ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 7, pp. 1466–1468. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © I.S. Nizamov, G.T. Gabdullina, L.A. Al'metkina, I.D. Nizamov, R.A. Cherkasov, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 7, pp. 1228–1230.

LETTERS TO THE EDITOR

O,O'-Ethylenedioxydiethylene bis[*S*-(triphenylplumbyl) (3,5-di-*tert*-butyl-4-hydroxyphenyl)phosphonodithioate]

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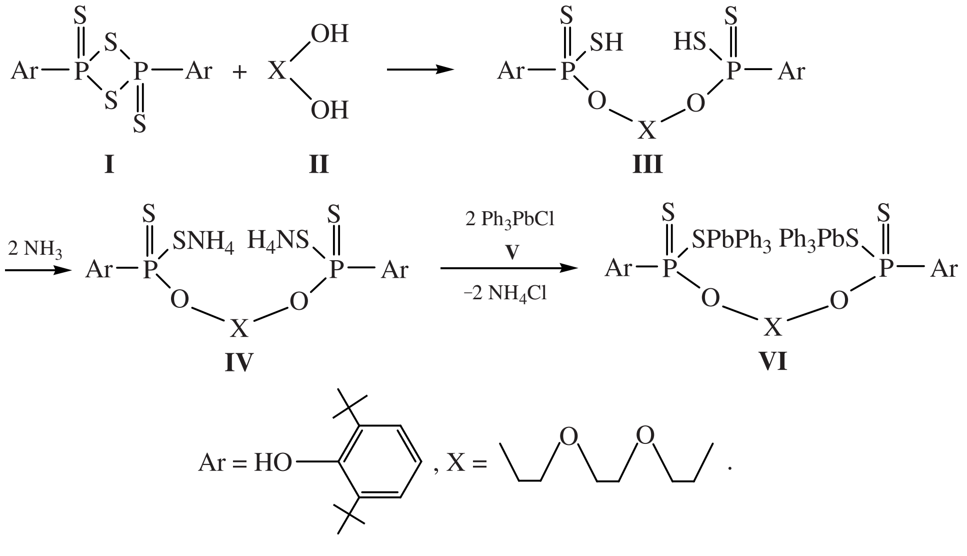
Received November 27, 2007

DOI: 10.1134/S1070363208070347

Sulfur-containing derivatives of four-coordinate phosphorus thio acids with a PS_2E structural fragment (E is a main subgroup element) are of great practical interest as additives to lubricant oils, regulators of rubber vulcanization, extractants, complex-forming agents, pesticides, etc. They are of interest for solving basic problems of organoelement chemistry, such as mutual influence of atoms in a heteroatomic group on an example of PS_2E system, electronic and steric structure, and stereochemistry. Earlier we synthesized highly biologically active oligomeric and monomeric *S*-trialkylplumbyl phosphorodithioates by the protodeplumbation of tetraalkylplumbanes with phosphorodithioic acids [1, 2].

In the present work we describe the synthesis of diplumbyl derivatives of bis(arylphosphonodithioic acids). Among them, bis(phosphonodithioic acids) with two terminal phosphorodithioyl groups are interesting ligands [3–6]. The first examples of stable bis(phosphonothioic acids) with methyl groups at the phosphorus atom have been synthesized by one of us by the reaction of 2,4-dimethyl-1,3,2λ^5,4λ^5-dithiadiphosphetane 2,4-disulfide with glycols at a 1:1 ratio in an Et_2O suspension at ~20° C [3]. At the same time, the corresponding bis(arylphosphonodithioic acids) could not be obtained pure by the reaction of 1,3,2λ^5,4λ^5-dithiaphosphetane 2,4-disulfides with aryl substituents at the phosphorus atom with glycols in acetonitrile at 70–80°C [4, 5]. From the reaction mixtures, dioxaphosphorinane sulfides, cyclic trithiopyrophosphonates, and thioacetamide have been isolated [4, 5]. These compounds, in our opinion, are by-products formed by the reaction of acetonitrile with bis (arylphosphonodithioic acid) as a primary product, since, as shown earlier, bis(methylphosphonodithioic acids) react with acetonitrile to give cyclic trithiopyrophosphonates and thioacetamide [6]. We found that the most convenient inert solvent for the reaction of 2,4-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,2λ^5,4λ^5-dithiadiphosphetane 2,4-disulfide (**I**) with triethylene glycol (**II**) is absolute benzene, that allowed us to obtain acid **III** at 50º within 1.5 h. Acid **III** was converted into the corresponding diammonium salt **IV** whose reaction with triphenylplumbane (**V**) gave ester **VI** as crystals.

***O,O'*-Ethylenedioxydiethylene bis[*S*-hydrogen (3,5-di-*tert*-butyl-4-hydroxyphenyl)phosphonodithioate] (III).** A mixture of 5.0 g of dithiadiphosphetane disulfide **I** and 1.2 g of glycol **II** in 15 ml of absolute benzene was heated for 1.5 h at 50°C with stirring and then cooled and filtered. The filtrate was evaporated for 1 h under a vacuum of 0.5 mm Hg at 40°C and 1 h under a vacuum of 0.06 mm Hg at 40°C to obtain 4.8 g (77%) of acid **III**. IR spectrum (film), ν, cm^{-1}: 3619 s [ν(O–H)]; 2958 s, 2873 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$]; 2478 m.br [ν(S–H)]; 1582 m, 1480 m [ν(C=C), Ar]; 1429 vs [$\delta_{as}(CH_3)$], 1036 vs.br [ν(P)O–C]; 957 s.br [ν(OC–C)]; 656 vs [ν(P=S)]; 504 m [ν(P–S)]. ^1H NMR spectrum, δ , ppm: 1.48 s [36H, $(CH_3)_3C$]; 2.37 m and 2.64 m (2H, S–H); 3.72 s (4H, $COCH_2CH_2OC$); 3.84 t (4H, $POCH_2CH_2O$, $^3J_{HH}$ 4.7); 4.39 d.t (4H, $POCH_2CH_2O$, $^3J_{HH}$ 4.7, $^3J_{PH}$ 10.0); 5.69



m (2H, O–H); 7.82 d (2H, C_6H_2P, $^3J_{PH}$ 16.2). ^{31}P NMR spectrum: δ_P 88.9 ppm. Found, %: C 54.18; H 7.63; P 8.06; S 17.11. $C_{34}H_{56}O_6P_2S_2$. Calculated, %: C 54.37; H 7.52; P 8.25; S 17.08.

***O,O'*-Ethylenedioxydiethylene bis[*S*-ammonium - (3,5-di-*tert*-butyl-4-hydroxyphenyl)phosphonodithioate] (IV).** Dry ammonia was bubbled for 1 h through solution of 1.2 g of acid **III** in 20 ml of benzene at ~20°C at stirring. Solution was then evaporated under vacuum (10 mm Hg) to a half of initial volume. The obtained precipitate was filtered and dried for 1 h under vacuum (0.02 mm Hg). It was separated 6.6 g (88%) of salt **IV**. mp 202–203°C. IR spectrum (vaseline oil), ν, cm^{-1}: 3634 s [ν(O–H)]; 3230 vs.v.br [ν(N^+H_4)]; 1581 m, 1459 s [ν(C=C, Ar)]; 1427 vs [$\delta_{as,s}$(CH_3)]; 1068 s, 1044 s [ν(P)O–C]; 949 s [ν(OC–C)]; 683 vs [ν(P=S)]; 507 m [ν(P–S)]. ^{1}H NMR spectrum, δ , ppm: 1.47 s [36H, $(CH_3)_3C$]; 3.59 t (4H, $POCH_2CH_2O$, $^3J_{HH}$ 4.1); 3.65 s (2H, $COCH_2CH_2OC$); 3.82 m (4H, $POCH_2CH_2$, $^3J_{HH}$ 4.4); 5.43 s and 5.45 s (8H, N^+H_4; 2H, OH); 7.94 d (2H, C_6H_2P, $^3J_{PH}$ 15.1); 7.96 d (2H, C_6H_2P, $^3J_{PH}$ 15.4). ^{31}P NMR spectrum: δ_P 109.7 ppm. Mass spectrum, *m/z* (I_{rel}, %): 780.6 (1). Found, %: C 52.68; H 7.38; N 3.30; P 8.04; S 16.35. $C_{34}H_{58}N_2O_6P_2S_4$. Calculated, %: C 52.28; H 7.48; N 3.57; P 7.93; S 16.42. *M* 780.4.

***O,O'*-Ethylenedioxydiethylene bis[*S*-(triphenylplumbyl) (3,5-di-*tert*-butyl-4-hydroxyphenyl)phosphonodithioate] (VI).** Plumbane **V**, 2.4 g, was added in portions to a suspension of 2.0 g of salt **IV** in 50 ml of benzene under dry argon. The mixture was heated for 2 h at 80°C under stirring, cooled, and filtered. The filtrate was evaporated for 1 h under a vacuum of 0.5 mm Hg at 40°C and for 1 h under a vacuum of 0.02 mm Hg at 40°C. The residue solidified on standing to give 3.0 g (72%) of compound **VI**, mp 64–65°C. IR spectrum (vaseline oil), ν, cm^{-1}: 3622 s [ν(O–H)]; 3088 w, 3061 w, 3036 w [ν(=C–H, Ar)]; 2958 vs, 2873 s [$\nu_{as,s}$(CH_3), $\nu_{as,s}$(CH_2)]; 1570 s, 1476 s [ν(C=C, Ar)]; 1430 vs [δ_{as}(CH_3)]; 1036 vs.br [ν(P)O–C]; 951 s.br [ν(OC–C)]; 692 m, 680 m [ν(P=S)]; 558 m, 508 m [ν(P–S)]; 442 s [ν(Pb–C), ν_{as}($PbPh_3$)]. ^{1}H NMR spectrum, δ , ppm: 1.49 s [36H, $(CH_3)_3C$]; 3.64 m (4H, $POCH_2CH_2O$); 4.07 m (4H, $POCH_2CH_2O$, $^3J_{HH}$ 4.5); 5.61 m (2H, O–H); 7.55 m, 7.73 m, and 7.86 m [30H, $(C_6H_5)_3Pb$]; 7.86 d [4H, C_6H_2P, $^3J_{PH}$ 20.4]. ^{31}P NMR spectrum: δ_P 98.7 ppm. Found, %: C 51.94; H 5.50; P 3.50; Pb 25.01; S 8.12. $C_{70}H_{84}O_6P_2Pb_2S_4$. Calculated, %: C 51.49; H 5.21; P 3.81; Pb 25.49; S 7.89.

The IR spectra were recorded on a Bruker Vector 22 FT–IR instrument (КBr). The ^{1}H NMR spectra were obtained on an Avance-600 spectrometer (600 MHz) in $CDCl_3$. The ^{31}P spectra were measured on a Bruker CXP-100 instrument (36.5 MHz) in C_6D_6 against external 85% H_3PO_4. The electron impact mass spectra were measured on a Finnigan MAT-212 instrument.

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