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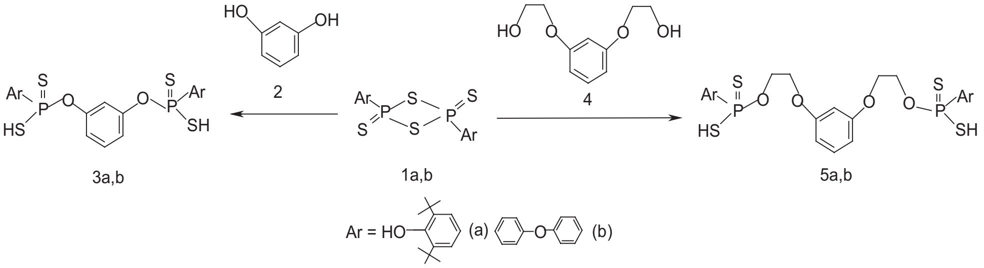
Novel bisaryldithiophosphonic acids were obtained by the reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with resorcinol and 1,3-bis(2-hydroxyethoxy)benzene.



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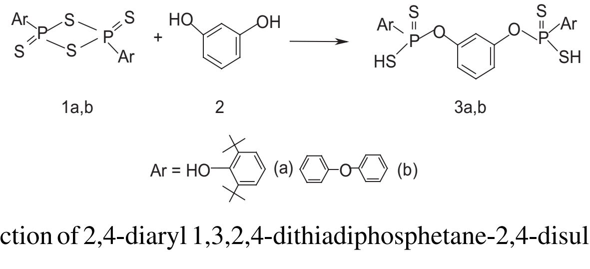
2,4-disulfides with alkylene glycols such as 1,4-butandiol and triethylene glycol (*4–7*). We now extend this approach to hydroxyphenols such as resorcinol and 1,3-bis(2-hydroxyethoxy) benzene.

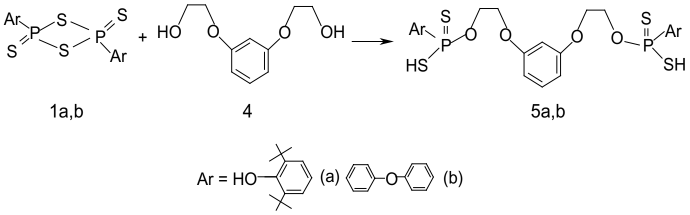
2. Results and discussion

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)-1,3,2λ^5-benzodioxaphosphole-2-thione, whereas with ethane-1,2-diols and 4,5-dihydro-1,3,2λ^5-dioxaphosphole-2-thione together with 2,4-bis(4-methoxyphenyl)-6,7-dihydro-1,5,3,2λ^5, 4λ^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 1,3,2λ^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 $\delta_P = 88.1$ 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 ^{1}H 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 [$(CH_3)_3C$, 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 [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.



Scheme 2. The reaction of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with 1,3-bis (2-hydroxyethoxy)benzene.

TOF mass spectrum of **3b** is attributable to the molecular ion $[M + H]^+$ (calculated molecular mass M of **3b** is 638.7).

The formation of products of similar structure could be expected using the 2-hydroxyethoxyl derivative of resorcinol. It should be noted that 1,3-bis(2-hydroxyethoxy)benzene **4** contains aliphatic hydroxyl groups in contrast to the aromatic ones found in resorcinol **2**. It is of considerable interest to compare the reactivity of hydroxyl compounds **2** and **4** toward 1,3,2,4-dithiadiphosphetane-2,4-disulfides. We have found that **4** reacts with dithiadiphosphetanes **1a** and **b** at room temperature to give O,O′-benzene-1,3-bis[ethoxy-2-(aryldithiophosphonic)] acids **5a** and **b** (Scheme 2).

The reactions of **1a** and **b** with **4** were performed under large dilutions in benzene similar to the procedure used for **2**. The formation of **5b** containing the 4-phenoxyphenyl substituents occurred within 2 h, whereas the reaction of dithiadiphosphetane **1b** with resorcinol **2** proceeded for 8 h to form thioacid **3b** with the same 4-phenoxyphenyl groups. Moreover, the products **3a** and **b** in the reactions of resorcinol **2** were prepared in yields of 67–85%. In contrast, the yields of **5a** and **b** in the reactions of 2-hydroxyethoxyl derivative **4** were increased to 91%. Thus, we have shown that **4** is more reactive than **2** toward **1a** and **b**. The ^{31}P NMR spectra of **5a** and **b** in benzene solutions revealed singlets at $\delta_P = 89.0$ and 87.6 ppm, respectively. The ^1H NMR spectrum of **5a** in $CDCl_3$ solution showed characteristic resonances due to the presence of the OCH_2CH_2O fragment attached to the phosphorus atom. The OCH_2CH_2OP protons appeared as a triplet in the region of $\delta = 4.27$ ppm with $^3J_{HH} = 5.2$ Hz in **5a**. A doublet of triplets observed in the region of $\delta = 4.57$ ppm has been assigned to the methylene protons (the OCH_2CH_2OP fragment) attached to the phosphorus atom via the oxygen with $^3J_{HH} = 5.2$ and $^3J_{PH} = 0.14.3$ Hz. The EI mass spectrum of **5b** exhibited a mass peak at m/e 727 for its molecular ion $[M]^+$. The MALDI TOF mass spectrum of **5a** exhibited a mass peak at m/e 821.8 for the ion $[M + Na]^+$ (calculated molecular mass M of **5a** is 799.1).

3. Conclusions

The reactions of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with resorcinol and 1,3-bis(2-hydroxyethoxy)benzene are of interest from the point of view of organothiophosphorus chemistry as they lead to new bisaryldithiophosphonic acids that may serve as the initial compounds on the way to some derivatives with potential biological activity.

4. Experimental

The IR spectra were obtained in KBr pellets, suspended in vaseline oil or as a liquid film, with a Bruker Vector-22 infrared spectrophotometer. The ^1H NMR spectra were taken on a Bruker

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 chromato-mass-spectrometer (sample directly introduced). Mass spectra MALDI TOF were run on an Ultrafex 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 80–81 °C. Anal. found: C, 57.32; H, 6.44; P, 8.63; S, 16.23. $C_{34}H_{48}O_4P_2S_4$ 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). ^{1}H 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-C_6HO_2P, $^4J_{HH} = 2.2$ Hz), 6.67 and 6.71 (two d, 1H, 5-C_6HO_2P, $^3J_{HH} = 8.3$ Hz), 7.07 and 7.13 (two d, 2H, 4,6-C_6HO_2P, $^3J_{HH} = 8.3$ Hz), 7.83 and 7.92 (two d, 4H, 2,6-C_6H_2P, $^3J_{PH} = 15.9$ Hz). MS (EI) m/e (I_{rel}): 711 $[M]^{+\cdot}$ (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 46–48 °C. Anal. found: C, 56.20; H, 3.91; P, 9.40; S, 20.46. $C_{30}H_{24}O_4P_2S_4$ 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). ^{1}H NMR: δ_H 1.19 (m, 2H, PSH), 6.94 (two d, 4H, 3,5-C_6H_2O, $^3J_{HH} = 7.4$ Hz), 7.02 (two d, 4H, 3,5-C_6H_2P, $^3J_{HH} = 7.9$ Hz), 7.18 (two d, 2H, 4-C_6HO, $^3J_{HH} = 7.4$ Hz and $^3J_{HH} = 7.4$ Hz), 7.34 (dd, 4H, 2,6-C_6H_2O, $^3J_{HH} = 7.4$ Hz), 7.83 (dd, 4H, 2,6-C_6H_2P, $^3J_{HH} = 7.9$ and $^3J_{PH} = 13.4$ Hz). MS (MALDI TOF, matrix – 1,8,9-trihydroxyanthracene) m/e: 639 $[M + H]^+$. ^{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 63–64 °C. Anal. Found: C, 57.10; H, 7.49; P, 7.42; S, 15.88. $C_{38}H_{56}O_6P_2S_4$ 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). ^{1}H NMR, δ_H: 1.46 [s, 36H, $(CH_3)_3C$, Ar], 3.00 (m, 2H, PSH), 4.27 (t, 4H, OCH_2CH_2OP, $^3J_{HH} = 5.2$ Hz); 4.57 (dt, 4H, OCH_2CH_2OP, $^3J_{HH} = 5.2$ and $^3J_{PH} = 14.3$ Hz); 5.65 (m, 2H, HO−Ar), 6.53 (m, 3H, 4,5,6-$C_6H_3O_2$), 7.18 (m, 1H, 2-C_6HO_2), 7.83 (d, 4H, 2,6-C_6H_2P, $^3J_{PH} = 16.4$ Hz). MS (MALDI TOF, matrix – 1,8,9-trihydroxyanthracene) m/e: 821.8 $[M + Na]^+$, 782 $[M - HO]^+$, 767.8 $[M - S]^+$, 750 $[M{-}S{-}HO]^+$. ^{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 (CH_2), 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). ^{1}H NMR, δ_H: 3.00 (m, 2H, PSH); 4.27 (t, 4H, OCH_2CH_2OP, $^3J_{HH} = 4.6$ Hz); 4.58 (dt, 4H, OCH_2CH_2OP, $^3J_{HH} = 4.6$ and $^3J_{PH} = 15.2$ Hz), 7.04 (m, 4H, 3,5-C_6H_2O; 4H, 3,5-C_6H_2P), 7.21 (two d, 2H, 4-C_6HO, $^3J_{HH} = 7.4$ Hz), 7.40 (dd, 4H, 2,6-C_6H_2O, $^3J_{HH} = 7.8$ Hz), 7.98 (dd, 4H, 2,6-C_6H_2P, $^3J_{HH} = 8.3$ and $^3J_{PH} = 14.8$ 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 $[M – S]^+$. ^{31}P NMR, δ_P: 87.6.

Acknowledgements

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