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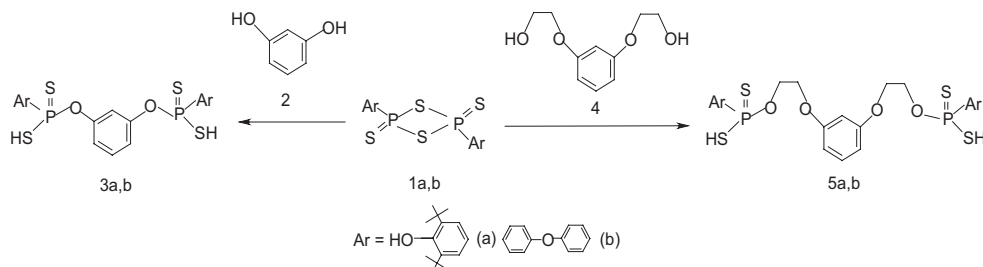
Reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with resorcinol and 1,3-bis(2-hydroxyethoxy)benzene

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Novel bisaryldithiophosphonic acids were obtained by the reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with resorcinol and 1,3-bis(2-hydroxyethoxy)benzene.



Keywords: 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides; resorcinol; 1,3-bis(2-hydroxyethoxy)benzene; bisaryldithiophosphonic acids

1. Introduction

Tetracoordinated organophosphorus thioacids, as well as their esters and salts, have a wide range of applications as lubricant additives, antioxidants, extractives, complexing agents, pesticides, etc. (1, 2). Bisdithiophosphonic acids are new types of tetracoordinated phosphorus thioacids bearing two dithiophosphoryl groups. 2,4-Dimethyl 1,3,2,4-dithiadiphosphetane-2,4-disulfide has been reported to react with alkylene glycols in 1:1 molar ratio in diethyl ether suspension at room temperature to give bisalkyldithiophosphonic acids (3). We have previously prepared bisaryldithiophosphonic acids in the reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-

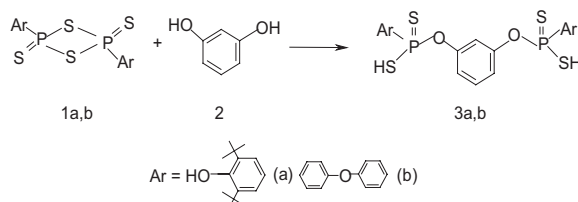
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2,4-disulfides with alkylene glycols such as 1,4-butandiol and triethylene glycol (4–7). We now extend this approach to hydroxyphenols such as resorcinol and 1,3-bis(2-hydroxyethoxy) benzene.

2. Results and discussion

The reaction of Lawesson-like reagents with compounds containing a pair of hydroxyl groups has been described (8). Lawesson's reagent has been reported to react with catechol to form 2-(4-methoxyphenyl)-1,3,2 λ^5 -benzodioxaphosphole-2-thione, whereas with ethane-1,2-diols and 4,5-dihydro-1,3,2 λ^5 -dioxaphosphole-2-thione together with 2,4-bis(4-methoxyphenyl)-6,7-dihydro-1,5,3,2 λ^5 ,4 λ^5 -dioxathiadiphosphepine-2,4-dithione are obtained (8). The reaction of 2,4-diferrocenyl 1,3,2,4-dithiadiphosphetane-2,4-disulfide with catechol or 3,5-di-*tert*-butylcatechol occurs in boiling toluene, resulting in the formation of 1,3,2 λ^5 -dioxaphosphole-2-thione derivatives (9). Thus, no bisaryldithiophosphonic acids were obtained in pure form in the reactions with catechols. Compounds isolated in previous studies (8, 9) seem to be secondary products. We have proposed that these reactions proceed via the intermediate formation of thermally unstable initial products containing the S P–O–X–O–P S fragment (where X = alkylene, arylene), which then decompose leading to the final products. To avoid the formation of secondary products, we have determined the optimal conditions for the formation of bisaryldithiophosphonic acids in the reactions with hydroxyphenols. We have chosen resorcinol as a homolog of catechol as a substrate for thiophosphorylation. It should be noted that the chemical behavior of resorcinol and 1,3,2,4-dithiadiphosphetane-2,4-disulfides has not been reported. The reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides **1a** and **b** with resorcinol **2** in benzene at room temperature over 10 days (for **1a**) or at 60 °C over 2 h (for **1b**) have brought about the formation of O,O'-(benzene-1,3-diyl)-1,3-bis(aryldithiophosphonic) acids **3a** and **b** (Scheme 1).

To avoid the formation of oligomers, we have carried out these reactions (Scheme 1) under large dilutions. Compounds **3a** and **b** are white crystalline solids. While bands of strong intensity for the hydroxyl groups in the region ν 3380 cm^{-1} in the IR spectra of **3a** and **b** are absent, they reveal the characteristic bands for S–H bonds ν 2538–2352 cm^{-1} . However, hydroxyl groups of the aryl substituent remained attached to **3a** and revealed a sharp band of medium intensity at ν 3618 cm^{-1} . The ^{31}P NMR spectra of **3a** and **b** in benzene solutions show singlets in the range of $\delta_{\text{P}} = 88.1$ and 87.9 ppm, respectively. These signals are typical for dithiophosphonic acids (10). In spite of **3a** and **b** containing two stereogenic centers at the phosphorus atoms, we observed only one singlet in their experimental ^{31}P NMR spectra. This phenomenon might be explained by a prototropic rearrangement in the S P–S heteroatom triad. Alternatively, the two chiral phosphorus atoms are perhaps too far apart and the ^{31}P peaks for the two diastereomers are accidentally equivalent. The ^1H NMR spectrum of **3a** in CDCl_3 solution exhibits two high-intensity singlets at $\delta = 1.47$ and 1.50 ppm for the methyl protons of the 3,5-di-*tert*-butyl-4-hydroxyphenyl groups $[(\text{CH}_3)_3\text{C}, \text{Ar}]$ in the ratio of $\sim 1 : 1$, indicating the formation of **3a** as a mixture of diastereoisomers. A mass peak at m/e 711 in the electron impact (EI) mass spectrum of **3a** is due to its molecular ion $[\text{M}]^+$ (calculated molecular mass M of **3a** is 711.0). A mass peak at m/e 639 observed in the MALDI



Scheme 1. The reaction of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with resorcinol.

Avance-600 spectrometer (600 MHz) in CDCl_3 . The ^{31}P NMR spectra were recorded with a Bruker Avance-400 (161.9 MHz) instrument in C_6H_6 with 85% H_3PO_4 as an external reference. Mass spectra (EI, 70 eV) were determined on a DFS Thermo Electron Corporation chromatomass-spectrometer (sample directly introduced). Mass spectra MALDI TOF were run on an Ultraflex Bruker (UV laser, 337 nm).

4.1. *O,O'-(Benzene-1,3-diyl)-1,3-bis(3,5-di-tert-butyl-4-hydroxyphenyldithiophosphonic) acid 3a*

Resorcinol **2** (0.11 g, 1.0 mmol) was added portionwise under dry argon under stirring at 20°C to the suspension of 0.6 g (1.0 mmol) of dithiadiphosphetane **1a** in 15 ml of anhydrous benzene, and stirring was continued for 8 h. The mixture was filtered and the filtrate was evaporated at reduced pressure (0.5 mm Hg) at 40°C for 1 h and then in vacuum (0.02 mm Hg) to give the residue that was solidified when stored. The yield of **3a** was 0.6 g (85%), mp $80\text{--}81^\circ\text{C}$. Anal. found: C, 57.32; H, 6.44; P, 8.63; S, 16.23. $\text{C}_{34}\text{H}_{48}\text{O}_4\text{P}_2\text{S}_4$ requires C, 57.44; H, 6.81; P, 8.71; S, 16.04%. IR (KBr pellet, ν_{max} , cm^{-1}): 3618 (H–O, Ar), 3085 (–C–H, Ar), 2959, 2913, 2913, 2872 (CH_3), 2538 (S–H, free), 2437 (S–H, bonded), 1594, 1478 (C–C, Ar), 1429 (CH_3), 1364 (CH_3), 1111, 1119 [(P)O–C], 973 (O–C), 660 (P S), 595 (P–S). ^1H NMR: δ_{H} 1.47 and 1.50 [two s, 36H, (CH_3)₃C, Ar], 2.59 (m, 2H, PSH), 5.03 (m, 2H, HO–Ar), 6.41 and 6.43 (two d, 1H, 2- $\text{C}_6\text{HO}_2\text{P}$, $^4J_{\text{HH}} = 2.2$ Hz), 6.67 and 6.71 (two d, 1H, 5- $\text{C}_6\text{HO}_2\text{P}$, $^3J_{\text{HH}} = 8.3$ Hz), 7.07 and 7.13 (two d, 2H, 4,6- $\text{C}_6\text{HO}_2\text{P}$, $^3J_{\text{HH}} = 8.3$ Hz), 7.83 and 7.92 (two d, 4H, 2,6- $\text{C}_6\text{H}_2\text{P}$, $^3J_{\text{PH}} = 15.9$ Hz). MS (EI) m/e (I_{rel}): 711 [M^+] (5). ^{31}P NMR, δ_{P} : 88.1.

4.2. *O,O'-(Benzene-1,3-diyl)-1,3-bis(4-phenoxyphenyldithiophosphonic) acid 3b*

Product **3b** (0.8 g, 67%) was obtained similarly from 1.0 g (1.9 mmol) of dithiadiphosphetane **1b** and (0.21 g, 1.9 mmol) resorcinol **2**, mp $46\text{--}48^\circ\text{C}$. Anal. found: C, 56.20; H, 3.91; P, 9.40; S, 20.46. $\text{C}_{30}\text{H}_{24}\text{O}_4\text{P}_2\text{S}_4$ requires C, 56.41; H, 3.79; P, 9.70; S, 20.08. IR (ν_{max} , cm^{-1}): 3064, 3030 (–C–H, Ar), 2352 (S–H), 1584, 1488 (C–C, Ar), 1122 [(P)O–C], 930 (O–C), 695 (P S), 520 (P–S). ^1H NMR: δ_{H} 1.19 (m, 2H, PSH), 6.94 (two d, 4H, 3,5- $\text{C}_6\text{H}_2\text{O}$, $^3J_{\text{HH}} = 7.4$ Hz), 7.02 (two d, 4H, 3,5- $\text{C}_6\text{H}_2\text{P}$, $^3J_{\text{HH}} = 7.9$ Hz), 7.18 (two d, 2H, 4- C_6HO , $^3J_{\text{HH}} = 7.4$ Hz and $^3J_{\text{HH}} = 7.4$ Hz), 7.34 (dd, 4H, 2,6- $\text{C}_6\text{H}_2\text{O}$, $^3J_{\text{HH}} = 7.4$ Hz), 7.83 (dd, 4H, 2,6- $\text{C}_6\text{H}_2\text{P}$, $^3J_{\text{HH}} = 7.9$ and $^3J_{\text{PH}} = 13.4$ Hz). MS (MALDI TOF, matrix – 1,8,9-trihydroxyanthracene) m/e : 639 [$\text{M} + \text{H}^+$]. ^{31}P NMR, δ_{P} : 87.9.

4.3. *O,O'-(Benzene-1,3-bis[ethoxy-2-(3,5-di-tert-butyl-4-hydroxyphenyldithiophosphonic)] acid 5a*

Product **5a** (0.8 g, 91%) was obtained similarly from 0.66 g (1.1 mmol) of dithiadiphosphetane **1a** and **4** (0.22 g, 1.1 mmol), mp $63\text{--}64^\circ\text{C}$. Anal. Found: C, 57.10; H, 7.49; P, 7.42; S, 15.88. $\text{C}_{38}\text{H}_{56}\text{O}_6\text{P}_2\text{S}_4$ requires C, 57.12; H, 7.06; P, 7.75; S, 16.05. IR (KBr pellet, ν_{max} , cm^{-1}): 3619 (H–O, Ar), 3009 (–C–H, AR), 2959, 2912, 2871 (CH_3 , CH_2), 2364, 2350 (S–H), 1590, 1492 (C–C, AR), 1430 (CH_3), 1364 (CH_3), 1043 [(P)O–C], 956 (O–C), 656 (P S), 507 (P–S). ^1H NMR, δ_{H} : 1.46 [s, 36H, (CH_3)₃C, Ar], 3.00 (m, 2H, PSH), 4.27 (t, 4H, $\text{OCH}_2\text{CH}_2\text{OP}$, $^3J_{\text{HH}} = 5.2$ Hz); 4.57 (dt, 4H, $\text{OCH}_2\text{CH}_2\text{OP}$, $^3J_{\text{HH}} = 5.2$ and $^3J_{\text{PH}} = 14.3$ Hz); 5.65 (m, 2H, HO–Ar), 6.53 (m, 3H, 4,5,6- $\text{C}_6\text{H}_3\text{O}_2$), 7.18 (m, 1H, 2- C_6HO_2), 7.83 (d, 4H, 2,6- $\text{C}_6\text{H}_2\text{P}$, $^3J_{\text{PH}} = 16.4$ Hz). MS (MALDI TOF, matrix – 1,8,9-trihydroxyanthracene) m/e : 821.8 [$\text{M} + \text{Na}^+$], 782 [$\text{M} - \text{HO}^+$], 767.8 [$\text{M} - \text{S}^+$], 750 [$\text{M} - \text{S} - \text{HO}^+$]. ^{31}P NMR, δ_{P} : 89.0.

4.4. *O,O'*-Benzene-1,3-bis[ethoxy-2-(4-phenoxyphenyldithiophosphonic)] acid **5b**

Product **5b** (1.0 g, 91%) was obtained similarly from 1.0 g (1.5 mmol) of dithiadiphosphetane **1b** and **4** (0.3 g, 1.5 mmol) as a paste. Anal. found: C, 56.36; H, 4.58; P, 8.64; S, 17.35. $C_{36}H_{32}O_6P_2S_4$ requires C, 56.18; H, 4.44; P, 8.52; S, 17.65. IR (liquid film, ν_{\max} , cm^{-1}): 3066, 3036 (–C–H, Ar), 2941, 2815 (CH₂), 2528 (S–H, free), 2443 (S–H, bonded), 1585, 1490 (C–C, Ar); 1041 [(P)O–C], 957 (O–C), 686 (P S), 530 (P–S). ¹H NMR, δ_H : 3.00 (m, 2H, PSH); 4.27 (t, 4H, OCH₂CH₂OP, ³*J*_{HH} = 4.6 Hz); 4.58 (dt, 4H, OCH₂CH₂OP, ³*J*_{HH} = 4.6 and ³*J*_{PH} = 15.2 Hz), 7.04 (m, 4H, 3,5-C₆H₂O; 4H, 3,5-C₆H₂P), 7.21 (two d, 2H, 4-C₆HO, ³*J*_{HH} = 7.4 Hz), 7.40 (dd, 4H, 2,6-C₆H₂O, ³*J*_{HH} = 7.8 Hz), 7.98 (dd, 4H, 2,6-C₆H₂P, ³*J*_{HH} = 8.3 and ³*J*_{PH} = 14.8 Hz). MS (EI) *m/e* (*I*_{rel}): 727 [M]⁺ (5). MS (MALDI TOF, matrix – the solution of sulfur in toluene) *m/e*: 727.5 [M + H]⁺, 695.4 [M – S]⁺. ³¹P NMR, δ_P : 87.6.

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