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LETTERS TO THE EDITOR

Phosphorus-Containing *N*-Alkylaldimmonium Salts

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Phosphorus-containing immonium salts were not described in the literature. Combination of thioester, thiophosphoryl, and immonium groups in one molecule should provide them with complexing properties and diverse biological activity.

Unsubstituted imines can be protonated by dithiophosphoric acid at the nitrogen atom [1, 2]. In contrast, *N*-alkyl-2-chloraldimines **Ia**–**Ic**, where the single chlorine atom is more mobile than the chlorine atoms in trichloromethyl and dichloromethylene groups of chloral and 2,2-dichloropropanal imines [3, 4], along with the protonation of the imine groups are likely to undergo nucleophilic substitution of Cl with dithiophosphate anion, as salts of dithioacids can be alkylated with alkyl halides [5].

We found that *N*-alkyl-2-chloraldimines **Ia**–**Ic** react with *O*,*O*-dialkyl dithioacids **IIa**–**IIc** to give *N*-alkyl-2-*O*,*O*-dialkyldithiophosphatoaldimmonium chlorides **IIIa**–**IIId**. The reaction proceeded in two stages. The first step is the protonation of the imine group to form immonium salt, *N*-alkyl-2-chloraldimmonium *O*,*O*-dialkyldithiophosphate **IV**, whose presence in the reaction mixture has been detected by ^{1}H and ^{31}P NMR spectroscopy. Thus, in the ^{1}H NMR spectrum of the reaction mixture the proton $N^{+}H$ resonates at 12 ppm. The chemical shift of the phosphorus atom in the ^{31}P NMR spectrum is 108 ppm. In comparison, the proton of $N^{+}H$ in the spectrum of *N*-*tert*-butyl-2-methylpropanimmonium *O*,*O*-diisopropyldithiophosphate **V** (synthesized as a model compound) resonates at 13.1 ppm; chemical shift of the phosphorus atom is 107.8 ppm.

In the second step of the reaction the chlorine atom in the salt **IV** was replaced by *O*,*O*-dialkyldithiophosphate group.

$$(Me)_2C(Cl)CH{=}NR^1 + (R^2O)_2P(S)SH$$
Ia–Ic **IIa, IIb**

$$\rightleftarrows (Me)_2C(Cl)\overset{\frown}{CH\cdots NHR^1}^{+}\ (R^2O)_2P(S)S^-$$
IV

$$\rightarrow (Me)_2CCH{=}N^{+}HR^1\ Cl^-$$
$$\Big|$$
$$SP(S)(OR^2)_2$$
IIIa–IIIe

III, R^1 = *t*-Bu, R^2 = *i*-Pr (**a**), Et (**b**), *n*-Bu (**c**); $R^1 = R^2$ = *i*-Pr (**d**); R^1 = Bz, R^2 = Et (**e**).

Composition and structure of the immonium salts **IIIa**–**IIIe** obtained were confirmed by elemental analysis, ^{1}H, ^{13}C, and ^{31}P NMR spectra.

***N*-*tert*-Butyl-2-(*O*,*O*-diisopropyldithiophosphato)-2-methylpropanimmonium chloride (IIIa).** 18.7 g (0.087 mol) of *O,O*-diisopropyldithiophosphoric acid **II** was added dropwise to a stirred solution of 14.1 g (0.087 mol) of *N*-*tert*-butyl-2-chloro-2-methylpropanimine **Ia** in 70 mL of CCl_4 at 0–5°C. Then the reaction mixture was warmed to 20°C, and the mixture was maintained at this temperature for 24 h. After the solvent removal the residue was dissolved in diethyl ether and cooled. The precipitated crystals were filtered off. Yield 20.5 g (81%), mp 147°C. ^{1}H NMR

spectrum ($CDCl_3$), δ, ppm: 1.18 d (12H, $\underline{Me}_2CHO$, $^3J_{HH}$ 6.1 Hz), 1.52 s (9H, CMe_3), 1.85 s (6H, CMe_2), 4.62 d. h (2H, CHOP, $^3J_{HH}$ 6.1, $^3J_{PH}$ 12.1 Hz), 8.76 s (CH=N), 14.25 br.s (1H, N^+H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.91 d and 23.34 d ($OCH\underline{Me}_2$, $^3J_{PC}$ 5.03 Hz), 27.56 s ($C\underline{Me}_3$), 28.34 d ($SC\underline{Me}_2$, $^3J_{PC}$ 8.05 Hz), 52.09 d (CS, $^2J_{PC}$ 4.02 Hz), 63.57 s ($\underline{C}Me_3$), 75.32 d ($Me_2\underline{CH}O$, $^2J_{PC}$ 8.05 Hz), 177.45 s ($CH=N^+$). ^{31}P NMR spectrum ($CDCl_3$): δ_P 85.20 ppm. Found, %: C 44.89; H 8.50; P 18.18; S 16.88. $C_{14}H_{31}ClNO_2PS_2$. Calculated, %: C 44.73; H 8.31; P 18.24; S 17.05.

***N-tert*-Butyl-2-(*O*,*O*-diethyldithiophosphato)-2-methylpropanimmonium chloride (IIIb)** was prepared similarly from 8.9 g (0.055 mol) of *N-tert*-butyl-2-chloro-2-methylpropanimine **Ia**, 50 mL of CCl_4 and 10.2 g (0.055 mol) of *O*,*O*-diethyldithiophosphoric acid **IIb**. Yield 14.5 g (76%), mp 112°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (6H, $CH_2\underline{Me}$, $^3J_{HH}$ 7.0 Hz), 1.45 s (9H, CMe_3), 1.80 s (6H, CMe_2), 4.09 d. q (4H, CH_2OP, $^3J_{HH}$ 7.0, $^3J_{PH}$ 10.3 Hz), 8.70 s (1H, $CH=N^+$), 14.31 br.s (1H, N^+H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 87.30 ppm. Found, %: C 41.57; H 7.97; P 8.81; S 18.18. $C_{12}H_{27}ClNO_2PS_2$. Calculated, %: C 41.43; H 7.82; P 8.90; S 18.42.

***N-tert*-Butyl-2-(*O*,*O*-dibutyldithiophosphato)-2-methylpropanimmonium chloride (IIIc)** was prepared similarly from 5.8 g (0.024 mol) of *N-tert*-butyl-2-chloro-2-methylpropanimine **Ia**, 50 mL of CCl_4 and 5.8 g (0.024 mol) of *O*,*O*-dibutyldithiophosphoric acid **IIc**. Yield 7.6 g (79%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.75 t (6H, $\underline{Me}CH_2$, $^3J_{HH}$ 7.1 Hz), 1.48 s (9H, CMe_3), 1.02–1.61 m (8H, CH_2CH_2), 1.82 s (6H, CMe_2), 3.62–4.02 m (4H, CH_2OP), 8.76 s (1H, $CH=N^+$), 13.46 br.s (1H, N^+H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 87.40 ppm. Found, %: C 47.69; H 8.84; P 7.59. $C_{16}H_{35}ClNO_2PS_2$. Calculated, %: C 47.57; H 8.73; P 7.67.

***N*-Isopropyl-2-(*O*,*O*-diisopropyldithiophosphato)-2-methylpropanimmonium chloride (IIId)** was prepared similarly from 14.7 g (0.1 mol) of *N*-isopropyl-2-chloro-2-methylpropanimine **Ib**, 50 mL of CCl_4 and 21.4 g (0.1 mol) of *O*,*O*-diisopropyldithiophosphoric acid **IIa**. Yield 29.2 g (81%), mp 64°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 d and 1.10 d (12H, $\underline{Me}_2CHO$, $^3J_{HH}$ 6.1 Hz), 1.35 d (6H, $\underline{Me}_2CHN$, $^3J_{HH}$ 6.3 Hz), 1.71 s (6H, CMe_2), 4.19 q and 4.12 q (1H, NCH, $^3J_{HH}$ 6.3 Hz), 4.59 d. h (2H, $O\underline{CH}Me_2$, $^3J_{HH}$ 6.1, $^3J_{PH}$ 12.1 Hz), 8.93 s (1H, $CH=N^+$), 14.06 br.s (1H, N^+H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.92 s ($N^+CH\underline{Me}_2$), 23.96 d and 23.82 d ($OCH\underline{Me}_2$, $^3J_{PC}$ 5.03 Hz), 27.89 d ($SC\underline{Me}_2$, $^3J_{PC}$ 7.04 Hz), 51.99 d (SC, $^2J_{PC}$ 5.08 Hz), 57.64 s (N^+CH), 75.43 d (CHOP, $^2J_{PC}$ 8.05 Hz), 178.30 s ($C=N^+H$). ^{31}P NMR spectrum ($CDCl_3$): δ_P 84.81 ppm. Found, %: C 43.23; H 8.14; P 8.69; S 17.54. $C_9H_{25}ClNO_2PS_2$. Calculated, %: C 43.11; H 8.08; P 8.56. S 17.70.

***N*-Benzyl-2-(*O*,*O*-diethyldithiophosphato)-*N-tert*-butyl-2-methylpropanimmonium chloride (IIIe)** was prepared similarly from 5.9 g (0.03 mol) of *N*-benzyl-2-methyl-2-chloropropanimine **Ic**, 25 mL of CCl_4 and 5.6 g (0.03 mol) of *O,O*-diethyldithiophosphoric acid **IIb**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 t (6H, $\underline{Me}CH_2$, $^3J_{HH}$ 7.0 Hz), 2.01 d (6H, CMe_2, $^4J_{PH}$ 1.2 Hz), 4.01–4.22 m (4H, $POCH_2$), 5.11 s (2H, $Ph\underline{CH}_2$), 7.36–7.80 m (5H, Ph), 8.61 s (1H, $CH=N^+$), 15.28 br.s (1H, N^+H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 87.64 ppm. Found, %: C 47.28; H 6.47; N 3.50; P 7.91. $C_{15}H_{25}Cl\cdot NO_3PS_2$. Calculated, %: C 47.18; H 6.60; N 3.67; P 8.11.

2-Methylpropanimmonium *O*,*O*-diisopropyldithiophosphate (V). A solution of 0.59 g (0.0047 mol) of *N-tert*-butyl-2-methylpropanimine in 5 mL of CCl_4 was added drop-wise to a stirred solution of 1 g (0.0047 mol) of *O,O*-diisopropyldithiophosphoric acid **II** in 5 mL of CCl_4 at 0°C. After 4 days in the ^{31}P NMR spectrum of the reaction mixture only one singlet was detected at δ_P 107.8 ppm corresponding to four-coordinated phosphorus atom surrounded with O_2PS_2. After the solvent removal, compound **V** was obtained. Yield 1.4 g (87%), mp 63°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 d (12H, $\underline{Me}_2CHO$, $^3J_{HH}$ 6.1 Hz), 1.38 d (6H, $\underline{Me}_2CH$, $^3J_{HH}$ 7.0 Hz), 1.63 s (9H, CMe_3), 3.63 sextet (1H, $\underline{CH}Me2$, $^3J_{HH}$ = 7.0 Hz), 4.75 d.h (2H, CHOP, $^3J_{HH}$ 6.1, $^3J_{PH}$ 12.1 Hz), 8.51 d (1H, $CH=N^+$, $^3J_{HH}$ 7.0 Hz), 13.1 br.s (1H, N^+H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 107.80 ppm. Found, %: C 49.40; H 9.38; N 4.26; P 8.93; S 18.61. $C_{14}H_{32}NO_2PS_2$. Calculated, %: C 49.24; H 9.45; N 4.10; P 9.07; S 18.77.

^1H and ^{13}C NMR spectra were recorded on AVANCE 400 WB spectrometer operating at 400.13 and 100.61 MHz, respectively, in $CDCl_3$, internal reference TMS. ^{31}P NMR spectra were registered on AVANCE 400 WB (161.98 MHz) and Bruker MSL-400 spectrometers (162 MHz), external reference 85% H_3PO_4.

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