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Reactions of *O*,*O*-Dialkyldithiophosphoric Acids with Non-Activated α-Olefins

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Abstract—Electrophilic addition reactions of *O*,*O*-dialkyldithiophosphoric acids to non-activated α-olefins proceeding in accordance with the Markovnikov's rule were studied. In the absence of a catalyst these reactions occur very slowly to give the products in low yields, while Lewis acid as a catalyst can greatly accelerate the reaction and increase the conversion in the Ad_E-processes. A similar acceleration of the addition processes and an increase in the reaction product yield occur at the action of ultrasound on the reaction medium.

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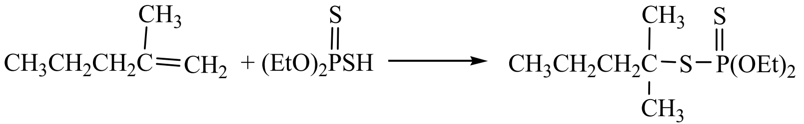
Synthetic results of the reactions of four-coordinated phosphorus thioacids with olefins depend significantly on the reogiochemistry of addition of thiophosphoric fragments to the double bonds of asymmetric olefins, i. e., on the possibility of formation of the carbon-carbon double bond adducts in accordance with or opposite to the Markovnikov's rule [1–9]. The unsaturated compounds containing electron-withdrawing groups adjacent to the double bond, for example, acrylonitrile, alkenyl acylates, etc., add *O*,*O*-dialkyldithiophosphoric acid against the Markovnikov's rule [2–4]. The reactions of *O*,*O*-dialkyldithiophosphoric acids with unsaturated compounds containing the electron-donating substituents (vinyl ethers, vinyl acetate) or asymmetric olefins (oct-1-ene, oct-2-ene, cycloalkenes, 2-methylprop-1-ene) result in the Markovnikov's adducts [1, 5–9]. In accordance with the Markovnikov's rule, the reaction of unactivated olefins with dithiophosphoric acids results in the adducts, which were not specifically purified from the phosphorus sulfides impurities [4, 6]. The explanation of this phenomenon lies in the fact that the starting olefins, especially those produced by the industry, contain the traces of peroxide compounds, which direct the addition of dithiophosphoric acid on the double bond against the Markovnikov's rule, i. e., in this case there is a radical addition [5]. The role of the phosphorus sulfides impurities, contained in the crude dithiophosphoric acid, is the destruction of the peroxides which favors the Markovnikov's adducts formation in the Ad-processes occurring by an ionic mechanism [5, 8]. Oct-1-ene, purified from peroxides, react with *O*,*O*-diethyldithiophosphoric acid to give exclusively the Markovnikov's adduct [6]. At the same time adding of cumene hydroperoxide to the reaction of *O*,*O*-diethyldithiophosphoric with oct-1-ene stimulates the radical anti-Markovnikov addition [6]. Diphenyl-dithiophosphinic acid reacts with oct-1-ene in the absence of additives at 130°C for 3 h to give *S*-2-methylheptyl diphenyldithiophosphinate, i. e. in accordance with the Markovnikov's rule [10]. Dialkyltetrathiophosphoric acids react with prop-1-ene or hex-1-ene (40–100°C, 1.5–16 h, pressure reactor) to form the Markovnikov's adducts [11].

Note that the reported reactions of dithiophosphoric acids with olefins [5–11] were carried out under rigid conditions, in which the addition processes can be complicated by the possibility of various rearrangements and other secondary reactions of the initially formed adducts. In this regard, we aimed to investigate the reactions of dithiophosphoric acids with the unactivated asymmetric olefins under the relatively mild conditions, avoiding the undesirable secondary processes, with use of catalysts or initiators. As the objects of the study α-olefins were selected of linear and vinylidene structure: hexadec-1-ene, octadec-1-ene, oct-1-ene and 2-methylpent-1-ene. It was found that in the absence of additives the reaction of 2-methylpent-1-ene **I** with *O*,*O*-diethyl dithiophosphoric acid **IIa** starts at 20°C and proceeds for six days to give *O*,*O*-diethyl *S*-1,1-dimethylbuthyl dithiophosphate **III** in 97% yield. The product was purified by vacuum distillation.



$$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2 + (EtO)_2\overset{\overset{S}{\|}}{P}SH \longrightarrow CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-S-\overset{\overset{S}{\|}}{P}(OEt)_2$$

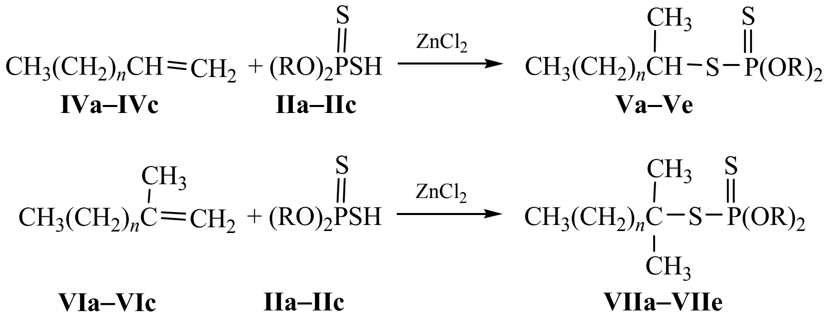
I **IIa** **III**

According to the ^{31}P NMR spectroscopy, the reaction of 2-methylpent-1-ene **I** with acid **IIa** at 20°C leads to the appearance of a singlet at δ_P 90.4 ppm in the ^{31}P NMR spectrum of the reaction mixture. In the ^{31}P NMR spectrum the signal intensity of the original acid **IIa** at 84.5 ppm [12] decreases gradually, and the signal of dithiophosphate **III** at 90.4 ppm increases. In the ^1H NMR spectrum of the product **III** the vinyl protons signals of the starting alkene **I** at δ 4.68 and 4.74 ppm disappear completely; the intense singlet signal originating from the six protons of two methyl groups at the C^2 carbon atom appears at δ 1.49 ppm. These data indicate clearly the formation of a Markovnikov's adduct **III** in the studided reaction. In the ^1H NMR spectrum the methylene group signals of protons of $PSCH_2$-moiety at δ 2.5–3.0 ppm are absent, which should occur in the case of the isomeric products formation owing to the alternative anti-Markovnikov addition process as described in [13]. The EI mass spectrum of the **III** contains a mass peak *m/z* 270.9 belonging to a $[M]^+$ molecular ion (calculated *M* 270.4).

However, the reaction of 2-methylpent-1-ene **I** with the acid **IIa** at room temperature in the absence of additives proceeds slowly, which makes this process low-productive. Meanwhile, this reaction can be accelerated by carrying it out at 80°C for 2 h in the absence of additives. In this case the product **III** is formed in 88% yield. Another possibility of the Ad-process intensification is the use of catalysts. Recently we found that the reaction of acid **IIa** with hexadec-1-ene at 20°C was accelerated in the presence of zinc chloride [14]; the adduct yield reached 76%. In the catalytic processes other Lewis acids $ZnCl_2$, $NiCl_2$, CuCl, $CuCl_2$, $FeCl_3$ have also been used, showing a high catalytic activity in the reactions of electrophilic addition of dithiophosphoric acids to the double bond of cyclic monoterpenes [camphene and *R*-(+)-limonene], which occur in accordance with the Markovnikov's rule [15, 16].

In this work we studied a possibility of using zinc chloride as a catalyst for the reaction of 2-methylpent-1-ene **I** with acid **IIa**. According to the ^{31}P NMR data, after stirring the starting reagents and 0.5 wt % of zinc chloride for 1 h at 20°C the amount of adduct **III** reaches 50%. After 8 h the reaction was completed, whereas in the absence of additives a long stirring (up to 6 days) at 20°C is required. According to the ^{31}P NMR data, in the reaction of acid **IIa** with hexadec-1-ene **IVa** at 80°C for 2 h in the absence of additives the conversion calculated on the phosphorus does not exceed 12%. The reactions of dithiophosphoric acids **IIa**–**IIc** with hexadec-1-ene **IVa**, octadec-1-ene **IVb**, and oct-1-ene **IVc** in the presence of zinc chloride (3.0 wt %) at 80°C over 2 h led to formation of *O*,*O*-dialkyl-*S*-2-methylalkyldithiophosphates **Va**–**Ve** as the major products in yields of 63–88%. According to the ^1H NMR spectral data, the used commercial samples of hexadec-1-ene, octadec-1-ene, and oct-1-ene contain vinylidene α-olefins as impurities (2%), 2 methylpentadec-1-ene **VIa**, 2-methylheptadec-1-ene **VIb**, and 2-methylhept-1-ene **VIc**, which react with the acids to form *O*,*O*-dialkyl-*S*-1,1-dimethylalkyldithiophosphates **VIIa**–**VIIe** as the minor products.

Dithiophosphates **Va** and **VIIa** were isolated from the reaction mixture by the column chromatography as an inseparable mixture of two compounds. The ^{31}P NMR spectrum of this mixture contains two singlet signals, at δ_P 94.5 and 90.2 ppm, in a 93:7 ratio (by the integral intensity). The main signal at δ_P 94.5 ppm corresponds to the product **Va**. The low-intensive signal at δ_P 90.2 ppm referred to the minor adduct **VIIa**. In the ^1H NMR spectrum of the mixture of dithiophosphates **Va** and **VIIa** there are doublet of quartets of triplets at δ 3.31 ppm ($^3J_{HH}$ 6.9, $^3J_{PH}$ 13.8 Hz) belonging to the methine proton of PSCH $(CH_3)CH_2$-moiety of the Markovnikov adduct **Va**. The methine proton of SCH- fragment is known to appear at δ 3.3–3.5 ppm [13]. In ^1H NMR spectrum of **Va** there is a doublet signal at δ 1.39 ppm ($^3J_{HH}$ 6.8 Hz)



$$\underset{\textbf{IVa–IVc}}{CH_3(CH_2)_nCH{=}CH_2} + \underset{\textbf{IIa–IIc}}{(RO)_2\overset{S}{\overset{\|}{P}}SH} \xrightarrow{ZnCl_2} \underset{\textbf{Va–Ve}}{CH_3(CH_2)_n\overset{CH_3}{\overset{|}{C}H}{-}S{-}\overset{S}{\overset{\|}{P}}(OR)_2}$$

$$\underset{\textbf{VIa–VIc}}{CH_3(CH_2)_n\overset{CH_3}{\overset{|}{C}}{=}CH_2} + \underset{\textbf{IIa–IIc}}{(RO)_2\overset{S}{\overset{\|}{P}}SH} \xrightarrow{ZnCl_2} \underset{\textbf{VIIa–VIIe}}{CH_3(CH_2)_n\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}S{-}\overset{S}{\overset{\|}{P}}(OR)_2}$$

R = Et (**IIa**), Pr-*i* (**IIb**), Bu-*i* (**IIc**); R = Et, *n* = 13 (**IVa, Va**); R = Pr-*i*, *n* = 13 (**IVa, Vb**); R = Pr-*i*, *n* = 15 (**IVb, Vc**); R = Pr-*i*, *n* = 5 (**IVc, Vd**); R = Bu-*i*, *n* = 5 (**IVc, Ve**); R = Et, *n* = 12 (**VIa, VIIa**); R = Pr-*i*, *n* = 12 (**VIa, VIIb**); R = Pr-*i*, *n* = 4 (**VIb, VIIc**); R = Pr-*i*, *n* = 4 (**VIc, VIId**); R = Bu-*i*, *n* = 4 (**VIc, VIIe**).

originating from the methyl protons of CH_3CHCP-group. The CI mass spectrum of the mixture of isomeric dithiophosphates **Va** and **VIIa** contains the mass peak with *m*/*z* 467 corresponding to their molecular ions $[M]^+$ (calculated *M* 466).

By the ^{31}P NMR spectroscopy data, the conversion in the reaction of acid **IIa** with hexadec-1-ene **IVa** in the presence of 2 wt % of zinc chloride at 20°C after stirring for 5 h was 26%, which is twice more than in the absence of a catalyst for the same period of time. The use of zinc chloride (1.3 wt %) in the reaction of acid **IIb** with hexadec-1-ene **IVa** and an increase in the reaction temperature to 80°C led to 100% consumption of the acid **IIa** within 1 h.

The reaction of acid **IIa** with oct-1-ene at 100°C is known to proceed in the absence of additives [6, 8]. We succeeded to perform the reaction of the acid **IIa** with oct-1-ene in the presence of 1 wt % of zinc chloride at 20°C over 10 h. Heating the mixture of acid **IIa** with oct-1-ene in the presence of 2.9 wt % of zinc chloride at 80°C for 2 h gives rise to products **Vd** and **VIId** in a yield of 71%. The esters **Vd** and **VIId** were isolated by the column chromatography as a mixture. In the ^{31}P NMR spectrum the singlet signal at δ_P 93.8 ppm corresponds to the adduct **Vd**. The signal at δ_P 90.8 ppm belongs to the minor product **VIId**. According to the ^1H and ^{31}P NMR spectral data, the compounds **Vd** and **VIId** are formed in 90:1 ratio.

In parallel with the catalytic action of Lewis acids, the reaction of dithiophosphoric acids with α-olefins can be accelerated by the ultrasound radiation, effect of which on the reaction mixtures is accompanied by a spontaneous increase in temperature [17, 18], as a rule, up to 170°C. Therefore the reactions under these conditions were performed using a jacketed reactor cooled by running water. We found that hexadec-1-ene **IVa** reacted with acid **IIa** under the influence of ultrasonic radiation of low frequency (22 kHz, power 400 W) at 60°C much faster, within 30 min. The products **Va** and **VIIa** were formed with a total yield of 74%. Note the coincidence of the physicochemical data and parameters of the NMR spectra of the adducts **Va** and **VIIa** obtained under the ultrasonic irradiation and in the presence of zinc chloride. Thus, the use of ultrasonic irradiation and catalysts like Lewis acids leads to a decrease in the reaction temperature and reduces the reaction time providing the satisfactory yield of the desired adducts.

In conclusion, it should be noted that the reactivity of 2-methylpent-1-ene in the reactions with dithiophosphoric acids is higher than that of oct-1-ene, hexadec-1-ene and octadec-1-ene (these olefins are almost comparable by the length of alkyl substituents). In the latter cases, the effect of the length of alkyl substituent chain on the activity of the olefin is not essential. The obtained results are consistent with the high activity of vinylidene α-olefins in comparison with the linear α-olefins in the reactions of electro-philic addition [19], which is due to the higher donor inductive effect of the two alkyl substituents at the double bond of the vinylidene α-olefins. These data can be useful in studying the thiophosphorylation reac-tions of higher industrial olefins, representing a complex mixture of olefins with different structures and reactivity, with use of the four-coordinated phosphorus thioacids [20–22].

EXPERIMENTAL

The IR spectra were recorded on a Tensor 27 IR Fourier-spectrometer (400–4000 cm^{-1}) from the samples as liquid films between KBr plates or from the

KBr pellets. The ^{31}P NMR spectra were measured on a Bruker CXP-100 spectrometer operating at 36.47 MHz relative to 85% H_3PO_4. A positive value of the chemical shift corresponds to the downfield displacement of the peak. The ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) and Bruker Avance-600 (600 MHz) spectrometers in $CDCl_3$ solutions. The ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (100.6 MHz) in $CDCl_3$ solutions. The EI and CI mass spectra were registered on a Finnigan MAT-212 and Trace MS Finnigan MAT mass spectrometers.

***O*,*O*-Diethyl *S*-1,1-dimethylbutyl dithiophosphate (III).** *a*. To a solution of 2.2 g of acid **IIa** in 1 ml of anhydrous benzene was added dropwise a solution of 1.0 g of pentene **I** in 2 ml of benzene while stirring under argon atmosphere at 20°C. The mixture was stirred for 6 days at 20°C and then evaporated at 40°C for 1 h at 0.5 mm Hg and for 1 h at 0.02 mm Hg. The residue (3.1 g, 97%) was distilled. Yield 2.4 g (75%), bp 102–103°C (0.04 mm Hg), n_D^{20} 1.5052. IR spectrum, ν, cm^{-1}: 2955 m, 2920 s, 2850 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$], 1468 m [$\delta_{as}(CH_3)$], 1390 m [$\delta_s(CH_3)$], 1021 v.s (POC), 966 s (OC–C), 664 m (P=S), 593 w.br (P–S). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.93 t (3H, $\underline{CH}_3CH_2$, $^3J_{HH}$ 7.3), 1.38 t [6H, $(\underline{CH}_3CH_2O)_2P$, $^3J_{HH}$ 7.3], 1.49 s (6H, CH_3CCH_3), 1.68 m (2H, CH_2), 4.28 d.q [4H, $(CH_3\underline{CH}_2O)_2P$, $^3J_{HH}$ 7.3, $^3J_{PH}$ 10.5]. Found, %: C 44.66; H 9.07; P 11.23; S 23.99. $C_{10}H_{23}O_2PS_2$. Calculated, %: C 44.72; H 8.57; P 11.46; S 23.72.

b. A mixture of 1.1 g of acid **IIa** and 1.0 g of pentene **I**, prepared at 20°C under argon atmosphere, was heated for 2 h at 80°C with stirring. After cooling to 20°C, the mixture was evaporated at 40°C for 1 h at 0.5 mm Hg. and for 1 h at 0.02 mm Hg. Yield 1.4 g (88%). ^{31}P NMR spectrum: δ_P 90.2 ppm. Found, %: C 44.43; H 8.69; P 11.33; S 24.01. $C_{10}H_{23}O_2PS_2$. Calculated, %: C 44.72; H 8.57; P 11.46; S 23.72.

c. To 1.1 g of acid **IIa** was added 0.1 g (0.5 wt %) of $ZnCl_2$ with stirring under argon atmosphere at 20° C. To the stirred mixture was added 0.5 g of pentene **I** at 20°C. The mixture was stirred for 8 h at 20°C, evaporated at 40°C for 1 h at 0.5 mm Hg and for 1 h at 0.02 mm Hg. Yield 1.5 g (94%). ^{31}P NMR spectrum: δ_P 90.6 ppm. Found, %: C 44.53; H 8.33; P 11.57; S 23.44. $C_{10}H_{23}O_2PS_2$. Calculated, %: C 44.72; H 8.57; P 11.46; S 23.72.

***O*,*O*-Diethyl *S*-2-methylpentadecyl dithiophosphate (Va) and *O*,*O*-diethyl *S*-1,1-dimethyltetradecyl dithiophosphate (VIIa).** *a*. A mixture of 5.0 g of acid **IIa** and 6.0 g of hexadecene **IVa**, distilled over sodium and containing pentadec-1-ene **VIa** impurity, and 0.1 g (2.0 wt %) of $ZnCl_2$ was heated for 2 h at 80°C. The mixture was diluted with 10 ml of Et_2O and washed with water (3×10 ml). The organic layer was separated, dried with calcium chloride, and evaporated at 40°C for 1 h at 0.5 mm Hg and for 1 h at 0.06 mm Hg. We obtained 7.7 g (70%) of a mixture of dithiophosphates **Va** and **VIIa**, 4.0 g of which was chromatographed on a column (silica gel, eluent – petroleum ether, bp 70–100°C). Yield 2.3 g (**Va** + **VIIa**), R_f 0.07 (petroleum ether n_D^{20} 1.4662. IR spectrum, ν, cm^{-1}: 2956 m, 2924 s, 2854 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$], 1466 m [$\delta_{as}(CH_3)$], 1389 m [$\delta_s(CH_3)$], 1019 v.s (POC), 958 s (OC–C), 662 m (P=S), 599 w.br (P–S). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.87 t (3H, $\underline{CH}_3CH_2CH_2$, $^3J_{HH}$ 6.8), 1.25 br.s (12H, CCH_2C), 1.35 t [6H, $(\underline{CH}_3CH_2O)_2P$, $^3J_{HH}$ 7.2], 1.39 d [3H, $\underline{CH}_3C(H)SP$, $^3J_{HH}$ 6.8], 1.59 m (2H, $PSCHCH_2\underline{CH}_2$), 1.66 m (2H, $PSCH\underline{CH}_2C$), 2.87 d.t (2H, $PS\underline{CH}_2CH_2$, $^3J_{HH}$ 7.7, $^3J_{PH}$ 23.9), 3.31 d.t.q [1H, $PS\underline{CH}(CH_3)CH_2$, $^3J_{HH}$ 6.9, $^3J_{PH}$ 13.8], δ_1 4.11 and δ_2 4.18 two m [4H, $(CH_3\underline{CH}_2O)_2P$]. ^{13}C NMR spectrum (the signal form of the $^{13}C–\{^1H\}$ spectrum is given in parentheses), δ_C, ppm (*J*, Hz): 14.1 s (q) ($\underline{C}H_3CH_2CH_2$, $^1J_{HC}$ 124.4), 15.1 d (d.q) ($\underline{C}H_3CH_2OP$, $^3J_{PC}$ 8.4, $^1J_{HC}$ 127.4), 22.7 s (t) ($CH_3\underline{C}H_2CH_2$, $^1J_{HC}$ 124.4), 27.1 s (t) ($\underline{C}H_2CH_2CH_2SP$, $^1J_{HC}$ 121.4), 29.7 br.s (t) ($C\underline{C}H_2C$, $^1J_{HC}$ 125.0), 32.0 s (t) ($CH_3CH_2\underline{C}H_2$, $^1J_{HC}$ 125.0), 38.2 d (t.d) ($PSCH\underline{C}H_2$, $^1J_{HC}$ 128.2, $^3J_{PC}$ 4.0), 41.0 d (d.d) ($PSCH_2\underline{C}H_2CH_2$, $^3J_{PC}$ 5.0), 41.3 d (d.d) ($PS\underline{C}H_2CH_2$, $^3J_{PC}$ 5.1), 46.3 d (d.d) [$PS\underline{C}H(CH_3)CH_2$, $^1J_{HC}$ 144.2, $^3J_{PC}$ 3.6], δ_1 63.68 two d (two t.d) [$(CH_3\underline{C}H_2O)_2P$, $^1J_{HC}$ 147.8, $^3J_{PC}$ 4.8] and δ_2 63.72 two d (two t.d) [$(CH_3\underline{C}H_2O)_2P$, $^1J_{HC}$ 147.8, $^3J_{PC}$ 5.4]. Found, %: C 58.79; H 10.24; P 7.71; S 15.91. $C_{20}H_{43}O_2PS_2$. Calculated, %: C 58.49; H 10.58; P 7.55; S 15.58.

b. A mixture of 1.9 g of acid **IIa** and 2.3 g of hexadec-1-ene **IVa**, containing pentadec-1-ene **VIa** impurity, was irradiated with ultrasound (22 kHz, 400 W) in a jacket reactor cooled with running water at 60°C for 30 min. After cooling to 20°C, the mixture was evaporated in a vacuum (0.02 mm Hg) at 50°C for 1 h. We obtained 3.1 g (74%) of a mixture of dithiophosphates **Va** and **VIIa**. ^{31}P NMR spectrum, δ_P, ppm: 94.4 and 90.3 in the 3:1 ratio. Found, %: C 54.32; H 10.80; P 7.71; S 15.84. $C_{20}N_{43}O_2PS_2$. Calculated, %: C 58.49; H 10.58; P 7.55; S 15.58.

_O_,_O_-Diisopropyl _S_-2-methylpentadecyl dithiophosphate (Vb) and _O_,_O_-diisopropyl _S_-1,1-dimethyltetradecyl dithiophosphate (VIIb) were obtained similarly from 3.4 g of acid **IIb**, 3.6 g of hexadecene **IVa**, containing pentadec-1-ene **VIa** impurity, and 0.1 g (2.9 wt %) of $ZnC1_2$. Yield 5.0 g (71%), 2.2 g of which was chromatographed on a column (silica gel, petroleum ether, bp 40–70°C), R_f 0.44 (petroleum ether), n_D^{20} 1.4715. IR spectrum, ν, cm^{-1}: 2978 m, 2924 s, 2854 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$], 1466 m [$\delta_{as}(CH_3)$], 1385 m, 1374 m [$\delta_s(CH_3)_2C_{gem}$], 972 v.s (POC), 655 m (P=S), 549 m (P–S). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 t (3H, $\underline{CH}_3CH_2$, $^3J_{HH}$ 7.1), 1.28 br.s [22H, $C(\underline{CH_2})_{11}C$], 1.36 m (1H, $CH_3\underline{CH}CH_2$, $^3J_{HH}$ 6.1), 1.40 d [12H, $(\underline{CH_3})_2CHOP$, $^3J_{HH}$ 6.1], 1.52 d [3H, $\underline{CH}_3C(H)SP$, $^3J_{HH}$ 6.7], 1.60 m (2H, $SCH_2CH_2\underline{CH_2}$, $^3J_{HH}$ 6.7), 1.71 m (2H, $PSCH_2\underline{CH_2}CH_2$, $^3J_{HH}$ 6.7), 2.05 d.t (2H, $PSCH\underline{CH_2}CH_2$, $^3J_{HH}$ 6.7), 2.88 d.t (2H, $PS\underline{CH_2}CH_2$, $^3J_{HH}$ 7.6, $^3J_{PH}$ 14.7), 3.38 d.t.q [1H, $PS\underline{CH}(CH_3)CH_2$, $^3J_{HH}$ 6.7, $^3J_{PH}$ 7.1], 4.83 m [2H, $(CH_3)_2\underline{CH}OP$, $^3J_{HH}$ 6.1], 4.92 m [2H, $(CH_3)_2\underline{CH}OP$, $^3J_{HH}$ 6.1]. ^{31}P NMR spectrum, δ_P, ppm: 92.8 and 87.3 in 11:1 ratio.

_O_,_O_-Diisopropyl _S_-2-methylheptadecyl dithiophosphate (Vc) and _O_,_O_-diisopropyl _S_-1,1-dimethylhexadecyl dithiophosphate (VIIc) were obtained similarly from 7.0 g of acid **IIb**, 8.3 g of octadecene **IVb**, containing heptadec-1-ene **VIb** impurity, and 0.2 g (2.9 wt %) of $ZnC1_2$. Yield 12.5 g (82%), 3.9 g of which was purified using a device for the molecular-film distillation at a temperature of 125°C (0.04 mm Hg), n_D^{20} 1.4581. IR spectrum, ν, cm^{-1}: 2977 m, 2924 m, 2853 m [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$], 1466 m [$\delta_{as}(CH_3)$], 1384 m, 1375 m [$\delta_s(CH_3)_2C_{gem}$], 981 s, 875 s (POC), 655 m (P=S), 548 m (P–S). ^{31}P NMR spectrum, δ_P, ppm: 92.7 and 87.3 in 2:1 ratio. Mass spectrum (EI), *m/z* (I_{rel}, %): 466.3 (1) $[M]^+$, 451.0 (1) $[M - Me]^+$, 423 (1) $[M - Pr\text{-}i]^+$. Found, %: C 61.42; H 11.37; P 6.74; S 13.67. $C_{24}H_{51}O_2PS_2$. Calculated, %: C 61.75; H 11.04; P 6.64; S 13.71. *M* 466.

_O_,_O_-Diisopropyl _S_-2-methylheptyl dithiophosphate (Vd) and _O_,_O_-diisopropyl _S_-1,1-dimethylhexyl dithiophosphate (VIId) were obtained similarly from 7.0 g of acid **IIb**, 3.6 g of octene **IVc**, containing heptene **VIc** and 0.2 g (2.9 wt %) of $ZnC1_2$. Yield 7.1 g (66%), 1.8 g of which was chromatographed on a column (silica gel, eluent – MeCN), R_f 0.86 (MeCN). IR spectrum, ν, cm^{-1}: 2978 v.s, 2931 v.s, 2879 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$], 1464 m [$\delta_{as}(CH_3)$], 1385 m [$\delta_s(CH_3)$], 1101 s (POC), 972 v.s. br (POC), 652 m (P=S), 513 w (P–S). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 t (3H, $\underline{CH}_3CH_2$, $^3J_{HH}$ 7.6), 1.28 br.s (8H, $C\underline{CH_2}C$), 1.37 d {12H, $[(\underline{CH_3})_2CHO]_2P$, $^3J_{HH}$ 5.1}, 1.52 d [3H, $\underline{CH}_3C(H)SP$, $^3J_{HH}$ 8.2], 1.60 m (2H, $PSCHCH_2\underline{CH_2}$), 1.76 m (2H, $PSCH\underline{CH_2}C$), 2.79 m (2H, $PS\underline{CH_2}CH_2$), 3.39 m [1H, $PS\underline{CH}(CH_3)CH_2$], 4.84 and 4.90 two m {4H, $[(CH_3)_2\underline{CH}O]_2P$}. ^{31}P NMR spectrum (MeCN), δ_P, ppm: 93.8 and 90.8 in 99:1 ratio. Found, %: C 51.37; H 9.73; P 9.88; S 19.56. $C_{14}H_{31}O_2PS_2$. Calculated, %: C 51.50; H 9.60; P 9.49; S 19.60.

_O_,_O_-Diisobutyl _S_-2-methylheptyl dithiophosphate (Ve) and _O_,_O_-diisobutyl-1,1-dimethylhexyl dithiophosphate (VIIe) were obtained similarly from 10.0 g of acid **IIc**, 4.6 g of octene **IVc**, containing heptene **VIc** impurity, and 0.1 g (1.0 wt %) of $ZnC1_2$. Yield 9.3 g (63%), 4.5 g of which was chromatographed on a column (silica gel, eluent – Et_2O), R_f 0.82 (Et_2O), n_D^{20} 1.4350. IR spectrum, ν, cm^{-1}: 2960 v.s, 2931 v.s, 2878 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$], 1469 m [$\delta_{as}(CH_3)$], 1393 m, 1369 [$\delta_s(CH_3)_2C_{gem}$], 998 v.s.br (POC), 963 m (OC–C), 854 m. br [$\nu_{as,s}(PO_2)$], 666 m (P=S), 553 w (P–S). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 t (3H, $\underline{CH}_3CH_2$, $^3J_{HH}$ 7.2), 0.97 br.s [8H, $C(\underline{CH_2})_4C$], 0.99 d {12H, $[(\underline{CH_3})_2CHCH_2O\}_2P$, $^3J_{HH}$ 7.2], 1.31 m [2H, $CH_2\underline{CH_2}CH_2SP$; 2H, $CH_2\underline{CH_2}C(H)SP$], 1.42 d [3H, $\underline{CH}_3C(H)SP$, $^3J_{HH}$ 6.6], 1.52 m {2H, $[(CH_3)_2\underline{CH}CH_2O]_2P$}, 1.61 m (2H, $PSCHCH_2\underline{CH_2}$), 1.76 m (2H, $PSCH\underline{CH_2}C$), 2.99 m (2H, $CH_2\underline{CH_2}SP$), 3.35 d.t.q [1H, $PS\underline{CH}(CH_3)CH_2$, $^3J_{HH}$ 7.2, $^3J_{HH}$ 6.6, $^3J_{PH}$ 13.2], 3.83 and 3.91 two m {4H, $[(CH_3)_2CH\underline{CH_2}O]_2P$, $^3J_{HH}$ 6.0}. ^{31}P NMR spectrm, δ_P, ppm: 94.9 and 92.5 in 1.5:1.0 ratio. Mass spectrum (CI), *m/z* (I_{rel}, %): 355.3 (17) $[M + H]^+$. Found, %: C 55.35; H 9.73; P 8.47; S 17.82. $C_{16}H_{35}O_2PS_2$. Calculated, %: C 54.20; H 9.98; P 8.74; S 18.05. *M* 354.3.

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