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> SHORT COMMUNICATIONS

## (+)-Dimethyl Tartrate in the Synthesis of Optically Active Bis-arylphosphonodithioic Acids

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Among four-coordinate phosphorus thio acids, promising thiophosphorylating agents are bis-dithiophosphonic acids having two terminal P(=S)SH fragments. Bis-dithiophosphonic acids with methyl groups on the phosphorus atoms were synthesized by reaction of methyl analog of Lawesson's reagent with glycols in diethyl ether [1]. After several unsuccessful attempts to synthesize stable bis-dithiophosphonic acids with aryl groups on the phosphorus atoms in acetonitrile [2, 3], we have developed a procedure for the preparation of bis-arylphosphonodithioic acids via reaction of homologs of Lawesson's reagent with triethylene glycol in benzene [4]. Despite the presence of different substituents at the four-coordinate phosphorus atoms in bisdithiophosphonic acid molecules, the proposed procedure did not ensure synthesis of optically active products owing to 1,3-prototropic migration in the S=P-SH heteroatom triad where the sulfur atoms become equivalent. Therefore, we presumed that optically active bisarylphosphonodithioic acids could be obtained using chiral glycols. Among the latter, of particular interest from the viewpoint of selective biological activity are naturally occurring diols, e.g., (+)-dimethyl L-tartrate

(I). We have found that 2,4-diaryl-1,3,2 $\lambda^5$ ,4 $\lambda^5$ -dithiadiphosphetane 2,4-disulfides **IIa** and **IIb** react with diol **I** to give optically active dimethyl 2,3-bis{[aryl(sulfanyl)phosphorothioyl]oxy}butanedioates **IIIa** and **IIIb**;  $[\alpha]_D^{22} = -13.6^\circ$  and  $-20.3^\circ$ , respectively ( $c = 1.0, C_6H_6$ ).

Dimethyl 2,3-bis{[(3,5-di-tert-butyl-4-hydroxyphenyl)(sulfanyl)phosphorothioyl]oxy}butanedioate (IIIa). Diol I, 2.1 g (11.8 mmol), was dissolved in a mixture of 20 ml of anhydrous benzene and 20 ml of chloroform, 7.0 g of compound IIa was added in small portions under stirring at 20°C in a stream of dry argon, and the mixture was heated for 1 h at 50°C and kept for ~12 h at 20°C. The mixture was filtered, the filtrate was evaporated at 40°C under reduced pressure (0.5 mm, 1 h), and the residue was evacuated for 1 h at 0.02 mm. Yield 9.0 g (99%). IR spectrum, v,  $cm^{-1}$ : 3446 (O-H), 2950, 2925, 2800 (C-H<sub>aliph</sub>), 2550 (S-H), 1742 (C=O), 1560, 1518 (C=C), 1430 (δ<sub>as</sub>CH<sub>3</sub>), 1144 (O-C), 684 (P=S), 618 (P-S). <sup>1</sup>H NMR spectrum, δ, ppm (J, Hz): 1.47 s and 1.48 s (18H each, t-Bu), 3.68 s and 3.71 s (3H each, CH<sub>3</sub>O), 5.70 m (2H, SH), 5.84 d and 5.85 d (1H each, CH,  ${}^{3}J_{HH} = 12.0$ ,  ${}^{3}J_{PH} = 16.5$ ), 7.90 d.d (2H, 2'-H, 6'-H,  ${}^{3}J_{HH} = 1.8$ ,  ${}^{3}J_{PH} = 16.5$ ).



Ar =  $3,5-(t-Bu)_2-4-HOC_6H_2(\mathbf{a}), 4-PhOC_6H_4(\mathbf{b}).$ 

<sup>31</sup>P NMR spectrum (C<sub>6</sub>H<sub>6</sub>):  $\delta_{\rm P}$  94.3 ppm. Mass spectrum (EI): m/z 778.5 ( $I_{\rm rel} = 5\%$ ) [M]<sup>+</sup>. Found, %: C 52.13; H 6.88; P 7.76; S 16.23. C<sub>34</sub>H<sub>52</sub>O<sub>8</sub>P<sub>2</sub>S<sub>4</sub>. Calculated, %: C 52.42; H 6.73; P 7.95; S 16.47. M 778.9.

Dimethyl 2,3-bis{[(4-phenoxyphenyl)(sulfanyl)phosphorothioyl]oxy}butanedioate (IIIb) was synthesized in a similar way from 1.0 g (5.6 mmol) of diol I and 3.0 g (5.7 mmol) of compound IIb. Yield 3.8 g (95%). IR spectrum, v, cm<sup>-1</sup>: 3065, 3063, 3024 (C-H<sub>arom</sub>), 2953, 2843 (C-H<sub>aliph</sub>), 2528 (S-H, free), 2430 (S-H, assoc.), 1765 (C=O), 1528, 1487 (C=C<sub>arom</sub>), 1436 (\delta<sub>as</sub>CH<sub>3</sub>), 1357 (\delta<sub>s</sub>CH<sub>3</sub>), 1109, 1061 (O–C), 694 (P=S), 534 (P–S). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm (J, Hz): 3.78 br.s (6H, CH<sub>3</sub>O), 5.87 d and 5.88 d (1H each, CH,  ${}^{3}J_{\text{HH}} = 12.5, {}^{3}J_{\text{PH}} = 16.5), 7.04 \text{ d.d } (4\text{H}, m\text{-H}, {}^{3}J_{\text{HH}} = 7.0, {}^{4}J_{\text{PH}} = 3.2); 7.09 \text{ d.d } (4\text{H}, \text{o'-H}, {}^{3}J_{\text{HH}} = 7.0);$ 7.23 d.d (2H, p'-H,  ${}^{3}J_{HH} = 7.3$ ), 7.42 m (4H, m'-H,  ${}^{3}J_{\text{HH}} = 7.7$ ), 8.01 d.d (4H, o-H,  ${}^{3}J_{\text{HH}} = 8.8$ ,  ${}^{3}J_{\text{PH}} = 14.7$ ). <sup>31</sup>P NMR spectrum (CHCl<sub>3</sub>): δ<sub>P</sub> 91.2 ppm. Found, %: C 50.96; H 3.67; P 8.47; S 18.26. C<sub>30</sub>H<sub>28</sub>O<sub>8</sub>P<sub>2</sub>S<sub>4</sub>. Calculated, %: C 50.98; H 3.99; P 8.77; S 18.15.

The IR spectra were recorded on a Bruker Vector 22 spectrometer with Fourier transform; samples were

examined as thin films. The <sup>1</sup>H NMR spectra were measured on a Bruker Avance-600 spectrometer (600 MHz) from solutions in CDCl<sub>3</sub>, and the <sup>31</sup>P NMR spectra were obtained on a Bruker CXP-100 instrument (36.5 MHz) using 85% H<sub>3</sub>PO<sub>4</sub> as external reference. The mass spectra (electron impact, 70 eV) were recorded on a Trace MS Finnigan MAT instrument with direct sample admission into the ion source. The optical rotations  $[\alpha]_D^{22}$  were determined on a Perkin– Elmer 341 polarimeter ( $\lambda$  589 nm, sodium halide lamp).

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