Recently Russian workers[5] described the product from **1a**, by a method that we believe to be similar to that of Moedritzer and Irani, as **3a**.

We have now studied the phosphonomethylation of several aminoalkanols with a view to fully identify the isolated products by ^{31}P, ^{13}C, ^{1}H NMR spectra. The

* Author to whom all correspondence should be addressed.

aminoalkanols studied were 2-aminoethanol **1a**, 2-amino-1-butanol **1b**, 2-amino-2-methyl-1-propanol **1c**, 1-amino-2-propanol **1d** and 2-amino-1-phenyl ethanol **1e**, 2-amino-2-methyl-1,3-propanediol **8** and 2-aminoethanethiol **10**. We also investigated the phosphonomethylation of 2-(methylamino)ethanol **4a** and 2-(ethylamino)ethanol **4b**.

The phosphonomethylation was performed by adding aqueous formaldehyde to a refluxing mixture of an aminoalkanol, water, phosphorous acid and conc. hydrochloric acid. The reaction mixture was refluxed for 3 h and then evaporated to obtain the crude product as a colorless syrup (Moedritzer and Irani's method[2]).

TABLE I

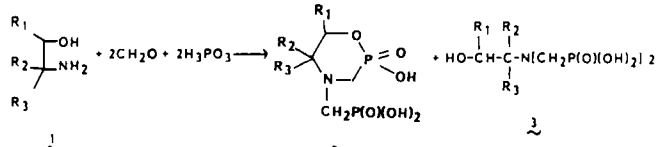
Spectral data of compounds **2a–2e**, **7a**, **7b** and **9**

Compound	^{31}P NMR (D_2O/H_3PO_4cap.)[a] (ppm)	^{13}C NMR (D_2O/Me_4Sicap.)[b]	^{1}H NMR (D_2O)[c]
2a	4.90(J_{PP} = 2.44 Hz) 7.53(J_{PP} = 2.44 Hz)	52.39(dd, 129.40 Hz, 3.66 Hz, CH_2) 55.76(dd, 139.16 Hz, 8.54 Hz, $\underline{C}H_2$) 55.76(t, 3.66 Hz, C_5) 63.31(d, 4.88 Hz, C_6)	3.45–3.75(m, 6H, CH_2) 4.30–4.60(m, 2H, OCH_2)
2b	4.40 7.68	10.63(s, CH_3), 19.15(s, $\underline{C}H_2$), 49.22(dd, 129.40 Hz, 3.66 Hz, CH_2) 50.93(dd, 137.94 Hz, 4.88 Hz, $\underline{C}H_2$) 64.12(d, 4.88 Hz, C_6) 65.50(t, 3.66 Hz)C_5)	1.04(t, 7 Hz, 3H, CH_3) 1.80(quintet, 7 Hz, 2H, CH_2) 3.42–3.82(m, 5H, CH_2, CH) 4.22–4.50(m, 2H, OCH_2)
2c	5.05 8.31	18.67(s, CH_3), 48.41(d, 129.39 Hz, CH_2) 49.87(dd, 137.33 Hz, 8.54 Hz, $\underline{C}H_2$) 66.04(dd, 7.32 Hz, 3.05 Hz, C_5) 71.75(d, 4.88 Hz, C_6)	1.44(s, 6H, CH_3) 3.40(dd, 12 Hz, 3 Hz, 2H, CH_2) 3.64(d, 12 Hz, 2H, CH_2) 4.20(d, 13 Hz, 2H, OCH_2)
2d	4.75 7.02	19.68(d, 8.55 Hz, CH_3)50.93(dd, 129.39 Hz, 3.66 HzCH_2), 55.68(dd, 137.94 Hz, 8.5 Hz CH_2), 59.98(unresolved triplet, C_5), 70.49(d, 3.66 Hz, C_6)	1.36(approx. d, 7 Hz, 3H, CH_3) 3.04–3.94(m, 6H, CH_2) 4.5–4.8(m, 1H, OCH)
2e	4.90(J_{PP} = 2.44 Hz) 6.72(J_{PP} = 2.44 Hz)	51.29(dd, 128.91 Hz, 3.91 Hz, CH_2) 55.97(dd, 136.72 Hz, 7.81 Hz, CH_2) 59.87(unresolved triplet, C_5) 75.19(d, 3.91 Hz, C_6) 127.52, 130.25, 130.77, 136.68(d, 9.76 Hz)	3.25–4.05(m, 6H, CH_2) 5.65(dt, J_{P-H} = 10 Hz, J_{H-H} = 3 Hz, 1H) 7.50(s, 5H, Ar)
7a	14.96	44.56(d, 4.88 Hz, CH_3), 56.98(d, 139.16 Hz, CH_2—P) 59.90(s, CH_2OH), 60.43(d, 8.54 Hz, N—CH_2)	2.42(s, 3H, CH_3) 2.60(d, J_{P-H} = 12 Hz, CH_2—P) 2.78(t, 7 Hz, 2H, N—CH_2) 3.72(t, 7 Hz, 2H, CH_2OH)
7b	15.20	11.83(s, CH_3), 50.81(d, 7.32 Hz, CH_2) 53.73(d, 139.16 Hz, CH_2—P), 56.57(d, 4.88 Hz, N$\underline{C}H_2CH_2OH$), 60.30(s, $\underline{C}H_2OH$)	1.06(t, 7 Hz, 3H, CH_3), 2.60–3.00(m, 6H), 3.72(t, 7 Hz, 2H, $C\underline{H}_2OH$)
9	8.36	13.07(s, CH_3), 49.06(d, 135.50 Hz) 68.01(t, 3.66 Hz, $NCCH_3$), 71.10 (s, OCH_2) 95.45(s, OCH_2O)	1.45(s, 3H, CH_3) 3.98(d, 13.5 Hz, 2H), 4.23(d, 14 Hz, 4H, CH_2P), 4.70 (d, 13.5 Hz, 2H), 4.92(d, 7 Hz, 1H), 5.35(d, 7 Hz, 1H)

[a] Recorded on a Jeol FX-60 spectrometer operating at 24.15 MHz.

[b] Recorded on a Jeol FX-60 spectrometer operating at 15.04 MHz.

[c] Recorded on a Perkin–Elmer R-32 spectrometer (90 MHz). The ^{1}H NMR spectra of all except **9** were recorded in D_2O with sodium salt of trimethylsilylpropionic acid as reference. The ^{1}H NMR spectrum of **9** was recorded in trifluoroacetic acid with Me_4Si as reference.



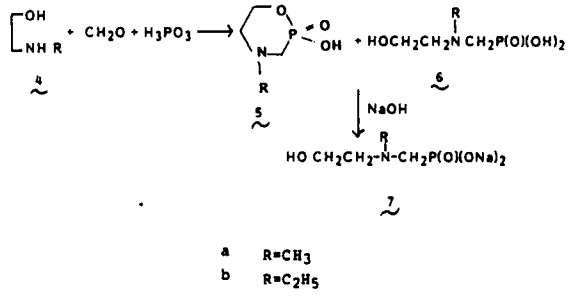
a $R_1=R_2=R_3=H$
b $R_1=R_2=H$, $R_3=C_2H_5$
c $R_1=H$; $R_2=R_3=CH_3$
d $R_1=CH_3$; $R_2=R_3=H$
e $R_1=C_6H_5$; $R_2=R_3=H$

Scheme 1

The crude product obtained from **1a** exhibited signals at 4.99 (d, $J = 1.8$ Hz), 8.12 (d, $J_{PP} = 1.8$ Hz) and 8.97 ppm in its ^{31}P NMR spectrum. When methanol was added to the crude product, a white crystalline solid separated out slowly. This solid was shown to be the cyclic ester **2a** from its ^{31}P NMR spectrum which contained signals at 4.90 (d, $J_{PP} = 2.4$ Hz) (P in the heterocyclic ring) and 7.53 ppm (d, $J_{PP} = 2.4$ Hz) (P in the methylene phosphonic acid) (Table I). The filtrate after the removal of **2a**, when examined by ^{31}P NMR, exhibited a major signal at 8.6 that split into a triplet when coupled to protons. However upon standing, only more of the cyclic ester **2a** precipitated out. Based on this observation, we assigned the signal at 8.97 ppm in the crude product to **3a**. From the ^{31}P NMR, the crude product appeared to be a 1:1 mixture of **2a** and **3a**. Thus phosphonomethylation of **1a** by Moedritzer and Irani's method[2] also yields a mixture of **2a** and **3a** (scheme-1) as does the Worms and Wollman's method.[4] The cyclic ester **2a** melted at 258–260°C. It is therefore likely that the product isolated by Moedritzer and Irani was **2a** and not **3a**.

Other aminoalkanols, **1b** and **1c**, containing primary amino and primary alcoholic functions gave crude products that exhibited spectra with similar characteristics except that in each case the cyclic ester **2** (**2b–2c**) was formed in greater amount than **3** (**3b–3c**) (ca 2:1). Aminoalkanols, **1d** and **1e**, containing primary amino and secondary alcoholic functions gave crude products which were also shown to be 2:1 mixtures of the cyclic ester structures (**2d** and **2e**) and the open chain structures (**3d** and **3e**). Only the cyclic esters **2** were isolated from the crude products by crystallization. Phosphonomethylation of 2-(alkylamino)ethanols **4** gave crude products that were shown to be 1:3 mixtures of the cyclic ester **5** and the open chain structure **6**. The crude products from 2-(alkylamino)-ethanols **4** failed to crystallize. These were treated with sodium hydroxide and disodium salts of [*N*-alkyl-*N*(2-hydroxyalkyl)amino] methanephosphonic acid **7** were isolated as colorless crystalline solids (scheme-2).

^{31}P NMR Spectra. The cyclic esters **2** exhibited two signals in the ^{31}P NMR spectra. The phosphorus in the heterocyclic ring appeared at about 4–5 ppm and the methylenephosphonic acid appeared at ca 7–8 ppm. The P–P coupling was observed in **2a** and **2e** and was about 2 Hz. The compounds **7** exhibited ^{31}P signal at ca 15 ppm.

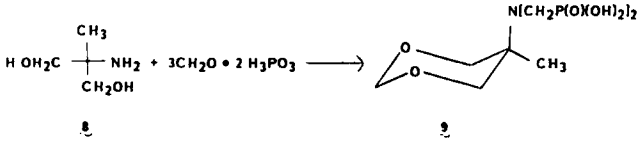


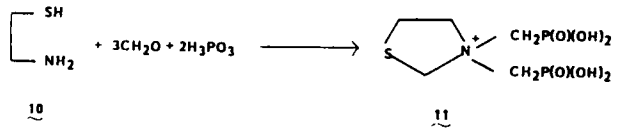
Scheme 2

^{13}C NMR spectra. ^{13}C NMR spectra were particularly useful in the characterization of the cyclic ester structures **2**. The compounds **2** showed the presence of two different methylene groups directly linked to phosphorus as expected. Each of these methylene groups appeared as a doublet of a doublet. The C_6 of the heterocyclic ring in **2** appeared as a doublet showing $^2J_{P-C}$ of 3–5 Hz. This carbon would be expected as a singlet in the alternate open chain structure **3** as observed in the case of **7**. Further the CH_3 group in **2d** and C_1 of phenyl group in **2e** appeared as doublets exhibiting $^3J_{P-C} = 9$ Hz. These would be expected as singlets in **3d** and **3e**. The ^{13}C NMR spectra of the disodium salts **7a** and **7b** showed the CH_2OH as singlet at ca 60.00 ppm in agreement with the open chain structures.

^1H NMR spectra. The ^1H NMR spectra were in complete accord with the cyclic ester structures for **2** and open chain structures for the disodium salts **7**. The ^1H NMR spectrum for **2c** was well resolved and exhibited a singlet for CH_3, a doublet of a doublet and a doublet assignable to two different CH_2 groups linked to phosphorus and a doublet at 4.20 ppm ($^3J_{P-H} = 13$ Hz) for -O CH_2 group. At the completion of this work, a report appeared confirming the cyclic ester structure of **2a** by x-ray diffraction studies.[6]

Phosphonomethylation of 2-amino-2-methyl-1,3-propanediol **8** gave a complex mixture (^{31}P NMR). When the crude product was dissolved in ethanol, the resulting solution slowly deposited a white crystalline solid. The ^{31}P NMR spectrum of this solid exhibited a single ^{31}P signal at +8.3 ppm that split into a triplet when coupled to protons. This suggested that there was no ring phosphorus in the structure of this product. In the ^{13}C NMR, this solid exhibited a triplet assignable to the carbon attached to nitrogen indicating the presence of two $—CH_2PO_3H_2$ groups. In addition, the ^{13}C NMR contained a signal at +95.45 ppm that is characteristic of the C-2 of the 1,3-dioxane structure. On the





Scheme 3

basis of this data, this solid was assigned the structure **9**, dimethylene diphosphonic acid of 5-amino-5-methyl-1,3-dioxane. It has been shown by other workers[7,8] that $N^+(CH_3)_3$ and other electronegative substituents attached to C-5 prefer axial position in the 1,3-dioxane series. In conformity with these studies, we propose that the structure **9** has a conformation in which methyl is equatorial and the N^+ group is axial. The proton magnetic resonance is in agreement with this structure. Our method appears to be the method of choice for preparing **9** in spite of its poor yield because 5-amino-5-methyl-1,3-dioxane is not easily accessible.

As reported previously[9] 2-aminoethanethiol **10** behaves much differently. Phosphonomethylation of **10** gave a crude product that exhibited ^{31}P signals at +6.11 and 7.83 ppm. The product which exhibited ^{31}P signal at +6.11 ppm was isolated and was shown to have the novel unexpected structure **11**.

EXPERIMENTAL

Melting points were determined on a melt-temp melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories and analytical division of Petrolite Corporation.

Phosphonomethylation of Aminoalkanols. A mixture of an aminoalkanol (0.2 mol), water (100 mL), phosphorous acid (0.4 mol) and conc. HCl (100 mL) was heated to reflux. Formaldehyde (66.6 mL of 36% aqueous, 0.8 mol) was added dropwise over a period of 2 h. The reaction mixture was refluxed for an additional 3 h and the solvent was removed on rotary evaporator. Water (200 mL × 3) was added and the solution was reevaporated to dryness to get the crude product as a colorless syrup.

4-(Phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2a**. The crude product obtained from 0.2 mol 2-aminoethanol **1a**, was dissolved in 20 mL water and methanol (200 mL) was added. The clear solution was allowed to stand whereupon 25.2 g (54%) of **2a** precipitated out as a white crystalline solid: mp darkens at 242°C and melts at 258–260°C.
Analysis. Calculated for $C_4H_{11}NO_6P_2$: N, 6.06; P, 26.84. Found: N, 6.07, P, 26.72.

5-Ethyl-4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2b**. The crude product obtained from 0.2 mol 2-amino-1-butanol **1b**, was dissolved in 200 mL ethanol. The sticky solid that separated after two days was collected by filtration. This was heated with a mixture of ethanol (50 mL) and water (5 mL) and filtered hot. There was isolated 14.5 g (28%) of **2b** as a white solid: mp 236–237°C.
Analysis. Calculated for $C_6H_{15}NO_6P_2$: C, 27.80; H, 5.79; N, 5.40; P, 23.94. Found: C, 27.42, H, 5.83; N, 5.35; P, 23.80.

5,5-Dimethyl-4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2c**. The crude product obtained from 0.2 mol 2-amino-2-methyl-1-propanol **1c**, was stirred with ethanol (500 mL). There was isolated 22.1 g (43%) of **2c** as a white crystalline solid: mp 235–237°C.
Analysis. Calculated for $C_6H_{15}NO_6P_2$: C, 27.80; H, 5.79; N, 5.40; P, 23.94. Found: C, 27.74; H, 5.62; N, 5.41; P, 23.80.

6-Methyl-4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2d**. The crude product obtained from 0.2 mol 1-amino-2-propanol **1d**, was dissolved in methanol. The clear solution was allowed to stand whereupon 24.8 g (49%) of **2d** precipitated out as a white crystalline solid: mp becomes sticky at 165°C and decomposes at 215°C.

Analysis. Calculated for $C_5H_{13}NO_6P_2 \cdot 0.3H_2O$: C, 23.96; H, 5.43; H, 5.59; P, 24.76; H_2O, 2.15. Found: C, 24.00; H, 5.71; N, 5.51; P, 24.60; H_2O, 2.29.

6-Phenyl-4-(phosphomethyl)-2-oxo-1,4,2-oxazaphosphorinane **2c**. The crude product obtained from 2-amino-1-phenylethanol (50 m mol) **1d**, was dissolved in ethanol (75 mL). The yield of **2e** which crystallized out slowly as a white solid was 7.1 g (46%): mp 235–236°C.
Analysis. Calculated for $C_{10}H_{15}NO_6P_2$: C, 39.09, H, 4.89; N, 4.56; P, 20.20. Found: C, 38.82; H, 5.01; N, 4.53; P, 19.90.

Phosphonomethylation of (N-alkylamino) ethanols. A mixture of an 2-(alkylamino)ethanol (0.1 mol), water (25 mL), phosphorous acid (0.1 mol) and conc HCl (25 mL) was heated to reflux. Formaldehyde (16.65 mL of 36% aqueous, 0.2 mol) was added dropwise over a period of 30 min. The reaction mixture was refluxed for an additional 3 h. The volatiles were removed on rotary evaporator. Water (50 mL × 3) was added to the residue and the solution was reevaporated to get the crude product as a viscous syrup.

Disodium salt of [N-(2-hydroxyethyl)-N-methylamino]methanephosphonic acid **7a**. The crude product obtained from 0.1 mol 2-(methylamino)ethanol, was refluxed with 64 g of 25% aq. NaOH for 3 h. After cooling to r.t., ethanol (250 mL) was added. The oil that precipitated out was separated from supernatant liquid and was dissolved in water (25 mL). Methanol (300 mL) was next added when a white solid precipitated out. The solid was collected by filtration and dissolved in methanol (175 mL) at rt. The solution was filtered to remove any suspended solid. The filtrate on warming deposited 7.0 g (30%) of **7a** as a white crystalline solid.
Analysis. Calculated for $C_4H_{10}NO_4PNa_2 \cdot H_2O$: C, 20.78; H, 5.19; N, 6.06; P, 13.42; H_2O, 7.79. Found: C, 20.89; H, 5.10; N, 6.04; P, 13.32; H_2O, 7.63.

Disodium salt of [N-Ethyl-N-(2-hydroxyethyl)amino]methanephosphonic acid **7b**. The crude product obtained from 0.1 mol 2-(ethylamino)ethanol was refluxed with 64 g of 25% aqueous sodium hydroxide for 5 h. After cooling to rt, ethanol (350 mL) was added and the precipitated solid (25.8 g) was collected by filtration. 5 g of this solid was dissolved in methanol (150 mL) and the solution was filtered and the filtrate was concentrated. There was obtained 1.0 g of **7b** as a colorless crystalline solid.
Analysis. Calculated for $C_5H_{12}NO_4PNa_2 \cdot 0.3H_2O$; C, 25.81; H, 5.42; N, 6.02; P, 13.34; H_2O, 2.32. Found: C, 25.81; H, 5.21; N, 5.92' P, 13.34; H_2O, 2.33.

5-[(Bis(phosphonomethyl))amino]-5-methyl-1,3-dioxane **9**. A mixture of 2-amino-2-methyl-1,3-propanediol (0.1 mol), water (50 mL), phosphorous acid (0.2 mol) and conc. HCl (50 mL) was heated to reflux. Formaldehyde (31.6 g of 38% aqueous, 0.4 mol) was added over a period of 30 min. The reaction mixture was refluxed for an addition 3 h and the solvent was removed on rotary evaporator. Water (50 mL × 3) was added and the solution was reevaporated to dryness to get the crude product as a colorless syrup. The crude product was dissolved in 100 mL ethanol and just enough water to obtain a clear solution. After four days, there was obtained 3.5 g of **9** as a colorless solid: mp 196–198°C with effervescence.
Analysis. Calculated for $C_7H_{17}NO_8P_2$: C, 27.54; H, 5.57; N, 4.59; P, 20.32. Found: C, 27.26; H, 5.56; N, 4.62; P. 20.12.

Phosphonomethylation of 2-Aminoethanethiol **10**. A mixture of 2-aminoethanethiol hydrochloride (0.05 mol), water (29.0 g), phosphorous acid (0.1 mol) and concentrated HCl (21.0 mL) was heated to reflux. Formaldehyde (36% aq, 0.2 mole) was added over a period of 45 minutes. The reaction mixture was refluxed for an additional 3 hours and then evaporated to dryness on rotary evaporator. Water (70 mL × 2) was added and the solution was reevaporated. The crude product was dissolved in water and allowed to stand. There was obtained 2.5 g of **11** as a white crystalline solid, mp 218°C decomp.
^{31}P NMR (D_2O/H_3PO_4Cap.) + 6.1; ^1H NMR 3.35 (t, $J_{HH} = 7$ Hz, 2H, S—CH_2), 4.06 (d, $J_{PH} =$ 13 Hz, 4H, CH_2—P), 4.12 (t, 2H, N—CH_2), 4.87 (s, 2H, S—CH_2N); ^{13}C NMR (D_2O/Me_4Si Cap) 27.92 (s, S—CH_2), 58.15 (d, $J_{P-C} = 133.06$ Hz, $NCH_2PO_3H_2$), 68.66 (unresolved t, N—CH_2 and N—CH_2—S).
Analysis. Calculated for $C_5H_{13}NO_6P_2S$; C, 21.66; H, 4.67; N, 5.05; P, 22.38; S, 11.55. Found: C, 21.66; H, 4.69; N, 5.00; P, 22.39; S, 11.55.

REFERENCES

1. Presented in Part at the 23rd Midwest Regional Meeting of the American Chemical Society, Iowa City, November 1988, Abstract 163.
2. K. Moedritzer and R. R. Irani, *J. Org. Chem.* **31,** 1603 (1966).
3. D. Redmore and B. Dhawan, *Phosphorus and Sulfur,* **16,** 233 (1983).
4. K. H. Worms and K. Wollman, *Z. Anorg. Allg. Chem.* **381,** 260 (1971).
5. N. V. Tsirul'nikova, V. Ya. Temkina, T. M. Sushitskaya and S. V. Rykov, *Zh. Obshch. Khim.,* **51,** 1028 (1981).
6. B. I. Makaranets, T. N. Polynova, M. A. Porai-Koshits and S. A. Il'ichev, *Izv. Akad. Nauk, SSSR, Ser. Khim.* 2649 (1984).
7. R. Van Cauwenberghe, M. Anteunis and L. Valckx, *Bull. Soc. Chim. Belg.* **83,** 285 (1974).
8. E. L. Eliel and S. A. Evans, *J. Amer. Chem. Soc.* **94,** 8587 (1972).
9. B. Dhawan and D. Redmore, *J. Heterocyclic Chem.* **25,** 1273 (1988).