

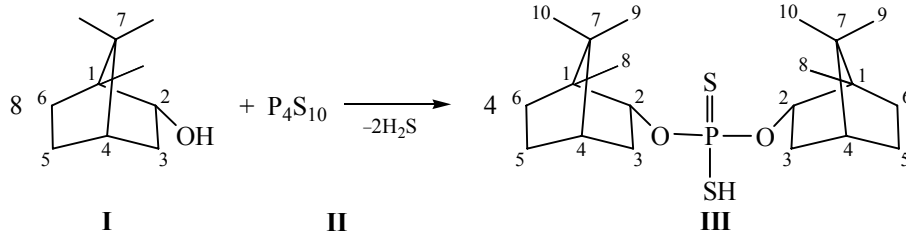
LETTERS
TO THE EDITOR**(1*S*)-endo(-)-Borneol in the Synthesis
of Optically Active Phosphorus Dithioacids**I. S. Nizamov^{a,b}, G. T. Gabdullina^a, L. A. Al'metkina^a,
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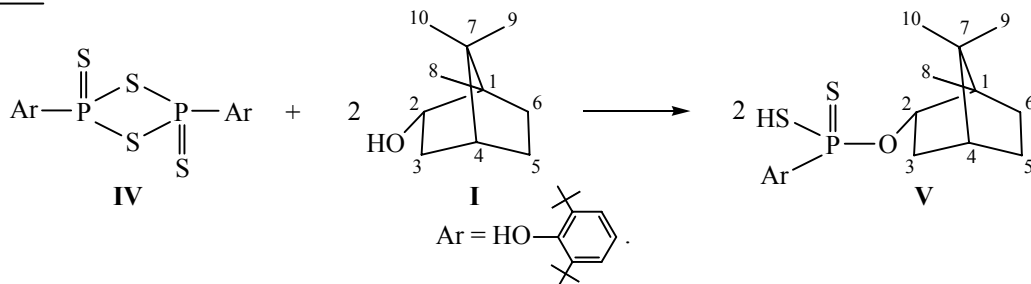
Recently we proposed a new approach to the synthesis of the biologically active compounds by the introduction of the chiral *O*-organyl substituents to the tetracoordinate phosphorus atom in dithiophosphoric and dithiophosphonic acids by the example of the reaction of (1*R*,2*S*,5*R*)-(-) and (1*S*,2*R*,5*S*)-(+)-menthols with tetraphosphorus decasulfide and 2,4-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,2,4-dithiodiphosphetane-2,4-disulfide, respectively [1, 2]. In these reactions the structure of the terpene fragment does not suffer the Wagner–Meerwein rearrangement type. These trans-

formations 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 tetraphosphorus decasulfide **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**.



The optical rotation value of dithiophosphate **III** ($[\alpha]_D^{22} -13.2^\circ$, c 1.0, C_6H_6) is in accordance with the corresponding characteristics of alcohol **I** ($[\alpha]_D^{23} -35.6^\circ$, c 5, EtOH) [3]. The ³¹P 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** ($[\alpha]_D^{22} -8.9^\circ$, c 1.0, C_6H_6).



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

Di{endo-(1S)-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 [$\nu_{\text{as,s}}(\text{CH}_3)$, $\nu_{\text{as,s}}(\text{CH}_2)$, $\nu_{\text{as,s}}(\text{CH})$], 2583 w (S–H_{free}), 2452 m.br (S–H_{bond}), 1479 m, 1454 m [$\delta_{\text{as}}(\text{CH}_3)$], 1390 m, 1367 m [$\delta_{\text{s}}(\text{CH}_3)_2\text{C}_{\text{gem}}$], 1009 v.s [(P)O–C], 992 s, 977 s, 951 s (OC–C), 772 m [$\nu_{\text{as,s}}(\text{PO}_2)$], 675 s (P=S), 540 m (P–S). ^1H NMR spectrum, δ_{H} , ppm (J , Hz): 0.90 s (3H, C^8H_3), 0.92 and 0.93 two s [6H, $(\text{CH}_3)_2\text{C}_{\text{cycle}}$], 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 , $^3J_{\text{HH}}$ 7.9, 7.5, 8.2 and 8.2), 2.32, 2.34, 2.35 and 2.36 four d (1H, C^4H , $^3J_{\text{HH}}$ 9.6 and 9.9), 3.38 m (1H, PSH), 4.80 d.t (1H, POC^2H , $^3J_{\text{HH}}$ 7.5, $^3J_{\text{PH}}$ 10.9). Found, %: C 59.80; H 8.49; P 7.89; S 15.62. $\text{C}_{20}\text{H}_{35}\text{O}_2\text{PS}_2$. Calculated, %: C 59.67; H 8.76; P 7.69; S 15.93.

{endo-(1S)-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 ($\text{C}=\text{C}-\text{H}$, Ar), 2954 v.s.br, 2928 s, 2875 s [$\nu_{\text{as,s}}(\text{CH}_3)$, $\nu_{\text{as,s}}(\text{CH}_2)$, $\nu_{\text{as,s}}(\text{CH})$], 2548 w (S–H_{free}), 2431 w (S–H_{bond}), 1583 m, 1481 m ($\text{C}=\text{C}$,

Ar), 1430 s [$\delta_{\text{as}}(\text{CH}_3)$], 1392 m, 1365 m [$\delta_{\text{s}}(\text{CH}_3)_2\text{C}_{\text{gem}}$], 1015 s [(P)O–C], 994 s, 978 s, 924 s (OC–C), 663 m (P=S), 514 m (P–S). ^1H NMR spectrum, δ_{H} , ppm, (J , Hz): 0.96 s (3H, C^8H_3), 0.99 and 1.01 two s [6H, $(\text{CH}_3)_2\text{C}_{\text{cycle}}$], 1.45 m (2H, C^5H_2), 1.52 s {18H, $[(\text{CH}_3)_3\text{C}]_2\text{Ar}$ }, 1.78 m (2H, C^6H_2), 2.02, 2.04, 2.06 and 2.07 four d (2H, C^3H_2 , $^3J_{\text{HH}}$ 9.2, 9.8, 8.9 and 10.5); 2.45, 2.46, 2.50 and 2.51 four d (1H, C^4H , $^3J_{\text{HH}}$ 7.5, 9.8, 9.8 and 9.5), 5.06 m (1H, P–OC²H), 5.35 m (1H, HO–Ar), 7.85 d (2H, 2,6– $\text{C}_6\text{H}_2\text{P}$, $^3J_{\text{PH}}$ 16.2). ^{31}P NMR spectrum: δ_{P} 86.4 ppm. Found, %: C 53.78; H 8.33; P 6.50; S 14.34. $\text{C}_{24}\text{H}_{39}\text{O}_2\text{PS}_2$. 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 ^1H 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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