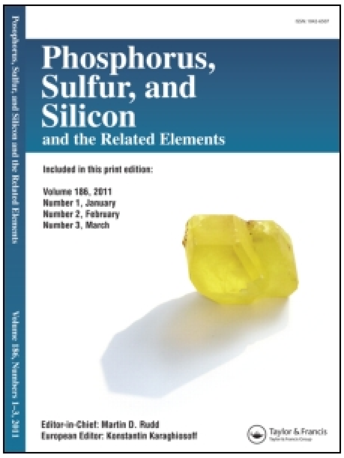

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# SYNTHESIS AND PROPERTIES OF CONDENSED UREIDOMETHYL PHOSPHONIUM SALTS

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# SYNTHESIS AND PROPERTIES OF CONDENSED UREIDOMETHYL PHOSPHONIUM SALTS[1]

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Urea, N-methylurea, and 1,3-dimethylurea react with tetrakis(hydroxymethyl)phosphonium chloride (THPC) in molar ratios lower than 4 : 1, forming condensed quaternary ureidomethyl phosphonium salts. The urea and N-methylurea products are polymeric gels, whereas the 1,3-dimethylurea products are cyclic crystalline solids. Some of the phosphonium salts are interconvertible through condensation or displacement reactions. Hydrolysis of the phosphonium salts, followed by oxidation, yields tertiary phosphine oxides having similar properties. The products were characterized by IR, NMR, and electron spectroscopy for chemical analysis (ESCA).

## INTRODUCTION

The reaction of urea with tetrakis(hydroxymethyl) phosphonium chloride (THPC) forms the basis for several of the flame retardant finishes developed for cotton over the past 25 years.[3] From a practical standpoint, the THPC/amide finish[4] and the PROBAN finish[5,6] are especially important. In the THPC/amide process, the urea and the partially neutralized THPC react in a 2 : 1 molar ratio during the curing of the impregnated fabric, and in the PROBAN process the urea and the THPC are condensed in a 0.5:1 molar ratio prior to the application of the finish.

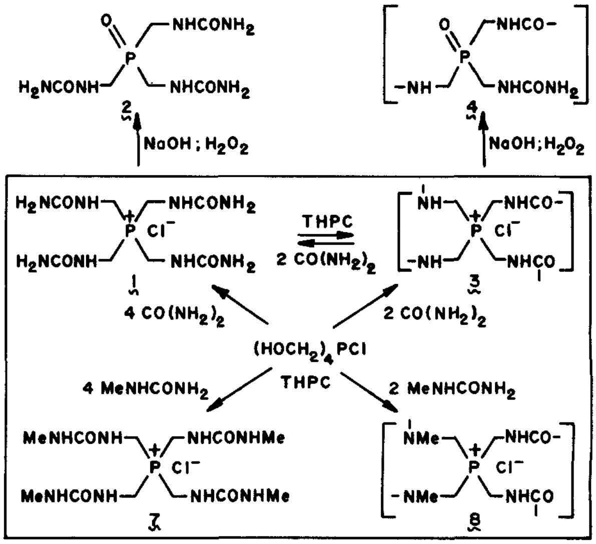
The reaction between urea and THPC is scarcely understood, though some advances have been made. Miller[7] found that the 0.5:1 precondensate of the PROBAN process remains in the quaternary phosphonium state, and that there is negligible formation of tertiary phosphine or phosphine oxide. Granzow[8] found that the phosphonium/phosphine equilibrium in a buffered 2 : 1 molar urea/TKP[9] solution is constant up to the point of gelation. We[10] reported the synthesis and properties of the 4 : 1 molar urea/THPC condensate, tetrakis(ureidomethyl)phosphonium chloride (**1**), a stable, water-soluble quaternary phosphonium salt. However, Kasem *et al.*[11] stated that the 1 : 1 molar urea/THPC polymer, prepared either in the solid state or in dimethylsulfoxide solution, contains no detectable chlorine and is therefore no longer quaternary.

In this paper, we report the synthesis and properties of the products obtained from urea and THPC in molar ratios lower than 4:1, and the corresponding products obtained from N-methylurea and 1,3-dimethylurea.

## RESULTS

### *Urea Derivatives*

The products obtained when urea is condensed with 80% THPC at 100°C are outlined in the box in Scheme 1.



SCHEME 1. Urea and N-methylurea derivatives.

When the molar ratio is 4:1 or higher, the product is the symmetrical quaternary phosphonium salt **1**, a colorless, water-soluble glass. Hydrolysis of **1** with sodium hydroxide, followed by oxidation with hydrogen peroxide, yields the symmetrical tertiary phosphine oxide **2**, which is also colorless and water-soluble.[10]

When the molar ratio was reduced to 2:1, the reaction mass gelled within 10 minutes, giving a 97.5% yield of the polymeric quaternary phosphonium salt **3**, friable, white solid, d. 230°C, which analyzed as a hemihydrate. A polymer structure was inferred from its insolubility in water and organic solvents. Hydrolysis of **3** with sodium hydroxide, followed by oxidation with hydrogen peroxide, yielded the polymeric tertiary phosphine oxide **4**, a white solid, d. 247°C, which was also insoluble in water and organic solvents.

Similar gels were formed when the molar ratio was changed to 1:1 or 3:1. The products, whose composition corresponded to structures intermediate between THPC and **1**, were the quaternary phosphonium salts **5** and **6**, both friable solids. Hydrolysis, followed by oxidation, yielded the tertiary phosphine oxides which, like **4**, were polymeric solids that were insoluble in water and organic solvents. No structures are assigned to **5**, **6**, or their hydrolysis products for the reasons given in the discussion below.

These condensations can also be carried out in refluxing toluene with the azeotropic removal of water. Reaction of urea with crystalline THPC in a 2:1 ratio, for example, gave a 97.1% yield of the quaternary phosphonium salt **3**, identical to the product described above. In benzene, owing to the lower reflux temperature, some water was displaced but the bulk of the product remained water soluble.

The ESCA spectra of polymers **3**, **5**, and **6** are reported in Table I, together with a few model compounds. The $P_{2p}$ and $Cl_{2p}$ peak positions are similar to those reported for other quaternary phosphonium salts.[12] The $C_{1s}$, $N_{1s}$, and $O_{1s}$ peak positions are similar to those of urea and methylenediurea. The $C_{1s}$ spectra clearly distinguish $CH_2$ from C=O, but do not distinguish among $CH_2$ groups attached to nitrogen, oxygen, or phosphorus. The $N_{1s}$ spectra of polymers **3**, **5**, and **6** show a slight increase in binding energy, coupled with a slight broadening of the full width at half height (FWHH), with increasing urea: THPC ratio. This result suggests that there is a difference between primary and secondary ureido nitrogens, but the effects are too subtle for characterizing the polymers.

The phosphonium salts **1** and **3** were found to be interconvertible. A 1:1 molar mixture of THPC and **1** in water gelled within 12 minutes at 100°C, giving a 96.1% yield of **3** (mp, IR). Conversely, a 2:1 molar mixture of urea and **3** in water cleared after two hours at 100°C, giving a 98.9% yield of **1** (IR, NMR). The latter reaction has become a key step in the large-scale synthesis of **2** from THPC or the corresponding sulfate, THPS.[13]

### *N-Methylurea Derivatives*

Condensation of N-methylurea with crystalline THPC in a 4:1 ratio in refluxing toluene, with the azeotropic removal of the water, gives the symmetrical quaternary phosphonium salt **7**, an amber water-soluble glass (Scheme 1).[10]

When the molar ratio was reduced to 2:1, the reaction mass gelled within 15 minutes, giving a quantitative yield of the polymeric quaternary

TABLE I

ESCA of condensed ureidomethyl phosphonium salts

| | Binding energy, eV | | | | | |
|---|---|---|---|---|---|---|
| Compound | $P_{2p}$ | $Cl_{2p}$ | $CH_{2(3)}$ $C_{1s}$ | C=O $C_{1s}$ | $N_{1s}$ (FWHH) | $O_{1s}$ |
| **5** | 131.5 | 196.5 | 283.9 | 287.4 | 398.8 (1.9) | 530.9 |
| **3** | 131.7 | 196.9 | 283.9 | 287.9 | 398.9 (2.0) | 531.0 |
| **6** | 131.7 | 196.9 | 284.3 | 287.9 | 399.0 (2.1) | 530.6 |
| **8** | 132.3 | 197.3 | 284.7 | 288.5 | 399.1 (2.0) | 532.1 |
| $CO(NH_2)_2^a$ | — | — | — | 288.5 | 399.3 | 534.8 |
| $MeNHCONH_2$ | — | — | 284.7 | 288.5 | 399.2 (1.8) | 531.1 |
| $CH_2(NHCONH_2)_2$ | — | — | 284.5 | 288.3 | 399.2 (2.0) | 530.9 |

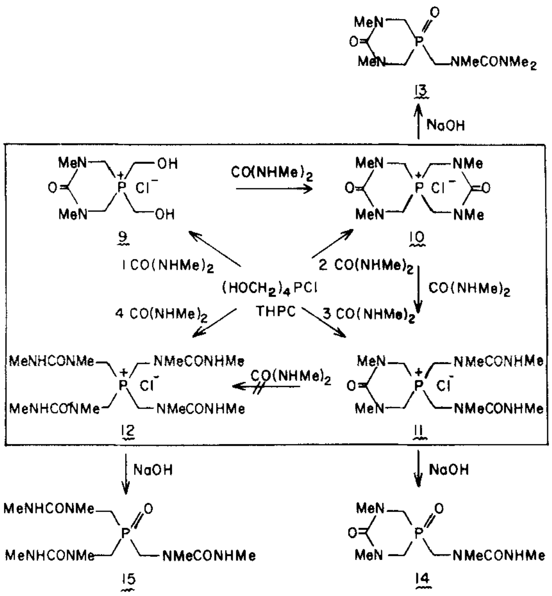
[a] From reference 21.

phosphonium salt **8**, a friable white solid, mp 210°C d. The product, like **3**, analyzed as a hemihydrate and was insoluble in water and organic solvents.

The ESCA spectra of polymer **8** and of N-methylurea are reported in Table I. The peak positions for **8** are slightly higher than those for polymers **3**, **5**, and **6** but within the expected ranges. The spectra distinguish $CH_2$ from C=O, but not $CH_2$ from $CH_3$ nor NH from $NH_2$.

### *1,3-Dimethylurea Derivatives*

The products obtained when 1,3-dimethylurea is condensed with crystalline THPC in refluxing toluene, with the azeotropic removal of the water, are outlined in the box in Scheme 2.



SCHEME 2. 1,3-Dimethylurea derivatives.

When the molar ratio is 4:1 or higher, the product is the crystalline quaternary phosphonium salt **12**, mp 194–194.5°C d. Hydrolysis of **12** with sodium hydroxide yields the crystalline tertiary phosphine oxide **15**, mp 226-227°C d, together with 1,1,3-trimethylurea. The extra methyl group in the latter originates from the methylene group in the cleavage fragment.[10]

When the molar ratio was reduced to 2:1, the same quantity of water was displaced, but the product, unlike the polymers obtained from urea and N-methylurea, was a crystalline, water-soluble quaternary phosphonium salt, mp 161–162°C (88.9% yield). The spiro structure **10** was established by IR, NMR, and molecular weight determination. The $^1H$ NMR spectrum showed a simple pattern of two signals ($CH_3$ and $CH_2$), each split into a doublet because of coupling with phosphorus. The PCH coupling constant was unusually large ($^2J_{PH} = 9.0$ Hz, compared to 4.0 Hz in **12**), as is often observed in cyclic organophosphorus compounds.[14]

Hydrolysis of **10** with sodium hydroxide gave the crystalline tertiary phosphine oxide **13**, mp 86–87°C (94.5% yield). The structure of the product was established by IR, NMR, and molecular weight determination. In this instance, P-C cleavage left an extra methyl group on the terminal nitrogen.

When the molar ratio was reduced to 1:1, the product, analyzed by $^1H$ NMR, was a mixture of THPC (10.6%), **10** (11.4%), and the quaternary phosphonium salt **9** (73.8%). The product, a colorless, viscous oil, also featured a large PCH coupling constant ($^2J_{PH} = 8.0$ Hz). It gave **10** in a 22.4% yield when condensed with 1,3-dimethylurea in a 1:1 ratio.

When the molar ratio was changed to 3:1, the product was a crystalline, water-soluble quaternary phosphonium salt, mp 196–197°C d. (67.5% yield), for which structure **11** was established by IR, NMR, and molecular weight determination. The ring-coupling constant ($^2J_{PH} = 6.5$ Hz) was in this instance smaller than the chain-coupling constant ($^2J_{PH} = 8.0$ Hz).

Hydrolysis of **11** with sodium hydroxide gave the crystalline tertiary phosphine oxide **14**, mp 142–143°C (91.8% yield), together with a 57.6% yield of 1,1,3-trimethylurea. The structure of the product was established by IR, NMR, and molecular weight determination. There was no evidence of ring cleavage.

The phosphonium salt **11** could also be prepared from **10** in a 90.1% yield by reaction with 1,3-dimethylurea in refluxing acetonitrile. The product was **11**, though an excess of 1,3-dimethylurea was present. Efforts to convert **11** to **12** by reaction with 1.3-dimethylurea in refluxing toluene or in the absence of solvent at 160°C were fruitless, the **11** being recovered intact in both cases. The driving force for the first step, which is unusual in that it constitutes the displacement of a tertiary urea by a secondary urea, is probably the relief of spiro ring strain.

Efforts to prepare the 1,3-diphenylurea (carbanilide) derivative of THPC corresponding to **10** were unsuccessful. Little reaction occurred in refluxing toluene, and in xylene the product was resinous.

## DISCUSSION

These experiments demonstrate that the reaction of ureas with THPC in molar ratios lower than 4:1 gives condensed quaternary phosphonium salts whose structures are either cyclic or polymeric, depending on the urea.

The 1,3-dimethylurea derivatives (Scheme 2) present no problem, because the urea is bifunctional. The methylene groups are linked to each other by 1,3-ureylene radicals,[15] forming 6-membered rings. The phosphonium salts **9** and **11** each contain a 6-membered ring, and the spiro phosphonium salt **10** contains two. Hydrolysis occurs in such a manner as to preserve the ring, if possible.

The structures of the urea and N-methylurea derivatives, however, are complicated by the increased functionality of the ureas. If the methylene groups are linked exclusively by 1,3-ureylene radicals, as shown in Scheme 1, the polymers will consist of networks of rings in random sizes which are multiples of six, interspersed with OH and $NHCONH_2$ end groups. Such structures are plausible for the 2:1 phosphonium salts **3** and **8**, but not for the 1:1 or 3:1 phosphonium salts **5** and **6** because the latter do not have sufficient functionality for crosslinking. The same argument applies to 1,1-ureylene radicals. The tendency of the urea and N-methylurea to form gels, therefore, is directly related to their increased functionality, but the extent of crosslinking must be small because it is not reflected in the elemental analyses. Efforts to determine the fine structure of the gels by ESCA spectroscopy were unsuccessful.

## EXPERIMENTAL

Melting points are uncorrected. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Enviro Analytical Laboratory, Knoxville, Tenn. IR spectra were taken on a Perkin-Elmer 137B with NaCl optics (w = weak, m = medium, s = strong, vs = very strong, br = broad). $^1H$ NMR spectra were taken on a Varian A-60A or a Varian EM360L, with TMS or DSS as an internal reference, and $^{31}P$ NMR spectra on a JEOL C-60-HL at 24.3 MHz, with 85% $H_3PO_4$ as an external reference (s = singlet, d = doublet, br = broad). ESCA were taken on a Varian IEE-15 equipped with a magnesium anode, the sample being mounted on a holder with double-backed adhesive tape.

Crystalline THPC, mp 149–149.5°C, was prepared from 80% THPC (Hooker Chemicals and Plastics Corp.) by azeotropic distillation with benzene followed by recrystallization from 2-propanol. Other reagents were used as obtained.

*Poly[bis(ureylenedimethyl)phosphonium chloride]*[15] (**3**). *A. In Toluene.* A mixture of THPC (9.53 g, 0.05 mol), urea (6.01 g, 0.10 mol), and toluene (25 ml) was heated to reflux in an apparatus fitted with a Dean-Stark trap for the azeotropic removal of the water. After 2.6 ml (72%) of water had been collected, evolution ceased (2 h). The product, which had separated during the reaction as a foamy white solid, was broken up, filtered, triturated under water and filtered again, giving 12.02 g (97.1%) of **3** as a brittle white solid, d. 230°C; IR (KBr) 1010 m, 1250 s, br, 1380 m, 1560 vs (NH, amide II), 1660 vs (C=O, amide I), 3000 m, and 3430 vs (NH) $cm^{-1}$.

*Anal.* Calcd for $C_6H_{12}ClN_4O_2P.0.5\ H_2O$: C, 29.10; H, 5.29; Cl, 14.32; N, 22.63; P. 12.51. Found: C, 28.96; H, 5.26; Cl, 14.10; N, 22.71; P. 12.39.

*B. In Water.* A mixture of 80% THPC (59.56 g, 0.25 mol) and urea (30.03 g, 0.50 mol) was heated to reflux in an oil bath. The urea dissolved at 100°C, giving a clear, colorless solution. A mildly exothermic reaction ensued, with steady refluxing, but within 10 min the mixture thickened and set up to a foamy gel. After cooling, the product was triturated under water, filtered, and dried over $P_2O_5$ in a vacuum desiccator, giving 60.34 g (97.5%) of **3** as a friable white solid, d. 230°C; IR (KBr) as above.

*Anal.* Found: C, 28.98; H, 5.32; Cl, 14.08; N, 22.67; P. 12.25.

*C. From* **1**. A solution of **1** (35.88 g, 0.10 mol) in water (15 ml) was heated to reflux and treated with 80% THPC (23.82 g, 0.10 mol) in a single portion. The solution started to thicken after 6 min and gelled after 12 min, immobilizing the stirrer. After heating at reflux for another 30 min, the product was cooled, triturated under water, filtered, and dried to constant weight in a vacuum oven at 80°C, giving 46.43 g (96.1%) of **3** as a friable off-white solid, d. 230°C; IR (KBr) as above.

*Polymer* **5**. Reaction of 80% THPC (23.82 g, 0.10 mol) and urea (6.01 g, 0.10 mol), following Procedure B, gave 18.28 g (85.2%) of **5** as a friable yellow gel, d. 240°C; IR (KBr) 1050 s (OC), 1250 s, 1380 m, 1560 vs (NH, amide II), 1670 s (C=O, amide I), 2940 s, and 3450 vs, br (NH and OH) $cm^{-1}$.

*Anal.* Calcd. for $C_5H_{12}ClN_2O_3P$: C, 27.98; H, 5.64; Cl, 16.52; N, 13.06; P, 14.43. Found: C, 28.29; H, 5.56; Cl, 16.12; N, 14.13; P, 14.19.

*Polymer* **6**. Reaction of 80% THPC (23.82 g, 0.10 mol) and urea (18.02 g, 0.30 mol), following Procedure B, gave 24.18 g (81.0%) of **6** as a friable pale-yellow gel, d. 208°C; IR (KBr) 1020 w, 1150 m, 1245 s, 1350 s, 1380 m, 1550 vs (NH, amide II), 1670 vs (C=O, amide I), 2970 w, and 3430 vs (NH) $cm^{-1}$.

*Anal.* Calcd. for $C_7H_{16}ClN_6O_3P$: C, 28.15; H, 5.40; Cl, 11.87; N, 28.14; P, 10.37. Found: C, 27.93; H, 6.05; Cl, 11.63; N, 27.64; P, 10.41.

*Tetrakis(ureidomethyl)phosphonium chloride* (**1**). A mixture of **3** (2.48 g, 0.01 mol), urea (1.20 g, 0.02 mol), and water (5 ml) was heated to reflux in an oil bath. The polymer gradually dissolved over 2 h. After heating for 1 h more, the solution was cooled, stripped in a rotary evaporator, and thoroughly dried in a vacuum desiccator, giving 3.55 g (98.9%) of **1** as pale-yellow, brittle glass, identical (IR, NMR) to the product prepared from THPC.[10]

*Poly[(ureidomethyl)(ureylenedimethyl)phosphine oxide]* (**4**). A slurry of **3** (6.03 g, 25 mmol) in 25 ml of water was purged with argon, treated with a solution of sodium hydroxide (1.00 g, 25 mmol) in 25 ml of water, and stirred for 24 h at room temperature. The slurry, still under argon, was treated with 30% hydrogen peroxide (2.84 g, 25 mmol), and allowed to cool. The product was collected on a filter, rinsed thoroughly with water, and dried under vacuum, giving 3.55 g (68.9%) of **4** as a white solid, d. 250°C. The analytical sample was further dried for 2h at 100°C/0.5 mm.

*Anal.* Calcd. for $C_5H_{11}N_4O_3P$: C, 29.13; H, 5.38; N, 27.18; P, 15.02. Found: C, 30.24; H, 5.79; N, 26.64; P, 14.92.

*Poly[bis(N-methylureylenedimethyl)phosphonium chloride]* (**8**). Reaction of THPC (9.53 g, 0.05 mol) with N-methylurea (7.41 g, 0.10 mol) in toluene (75 ml), following Procedure A, gave 2.3 ml (64%) of water and 14.02 g (101.7%) of **8** as a friable white solid, mp 210°C d.; IR (KBr) 1550 s (NH, amide II), 1660 s (C=O, amide I), and 3450 vs (NH) $cm^{-1}$.

*Anal.* Calcd. for $C_8H_{16}ClN_4O_2P \cdot 0.5\ H_2O$: C, 34.85; H, 6.22; Cl, 12.86; N, 20.33; P, 11.23. Found: C, 34.75; H, 6.10; Cl, 12.74; N, 20.19; P, 11.07.

*3,9-Dioxo-2,4,8,10-tetramethyl-2,4,8,10-tetraaza-6-phosphoniaspiro[5.5] undecane chloride* (**10**). *D. In toluene.* A mixture of crystalline THPC (19.06 g, 0.1 mol), 1,3-dimethylurea (17.62 g, 0.2 mol), and toluene (150 ml) was heated to reflux in an apparatus fitted with a mechanical stirrer and a Dean-Stark trap for azeotropic removal of the water. The mixture was held at reflux until the evolution of water ceased; 7.2 ml (100.0%) of water was collected in 4 h, half of it during the first 15 min. The product, which had separated during the reaction as a mass of white solids, was broken up, triturated under acetonitrile,[16] filtered, and dried, giving 26.21 g (86.3%) of **10** as a white, crystalline solid, mp 158–159°C and resolidifying. Two recrystallizations from 2-propanol (12 ml/g) gave pure **10**, mp 161–162°C and resolidifying, then mp 217°C d; IR (KBr) 757 m, 910 m, 1035 m, 1160 m, 1210 s, 1250 m, 1370 m, 1385 s, 1410 m, 1430 m, 1455 m, 1490 vs, 1660 s (C=O, amide I), 2900 m, 3000 m, and 3500 m (OH) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta$ 2.89 (d, 12H, $CH_3$, J = 2.5 Hz) and 4.55 (d, 8H, $CH_2$, J = 9.0 Hz) ppm; $^{31}P$ NMR ($H_2O$), $\delta$ 29.8 ppm.

*Anal.* Calcd. for $C_{10}H_{20}ClN_4O_2P \cdot 0.5\ H_2O$: C, 39.54; H, 6.97; Cl, 11.67; N, 18.45; P, 10.20; mol. wt., 304. Found: C, 39.38; H, 6.95; Cl, 11.94; N, 18.33; P, 10.11; mol. wt. (osmometric in $H_2O$), 166, 172.

The phosphonium salt **10** is soluble in water, the lower alcohols, and dimethylsulfoxide and insoluble in other common organic solvents. It can be recrystallized from 2-propanol or acetonitrile.

*5,5-Bis(hydroxymethyl)-1,3-dimethyl-2-oxo-1,3-diaza-5-phosphoniacyclohexane chloride* (**9**). Reaction of crystalline THPC (19.06 g, 0.1 mol) with 1,3-dimethylurea (8.81 g, 0.1 mol) and toluene (75 ml), following Procedure D, yielded 3.7 ml (103%) of water and 23.40 g (95.9%) of a colorless, viscous oil that (analyzed by NMR) consisted of THPC (2.03 g, 10.6%), **10** (3.45 g, 11.4%), and **9** (17.92 g, 73.8%). For **9**, $^1H$ NMR ($D_2O$) $\delta$ 2.99 (d, 6H, $CH_3$, J = 2.0 Hz), 4.30 (d, 4H, $CH_2N$, J = 8.0 Hz), and 4.90 (s, 4H, $CH_2O$) ppm.

Half of this oil (11.70 g, 0.05 mol) was treated with 1,3-dimethylurea (4.40 g, 0.05 mol) and toluene (75 ml) and heated at reflux for 7 h, giving 1.4 ml (78%) of water and 3.40 g (22.4%) of **10** (IR, NMR). The remainder of the product (10.74 g) was a colorless glass.

*5,5-Bis(1,3-dimethylureidomethyl)-1,3-dimethyl-2-oxo-1,3-diaza-5-phosphoniacyclohexane chloride* (**11**). *E. From THPC.* Reaction of crystalline THPC (19.06 g, 0.1 mol) with 1,3-dimethylurea (26.44 g, 0.3 mol) in toluene (75 ml), following Procedure D, gave 6.8 ml (94%) of water and 25.85 g (67.5%) of **11** as a white, crystalline solid, mp 191–192.5°C d. The remainder (11.89 g) was a viscous yellow oil. Two recrystallizations from 2-propanol (5 ml/g), followed by thorough drying in a vacuum at 100°C, gave pure **11**, mp 196–197°C d; IR (Nujol) 902 s, 1140 m, 1150 m, 1195 m, 1240 m, 1255 m, 1530 s (NH, amide II), 1580 vs, 1670 s (C=O, amide I), and 3230 s (NH) $cm^{-1}$; $^1H$ NMR ($D_2O$) $\delta$ 2.74 (s, 6H, chain 3-$CH_3$), 2.90 (d, 6H, ring 1- and 3-$CH_3$, J = 2.0 Hz), 2.99 (d, 6H, chain 1-$CH_3$, J = 2.0 Hz), 3.90 (d, 4H, chain $CH_2$, J = 8.0 Hz), and 4.26 (d, 4H, ring $CH_2$, J = 6.5 Hz) ppm.[17]

*Anal.* Calcd. for $C_{13}H_{28}ClN_6O_3P$: C, 40.78; H, 7.37; Cl, 9.26; N, 21.96; P, 8.09; mol. wt., 383. Found: C, 40.43; H, 7.04; Cl, 8.95; N, 21.83; P, 8.06; mol. wt. (osmometric in $H_2O$), 234.

The phosphonium salt **11** is soluble in water and the lower alcohols and insoluble in other common organic solvents.

*F. From* **10**. A mixture of **10** (2.95 g, 0.01 mol), 1,3-dimethylurea (1.76 g, 0.02 mol), and acetonitrile (5 ml) was heated to reflux in an oil bath, whereupon all solids dissolved. The solution was held at reflux for 2h, cooled, and stripped under vacuum, leaving 4.91 g of product that gradually solidified. The product was extracted with benzene in a Soxhlet extractor to remove the excess 1,3-dimethylurea and stripped again, giving 3.45 g (90.1%) of **11** as a white, crystalline solid, mp 175–182°C. One recrystallization from 2-propanol gave pure **11**, mp 194–195°C d., identical (IR, NMR) to the product prepared from THPC.

*1,3-Dimethyl-5(1,3,3-trimethylureidomethyl)-1,3-diaza-5-phosphorinan-2,5-dione* (**13**). A solution of **10** (14.74 g, 0.05 mol), sodium hydroxide (2.00 g, 0.05 mol), and water (50 ml) was heated for 1 h at reflux,[18] allowed to cool, neutralized with 6*N* hydrochloric acid, and stripped to dryness on a rotary evaporator. The residue was shaken with acetone (100 ml), filtered to remove sodium chloride, and stripped again, giving 13.05 g (94.5%) of **13** as a white, crystalline solid, mp 86–87°C after recrystallization from ethyl acetate; IR (Nujol) 1110 m, 1150 m, 1175 m, 1230 m, 1490 s, and 1620 vs (C=O, amide I) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.86 (s, 6H, chain 3-$CH_3$), 2.93 (d, 6H, ring 1- and 3-$CH_3$, J = 2.0 Hz), 3.10 (s, 3H, chain 1-$CH_3$), 3.61 (d of d, 4H, ring $CH_2$, J = 2.0 and 7.0 Hz), and 3.70 (s, 2H, chain $CH_2$) ppm.[19]

*Anal.* Calcd. for $C_{10}H_{21}N_4O_3P$: C, 43.47; H, 7.66; N, 20.28; P, 11.21; mol. wt., 276. Found: C, 43.49; H, 8.18; N, 20.31; P, 11.24; mol. wt. (osmometric in $H_2O$), 282.

The phosphine oxide **13** is soluble in water, ethanol, chloroform, acetone, and benzene and insoluble in ether and carbon tetrachloride. It can be recrystallized from ethyl acetate (1 ml/g) or 2-propanol (0.5 ml/g) and distils without decomposition at 222°C/0.5 mm.

*1,3-Dimethyl-5(1,3-dimethylureidomethyl)-1,3-diaza-5-phosphorinan-2,5-dione* (**14**). A solution of **11** (9.57 g, 0.025 mol) in 25.0 ml of 1*N* sodium hydroxide was heated briefly to reflux, allowed to cool, neutralized with 1*N* hydrochloric acid, and stripped to dryness in a rotary evaporator. The residue was shaken with ethanol (25 ml), filtered to remove sodium chloride, stripped again, and triturated with benzene (25 ml) to remove 1,1,3-trimethylurea (1.47 g [57.6%], mp 70–71°C after recrystallization from cyclohexane).[10] The residue (6.02 g, 91.8%) was a white, crystalline solid, mp 137–140°C. Two recrystallizations from acetonitrile (2 ml/g), followed by vacuum drying for 3 h at 100°C, gave pure **14**, mp 142–143°C; IR (Nujol) 870 m, 1150 s, 1175 vs (P = 0), 1220 m, 1480 s, 1550 s (NH, amide II), 1620 vs (C=O, amide I), and 3370 s (NH) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.80 (d, 3 H, chain 3-$CH_3$, J = 4.5 Hz, collapsing to s with $D_2O$), 2.96 (d, 6 H, ring 1- and 3-$CH_3$, J = 2.0 Hz), 3.08 (s, 3 H, chain 1-$CH_3$), 3.70 (s, 2 H, chain $CH_2$), 3.74 (d of d, 4 H, ring $CH_2$, J = 3.0 and 23.5 Hz), and 5.5 (m, NH, vanishing with $D_2O$) ppm.[20]

*Anal.* Calcd. for $C_9H_{19}N_4O_3P$: C, 41.22; H, 7.30; N, 21.37; P, 11.81; mol. wt., 262. Found: C, 41.25; H, 7.64; N, 21.48; P, 11.94; mol. wt. (osmometric in $H_2O$), 270.

The phosphine oxide **14** is soluble in water, ethanol, 2-propanol, chloroform, and dimethylsulfoxide and insoluble in other common organic solvents. When recrystallized from acetonitrile it forms a hemisolvate, mp 112–113°C [$^1H$ NMR: $\delta$ 2.33 (s, 1.5 H, $CH_3CN$)], which is stable to vacuum drying for 2 h at 82°C.

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16. Acetonitrile removed a resinous byproduct (4.09 g) that was not soluble in toluene.
17. The $CH_2$ chemical shifts were assigned by comparison with **9**, **10**, and **12**, and the $CH_3$ chemical shifts by comparison with **14**.
18. In another experiment, the reaction was only 58% complete after 18 h at room temperature.
19. In $D_2O$, the signals appeared at $\delta$ 2.89 (s), 2.94 (d, J = 2.0 Hz), 3.07 (s), 3.82 (d of d, J = 4.0 and 12.0 Hz), and 3.87 (s) ppm, respectively. Increasing the field strength to 80 MHz (Varian CFT-20, $^1H$ probe) did not alter the pattern of the methylene segment of the spectrum.
20. In $D_2O$, the signals appeared at $\delta$ 2.68 (s), 2.88 (d, J = 2.0 Hz), 2.95 (d, J = 0.5 Hz), 3.80 (s), and 3.83 (d for d, J = 4.0 and 21.5 Hz) ppm, respectively. The splitting of the chain 1-$CH_3$ group ($^4J_{PH}$ = 0.5 Hz) was only visible after five-fold expansion.
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