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LETTERS
TO THE EDITOR

Reaction of Elemental Phosphorus (P_4) and Sulfur with Amines in the Presence of Alkylene Glycols: New Method to Prepare Octathiotetraphosphetane Ammonium Salts

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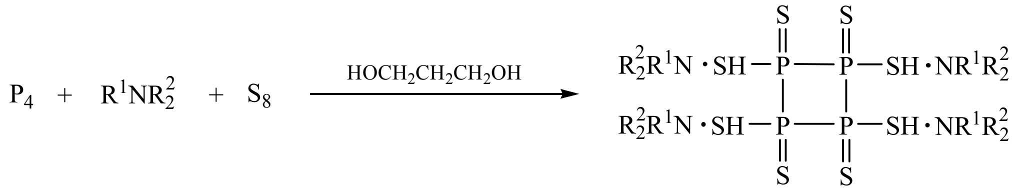
Syntheses based on cleavage of the phosphorus–phosphorus bond in the molecule of elemental (white) phosphorus open the easiest and environmentally friendly opportunities to prepare many useful organophosphorus compounds [1–3].

We have recently demonstrated that reactions of white phosphorus (P_4) and elemental sulfur with proton-donating reagents easily proceed in the presence of amines [4–6], yielding ammonium salts of phosphorous and hypophosphorous acids and diesters of dithiophosphoric acid. The reaction of white phosphorus and sulfur with aliphatic thiols in the presence of amines has been shown to give the four-membered cyclic phosphorus compounds, ammonium salts of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane [7,8], with moderate yields. These salts were prepared previously [9, 10] along with other cyclic thiophosphates via the reaction of white phosphorus with polysulfides, hydrogen sulfide, and amines.

Extending the above-listed results, herein we demonstrate a new method to yield octathiotetraphosphetane via the reaction of P_4, sulfur, and amines in the presence of 1,3-propanediol as protonodonor. The reaction was carried out in acetonitrile at 55–70ºC during 8–10 h. The conversion of phosphorus was complete, and no hydrogen sulfide formation was observed. By cooling the reacted mixture down, we isolated compounds revealing the δ_P 120–122 ppm signal in ^{31}P NMR spectra, identified as octathiophosphetane ammonium salts (Scheme 1).

The salts obtained crystallized readily. Physicochemical and spectral parameters of the products **Ia**–**Ie** completely coincided with those of the compounds obtained via the reaction of P_4, sulfur, and amines in the presence of thiols. The latter products were studied by IR, Raman, ^{31}P NMR, and ^{1}H NMR spectroscopy in combination with Density Functional Theory simulation; structure of the salts **Ia**–**Ic** was confirmed by X-ray diffraction analysis [7, 8].

Scheme 1.



Ia–**Ie**

$R^1 = R^2 = Et$ (**a**); $R^1 = H$, $R^2 = –(CH_2)_5–$ (**b**); $R^1 = H$, $R^2 = Et$ (**c**); $R^1 = Me$, $R^2 = (CH_2CH_2)_2O$ (**d**); $R^1 = CH_2C_6H_5$, $R^2 = Me$ (**e**).

Octathiotetraphosphetane ammonium salts are heterocyclic compounds containing functional groups in their molecules; therefore, they can be of interest for medical and biological studies. They form metal complexes with transition metal halides [11] and are potentially active antifungal agents (*Candida albicans*) [12].

Synthesis of tetrakis(ammonium) salts of 1,2,3,4-tetrathio-1,2,3,4-tetrathioxotetraphosphetane Ia–Ie *(general procedure).* 33 mmol of amine was added at room temperature under argon to a solution of 1 g (32 mmol) of white phosphorus, 2.1 g (64.6 mmol) of sulfur, and 2.5 g (33 mmol) of 1,3-propanediol in 8–10 mL of acetonitrile. The mixture was stirred during 8–10 h at 65–80ºC and then evaporated under reduced pressure. The so formed crystals were filtered off, dissolved in acetonitrile, and precipitated with diethyl ether. Physico-chemical and spectral features of the products **Ia–Ie** agreed with the reference data [7, 8].

1,2,3,4-Tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(triethylammonium) salt Ia. Yield 1.3 g (21%), yellow crystals, mp 96-110ºC. IR spectrum (KBr), ν, cm^{-1}: 2678, 2491 (HN^+), 660, 565 (P–S), 390 (P–P). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.33–1.38 m (36H, CH_3), 3.2-3.38 m (24H, CH_2). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 122. Found, %: C 36.16; H 7.84; N 7.00; P 15.48; S 32.65. $C_{24}H_{64}N_4P_4S_8$. Calculated, %: C 36.55; H 8.12; N 7.11; P 15.74; S 32.49.

1,2,3,4-Tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(piperidinium) salt Ib. Yield 2.6 g (44.6%), white fine crystalline powder, mp 196–210ºC. IR spectrum (KBr), ν, cm^{-1}: 2465 (HN^+), 656, 566 (P–S), 390 (P–P). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.67–1.77 m (24H, $(CH_2)_3$), 3.16-3.18 m [16H, $N(CH_2)_2$]. ^{31}P NMR spectrum (D_2O), δ_P, ppm: 123. Found, %: C 32.86; H 6.29; N 7.27; P 16.85; S 35.88. $C_{20}H_{48}N_4P_4S_8$. Calculated, %: C 33.15; H 6.63; N 7.73; P 17.13; S 35.36.

1,2,3,4-Tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(diethylammonium) salt Ic. Yield 1.2 g (22%), light-yellow crystals, mp 156–168ºC. IR spectrum (KBr), ν, cm^{-1}: 2465 (HN^+), 656, 566 (P–S), 390 (P–P). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.23–1.27 m (24H, CH_3), 3.03-3.08 m (16H, CH_2). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 124. Found, %: C 28.11; H 6.89; N 8.30; P 18.51; S 38.90. $C_{16}H_{48}N_4P_4S_8$. Calculated, %: C 28.40; H 7.10; N 8.28; P 18.34; S 38.87.

1,2,3,4-Tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(methylmorpholinium) salt Id. Yield 1.46 g (23%), white powder, mp 137–144ºC. IR spectrum (KBr), ν, cm^{-1}: 2704, 2461 (HN^+), 656, 565 (P–S), 390 (P–P). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 2.88 s (12H, CH_3) 3.3 m (16H, NCH_2), 3.94 m (16H, OCH_2). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 121. Found, %: C 30.17; H 6.03; N 6.75; P 15.65; S 32.83. $C_{20}H_{48}N_4O_4P_4S_8$. Calculated, %: C 30.46; H 6.09; N 7.11; P 15.74; S 32.49.

1,2,3,4-Tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(dimethylbenzylammonium) salt Ie. Yield 0.8 g (12%), white powder, mp 113–115ºC. IR spectrum (KBr), ν, cm^{-1}: 2678, 2466 (HN^+), 657, 566 (P–S), 391 (P–P). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 2.83 s (24H, CH_3) 4.32 m (8H, NCH_2), 7.47–7.54 m (20H, H_{Ar}). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 123. Found, %: C 46.80; H 6.23; N 6.01; P 13.10; S 27.93. $C36H_{56}N_4O_4P_4S_8$. Calculated, %: C 46.75; H 6.06; N 6.06; P 13.42; S 27.71.

IR spectra were recorded with the Bruker Tensor-27 Fourier spectrometer (KBr, 4000-400 cm^{-1}). ^{1}H NMR spectra were recorded with the Bruker MSL-400 (162.0 MHz) spectrometer with internal TMS reference. ^{31}P NMR spectra were recorded with the Bruker CPX (36.48 MHz) spectrometer with 85% phosphoric acid reference. C, H, N, and S content were determined using the CHN-3 analyzer. Content of phosphorus was evaluated by means of the standard pyrolysis procedure.

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