REACTIONS OF PHOSPHORUS PENTACHLORIDE WITH N,N′-DIALKYL- AND N-ALKYL-N′-ACETYLUREAS

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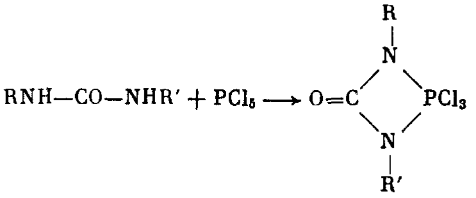
N,N′-dialkylureas are phosphorylated by phosphorus pentachloride to give cyclic trichlorodiazaphosphetidinones. The formation of these derivatives in the reaction of N-methyl-N′-chloroacetylurea with PCl_5 is accompanied by the chlorination of the N-acetyl fragment.

In our previous work [1], we have shown that halophilic reactions involving pentavalent phosphorus halides may proceed by an alternative pathway due to ionized forms. In order to obtain pentacoordinated trigonal-bipyramidal phosphorus incapable of the following ionic dissociation:

$$R_nPCl_{5-n} \rightarrow [R_nPCl_{4-n}]^+ + Cl^- \qquad (1)$$

we carried out the reactions of several N,N′-disubstituted ureas with phosphorus pentachloride.

We should note that such transformations have been used mainly for the case of N,N′-dimethylurea [2]. The reactions with PCl_5 for N,N′-dialkylureas, obtained by the hydrolysis of the corresponding isocyanates, were carried out by cyclization with a 1:1 reagent ratio since chlorination of the endocyclic carbonyl group may occur in the presence of excess PCl_5 [3].

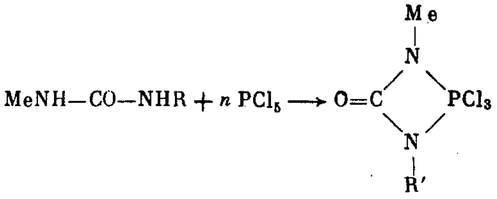


(2)

(I)—(IV)

$R = R' = Me$ (I); $R = R' = Et$ (II); $R = R' = n\text{-}Bu$ (III); $R = Me$, $R = n\text{-}Pr$ (IV).

However, cyclization proceeds for N-methyl-N′-chloroacetylureas only with a greater amount of PCl_5. In this case, the endocyclic acetyl fragment remains unaltered and chlorination of the exocyclic acetyl fragment occurs accompanied by the formation of α-chlorovinyl and chloroalkyl derivatives (V)-(VII)



(3)

(V)—(VII)

$R = COCH_2Cl$, $R' = CCl_2{-}CHCl_2$, $n = 3$ (V); $R = COCH_2Cl$, $R' = C(Cl){=}CHCl$, $n = 2$ (VI);
$R = COCCl_3$, $R' = C_2Cl_5$, $n = 2$ (VII).

The structure of the phosphorylated ureas obtained was demonstrated by PMR, ^{31}P NMR, and ^{35}Cl NQR spectroscopy. Thus, the $\delta^{31}P$ chemical shifts lie in the region characteristic for pentacoordinated phosphorus (47-60 ppm), while the multiplicity of the spectra without proton decoupling indicates the presence of two alkyl groups coupled with the phosphorus atom. This is possible only in the case of a diazaphosphetidine ring. The ^{35}Cl NQR spectra,

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which display signals characteristic for chlorine atoms in the P-Cl bond in $(Cl_3PNR)_2$ compounds [4,5], indicate the trigonal-bipyramidal structure of the diazaphosphetidinones obtained. The high-frequency signals at 30-31 MHz are assigned to the quasiequatorial chlorine atoms, while the low-frequency signals at 26-27.6 MHz are assigned to the quasiaxial chlorine atoms.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were taken on a Bruker WP-200 SY spectrometer at 200.13 and 81.026 MHz, respectively, using $CDCl_3$ as the internal standard for the ^1H NMR spectra and 85% H_3PO_4 as the external standard for the ^{31}P NMR spectra. The ^{35}Cl NQR spectra were obtained on an IS-3 spectrometer at 77 K.

2,2,2-Trichloro-1,3-dimethyldiazaphosphetidinone (I). A sample of 41.7 (0.2 mole) PCl_5 was added to a solution of 17.6 g (0.2 mole) N,N′-dimethylurea in 80 ml CCl_4. The mixture was stirred at reflux until hydrogen chloride was no longer released. The solution was separated from the upper oily phase and evaporated. The residue was distilled in vacuum to give 30.4 g (68%) (I), bp 70-72°C (0.7 mm) (78-79°C (1.5 mm) [2]). ^{31}P NMR spectrum (δ, ppm): −61.1 (J_{PH} = 21.0 Hz), ^{35}Cl NQR spectrum (ν^{77} MHz, signal/noise ratio): 30.328 (38), 25.848 (20).

2,2,2-Trichloro-1,3-diethyldiazaphosphetidinone (II) was obtained by analogy from 4.6 g (0.04 mole) N,N′-diethylurea and 8.4 g (0.04 mole) PCl_5 in 50 ml CCl_4. The yield of (II) was 6.8 g (68%), bp 72-74°C (0.3 mm). Found: C, 23.76; H, 3.77; P, 12.24%. Calculated for $C_5H_{10}Cl_3N_2OP$: C, 23.85; H, 3.97; P, 12.32%. ^{31}P NMR spectrum (δ, ppm): −62.4 (J_{PH} = 27.9 Hz). PMR spectrum (δ, ppm): 3.14 d.m (2H, CH_2, J_{HP} = 27.9 Hz).

2,2,2-Trichloro-1,3-dibutyldiazaphosphetidinone (III) was obtained by analogy from 8.8 g (0.05 mole) N,N′-dibutylurea and 10.7 g (0.05 mole) PCl_5 in 100 ml CCl_4. The yield of (III) was 9.5 g (62%), bp 110-112°C (0.4 mm). Found: C, 32.42; H, 6.02; P, 10.38%. Calculated for $C_9H_{18}Cl_3N_2OP$: C, 32.36; H, 5.85; P, 10.24%. ^{31}P NMR spectrum (δ, ppm): −61.4 (J_{PH} = 27.8 Hz). PMR spectrum (δ, ppm): 3.21 d.d (2H, CH_2, J_{HP} = 27.8 Hz), 1.57 m (2H, CH_2), 1.29 m (2H, CH_2), 0.86 t (3H, CH_3). ^{35}Cl NQR spectrum (ν^{77} MHz, signal/noise ratio): 30.895 (10), 30.749 (15), 29.963 (22), 25.971 (5), 25.708 (4).

2,2,2-Trichloro-1-methyl-3-propyldiazaphosphetidinone (IV) was obtained by analogy from 23.2 g (0.2 mole) N-methyl-N′-propylurea and 45.7 g (0.2 mole) PCl_5 in 200 ml CCl_4. The yield of (IV) was 22.6 g (45%), bp 76-78°C (0.3 mm). Found: C, 23.74; H, 3.72; P, 12.69%. Calculated for $C_5H_{10}Cl_3N_2OP$: C, 23.85; H, 3.97; P. 12.32%. ^{31}P NMR spectrum (δ, ppm): −60.8 (J_{PH}' = 19.3, J_{PH}'' = 30.2 Hz). PMR spectrum (δ, ppm): 2.65 d (3H, CH_3, J_{HP}' = 19.3 Hz), 3.19 d.t (2H, CH_2, J_{HP}'' = 30.2 Hz), 1.65 m (2H, CH_3). ^{35}Cl NQR spectrum (ν^{77} MHz, signal/noise ratio): 30.444 (28), 29.906 (30), 26.123 (21).

2,2,2-Trichloro-1-methyl-3-(1,1,2,2-tetrachloroethyl)diazaphosphetidinone (V). A sample of 1.0 g (0.007 mole) N-methyl-N′-chloroacetylurea was added to a suspension of 4.4 g (0.021 mole) PCl_5 and the mixture was stirred at ~20°C until hydrogen chloride was no longer released. The solvent was evaporated and the residue was cooled. The crystalline precipitate was washed with cold nitromethane and dried in vacuum to give 1.8 g (72%) (V), mp 77-84°C (dec.). Found: C, 12.80; H, 1.08; N, 9.38; Cl, 65.80%. Calculated for $C_4H_4Cl_7N_2OP$: C, 12.80; H, 1.08; N, 7.47; P, 8.25; Cl, 66.15%. ^{31}P NMR spectrum (δ, ppm): −69.1 (J_{PH} = 24.4 Hz). PMR spectrum (δ, ppm): 3.10 d (3H, CH_3, J_{HP} = 23.9 Hz), 6.84 d (1H, $HCCl_2$, J_{HP} = 1.0 Hz).

2,2,2-Trichloro-1-methyl-3-(1,2-dichloroethenyl)diazaphosphetidinone (VI). A sample of 2.2 g (0.015 mole) N-methyl-N′-chloroacetylurea was added to a suspension of 6.0 g (0.03 mole) PCl_5 in 25 ml benzene. The mixture was stirred at ~20°C until hydrogen chloride was no longer evolved. The solvent was evaporated in vacuum and the residue was diluted with benzene and filtered off. The solution was evaporated to give 4.4 g (78%) (VI) as a thick, yellow oil, which turns red upon storage. Found: C, 20.06; H, 1.26; P, 9.20% Calculated for $C_4H_4Cl_5N_2OP$: C, 15.78; H, 1.33; P, 10.18%. ^{31}P NMR spectrum (δ, ppm): −58.1 (J_{PH} = 23.3 Hz). PMR spectrum (δ, ppm): 2.96 d (3H, CH_3, J_{HP} = 23.2 Hz), 6.42 d (1H, HCCl=). ^{35}Cl NQR spectrum (ν^{77} MHz, signal/noise ratio): 36.311 (25), 35.275 (27) (CCl), 30.956 (23), 27.016 (12) (PCl_3).

2,2,2-Trichloro-1-methyl-3-perchloroethyldiazaphosphetidinone (VII). A sample of 2.0 g (0.009 mole) N-methyl-N′-trichloroacetylurea was added to a suspension of 3.8 g (0.018 mole) PCl_5 in 30 ml benzene. The mixture was stirred at ~20°C until the reagents dissolved completely. The solution was filtered and evaporated in vacuum to give 3.2 g (87%) (VII), mp 84°C (final crystallization). Found: C, 9.22; H, 0.80; P, 6.55%. Calculated for $C_4H_3Cl_8N_2OP$: C, 11.72; H, 0.74; P, 7.56%. ^{31}P NMR spectrum (δ, ppm): −47.2 (J_{PH} = 26.1 Hz). PMR spectrum

(δ, ppm): 3.11 d (CH_3, J_{HP} = 25.6 Hz). ^{35}Cl NQR spectrum (ν^{77} MHz, signal/noise ratio): 40.580 (6), 40.140 (6), 39.850 (5) (CCl_3), 38.670 (7), 38.054 (9), (CCl), 31.823 (14), 31.673 (13), 27.583 (6) (PCl_3).

LITERATURE CITED

1. V. K. Dmitriev and B. V. Timokhin, Zh. Obshch. Khim., 53, No. 9, 2149 (1983).
2. H. Ulrich and A. A. R. Saygh, Angew. Chem., 76, No. 14, 647 (1964).
3. M. Becke-Goehring and H. Scwind, Z. Anorg. Allg. Chem., 372, 285 (1970).
4. W. P. Dalgleich and A. L. Porte, J. Magn. Reson., 20, No. 2, 359 (1975).
5. G. E. Kibrik, V. S. Kozlov, I. A. Kyuntsel', et al., Khim. Fiz., 4, No. 8, 1076 (1985).

CRYSTAL STRUCTURE OF $1H^+,10H^+$-1,10-DIAZONIA-18-CROWN-6 DIETHYLDITHIOPHOSPHATE

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An x-ray diffraction structural analysis was carried out on $1H^+,10H^+$-1,10-diazonia-18-crown-6 diethyldithiophosphate, which exists in the crystal as isolated ionic hydrogen-bonded complexes $[H_2DA18C6]^{2+}\cdot 2(EtO)_2PS_2^-$ with strong inter-ion N-H···S hydrogen bonds. The centrosymmetric DA18C6 dication has an unusual two-cornered conformation stabilized by a pair of weak intra-ring furcated O···H(N)···O hydrogen bonds.

In this communication, results are given for an x-ray diffraction structural analysis for crystals of $1H^+,10H^+$-1,10-diazonia-18-crown-6 diethyldithiophosphate (I). The structure of (I) holds interest in the study of the possible conformations, intra-ring hydrogen bonds, and means of coordination of 1,10-diaza-18-crown-6 (DA18C6) by various molecules in the absence of metal cations.

Thiophosphate (I) is a salt and exists in the crystal as isolated ionic hydrogen-bonded complexes $[H_2DA18C6]^{2+}\cdot 2(EtO)_2PS_2^-$ (see Fig. 1). The centrosymmetric DA18C6 dication (with two protonated hydrogen atoms) is found at a crystallographic center of inversion i(000) and two $(EtO)_2PS_2^-$ anions are linked to this dication by hydrogen bonds.

Major bond lengths: $P{-}S^1$ = 1.938(1), $P{-}S^2$ = 1.961(1), $P{-}O^1$ = 1.567(3), $P{-}O^2$ = 1.559(3), $N^1{-}C^2$ = 1.496(4), $N^1{-}C^{9'}$ = 1.491(4), $C^2{-}C^3$ = 1.486(5), $C^3{-}O^4$ = 1.417(4), $O^4{-}C^5$ = 1.416(4), $C^5{-}C^6$ = 1.483(5), $C^6{-}O^7$ = 1.420(4), $O^7{-}C^8$ = 1.406(4), $C^8{-}C^9$ = 1.481(5), $H^{1.1}{-}N^1$ = 0.93(5), and $H^{1.2}{-}N^1$ = 0.85(4) Å. Major bond angles: S^1PS^2 = 117.87(6), S^1PO^1 = 106.1(2), S^1PO^2 = 109.7(2), S^2PO^1 = 112.8(1), S^2PO^2 = 111.0(1), O^1PO^2 = 97.3(2), $C^{9'}N^1C^2$ = 116.2(3), $N^1C^2C^3$ = 111.5(3), $C^2C^3O^4$ = 107.3(3), $C^3O^4C^5$ = 111.7(2), $O^4C^5C^6$ = 109.9(3), $C^5C^6O^7$ = 110.4(3), $C^6O^7C^8$ = 112.8(3), $O^7C^8C^9$ = 108.5(3), $C^8C^9N^{1'}$ = 110.6(3), and $H^{1.1}N^1H^{1.2}$ = 107(4)°. The phosphorus atom in the $(EtO)_2PS_2^-$ anion with a delocalized P=S bond has distorted tetrahedral coordination. The $S{=\!=\!=}P{=\!=\!=}S$ bond angle is greatest and the O-P-O bond angle is least. Both ethoxy groups undergo strong thermal oscillations in the structure of (I) and are probably somewhat disordered. Thus, their geometrical parameters are quite distorted but this may be an artifact; torsion angles $PO^1C^{10}C^{11}$ = −170 and $PO^2C^{12}C^{13}$ = −175°. The intra-ring torsion angles are: $C^{9'}N^1C^2C^3$ = −64.3, $N^1C^2C^3O^4$ = −58.0, $C^2C^3O^4C^5$ = 177.8, $C^3O^4C^5C^6$ = 171.5, $O^4C^5C^6O^7$ = 67.3, $C^5C^6O^7C^8$ = 175.5, $C^6O^7C^8C^9$ = 171.9, $O^7C^8C^9N^{1'}$ = 57.1, and $C^8C^9N^{1'}C^{2'}$ = 177.6°. N^1 and $N^{1'}$ in the macroheterocycle in (I) deviate from the plane of the four oxygen atoms in opposite directions by 0.447(3) and −0.447(3) Å. The intra-ring distances are: $N^1\cdots N^{1'}$ = 6.320(3), $O^4\cdots O^{4'}$ = 5.574(2), and $O^7\cdots O^{7'}$ = 4.750(2) Å.

The DA18C6 dication in (I) has a two-cornered conformation [1]. Two gauche bonds (−−) and (++) converge at C^2 and $C^{2'}$. Such a conformation has not yet been reported for DA18C6 and differs from the two-cornered conformations of the DA18C6 dication in the $[H_2DA18C6]^{2+}$.

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