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LETTERS TO THE EDITOR

Disproportionation of Diethylarsanyl *N*,*N*-Diethyl(3,5-di-*tert*-butyl-4-hydroxyphenyl)-phosphonamidodithioate

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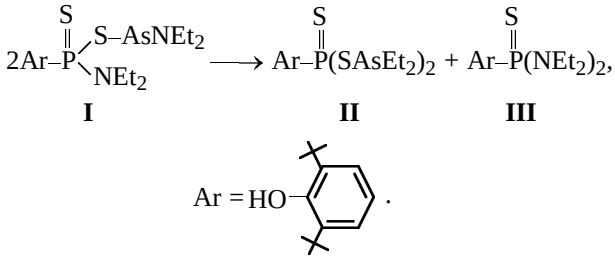
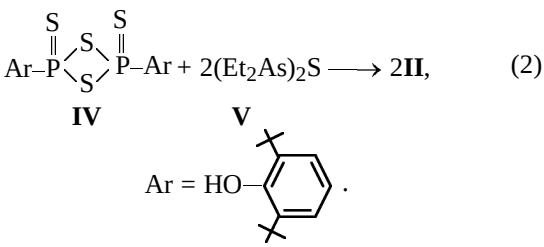
S-Organoelement derivatives of four-coordinate phosphorus thioacids containing a P(S)SE fragment (E = P, As) often exhibit low thermal stability. In particular, diorganylphosphanyl *N*,*N*-dialkylarylphosphonamidodithioates with the R_2N–P(S)S–P< fragment, regarded as the products of insertion of monomeric fragments of 2,4-diaryl-1,3,2,4-dithiadiphosphetane 2,4-disulfides into the N–P bond of aminophosphines, transform under heating to the sulfides of the starting aminophosphines and the products of condensation of arylmetadithiophosphonates [1]. We have previously prepared diorganylarsanyl *N*,*N*-dialkylarylphosphonamidodithioates containing an R_2N–P(S)S–As< fragment by the reactions of 2,4-diaryl-1,3,2,4-dithiadiphosphetane 2,4-disulfides with aminoarsines [2]. We found that, contrary to the compounds with the R_2N–P(S)SP< fragment, diethylarsanyl *N*,*N*-diethyl(3,5-di-*tert*-butyl-4-hydroxyphenyl)phosphonamidodithioate **I** disproportionates at 70°C within 1 h to form crystalline bis(diethylarsanyl) 3,5-di-*tert*-butyl-4-hydroxyphenylphosphonotrithioate **II**. The second reaction product, *N*,*N*,*N*',*N*'-tetraethyl-3,5-di-*tert*-butyl-4-hydroxyphenylphosphonothiodiamide **III**, could not be isolated because of its lability [reaction (1)].



(1)

The structure of **II** was comfirmed by an independent synthesis from 2,4-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **IV** and bis(diethylarsanyl) sulfide **V** at ~20°C for 1 h [reaction (2)].



(2)

The physicochemical constants and spectral characteristics of samples of **II** prepared by these two

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methods are identical. The molecular structure of **II** was determined by single crystal X-ray diffraction. Each arsenic atom in **II** is bound with only one sulfur atom. Dimeric associates are absent. Complete results of the X-ray diffraction analysis will be reported later.

Bis(diethylarsanyl)3,5-di-*tert*-butyl-4-hydroxyphenylphosphonotrithioate II. *a*. Diethylarsanyl *N*,*N*-diethyl(3,5-di-*tert*-butyl-4-hydroxyphenyl)phosphonamidodithioate **I** prepared from 4.1 g of dithiaphosphetane disulfide **IV** and 2.8 g of diethyl(diethylamino)arsine in 10 ml of anhydrous benzene at ~20°C similarly to the procedure from [2] was heated for 1 h at 70°C. The resulting mixture was filtered, and the filtrate was evaporated for 2 h in a vacuum (0.02 mm) to obtain 1.3 g (31%) of **II**, mp 126–127°C. IR spectrum, ν, cm^{-1}: 3550 m.br [ν(OH)], 1580 m [ν(C=C) Ar], 1428 s [ν(Ph)], 1300 m [β(=CH), ν(Ph)], 1260 m [ω, $\tau(CH_2)_2$], 1140 m [$\rho(CH_3)$], 1110 s [ν(PAr)], 1045 w, 1025 w [ν(AsC)], 665 m.br [ν(P=S)], 615 m [δ(Ph)], 594 m, 520 m, 494 m [ν(PS), $\nu(AsC_2)$]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.44 m [18H, $(CH_3)_3C$], 1.49 t {12H, $[(CH_3CH_2)_2AsS]_2P$, $^3J_{HH}$ 7.7}, 2.58 q {8H, $[(CH_3CH_2)_2AsS]_2P$, $^3J_{HH}$ 7.7}, 7.60 m (1H, OH), 7.90 d (2H, 2,6-C_6H_2, $^3J_{PH}$ 16.0). ^{31}P NMR spectrum, δ_P, ppm: 76.7. Found, %: C 44.19; H 6.71; As 24.86; P 4.84; S 15.83. $C_{22}H_{41}As_2OPS_2$. Calculated, %: C 44.14; H 6.92; As 25.05; P 5.18; S 16.03.

b. To a solution of 1.9 g of diarsanyl sulfide **V** in 10 ml of anhydrous benzene, 1.9 g of dithiaphosphetane disulfide **V** was added in portions at ~20°C with stirring under dry argon. The mixture was stirred for 1 h at 20°C, and the resulting solution was allowed to stand for a week at ~20°C. The precipitate thus formed was filtered off and washed with benzene. After recrystallization from benzene, 0.5 g (13%) of **II** was obtained, mp 125–126°C.

The IR spectra were recorded on a UR-20 spectrometer (mulls in mineral oil, KBr). The ^{1}H NMR spectra were obtained on a Bruker MSL-400 spectrometer (400 MHz) in C_6D_6 against internal TMS. The ^{31}P NMR spectra were measured on a Bruker CPX-100 spectrometer (36.5 MHz, C_6H_6) against external 85% H_3PO_4.

X-ray diffraction studies were carried out on an Enraf–Nonius CAD-4 four-circle diffractometer (λMoK_α 0.71073 Å). The crystals of **II** are monoclinic, unit cell parameters at –150°C: *a* 12.070(8), *b* 12.58(2), *c* 12.93(1)Å, β 103.89°, *V* 2815 $Å^3$, *Z* 4, space group $P2_1/n$. The structure was solved by the direct method using the SIR program [3] and MoLEN program package [4].

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