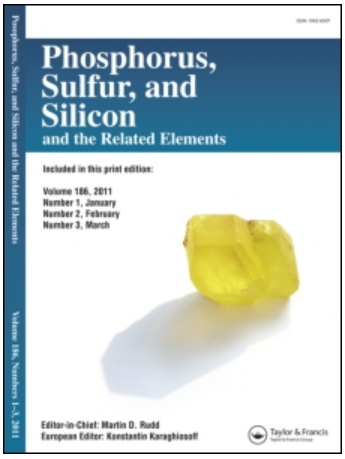

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SYNTHESIS OF SOME CARBONYL DERIVATIVES OF TRIS(AMINOMETHYL)PHOSPIE OXIDE

Arlen W. Frank[a]
[a] U.S. Department of Agriculture, Southern Regional Research Center, ARS, New Orleans, Louisiana

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SYNTHESIS OF SOME CARBONYL DERIVATIVES OF TRIS(AMINOMETHYL)PHOSPHINE OXIDE[1]

ARLEN W. FRANK

Southern Regional Research Center, ARS, U.S. Department of Agriculture, New Orleans, Louisiana 70179

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Miscellaneous phosphorylated carbamates, ureas and thioureas of potential value as flame retardants for cotton have been synthesized from a key intermediate, tris(aminomethyl)phosphine oxide (**1**), whose synthesis we recently described. Reactions were carried out between **1** and representative chloroformates, isocyanates, thiocyanates and ureas, and with carbonyl sulfide and carbon disulfide. An improved procedure was developed for the thermal cyclization of the carbonyl sulfide and carbon disulfide adducts.

INTRODUCTION

Polymers containing the PCH_2N group are useful as flame retardant finishes for cotton.[2] Fabrics treated with these finishes, however, are sometimes deficient with respect to hand, strength, easy care properties, or resistance to chlorine bleach. A goal of the Center's research program is to overcome these deficiencies through structural modification of the polymers. One of the key reagents for this work is tris(aminomethyl)phosphine oxide (**1**), whose synthesis we have recently described.[3–5] This paper concerns the reactions of **1** with carbonyl reagents to give miscellaneous phosphorylated carbamates, ureas and thioureas that should be useful for the preparation of modified polymer finishes.

RESULTS AND DISCUSSION

Carbamate Derivatives

Reaction of **1** with the alkyl chloroformates **2a–d** in water at 10–15°C gave the tris(*N*-carbalkoxylaminomethyl)phosphine oxides **3a–d** in 86–97% yield (Eq. (1)):[6]

$$\underset{\mathbf{1}}{(NH_2CH_2)_3PO} + 3\ ClCO_2R + 3\ NaOH \longrightarrow \underset{\mathbf{3}}{(RO_2CNHCH_2)_3PO} + 3\ NaCl + 3\ H_2O \qquad (1)$$

$\mathbf{2}$: a, R = Me; b, R = Et; c, R = i-Pr; d, R = n-Bu

The products were all new except the methyl derivative **3a**, which had been prepared previously from the phosphonium chloride **4a** by ammonolysis followed by oxidation.[7,8] Application of this method to the phosphonium chlorides **4b–d** gave the corresponding tertiary phosphine oxides **3b–d** in 26–87% yield (Eq. (2)):

$$\underset{\mathbf{4}}{(RO_2CNHCH_2)_4PCl} + NH_4OH + H_2O_2 \longrightarrow \underset{\mathbf{3}}{(RO_2CNHCH_2)_3PO} + RO_2CNHCH_2OH + NH_4Cl + H_2O \quad (2)$$

a, R = Me

b, R = Et

c, R = i-Pr

d, R = n-Bu

The products of the two methods were identical.

Urea Derivatives

The tris(ureidomethyl)phosphine oxides **6b, c** were prepared without difficulty in 91–97% yield by the reaction of **1** with the isocyanates **5b, c** in acetonitrile, with ice-bath cooling to moderate the exotherm (Eq. (3)):

$$\underset{\mathbf{1}}{(NH_2CH_2)_3PO} + 3\ RNCO \longrightarrow \underset{\mathbf{6}}{(RNHCONHCH_2)_3PO} \quad (3)$$

$\mathbf{5}$

a, R = H

b, R = Me

c, R = Ph

The products were identical to those reported previously for the reaction of tris(hydroxymethyl)phosphine with methyl- or phenylurea, whose structures had been assigned on the basis of spectroscopic evidence.[9,10] The present work confirms these assignments, for the structures of the products of Eq. (3) are unambiguous.

For the unsubstituted tris(ureidomethyl)phosphine oxide **6a** (TUPO), isocyanic acid (**5a**) was generated *in situ* by the reaction of sodium cyanate with the crystalline trihydrochloride of **1** in aqueous solution. The product, unlike earlier preparations,[11,12] was a white crystalline solid, mp 180–182°C dec., whose NMR spectrum showed a single signal for the CH_2 protons at δ_H 3.74 ppm, split into a doublet by coupling with the phosphorus, and a single signal for the phosphorus at δ_P 38.3 ppm, split into a septet by coupling with the six CH_2 protons. TUPO products prepared from tetrakis(ureidomethyl)phosphonium chloride (TUPC)[11] or octakis(ureidomethyl)diphosphonium sulfate (TUPS)[12] by hydrolysis followed by oxidation were both viscous colorless resins. Their NMR spectra showed other signals in the CH_2 region, but the main feature of both was the CH_2 signal for **6a**.

The tris(ureidomethyl)phosphine oxides **6a, b** were also prepared in 79–81% yield by the reaction of **1** with the ureas **7a, b** (Eq. (4)):[13]

$$(NH_2CH_2)_3PO + 3\ CO(NHR)_2 \longrightarrow (RNHCONHCH_2)_3PO + 3\ RNH_2 \quad (4)$$

1 **7** **6**

a, R = H

b, R = Me

Reaction of **1** with a large excess of urea was over after several hours at reflux in aqueous solution, but reaction with 1,3-dimethylurea was negligible under these conditions. In the absence of a solvent, **1** reacted smoothly with a large excess of 1,3-dimethylurea giving tris(3-methylureidomethyl)phosphine oxide (**6b**) after 3.5 hours at 145–155°C. This method too gives a product of unambiguous structure.

Thiourea Derivatives

Reaction of **1** with ethyl isothiocyanate in acetonitrile under the conditions of Eq. (3) gave tris(3-ethylthioureidomethyl)phosphine oxide (**8b**) in 92.2% yield (Eq. (5)):

$$(NH_2CH_2)_3PO + 3\ RNCS \longrightarrow (RNHCSNHCH_2)_3PO \quad (5)$$

1 **8**

a, R = H

b, R = Et

No reaction occurred between sodium or potassium thiocyanate and the trihydrochloride of **1** in water, nor between **1** and carbon disulfide and sodium hydroxide followed by ethyl chloroformate.[14] The anticipated products were **8a** and $(SCNCH_2)_3PO$, respectively.

Thiocarbamate Derivatives

Reaction of **1** with carbonyl sulfide or carbon disulfide in ethanol solution at room temperature gave the 1 : 1 adducts **9a, b** in 90–95% yield (Eq. (6)):

(6)

1 **9**

a, X = O, Y = S

b, X = Y = S

c, X = Y = O

TABLE I

^{1}H NMR data for the adducts **9a–c**[a]

Assignment	9a	9b	9c[b]
		In D_2O	
α	3.40 (6)	3.43 (6)	3.38 (6)
β	3.44 (6)	3.43 (6)	3.38 (6)
γ	3.88 (6)	4.50 (7)	3.77 (4.5)
		In D_2O / NaOD	
α	3.14 (5)	3.21 (5.5)	3.15 (5.5)
β[c]	3.20 (6)	3.21 (5.5)	3.17 (6)
γ	3.78 (6)	4.39 (7)	3.66 (5.5)

[a] δ_H in ppm, J (in parentheses) in Hz.
[b] Data from ref. 3.
[c] The doublet for pure **1** shifts almost imperceptibly from 3.22 (6) in D_2O to 3.21 (6) in D_2O/NaOD.

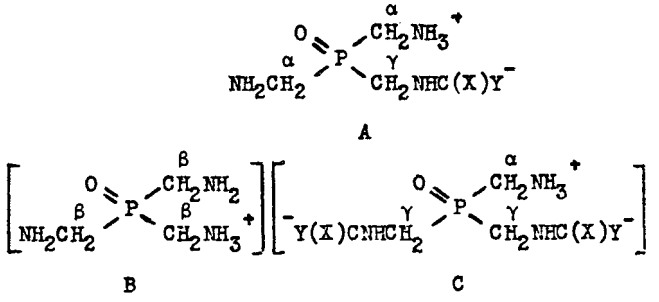
As in the reaction of **1** with carbon dioxide that gave **9c**,[3] the initial products were low-melting fluffy solids that changed on exposure to air (moisture) to compact crystalline solids. The carbon disulfide adduct **9b** was water-soluble when first prepared, but separated within an hour becoming almost totally insoluble.

The reaction of **1** with carbon disulfide could also be carried out in methanol or ethanol at reflux; no adduct is formed under these conditions between **1** and carbon dioxide.[3] In higher-boiling solvents, the carbon disulfide adduct cyclized to a thiourea (see below).

No reaction occurred when the carbon dioxide adduct **9c** was treated with carbon disulfide in methanol or ethanol, either in the presence or absence of water. Carbon dioxide is displaced from benzylamine carbamate or ethylenediamine carbamate under these conditions, giving the corresponding dithiocarbamate in high yield.[15,16]

The ^{1}H NMR spectra of **9a** and **9b** resembled **9c** in gross features but differed in detail. All three showed a pair of doublets for the three methylene groups in a ratio of 4 : 2, but the stronger doublet in **9a** was further split into a pair of overlapping doublets. Upon the addition of NaOD to the D_2O solutions, all of the signals shifted upfield but only the stronger doublet of **9c** split into a pair of overlapping doublets (Table I).

The structure of **9c**, based on an analysis of its ^{1}H and ^{13}C NMR spectra, was previously established to be an equimolar mixture of monocarbamate salt A and dicarbamate salt BC (X = Y = O):[3]

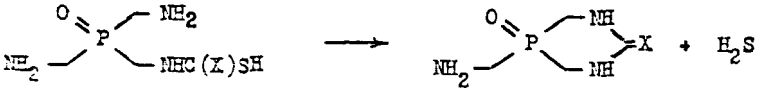


The behavior of **9a** and **9b** suggests that they too are equimolar mixtures of A and BC (X = O, Y = S and X = Y = S, respectively), though the evidence for **9b** is not conclusive. The signals for the unsubstituted aminomethylene groups α and β are distinct in **9a**, but coincide in **9b** and **9c** in D_2O and in **9b** in NaOD. In D_2O, the signals within each A and B component are averaged by proton exchange between the nitrogens. The signals for the substituted aminomethylene groups γ appear farther downfield and coincide in all three adducts.

The mass spectra of **9b** and **9c** were profoundly influenced by their thermal instability, discussed in the next section. The carbon dioxide adduct **9c**, which reverts to its components when heated, showed lines at m/e 138 (protonated **1**) and 44 (CO_2), together with lines at 108 and 78 ascribed to the cleavage of one or two $CH_2NH_2^+$ fragments from the protonated **1**. The carbon disulfide adduct **9b**, which cyclizes with the loss of H_2S when heated, showed lines at m/e 179 (**9b** − H_2S) and 34 (H_2S), together with a strong line at 149 ascribed to the cleavage of the remaining $CH_2NH_2^+$ fragment from the cyclized **9b**. The loss of $CH_2{=}NH_2^+$ (m/e 30) is a common pathway for fragmentation of aliphatic amines of the type RCH_2NH_2.[17] No molecular ions of the salts A or BC were detected.

Cyclic Urea and Thiourea Derivatives

When heated to 100°C or above, the adducts **9a, b** cyclized with the evolution of hydrogen sulfide giving 5-aminomethyl-1,3-diaza-5-phosphorinan-2,5-dione (**10a**) and its 2-thio derivative (**10b**), respectively (Eq. (7)):



9 **10** (7)

a, X = O

b, X = S

The isolation of **10a, b** from the reaction mixture in satisfactory yield and purity proved to be difficult. Table II summarizes the results of cyclization experiments on **9b** carried out under a variety of conditions. Cyclization in water, under the conditions of Hofmann's original paper on ethylenethiourea,[18] gave a moderate yield of **9b**-free **10b**, together with 27% of **1** owing to hydrolytic cleavage of the **9b**. The use of hydrochloric acid, said to be beneficial for such cyclizations,[19,20] caused even more extensive cleavage. Cyclization in neutral solvents such as *n*-butanol, diethyl carbonate or anisole, or basic solvents such as pyridine, gave **10b** contaminated with unreacted **9b** and other unidentified by-products. Cyclization in glacial acetic acid gave no **10b** at all. The use of benzaldehyde to protect the free amine group by Schiff base formation produced no improvement, nor did omission of the solvent.

The best results were obtained by cyclization of **9a** or **9b** in boiling water in the presence of an excess of calcium hydroxide. No hydrogen sulfide was liberated until the mixture was acidified. The preferred method was to treat the solution, after filtering off the excess calcium hydroxide, with carbon dioxide at 70°C until the

TABLE II

Cyclization of **9b** to **10b**

Temp. °C	Solvent	Time hr	Product, **10b**	% Yield Other
100	H_2O	2	67	0 (**9b**), 27 (**1**)
100	H_2O (HCl)[a,b]	1	28	68 (**1**)
100	H_2O [$Ca(OH)_2$][c]	2	90	10.8 (**12**), 0 (**9b**)
115.5	Pyridine	2	56	16 (**9b**)
117	*n*-Butanol	2	69	7 (**12**), 9 (**9b**)
117	*n*-Butanol	5	51	8 (**9b**)
118	Acetic acid	3	0	Oil[d]
126	$(EtO)_2CO$	1	68	18 (**9b**)
126	$(EtO)_2CO$ (PhCHO)[c]	1	48	0 (**9b**)
126	$(EtO)_2CO$ (PhCHO)[a]	1	49	
138	None (vacuum)	2	57	34 (**1**)
155	Anisole	2	52	
175	None (1 atm)	0.25	0[e]	

[a] One mol reagent per mol **9b**.
[b] The presence of HCl is beneficial for the preparation of ethylenethiourea.[19,20]
[c] Two mols reagent per mol **9b**.
[d] NMR: δ_H (D_2O) 2.07 (t, 3 H, CH_3, J = 2 Hz) and 3.85 (d, 2 H, CH_2, J = 6 Hz) ppm.
[e] Sandy solid insoluble in water.

hydrogen sulfide was expelled; heating was necessary to prevent the latter from dissolving the calcium carbonate.[21]

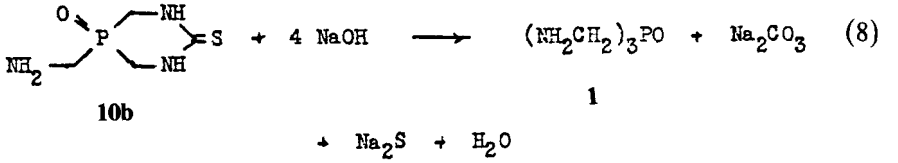
The 2-oxo product, mp 198–199°C, isolated in 73.0% yield, was identical to the by-product of the alkaline hydrolysis of **3a**,[3] confirming its identity as **10a**. The 2-thio product, mp 207–208°C, isolated in 74.9% yield, was identified as **10b** by its IR spectrum, which showed a very strong doublet at 1227–1242 cm^{-1} (C=S) and no C=O, and by its ^1H NMR spectrum, which showed a 2 : 2 : 2 doublet/triplet/singlet pattern similar to that of **10a**. Under identical conditions, the carbon dioxide adduct **9c** simply regenerated the amine **1**, no trace of **10a** being detected. The same behavior is observed when **9c** is heated in the absence of a solvent.[3]

The proton-decoupled ^{31}P NMR spectra of **10a** and **10b** showed a single signal for the phosphorus resonance at δ_P 32.3 and 25.6 ppm, respectively, but the undecoupled spectra both exhibited far greater peak spread and multiplicity than expected. The J_{PH} couplings reported[3] for **10a**, for example, translate to a $\pm$7.0 Hz peak spread for phosphorus, yet the observed peak spread was $\pm$27.3 Hz. If the triplet/singlet portion of the ^1H NMR spectra, representing the four ring protons of **10a** and **10b**, are reconfigured as a 1 : 2 : 1 triplet of doublets, the phosphorus peak spreads become $\pm$27.5 and $\pm$28.0 Hz, respectively, in excellent agreement with those observed. Despite the multiplicity, 14 of the 25 lines of **10a** and 17 of the 27 lines of **10b** were positively identified in their ^{31}P NMR spectra. Two of the four ring protons in each compound are therefore magnetically equivalent and two are not, but it is not possible to determine which is which.

The ^{13}C NMR spectra of **10a** and **10b** were consistent with the assigned structures. The chain carbon and the ring carbons C_4 and C_6 appeared as a pair of signals in the δ_C 37–39 ppm region, each split into a doublet by coupling with phosphorus and further split into a doublet of triplets by coupling with the geminal protons. The

C=X carbon appeared at 159.8 ppm in **10a** and 177.8 ppm in **10b**, each split into a doublet by coupling with phosphorus. These assignments are very similar to those reported for the phosphorus-free propyleneureas and -thioureas.[22]

The 2-thio compound **10b** was unexpectedly sensitive to base, regenerating the triamine **1** within a day at room temperature (Eq. (8)). Neither **10a** nor ethylenethiourea exhibit this behavior. Thioureas are often very difficult to hydrolyze.[23]

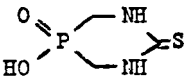


10b **1**

(8)

In contrast, **10b** appeared to be stable indefinitely to acid. It formed crystalline 1 : 1 salts (**11a–c**) with hydrochloric acid, sulfuric acid and oxalic acid that were, like those of **10a**,[3] soluble in the concentrated acids.

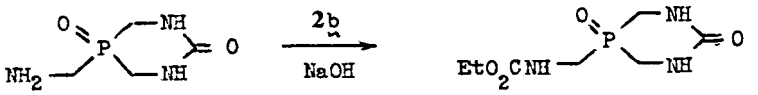
A by-product of the cyclization of **9b**, separated from the main product by anion exchange chromatography, was identified by IR, ^1H NMR, ^{31}P NMR, ^{13}C NMR and elemental analysis as the phosphinic acid **12**:



12

This by-product, unlike **10b**, was stable to base as well as to acid. Since neither **10a** nor **10b** undergoes C—P bond cleavage upon refluxing with aqueous calcium hydroxide, and **1** is known to be stable under these conditions,[3] the source of the **12** is unknown.

The cyclic amine **10a** reacted with ethyl chloroformate (**2b**) under the conditions of Eq. (1) giving the carbamate derivative **13** in 83% yield (Eq. (9)):



10a **13**

(9)

EXPERIMENTAL[24]

Reagents. Tris(aminomethyl)phosphine oxide (**1**) was prepared from the carbamate **3a** by hydrolysis with calcium hydroxide.[3] The ^1H NMR spectrum of the neat liquid, not reported previously, exhibited signals at δ_H 2.58 (s, 6 H, NH_2) and 3.17 (d, 6 H, CH_2, J = 6.0 Hz) ppm. The methylene protons were coupled to phosphorus (as in D_2O, where δ_H = 3.22 ppm; d, 6 H, CH_2, J = 6.0 Hz)[4] but not to NH_2. The trihydrochloride, dec. 239°C,[4] was prepared by treating **1** with 6*N* hydrochloric acid, filtering, rinsing the crystalline salt with 6*N* hydrochloric acid followed by ethanol, and air-drying. The carbon

dioxide adduct **9c** was prepared from **1** as previously described.[3] The phosphonium chlorides **4a–d** were prepared by the reaction of tetrakis(hydroxymethyl)phosphonium chloride with the appropriate alkyl carbamate.[7] Carbonyl sulfide was prepared from thiocyanic acid[15] or obtained from a commercial lecture bottle; the results were the same. Other reagents were commercial products and were used as obtained.

Methods. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared (IR) spectra were taken on a Perkin-Elmer 137B (m = medium, s = strong, vs = very strong, br = broad, sh = shoulder). Nuclear magnetic resonance (NMR) spectra were taken on a Varian EM-360L (^{1}H) or a Varian CFT-20 (^{13}C and ^{31}P), with TMS or DSS as an internal reference for the ^{1}H spectra, dioxane as an internal reference for the ^{13}C spectra,and 85% phosphoric acid as an external reference for the ^{31}P spectra (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Chemical shifts are given relative to TMS (δ_H and δ_C) or H_3PO_4 (δ_P), downfield positive. Mass spectra were taken on a Finnigan 4000 GC-MS at 70 eV, the sample being injected into the probe, heated in ballistic fashion to 300°C, and scanned from m/e 33 to 450.

Tris(N-carbethoxylaminomethyl)phosphine Oxide (**3b**)

A. From **1**. Ethyl chloroformate (8.14 g, 0.075 mol) was added dropwise to a solution of **1** (6.86 g, 0.05 mol) in water (15 ml) over a 10 min period at 10–15°C with ice-bath cooling and mechanical stirring. Solids separated from the start. The mixture was diluted with ice-water (15 ml) and treated simultaneously with ethyl chloroformate (8.14 g, 0.075 mol) and 50% sodium hydroxide solution (12.00 g, 0.05 mol) over a 10 min period at 10–15°C. The mixture, now neutral, was allowed to warm to room temperature and was then filtered, giving 15.65 g (88.6%) of **3b** as a white solid, mp 155–165°C. Another 0.73 g was recovered from the filtrate by extraction with chloroform; total yield, 16.38 g (92.8%). One recrystallization from ethanol gave pure **3b** as a white, crystalline solid, mp 158–158.5°C; IR (KBr): 1024m, 1136s (P=O), 1250s, 1290m, 1522s (NH, amide II), 1550s, 1700vs (C=O, amide I), 3205m, sh (NH) and 3345m cm^{-1}; NMR: δ_H ($CDCl_3$) 1.27 (t, 9 H, CH_3, J = 7 Hz), 3.72 (t, 6 H, CH_2P, J = 6 Hz; d, J = 5 Hz with D_2O), 4.14 (q, 6 H, CH_2C, J = 7 Hz) and 6.60 (t, 3 H, NH, J = 6 Hz, vanishing with D_2O) ppm; δ_P ($CDCl_3$) 44.8 ppm.

Anal. Calcd. for $C_{12}H_{24}N_3O_7P$: C, 40.79; H, 6.85; N, 11.90; P, 8.77. Found: C, 40.73; H, 6.77; N, 11.89; P, 9.04.

The ethyl ester **3b** is soluble in chloroform and insoluble in water, acetone or carbon tetrachloride. It can be recrystallized from ethanol (3 ml/g) or acetonitrile (5 ml/g). When heated above its mp it gasses gently at 195–205°C without discoloration.

B. From **4b**. Conc. ammonium hydroxide (3 ml) was added to a stirred solution of **4b** (4.75 g, 0.01 mol) in water (20 ml) in an apparatus previously purged with argon. Solids separated within one minute. After 1 hr the mixture, still under argon, was treated dropwise with 3% hydrogen peroxide (11.3 ml, 0.01 mol) over a 10 min period at room temperature, stirred for 1 hr. and filtered, giving 2.66 g (75.4%) of **3b** as a white crystalline solid, mp 156–157°C. Another 0.42 g, mp 152–154°C, was recovered from the filtrate by extraction with chloroform and rinsing the product with water and with acetone; total yield, 3.08 g (87.2%). The identity of the product was confirmed by IR and ^{1}H NMR.

Tris(N-carbomethoxylaminomethyl)phosphine Oxide (**3a**). Prepared by method A in 96.8% yield or by method B (see ref. 8 for details) in 88.0% yield. To remove by-product sodium chloride, the product was shaken with glacial acetic acid (10 ml/g), filtered, stripped under vacuum, shaken with ethanol, and collected on a filter. Mp, IR, ^{1}H NMR as previously reported;[3,7] NMR: δ_P (d_6-DMSO) 40.6 ppm.

Tris(N-carboisopropoxylaminomethyl)phosphine Oxide (**3c**). Prepared by method A in 90.2% yield or by method B in 82.0% yield. One recrystallization from water gave pure **3c** as colorless needles, mp 159–159.5°C; IR (KBr): 860m, 1105s, 1136s (P=O), 1170s, 1220m, 1250vs, 1290s, 1372m, 1383m, 1530s (NH, amide II), 1684vs (C=O, amide I), 2970s, and 3310s (NH) cm^{-1}; NMR: δ_H ($CDCl_3$) 1.25 (d, 18 H, CH_3, J = 6 Hz), 3.72 (t, 6H, CH_2, J = 5.5 Hz, collapsing with D_2O to d, J = 6 Hz), 4.92 (septet, 3 H, CH, J = 6 Hz), and 6.47 (t, 3 H, NH, J = 5.5 Hz, vanishing with D_2O) ppm; δ_P ($CDCl_3$) 44.6 ppm.

Anal. Calcd. for $C_{15}H_{30}N_3O_7P$: C, 45.56; H, 7.65; N, 10.63; P, 7.83. Found: C, 45.65; H. 7.47; N, 10.61; P, 7.56.

The isopropyl ester **3c** is non-hygroscopic, soluble in ethanol and acetone, and insoluble in water, ether, benzene and cyclohexane. It can be recrystallized from water (17 ml/g) or isopropyl alcohol (2 ml/g), and decomposes without discoloration at 189°C.

Tris(N-carbo-n-butoxylaminomethyl)phosphine Oxide (**3d**). Prepared by method A in 86.3% yield or by method B in 25.8% yield. In method B, ethanol (10 ml) was added to the water (20 ml) to help dissolve the

4d. One recrystallization from cyclohexane gave pure **3d** as a white crystalline solid, mp 96–96.5°C; IR (KBr): 773m, 1020m, 1139s (P=O), 1256s, 1307s, 1391m, 1460m, 1524s (NH, amide II), 1700vs (C=O, amide I), 2865m, 2950s, 3225m, and 3300s (NH) cm^{-1}; NMR: δ_H ($CDCl_3$) 0.93 (t, 9 H, CH_3, J = 6 Hz), 1.1–1.8 (m, 12 H, CH_2CH_2), 3.72 (t, 6 H, CH_2P, J = 6 Hz, collapsing with D_2O to d, J = 6 Hz), 4.08 (t, 6 H, CH_2O, J = 6 Hz), and 6.57 (t, 3 H, NH, vanishing with D_2O) ppm; δ_P ($CDCl_3$) 44.9 ppm.

Anal. Calcd. for $C_{18}H_{36}N_3O_7P$: C, 49.42; H, 8.30; N, 9.61; P, 7.08. Found: C, 49.47; H, 8.32; N, 9.60; P, 7.27.

The *n*-butyl ester **3d** is non-hygroscopic, soluble in the common organic solvents, and insoluble in water. It can be recrystallized from cyclohexane (7 ml/g), and decomposes without discoloration at 227–230°C.

Tris(ureidomethyl)phosphine Oxide (**6a**)

C. Urea Method. A mixture of **1** (5.48 g, 0.04 mol), urea (21.62 g, 0.36 mol), and water (50 ml) was heated in an oil bath for 5 hr at reflux with constant stirring. After cooling, the solution was stripped of water under reduced pressure. The residue, a mixture of **6a** and urea, was thoroughly dried under vacuum and was then extracted with ethanol for 8 hr in a Soxhlet extractor, giving 8.62 g (81.0%) of **6a** as a white crystalline solid, mp 179–181°C dec.; IR (Nujol): 853m, 1135s, 1165s (P=O), 1195m, 1270m, 1540–1580vs, br (NH, amide II), 1635vs (C=O, amide I), 3340s (NH), and 3500s (NH) cm^{-1}; NMR: δ_H (D_2O) 3.74 (d, 6 H, CH_2, J = 4.5 Hz); δ_H (d_6-DMSO) 3.47 (t, 6 H, CH_2, J = 5 Hz), 5.85 (s, 6 H, NH_2), and 6.41 (t, 3 H, NH, J = 5 Hz) ppm; δ_P (D_2O) 38.3 (septet, J_{PH} = 4.6 Hz) ppm.

Anal. Calcd. for $C_6H_{15}N_6O_4P$: C, 27.07; H, 5.68; N, 31.58; P, 11.63; mol. wt., 266.21. Found: C, 26.87; H, 5.52; N, 31.38; P, 11.51; mol. wt. (osmometric in H_2O), 256.

The ureide **6a** is soluble in water, acetic acid, DMSO and hot dimethylformamide, and insoluble in the common organic solvents.

D. Isocyanic Acid Method. A solution of **1** trihydrochloride (7.40 g, 0.03 mol), sodium cyanate (5.85 g, 0.09 mol), and water (50 ml) was stirred overnight in a loosely stoppered flask. The ^1H NMR spectrum of the aqueous solution showed only the sharp **6a** doublet at δ_H 3.74 (4.5 Hz). The solution was acidified with 6*N* hydrochloric acid, and after the gassing ceased it was transferred to a 19 × 600 mm chromatographic column half filled with a 1 : 1 blend of Rexyn 101 (H) and Rexyn 201 (OH) ion exchange resins and eluted with water. The effluent, tested and found to be salt-free, was stripped of water under reduced pressure. The residue was rubbed with ethanol, filtered and dried, giving 2.78 g (69.5%) of **6a** as a white crystalline solid, mp 180–182°C dec., identical (IR, ^1H NMR) to the product described above.

E. From TUPC or TUPS. The ^1H NMR spectra of TUPO solutions prepared from TUPC[11] or TUPS[12] both showed a strong signal for **6a** at δ_H 3.74 ppm, but the presence of extra signals in the 3.5 to 4.5 ppm region made it impossible to determine their purity. The TUPC product, reflecting the purity of the starting material, had the fewer extra signals.

Tris(3-methylureidomethyl)phosphine Oxide (**6b**)

F. Isocyanate Method. A slurry of **1** (5.48 g, 0.04 mol) in acetonitrile (25 ml) was treated dropwise with a solution of methyl isocyanate (6.85 g, 0.12 mol) in acetonitrile (25 ml) over a 15 min period, with ice-bath cooling applied to control the exotherm. Solids separated all through the addition. After 2 hr stirring, the product was collected on a filter, rinsed with acetonitrile and dried, giving 12.02 g (97.5%) of **6b** as a white crystalline solid, mp 228°C dec. One recrystallization from ethanol/water gave pure **6b**, mp 232°C dec., identical (IR, ^1H NMR) to the product prepared from tris(hydroxymethyl)phosphine.[9]

G. Urea Method. A mixture of **1** (5.48 g, 0.04 mol) and 1,3-dimethylurea (31.72 g, 0.36 mol) was heated in an oil bath at 145–155°C until an NMR test showed that the reaction was complete (3.5 hr). After cooling, the product was shaken with acetone for 2 hr to remove the unreacted 1,3-dimethylurea, filtered, and rinsed with acetone, giving 9.74 g (79.0%) of **6b** as a white crystalline solid, identical (IR, ^1H NMR) to the product described above. Most of the excess 1,3-dimethylurea (20.42 g, 96.5%) was recovered from the filtrate.

Tris(3-phenylureidomethyl)phosphine Oxide (**6c**). Reaction of **1** with phenyl isocyanate in acetonitrile according to procedure F gave **6c**, mp 261°C dec., in 90.8% yield, identical (IR, ^1H NMR) to the product prepared from tris(hydroxymethyl)phosphine;[9] NMR: δ_H (CF_3CO_2H) 4.43 (d, 6 H, CH_2, J = 3.5 Hz) and 7.1–7.7 (m, 15 H, C_6H_5) ppm.

Tris(3-ethylthioureidomethyl)phosphine Oxide (**8b**). Reaction of **1** with ethyl isothiocyanate in acetonitrile according to procedure F gave **8b** as a white crystalline solid, mp 168–171°C, in 92.2% yield. One

recrystallization from ethanol gave an analytical sample, mp 174–175°C; IR (KBr): 873m, 1075m, 1150s (P=O), 1200m, 1259s, 1297s, 1339s, 1377s, 1443m, 1505s, sh, 1543vs, 2915m, 2960m, 3050m, 3215vs (NH), and 3370m, sh cm^{-1}; NMR: δ_H (d_6-DMSO) 1.12 (t, 9 H, CH_3, J = 7 Hz), 3.41 (q, 6 H, CH_2C, J = 7 Hz), 4.17 (d, 6 H, CH_2P, J = 4.5 Hz), and 7.79 (br s, 3 H, NH) ppm; δ_P (d_6-DMSO) 43.4 ppm.

Anal. Calcd. for $C_{12}H_{27}N_6OPS_3$: C, 36.16; H, 6.83; N, 21.09; P, 7.77; S, 24.13. Found: C, 35.39; H, 7.04; N, 20.70; P, 7.78; S, 23.93.

The thioureide **8b** is soluble in DMSO and dimethylformamide, and insoluble in chloroform. It can be recrystallized from ethanol (5 ml/g) or water (30 ml/g).

[*Bis(aminomethyl)phosphinyl*]*methylthiocarbamic Acid* (**9a**). A stream of carbonyl sulfide was passed into a solution of **1** (27.42 g, 0.2 mol) in ethanol (500 ml) over a 3 hr period with constant stirring. Solids started to separate within 10 min. The solids were collected on a filter, rinsed thoroughly with ethanol, and vacuum dried over potassium hydroxide pellets, giving 37.31 g (94.6%) of **9a** as a white crystalline solid, mp 107–108°C dec.; IR (KBr): 807m, 815m, 916m, 1130s, 1155vs (P=O), 1180s, 1220m, 1365m, 1385m, 1470vs, 1540s, 1600s (C=O), 2330w (NH^+), 2850s, and 3280s (NH) cm^{-1}; NMR: see Table I.

Anal. Calcd. for $C_4H_{12}N_3O_2PS$: C, 24.36; H, 6.14; N, 21.31; P, 15.70; S, 16.26. Found: C, 24.45; H, 6.39; N, 21.47; P, 15.81; S, 16.34.

The thiocarbamate **9a** is soluble in water and insoluble in organic solvents.

[*Bis(aminomethyl)phosphinyl*]*methyldithiocarbamic Acid* (**9b**). Carbon disulfide (19.03 g, 0.25 mol) was added over a 15 min period to a solution of **1** (13.71 g, 0.1 mol) in ethanol (300 ml) with rapid stirring. Solids separated at once, and the mixture warmed to the touch. After the addition, the mixture was stirred slowly for 4 hr at room temperature, filtered, and the filter cake rinsed thoroughly with ethanol and vacuum dried, giving 19.31 g (90.5%) of water-soluble off-white solid, mp 59.5°C dec.; NMR: δ_H (D_2O) 3.43 (d, 4 H, CH_2, J = 6 Hz) and 4.50 (d, 2 H, CH_2, J = 7 Hz) ppm. The product was dissolved in water (20 ml), set aside for 3 hr and then filtered, giving 11.53 g (54.1%) of water-insoluble solid. One recrystallization from water (4 ml/g) gave pure **9b** as an off-white crystalline solid, mp 120–122°C; IR (KBr): 692w, 780s, 818m, 851vs, 970vs, 1015w, 1045m, 1160vs (P=O), 1220m, 1255w, 1300m, 1370w, 1470s br, 1585m, 2300–2600m (NH^+), 2920vs, and 3170s (NH) cm^{-1}; NMR (D_2O/NaOD): see Table I; Mass spectrum (% rel. abundance, ion fragment): m/e 180 (6), 179 (81, P–H_2S, **10b**), 150 (100, $S{=}C[NHCH_2]_2POH^+$), 149 (32, $S{=}C[NHCH_2]_2PO^+$), 72 (14), 70 (14), 69 (10), 44 (14), 43 (14), and 34 (H_2S).

Anal. Calcd. for $C_4H_{12}N_3OPS_2$: C, 22.53; H, 5.67; N, 19.71; P, 14.52; S, 30.07. Found: C, 22.46; H, 5.77; N, 19.58; P, 14.79; S, 30.41.

The dithiocarbamate **9b** is insoluble in water, carbon disulfide and organic solvents.

[*Bis(aminomethyl)phosphinyl*]*methylcarbamic Acid* (**9c**). Mass spectrum (% rel. abundance, ion fragment): m/e 138 (12, $[NH_2CH_2]_3POH^+$), 137 (8, **1**), 108 (33, $[NH_2CH_2]_2POH^+$), 107 (19), 90 (14), 89 (10), 79 (58), 78 (100, $NH_2CH_2POH^+$), 77 (38), 60 (17), 59 (43), 47 (10, PO^+), 44 (70, CO_2), 43 (29), and 41 (11).

5-Aminomethyl-1,3-diaza-5-phosphorinan-2,5-dione (**10a**). A mixture of **9a** (3.94 g, 0.02 mol), calcium hydroxide (2.96 g, 0.04 mol) and water (100 ml) was purged with argon and heated in an oil bath for 2 hr. at reflux with constant stirring. After cooling, the mixture was filtered, giving 2.44 g (82.4%) of recovered calcium hydroxide that had a greenish cast. The filtrate and washings were heated to 70°C, sparged with carbon dioxide [*Caution*: H_2S evolved] followed by argon, cooled, and filtered again, giving 0.73 g (18.2%) of calcium carbonate. The filtrate was stripped of water under reduced pressure, giving 4.09 g of white crystalline solid consisting (NMR, D_2O) of **10a** and **1** in a molar ratio of 3 : 1. To remove the latter, the solid was dissolved in water (10 ml), heated to boiling for 15 min, concentrated to low volume, diluted with ethanol (200 ml) and filtered, giving 2.38 g (73.0%) of **10a** as a white crystalline solid, mp 198–199°C; NMR: δ_H (D_2O) 3.38 (d, 2 H, chain CH_2, J = 5.5 Hz), 3.72 (d, 1 H, ring CH, J = 12.5 Hz), 3.73 (d, 2 H, ring CH, J = 11 Hz) and 3.74 (d, 1 H, ring CH, J = 9.5 Hz) ppm; δ_C (D_2O) 37.01 (d of t, chain CH_2, J_{PC} = 75.3 Hz, J_{CH} = 138.6 Hz), 37.66 (d of t, ring CH_2, J_{PC} = 66.7 Hz, J_{CH} = 142.6 Hz) and 159.77 (d, C=O, J_{PC} = 7.0 Hz) ppm; δ_P(D_2O) 32.3 ppm.

5-Aminomethyl-2-thio-1,3-diaza-5-phosphorinan-2,5-dione (**10b**). A mixture of **9b** (21.33 g, 0.1 mol), calcium hydroxide (14.82 g, 0.2 mol) and water (500 ml) was purged with argon and heated in an oil bath for 2 hr at reflux with constant stirring. The solids acquired a greenish cast. After cooling, the mixture was filtered, giving 10.07 g (67.9%) of recovered calcium hydroxide. The filtrate, clear and colorless, was heated to 70°C, sparged with carbon dioxide until no more solids separated [*Caution*: H_2S evolved], and filtered again giving 5.41 g (0.054 mol) of calcium carbonate. The filtrate was concentrated to low volume and percolated through a 19 × 600 mm chromatographic column charged with 60 g of Dowex 50W-X8 cation exchange resin. The resin was eluted with water until all of the by-product **12** (see below) was

removed, then with 2*N* hydrochloric acid to displace the main product (**10b**) as the hydrochloride **11a**. The eluate fractions were stripped, rinsed with ethanol and vacuum dried, giving 19.41 g (90.0%) of **11a** as a white crystalline solid.

A 2.15 g portion of **11a** was dissolved in 25 ml of water and percolated through a 10 × 500 mm chromatographic column containing 7.5 g of Rexyn 201 (OH) anion exchange resin. The resin was eluted with water (300 ml) and the eluate fractions stripped and rinsed with ethanol, giving 1.34 g (74.9%) of **10b**, mp 207–208°C dec. after one recrystallization from water; IR (KBr): 635m, 728m, 777m, 855s, 928m, 955m, 1025m, 1082w, 1160vs (P=O), 1227, 1242vs (C=S), 1282w, 1412m, 1479w, 1531vs, 1567–1580s, 2870s, 2960s, 3180s, 3300vs (NH), and 3410w cm^{-1}; NMR: δ_H (D_2O) 3.46 (d, 2 H, chain CH_2, J = 5 Hz), 3.89 (d, 1 H, ring CH, J = 13.5 Hz), 3.90 (d, 2 H, ring CH, J = 12 Hz) and 3.91 (d, 1 H, ring CH, J = 10.5 Hz) ppm; δ_C (D_2O) 37.28 (d of t, chain CH_2, J_{PC} = 75.9 Hz, J_{CH} = 138.6 Hz), 38.83 (d of t, ring CH_2, J_{PC} = 65.0 Hz, J_{CH} = 143.6 Hz) and 177.8 (d, C=S, J_{PC} = 10 Hz) ppm; δ_P (D_2O) 25.6 ppm.

Anal. Calcd. for $C_4H_{10}N_3OPS$: C, 26.81; H, 5.63; N, 23.46; P, 17.28; S, 17.89. Found: C, 26.90; H, 5.76; N, 23.46; P, 17.52; S, 17.97.

The thioureide **10b** is soluble in water and DMSO, and insoluble in organic solvents.

Salts of **10b** (**11a–c**). A portion of the **10b** eluted from the Dowex 50W-X8 column with 2*N* hydrochloric acid (above) was recrystallized twice from water, giving pure **11a** as a white crystalline solid, mp 247°C dec.; IR (KBr): 718m, 752m, br, 786m, 833s, 864m, 1020s, 1068m, 1085s, 1163vs (P=O), 1230s, 1244vs (C=S), 1400m, 1443m, 1485s, 1538vs (NH), 2545s, and 2780–3225vs (NH) cm^{-1}; NMR: δ_H (D_2O) 3.80 (d, 2 H, chain CH_2, J = 7.5 Hz) and 3.90 (d, 4 H, ring CH_2, J = 12.5 Hz) ppm.

Anal. Calcd. for $C_4H_{11}ClN_3OPS$: Cl, 16.44; N, 19.49; P, 14.36. Found: Cl, 16.79; N, 19.66; P, 14.61.

The hydrochloride **11a** was also prepared by dissolving **10b** in 12*M* hydrochloric acid, filtering to remove impurities, stripping to dryness, rinsing with ethanol, and air-drying. The sulfate and oxalate salts were similarly prepared from **10b** and 9*M* sulfuric acid or 0.5*M* oxalic acid solutions. The sulfate salt **11b** was a white crystalline solid, mp 201°C dec.; NMR: δ_H (D_2O) 3.80 (d, 2 H, chain CH_2, J = 8.5 Hz) and 3.98 (d, 4 H, ring CH_2, J = 12.5 Hz) ppm. The oxalate salt **11c** was a white crystalline solid, mp 155°C dec.; NMR: δ_H (D_2O) 3.79 (d, 2 H, chain CH_2, J = 8.5 Hz) and 3.96 (d, 4 H, ring CH_2, J = 12.5 Hz) ppm.

The salts **11a–c** are soluble in water and conc. acid solutions and insoluble in organic solvents.

5-Hydroxy-2-thio-1,3-diaza-5-phosphorinan-2,5-dione (**12**). The Dowex 50W-X-8 chromatographic fractions containing the by-product (see foregoing experiment) were stripped, rinsed with ethanol and vacuum dried, giving 1.79 g (10.8%) of **12** as a white crystalline solid, dec. 212°C (frothing) after two recrystallizations from water/ethanol; IR (KBr): 625m, 700m, 837s, 988vs, 1005vs, 1064s, 1179s (P=O), 1228m, 1245s (C=S), 1418m, 1520–1538vs (NH, amide II), 1613–1639m, 2860w, 2910w, 2920w, 3270s (NH) and 3370s cm^{-1}; NMR: δ_H (D_2O) 3.42 (d, 4 H, CH_2, J = 13 Hz) ppm, shifting to 3.28 ppm with NaOD and to 3.58 ppm with DCl; δ_C (D_2O) 42.50 (d of t, CH_2, J_{PC} = 95.4 Hz, J_{CH} = 140.4 Hz) and 176.0 (d, C=S, J_{PC} = 10 Hz) ppm; δ_P (D_2O) 13.1 (quintet, J_{PH} = 13 Hz) ppm.

Anal. Calcd. for $C_3H_7N_2O_2PS$: C, 21.69; H, 4.25; N, 16.87; P, 18.64; S, 19.30; mol. wt., 166.14. Found: C, 22.01; H, 4.66; N, 16.98; P, 18.51; S, 18.69; mol. wt. (osmometric in H_2O), 118.

The acid **12** is soluble in water and hot DMSO, and insoluble in organic solvents.

Alkaline Hydrolysis of **10b**. The ^1H NMR spectrum of **10b** in D_2O/NaOD, taken immediately, showed the characteristic doublet/triplet/singlet pattern of **10b**, shifted about 15 Hz upfield of its position in D_2O, but after 24 hr only the doublet for **1** at 190, 196 Hz remained. The same behavior was observed whether 40% NaOD (3–4 drops) was added to a D_2O solution of **10b** itself or to a D_2O solution of its hydrochloride, sulfate or oxalate salts **11a–c**.

In contrast, the spectrum of **10b** in D_2O containing 38% DCl (3–4 drops) appeared to be stable indefinitely, showing the characteristic pair of doublets for the hydrochloride **11a** even after 5 min in a boiling water bath.

5-(N-Carbethoxylaminomethyl)-1,3-diaza-5-phosphorinan-2,5-dione (**13**). Ethyl chloroformate (1.09 g, 0.01 mol) and 50% sodium hydroxide solution (0.80 g, 0.01 mol) were added simultaneously to a solution of **10a** (1.63 g, 0.01 mol) in water (10 ml) over a 5 min period at 10–15°C with ice-bath cooling and mechanical stirring. No solids separated. The solution was stripped under reduced pressure, leaving a solid residue. After drying, the residue was shaken with glacial acetic acid (60 ml) for 2 hr on a mechanical shaker, filtered to remove the sodium chloride, and stripped again. The residue, rinsed with acetone and air-dried, weighed 1.95 g (83.0%). One recrystallization from ethanol/water gave pure **13** as a white crystalline solid, mp 225°C dec.; IR (KBr): 767s, 800m, 871m, 935m, 1053s, 1090m, 1112s, 1152s (P=O), 1180m, 1214m, 1225m, 1244s, 1282m, 1337s, 1374s, 1425s, 1447s, 1462s, 1520s (NH, amide II), 1655s, 1695vs (C=O, amide I), 2940s, 3070s, and 3230s (NH) cm^{-1}; NMR: δ_H (D_2O) 1.22 (t, 3 H, CH_3,

J = 7 Hz), 3.74 (d, 1 H, ring CH, J = 12.5 Hz), 3.745 (d, 2 H, ring CH, J = 11.5 Hz), 3.75 (d, 1 H, ring CH, J = 10.5 Hz), 3.97 (d, 2 H, chain CH_2P, J = 5 Hz) and 4.12 (q, 2 H, CH_2C, J = 7 Hz) ppm; δ_P (D_2O) 29.3 ppm.

Anal. Calcd. for $C_7H_{14}N_3O_4P$: C, 35.75; H, 6.00; N, 17.87; P, 13.17. Found: C, 35.50; H, 6.24; N, 17.99; P, 13.38.

The carbamate **13** is soluble in water and in hot alcohols, and insoluble in the common organic solvents.

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