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CHEMISTRY

Reaction of Red Phosphorus (P_n) with Alkanethiolate Anions

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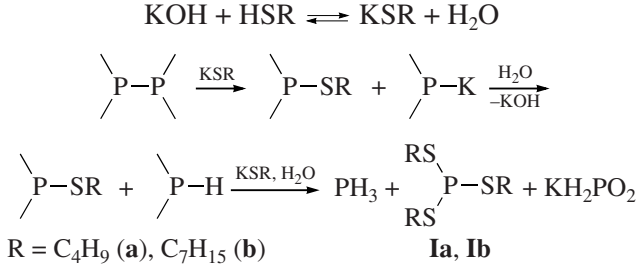
In recent years, the cleavage of P–P bond of elemental phosphorus under the action of nucleophiles has been extensively studied [1, 2]. From the viewdpoint of basic research, these studies fundamentally supplement the existing paradigms in phosphorus chemistry, and from the viewpoint of synthetic methodology, they open the shortest and environmentally benign ways to the organophosphorus compounds of practical importance [2]. The possibility of preparative use of phosphorus-centered nucleophiles produced by the cleavage of P–P bonds of white phosphorus under the action of anions of bases (hydroxide anions) was reported for the first time in [3]. Successful attempts to utilize in organophosphorus synthesis less reactive but nontoxic red phosphorus, which is more safe to handle as compared with white phosphorus, were made by the authors [4, 5] who accomplished the cleavage of P–P bond of three-dimensional macromolecule of this allotrope of phosphorus in alkali metal–liquid ammonia systems. A direct one-pot synthesis of tristyrylphosphine [6] from phenylacetylene and red phosphorus in KOH–HMPA (hexamethylphosphoramide) superbasic system laid the foundation of the systematic use of phosphorus-centered nucleophiles generated by the cleavage of P–P bond in the presence of bases for the synthesis of unavailable or unknown organophosphorus compounds.

At present, the cleavage of P–P bond in the macromolecule of red phosphorus under the action of hydroxide anions in superbasic media is a key stage in novel one-pot syntheses of a wide variety of phosphines and phosphine oxides [2], which were obtained previously by multistep reactions from toxic and aggressive phosphorus halides.

The data on the cleavage of P–P bond of elemental phosphorus with sulfur-centered nucleophiles produced from thiols seems to be confined to the synthesis of trialkyl trithiophosphites [7], salts of *S*,*S*-diphenyl dithiophosphoric acid, or triphenyl thiophosphate from white phosphorus [8]. The supramolecule of red phosphorus is much less reactive in comparison with white phosphorus; therefore, its cleavage under the action of sulfur nucleophiles has been unknown so far. We have found recently that hydrosulfide anions in DMSO (dimethyl sulfoxide) media disaggregate the cross-linked macromolecule of red phosphorus to form trithio- and tetrathiophosphates [9].

In this work, we carried out and studied for the first time the reaction of red phosphorus with potassium alkanethiolates. The reaction was accomplished on heating the reagents in DMSO (125–128°C, 4 h).

The sequential cleavage of P–P bonds in P_n macromolecule with thiolate anion was expected to proceed through intermediate compounds containing P–H and P–SR bonds to form finally PH_3, $(RS)_3P$ (**Ia**, **Ib**), and KH_2PO_2 (Scheme 1).



Scheme 1.

Indeed, the reaction resulted in the formation of these compounds identified by ^{31}P NMR spectroscopy.

Unexpectedly, we isolated potassium *S*,*S*-dialkyl trithiophosphates (**IIa**, **IIb**) from reaction mixtures in 13–15% yield (not optimized). These compounds seem

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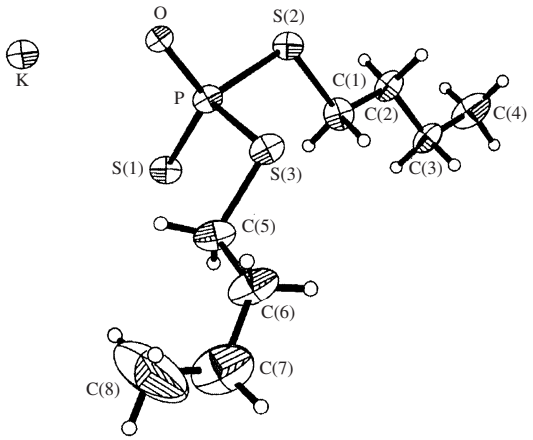


Fig. 1. Molecule of trithiophosphate **IIa**: the selected bond lengths (Å): P–O, 1.473(7); P–S(1), 1.931(4); P–S(2), 2.074(4); P–S(3), 2.094(4); bond angles: O–P–S(1), 117.4(3)°; O–P–S(2),103.6(3)°; S(1)–P–S(2), 113.1(2)°; O–P–S(3), 110.7(3)°; S(1)–P–S(3), 110.0(2)°; S(2)–P–S(3), 100.6(2)°.

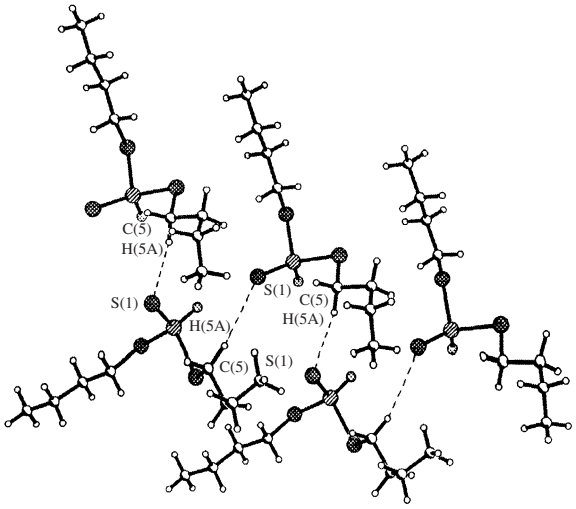
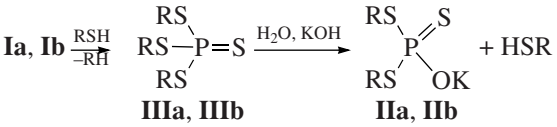


Fig. 2. Intermolecular hydrogen contacts in the crystal structure of trithiophosphate **IIa**, Å: S(1)···C(5), 3.30(1), Å; S(1)···H(5A), 2.89 Å, C(5)–H(5A), 0.99 Å; S(1)···C(5)–H(5A), 165° (the sum of van der Waals radii is 3.50 Å for S···C and 3.0 Å for S···H [14]).

to result from the oxidation of trialkyl trithiophosphites (**Ia**, **Ib**) with thiols to afford trialkyl tetrathiophosphates (**IIIa**, **IIIb**) [10] and their subsequent alkaline hydrolysis (Scheme 2).



R = C_4H_9 (**a**), C_7H_{15} (**b**)

Scheme 2.

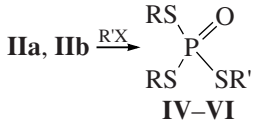
Tetrathiophosphates **IIIa** and **IIIb** were identified in the reaction mixture by ^{31}P NMR spectroscopy.

Under the conditions studied, conversion was 78–85% for phosphorus and 87–91% for thiols (the latter produce not only P–S and P=S bonds but also undergo oxidation to give dialkyl disulfides in 50–56% yields).

The structure of compounds **IIa** and **IIb** was confirmed by X-ray diffraction study, the data of elemental analysis, NMR and IR spectroscopy.

The crystal structure of salt **IIa** is formed by *S,S*-dibutyl trithiophosphate anion and K^+ ion (Fig. 1), occupying general positions in unit cell. The P–O distance in the anion is 1.473(7) Å, the length of P=S double bond is 1.931(4) Å, while the lengths of ordinary P–S bonds are 2.074(4)–2.094(4) Å. These data are comparable with the data for P–O and P=S bond distances (1.47–1.49 Å and 1.93–1.94 Å, respectively) and P–S bond distance (2.08–2.11 Å) in similar compounds [11]. At the same time, it should be noted that there are one of the shortest P–O and K–O bonds, the latter vary within 2.669(7)–2.732(7) Å [12] (the sum of ionic radii of K and O atoms is 2.69 Å [13]). The crystal structure involves short intermolecular C–H…S contacts between the anions, which unites them into chains (Fig. 2).

Previously unknown potassium trithiophosphates **IIa** and **IIb** are promising reagents for the targeted synthesis of organic compounds containing phosphorus and sulfur. For example, the salts are readily alkylated with organic halides to form *S,S,S*-trialkyl trithiophosphates **IV**–**VI** (Scheme 3).



R = C_4H_9, R' = CH_3 (**IV**); R' = CH_2=$CHCH_2$ (**V**);

R = C_7H_{15}, R' = CH_3 (**VI**); X = Br, I

Scheme 3.

The reaction leads to the quantitative rearrangement of thiophosphoryl fragment into phosphoryl (>P(=S)–O– ⟶ >P(=O)–S–).

Thus, we carried out for the first time the direct reaction of red phosphorus with alkanethiolate anions (generated in situ from alkanethiols and potassium hydroxide) to produce potassium *S,S*-dialkyl trithiophosphates, promising intermediates for organophosphorus synthesis. The found reaction is a fundamental complement to the up-to-date knowledge on the reactivity of P–P bond in the supramolecule of red phosphorus.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded on a Bruker 400DPX spectrometer (operating at 400.13 and 161.98 MHz, respectively) using hexamethyldisiloxane and

85% H_3PO_4 as internal and external reference, respectively. IR spectra were recorded on a Bruker ISF-25 spectrophotometer. Mass spectra with electronic ionization (70 eV) were obtained on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, detected mass range 34–450, capillary column, SPB-5 phase). X-ray diffraction study of crystals of **IIa** was performed at 123 K on a Bruker SMART APEX2 CCD diffractometer (MoK_α radiation). GLC analysis was carried out on a LKhM-8MD chromatograph (column 1.2 m × 3 mm), 1% of PEG 20000 on NaCl, column temperature 100°C, injector temperature 250°C, helium carrier gas, flow rate 2 L/h).

General procedure for the synthesis of salts IIa and IIb. A mixture of 2.38 g (36.6 mmol) of pulverized KOH · 0.5H_2O and 4.84 g (36.6 mmol) of $C_7H_{15}SH$ in 50 mL of DMSO was heated with stirring at 60°C until complete homogenization. Red phosphorus (0.71 g, 22.9 mmol) was added to the obtained potassium thiolate solution and the reaction mixture was stirred at 125–128°C for 4 h, evolution of PH_3 is observed (qualitative reaction with aqueous solution of $CuSO_4$). The reaction mixture was cooled and filtered, the precipitate was washed on filter with DMSO (10 mL), H_2O (10 mL), acetone (10 mL), ether (10 mL), dried in vacuum to give 0.16 g of red phosphorus (conversion is 78%). The filtrate was combined with DMSO and H_2O washings and analyzed by NMR and GLC. ^{31}P NMR spectrum showed signals at (δ, ppm) 3.4 (t, $^1J_{PH}$ = 464 Hz), 73.6, 98.1, and 118.5 in 70 : 26 : 3 : 1 ratio related to KH_2PO_2, $(C_7H_{15}S)_2P(S)OK$ (**IIb**), $(C_7H_{15}S)_3P(S)$ (**IIIb**), and $(C_7H_{15}S)_3P$ (**Ib**), respectively. According to GLC data, the filtrate contains also 0.45 g of Me_2S, 0.45 g of $C_7H_{15}SH$ (conversion is 91%), and 0.57 g (12%, hereinafter the yield is calculated with an allowance for the conversion of the thiol) of $C_7H_{15}SMe$ (as a result of the known reaction of thiols with KOH–DMSO system [15], identified by comparison with authentic sample by GLC and GC–MS). The filtrate was diluted with water (1 : 1), treated with 5% aqueous solution of hydrochloric acid to pH 4, extracted with ether (5 × 30 mL), the extract was washed with water (5 × 30 mL) and dried with K_2CO_3. The ether was distilled off at atmospheric pressure, $C_7H_{15}SH$ and $C_7H_{15}SMe$ were distilled in a vacuum. The residue was washed with hexane (5 × 5 mL) and dried in vacuum to give 0.63 g (15%) of potassium diheptyl trithiophosphate (**IIb**) as white crystals, mp 114–116°C. For $C_{14}H_{30}KOPS_3$ anal. calcd. (%): C, 44.17; H, 7.94; P, 8.14; S, 25.27. Found (%): C, 43.77; H, 7.65; P, 7.72; S, 24.79. ^{1}H NMR ($CDCl_3$, δ_P, ppm): 0.89 (t, 6H, Me, $^3J_{HH}$ = 6.72 Hz), 1.20–1.45 (m, 16H, CH_2), 1.68 (m, 4H, **C**$\mathbf{H}_2$$CH_2S$), 2.88 (m, 4H, CH_2S). ^{31}P NMR ($CDCl_3$, δ_P, ppm): 86.5. IR (KBr, ν, cm^{-1}): 635 (P=S). The hexane was distilled off, and the residue was dried in a vacuum to give 2.44 g (56%) of diheptyl disulfide.

Potassium *S,S*-dibutyl trithiophosphate (IIa) was obtained similarly to salt IIb. Yield 0.42 g (13%, butanethiol conversion is 87%), white crystals, mp 98–100°C. For $C_8H_{18}KOPS_3$ anal. calcd. (%): C, 32.41; H, 6.12; P, 10.45; S, 32.44. Found (%): C, 32.90; H, 5.94; P, 9.97; S, 32.47. ^{1}H NMR ($CDCl_3$, δ_P, ppm): 0.92 (t, 6H, Me, $^3J_{HH}$ = 7.29 Hz), 1.42 (m, 4H, **C**$\mathbf{H}_2$Me), 1.67 (m, 4H, CH_2CH_2S), 2.90 (m, 4H, CH_2S). ^{13}C NMR ($CDCl_3$, δ_P, ppm): 13.42 (Me), 21.85 (CH_2), 31.69 (d, CH_2, J_{CP} = 5.53), 35.24 (d, CH_2, J_{CP} = 2.58). ^{31}P NMR ($CDCl_3$, δ_P, ppm): 85.6. IR (KBr, ν, cm^{-1}): 645 (P=S). The conversion of red phosphorus was 85%, the yield of dibutyl disulfide was 50%. The main crystallographic and experimental data for **IIa**: $C_8H_{18}KOPS_3$, M = 296.47, orthorhombic, space group Iba_2, a = 16.772(4), b = 24.884(7), c = 6.872(2) Å, U = 2867.8(1) Å^3, Z = 8, D_{calcd} =1.37 g m^{-3}, μ = 0.890 mm^{-1}, $2\theta_{max}$ = 49.42°, 6618 total reflections, 2296 reflections measured, 127 refined parameters, R = 0.089 for 1422 reflections with $F_0 > 4\sigma(F_0)$.

General procedure for the synthesis of trithiophosphates IV–VI. A solution of organyl halide (CH_3I, CH_2=$CHCH_2Br$, 2.0 mmol) in 1 mL of tetrahydrofuran (THF) was added to a solution of potassium *S,S*-dialkyl trithiophosphate (1.0 mmol) in 4 mL of THF. The reaction mixture was stirred at ambient temperature for 1 h, the resulting precipitate was filtered off, the THF was removed from the filtrate at reduced pressure, and the residue was dried in vacuum.

***S,S*-Dibutyl *S*-methyl trithiophosphate (IV).** Yield 0.26 g (95%), yellow oil. For $C_9H_{21}OPS_3$ anal. calcd. (%): C, 39.68; H, 7.77; P, 11.37; S, 35.31. Found (%): C, 39.55; H, 7.40; P, 10.89; S, 34.97. ^{1}H NMR ($CDCl_3$, δ_P, ppm): 0.93 (t, 6H, Me, $^3J_{HH}$ = 7.29 Hz), 1.43 (m, 4H, **C**$\mathbf{H}_2$Me), 1.73 (m, 4H, **C**$\mathbf{H}_2$$CH_2S$), 2.41 (d, 3H, MeS, $^3J_{PH}$ = 15.87 Hz), 2.98 (m, 4H, CH_2S). ^{31}P NMR ($CDCl_3$, δ_P, ppm): 61.9. IR (KBr, ν, cm^{-1}): 1202 (P=O). MS (*m*/*z*): 272 $[M]^{+\bullet}$.

S-Allyl *S,S*-dibutyl trithiophosphate (V). Yield 0.29 g (97%), light yellow liquid. For $C_{11}H_{23}OPS_3$ anal. calcd. (%): C, 44.26; H, 7.77; P, 10.38; S, 32.23. Found (%): C, 44.45; H, 8.01; P, 10.78; S, 32.69. ^{1}H NMR ($CDCl_3$, δ_P, ppm): 0.93 (t, 6H, Me, $^3J_{HH}$ = 7.29 Hz), 1.44 (m, 4H, **C**$\mathbf{H}_2$Me), 1.73 (m, 4H, **C**$\mathbf{H}_2$$CH_2S$), 2.99 (m, 4H, CH_2**C**$\mathbf{H}_2$S), 3.62 (m, 2H, CH_2=CH**C**$\mathbf{H}_2$S), 5.17 (d, 1H, H_{cis}, =CH_2, $^3J_{HH}$ = 9.86 Hz), 5.29 (d, 1H, H_{trans}, =CH_2, $^3J_{HH}$ = 16.77 Hz), 5.94 (m, 1H, =CH). ^{31}P NMR ($CDCl_3$, δ_P, ppm): 64.9. IR (film, ν, cm^{-1}): 1201 (P=O).

***S,S*-Diheptyl S-methyl trithiophosphate (VI).** Yield 0.22 g (62%), yellow oil. For $C_{15}H_{33}OPS_3$ anal. calcd. (%): C, 50.52; H, 9.33; P, 8.69; S, 26.98. Found (%): C, 45.01; H, 7.93; P, 6.31; S, 30.76. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 (t, 6H, Me, $^3J_{HH}$ = 6.68 Hz),

1.20–1.44 (m, 16H, CH_2), 1.74 (m, 4H, $\mathbf{CH}_2CH_2S$), 2.42 (d, 3H, MeS, $^3J_{PH}$ = 15.96 Hz), 2.97 (m, 4H, CH_2S). ^{31}P NMR ($CDCl_3$, δ_P, ppm): 66.6. IR (film, ν, cm^{-1}): 1204 (P=O). MS (*m*/*z*): 356 $[M]^{+\bullet}$.

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