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LETTERS TO THE EDITOR

(1*S*)-*endo*-(–)-Borneol in the Synthesis of Optically Active Phosphorus Dithioacids

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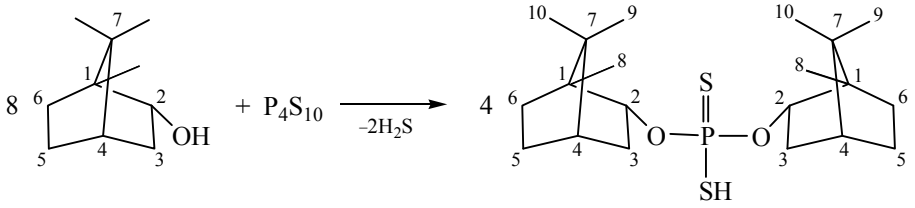
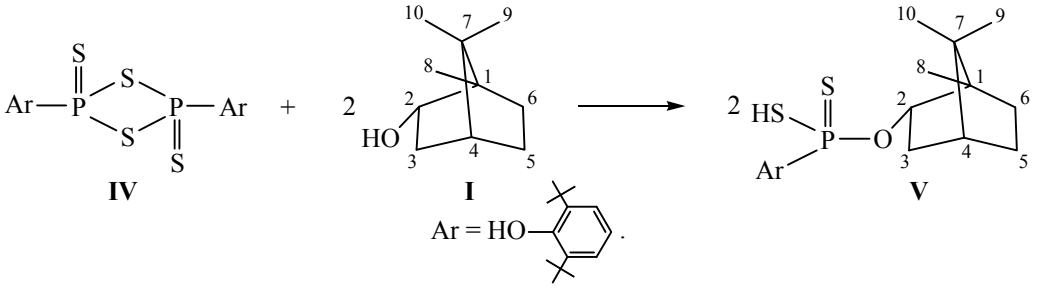
Recently we proposed a new approach to the synthesis of the biologically active compounds by the introduction of the chiral *O*-organyl substituents to the tetracoordinate phosphorus atom in dithiophosphoric and dithiophosphonic acids by the example of the reaction of (1*R*,2*S*,5*R*)-(–)- and (1*S*,2*R*,5*S*)-(+)-menthols with tetraphosphorus decasulfide and 2,4-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,2,4-dithiodiphoshetane-2,4-disulfide, respectively [1, 2]. In these reactions the structure of the terpene fragment does not suffer the Wagner–Meerwein rearrangement type. These transformations may proceed in the thiophosphorylation of other terpene molecules, for example, of the bicyclic terpene alcohols. As a result of their reaction with the phosphorus sulfides yielding the phosphorus dithioacids the optical activity loss may occur. In order to test this hypothesis, (1*S*)-*endo*-(–)-borneol **I**, one of the most accessible bicyclic terpenols, was chosen to react with the tetraphosphorusdecasulfide **II**. The reaction proceeds in anhydrous benzene at 50°C over 1 h to give di{*endo*-(1*S*)-trimethylbicyclo[2.2.1]hept-2-yl}-(–)-dithiophosphoric acid **III**.



I **II** **III**

The optical rotation value of dithiophosphate **III** ($[\alpha]_D^{22}$ –13.2°, *c* 1.0, C_6H_6) is in accordance with the corresponding characteristics of alcohol **I** ($[\alpha]_D^{23}$ –35.6°, *c* 5, EtOH) [3]. The ^{31}P NMR spectrum of **III** contains a singlet at δ_P 86.9 ppm that is characteristic of dithiophosphoric acids [4]. Under the same conditions, the reaction of terpenol **I** with 2,4-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **IV** gives rise to the optically active acid **V** ($[\alpha]_D^{22}$ –8.9°, *c* 1.0, C_6H_6).



IV **I** **V**

Thus, the thiophosphorylation of terpenol **I** with the tetraphosphorusdecasulfide and 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfide did not result in the loss of the optical activity. The ^{1}H NMR spectral data proved that the structure of the borneol fragment in the molecules of **III** and **V** remained unchanged.

Di{*endo*-(1*S*)-trimethylbicyclo[2.2.1]hept-2-yl}-(–)-dithiophosphoric acid (III). To a solution of 1.7 g of terpenol **I** in 20 ml of anhydrous benzene at 20°C was added in portions 0.9 g of phosphorus sulfide **II** under argon with stirring. The mixture was heated for 1 h at 50°C. After cooling, the mixture was filtered. The solvent was evaporated from the filtrate within 1 h in a vacuum (0.5 mm Hg) at 40°C and for 1 h at 0.02 mm Hg at 40°C. The residue (1.8 g, 77%) was purified by the column chromatography (silica gel 0.060–0.200 μm, eluent is benzene), R_f 0.41 (hexane), n_D^{20} 1.5222. IR spectrum, ν, cm^{-1}: 2955 v.s.br, 2880 v.s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$, $\nu_{as,s}(CH)$], 2583 w (S–H_{free}), 2452 m.br (S–H_{bond}), 1479 m, 1454 m [$\delta_{as}(CH_3)$], 1390 m, 1367 m [$\delta_s(CH_3)_2C_{gem}$], 1009 v.s [(P)O–C], 992 s, 977 s, 951 s (OC–C), 772 m [$\nu_{as,s}(PO_2)$], 675 s (P=S), 540 m (P–S). ^{1}H NMR spectrum, δ_H, ppm (*J*, Hz): 0.90 s (3H, C^8H_3), 0.92 and 0.93 two s [6H, $(CH_3)_2C_{cycle}$], 1.32 m (2H, C^5H_2), 1.75 m (2H, C^6H_2), 1.90, 1.93, 1.94 and 1.96 four d (2H, C^3H_2, $^3J_{HH}$ 7.9, 7.5, 8.2 and 8.2), 2.32, 2.34, 2.35 and 2.36 four d (1H, C^4H, $^3J_{HH}$ 9.6 and 9.9), 3.38 m (1H, PSH), 4.80 d.t (1H, POC^2H, $^3J_{HH}$ 7.5, $^3J_{PH}$ 10.9). Found, %: C 59.80; H 8.49; P 7.89; S 15.62. $C_{20}H_{35}O_2PS_2$. Calculated, %: C 59.67; H 8.76; P 7.69; S 15.93.

***O*-{*endo*-(1*S*)-Trimethylbicyclo[2.2.1]hept-2-yl}-(–)-3,5-di-*tert*-butyl-4-hydroxyphenyldithiophosphonic acid (V)** was obtained similarly from 0.6 g of alcohol **I** and 1.1 g of disulfide **IV**. Yield 1.2 g (73%), R_f 0.75 (benzene). IR spectrum, ν, cm^{-1}: 3685 s (H–O, Ar), 3090 w, 3072 w, 3034 w (⋯C–H, Ar), 2954 v.s.br, 2928 s, 2875 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$, $\nu_{as,s}(CH)$], 2548 w (S–H_{free}), 2431 w (S–H_{bond}), 1583 m, 1481 m (C⋯C, Ar), 1430 s [$\delta_{as}(CH_3)$], 1392 m, 1365 m [$\delta_s(CH_3)_2C_{gem}$], 1015 s [(P)O–C], 994 s, 978 s, 924 s (OC–C), 663 m (P=S), 514 m (P–S). ^{1}H NMR spectrum, δ_H, ppm, (*J*, Hz): 0.96 s (3H, C^8H_3), 0.99 and 1.01 two s [6H, $(CH_3)_2C_{cycle}$], 1.45 m (2H, C^5H_2), 1.52 s {18H, $[(CH_3)_3C]_2Ar$}, 1.78 m (2H, C^6H_2), 2.02, 2.04, 2.06 and 2.07 four d (2H, C^3H_2, $^3J_{HH}$ 9.2, 9.8, 8.9 and 10.5); 2.45, 2.46, 2.50 and 2.51 four d (1H, C^4H, $^3J_{HH}$ 7.5, 9.8, 9.8 and 9.5), 5.06 m (1H, P–OC^2H), 5.35 m (1H, HO-Ar), 7.85 d (2H, 2,6-C_6H_2P, $^3J_{PH}$ 16.2). ^{31}P NMR spectrum: δ_P 86.4 ppm. Found, %: C 53.78; H 8.33; P 6.50; S 14.34. $C_{24}H_{39}O_2PS_2$. Calculated, %: C 63.40; H 8.65; P 6.81; S 14.11.

The IR spectra were recorded on an infrared Fourier spectrometer Bruker Vector 22 from KBr pellets. The ^{1}H NMR spectra were obtained on a Bruker Avance-600 spectrometer (600 MHz) from $CDCl_3$ solutions. The ^{31}P NMR spectra were recorded on a Bruker Avance 400 instrument (161.98 MHz) from benzene solutions with external reference 85% H_3PO_4. The optical rotation was determined on a Perkin Elmer 341 polarimeter (λ 589 nm, sodium-halogen lamp, *l* 55 mm).

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