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LETTERS TO THE EDITOR

Reaction of 2,4-Diaryl-1,3-dithia-2,4-diphosphetane-2,4-disulfides with Resorcinol

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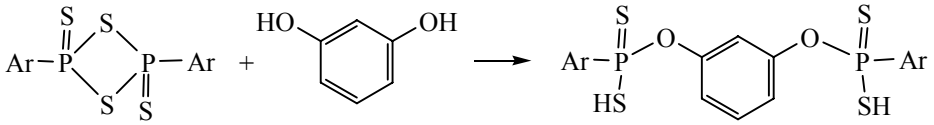
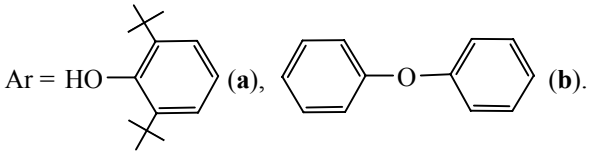
Bisdithiophosphonic acids containing two α,ω-dithiophosphoryl groups [1, 2] are of interest as the podand-like compounds in substitution, intercalation, addition, and complexation reactions to create on their basis antioxidants for polymers, antioxidant additives for lubricating oils, corrosion inhibitors, extractants of metal ions, etc. [3–9]. The reactions of 2,4-dialkyl- or diaryl-1,3-dithia-2,4-diphosphetane-2,4-disulfides with glycols are used to obtain bisdithiophosphonic acids [1–8]. At the same time the reaction of catechol with 2,4-diferrocenyl-1,3-dithia-2,4-diphosphetane-2,4-disulfide results in 1,3,2-dioxaphospholane derivative [10], which is a secondary product formed during the desulfurization of the intermediate phenylene bisdithiophosphonic acid. In contrast, resorcinol **II** was found to react with 2,4-diaryl-1,3-dithia-2,4-diphosphetane-2,4-disulfides **Ia** and **Ib** in benzene at 20°C for 10 days (**Ia**) or at 60°C for 2 h (**Ib**) to give *O*,*O*'-(benzene-1,3-diyl) bis(aryldithiophosphonic) acids (**IIIa**, **IIIb**) as solids. The ^{31}P NMR spectra of acids **IIIa** and **IIIb** contain one characteristic signal [11] at 88.1 and 87.9 ppm, respectively.



Ia, Ib **II** **IIIa, IIIb**



(**a**), (**b**).

***O*,*O*'-(Benzene-1,3-diyl) bis(3,5-di-*tert*-butyl-4-hydroxyphenyldithiophosphonate) (IIIa).** To a suspension of 0.6 g of phosphetane **Ia** in 15 ml of anhydrous benzene under an argon atmosphere at 20°C was added by portions 0.11 g of resorcinol **II**. The mixture was stirred at 20°C for 8 h, then filtered and evaporated at 40°C within 1 h at 0.5 Hg mm and for 1 h at 0.02 Hg mm. Yield 0.6 g (85%), mp 80–81°C. IR spectrum, ν, cm^{-1}: 3618 m (H–O), 3085 w (⋯C–H, Ar), 2959 s, 2913 s, 2872 m [$\nu_{as,s}(CH_3)$], 2538 w.br (S–H), 2437 w.br (S–H), 1594 m, 1478 s (C⋯C, Ar), 1429 v.s [$\delta_{as}(CH_3)$], 1364 m [$\delta_s(CH_3)$], 1111 s, 1119 v.s [(P)O–C], 973 s (O–C), 660 m (P=S), 595 m (P–S). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 s and 1.50 s [36H, $(CH_3)_3C$], 2.59 m (2H, PSH), 5.03 m (2H, HO), 6.42 t (1H, 2-C_6HO_2P, $^4J_{HP}$ 2.2), 6.69 t (1H, 5-C_6HO_2P, $^3J_{HH}$ 8.3), 7.07 d and 7.13 d (2H, 4,6-C_6HO_2P, $^3J_{HH}$ 8.3), 7.83 d and 7.92 d (4H, 2,6-C_6H_2P, $^3J_{PH}$ 15.9). Mass

spectrum (EI), *m*/*z* (I_{rel}, %): 711 (5) $[M]^+$. Found, %: C 57.32; H 6.44; P 8.63; S 16.43. $C_{34}H_{48}O_4P_2S_4$. Calculated, %: C 57.44; H 6.81; P 8.71; S 16.04. M 711.0.

***O*,*O*'-(Benzene-1,3-diyl) bis(4-phenoxyphenyldithiophosphonate) (IIIb)** was prepared similarly from 1.0 g of phosphetane **Ib** and 0.21 g of resorcinol **II**. Yield 0.8 g (67%), mp 46–48°C. IR spectrum, ν, cm^{-1}: 3064 w, 3030 w (⋯C–H, Ar), 2352 w.br (S–H), 1584 v.s, 1488 v.s (C⋯C, Ar), 1122 s [(P)O–C], 930 v.s.br (O–C), 695 s (P=S), 520 m (P–S). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19 m (2H, PSH), 6.94 two d (4H, 3,5-C_6H_2O, $^3J_{HH}$ 7.4), 7.02 two d (4H, 3,5-C_6H_2P, $^3J_{HH}$ 7.9), 7.18 two d (2H, 4-C_6HO, $^3J_{HH}$ 7.4), 7.34 d.d (4H, 2,6-C_6H_2O, $^3J_{HH}$ 7.4), 7.83 d. d (4H, 2,6-C_6H_2P, $^3J_{HH}$ 7.9, $^3J_{PH}$ 13.4). Mass spectrum (MALDI TOF), *m*/*z*: 638 $[M]^+$. Found, %: C 56.20; H 3.91; P 9.40; S 20.46. $C_{30}H_{24}O_4P_2S_4$. Calculated, %: C 56.41; H 3.79; P 9.70; S 20.08. *M* 638.7.

The IR spectra were recorded on a Bruker Vector 22 IR Fourier-spectrometer (KBr pellets or mulls in mineral oil). The ^{1}H NMR spectra were registered on a Bruker Avance-600 (600 MHz) spectrometer in $CDCl_3$; the ^{31}P NMR spectra, on a Bruker CXP-100 (36.5 MHz) spectrometer in benzene relative to external 85% H_3PO_4. The mass spectra (EI) were measured on a DFS Thermo Electron Corporation (70 eV). The MALDI TOF mass spectra were obtained on an Ultrafex Bruker (UV, 337 nm, matrix 1,8,9-trihydroxyanthracene).

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