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LETTERS TO THE EDITOR

Reaction of *O,O*-Diethyl Phosphorodithioic Acid with Hexadec-1-ene. Catalysis with Zinc Chloride

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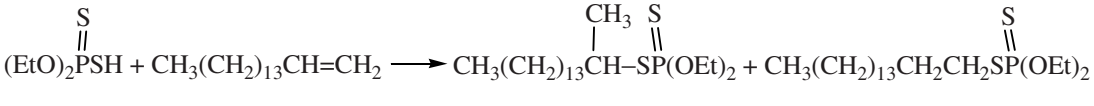
As shown earlier [1–6] the regiochemistry of addition of *O,O*-diethyl phosphorodithioic acid (**I**) to unsymmetrical alkenes, i.e. formation of Markovnikov or anti-Markovnikov products, is defined by the nature of substituents at the double bond and, in some cases, on the presence or absence of catalysts in the reaction mixture. Alkenes with electron-acceptor groups at the double bond take up dithio acid **I** under base catalysis or without it occurs against Markovnikov's rule [2]. The reactions of unactivated aliphatic alkenes (oct-1- and oct-2-enes, cyclohexene, diisobutylene) at 100°C give rise to Markovnikov products [4–6]. Phos-phorodithioc acids not been subjected to special purification with aqueous sodium carbonate [4–6] contain an admixture of phosphorus sulfide (P_4S_{10}) which can destroy peroxide admixtures in commercial alkenes and thus favors formation of Markovnikov products. At the same time, cumene hydroperoxide additive in a mixture of dithio acid **I** and oct-1-ene favors an anti-Markovnikov reaction pathway. The reaction of commercial oct-1-ene (with a natural content of per-oxides) with purified dithio acid **I** provides a mixture of two isomeric Markovnikov adducts [6].

Reported reactions were all performed under fairly rigid conditions, which, in the case of phosphorus dithio acid derivatives, frequently accompanied by rearrangements and side reactions. It was interesting to study these reactions under milder conditions to exclude secondary processes and also to try Lewis acids as catalysts for more facile reactions. To our knowledge, such approach has never been applied in the above-described reactions.

In this connection we studied reaction of dithio acid **I** with hexadec-1-ene (**II**) at about 20ºC in the absence of catalysts and solvents. After 50 days, the ^{31}P NMR spectrum contained four signals. The signals of two adducts are located at δ_P 94.2 (integral intensity 74%) and 90.1 ppm (11%), and the signal of starting acid **I,** at δ_P 84.4 ppm (6%). The signal at δ_P 63.1 ppm (9%) can be assigned to a Pishchimuka rearrangement product [7]. The latter product and and acid **I** are easily removable from the mixture by washing with water. *O,O*-Diethyl hexadecyl phosphorodithioates as a mixture of isomers IIIa and IIIb were isolated by column chromatography. The ^{31}P NMR spectrum of the mixture contained two signals at δ_P 94.2 (93%) and 90.1 ppm (7%). Both signals appear in a region characteristic of trialkyl phosphorodithioates with a thionic sulfur atom [7].



I **II** **IIIa** **IIIb**

The regiochemistry of the addition of acid **I** to alkene **II** was established by an analysis of the ^{1}H NMR spectra of the isolated products. In the ^{1}H NMR spectrum of compound **IIIa,** the PSC*H*$(CH_3)CH_2$ methine proton should give a doublet of triplets of quartets in the region of δ 3.0–3.5 ppm, whereas the PC*H*$_2$CH$_2$ methylene protons of adduct **IIIb** should appear as a doublet of triplets at δ 2.5–3.0 ppm. Actually, in the ^{1}H NMR spectrum of the isolated isomeric mixture shows the corresponding signals at δ 3.31 and 2.87 ppm (6 : 1). Based on the ^{1}H NMR spectra we can conclude that the major signal at δ_P 94.2 ppm in the ^{31}P NMR spectrum belongs to Markovnikov adduct **IIIa**, while the minor signal at δ_P 90.1 ppm belongs to isomer **IIIb**. Thus, phosphorodithioic acids prefer to add to hexadec-1-ene according to the Markovnikov rule.

In the presence of anhydrous $ZnCl_2$ (1 wt %), the reaction rate increases essentially. According to the ^{1}H and ^{31}P NMR spectra, products **IIIa** and **IIIb** are formed in the same ratio as without a catalyst, at room temperature for 1 day.

***O,O*-Diethyl hexadecyl phosphorodithioates IIIa, IIIb.** A mixture of 5.0 g of acid **I** and 6.0 g of alkene **II** was left to stand at ~20°C for 50 days, diluted with 10 ml of Et_2O, and washed with three 10-ml portions of water. The organic layer was separated and dried over $CaCl_2$. The drying agent was removed, and the filtrate was evaporated at 40ºC first for 1 h under a vacuum of 0.5 mm Hg and then 1 h under a vacuum of 0.006 mm Hg to obtain 7.7 g (70%) of a mixture of compounds **IIIa** and **IIIb**. Part of the resulting material (4.0 g) was subjected to column chromatography on silica gel (eluent petroleum ether, bp 70–100°C) to isolate 2.3 g of a mixture of compounds **IIIa** and **IIIb**. R_f 0.07, 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 [$\delta_{as}(CH_3)$, $\delta_s(CH_2)$,]; 1389 m [$\delta(CH_3)$]; 1019 vs [ν(P)O–C]; 958 s [ν(OC–C)]; 662 m [ν(P=S)]; 599 w, br [ν(P–S)]. ^{1}H NMR spectrum, $CDCl_3$, δ, ppm, (*J*, Hz): 0.87 t (3H, C*H*$_3$CH$_2$CH$_2$, $^3J_{HH}$ 6.8); 1.25 br.s (12H, CC*H*$_2$C); 1.35 t [6H, (C*H*$_3$CH$_2$O)$_2$P, $^3J_{HH}$ 7.2]; 1.39 d [3H, C*H*$_3$CHSP, $^3J_{HH}$ 6.8 from **IIIa**]; 1.59 (m, 2H, PSCHCH$_2$C*H*$_2$); 1.66 m (2H, PSCHC*H*$_2$C); 2.87 d.t (2H, PSC*H*$_2$CH$_2$, $^3J_{HH}$ 7.7, $^3J_{PH}$ 23.9 from **IIIb**]; 3.31 d.t.q (1H, PSC*H*(CH_3) CH$_2$, $^3J_{HH}$ 6.9, $^3J_{HH}$ 6.9, $^3J_{PH}$ 13.8 from **IIIa**]; δ_1 4.11 m and δ_2 m [4H, (CH$_3$C*H*$_2$O)$_2$P, $^3J_{HH}$ 7.2]. ^{13}C NMR spectrum (shape of the ^{13}C–{^{1}H} signal), δ, ppm, (*J*, Hz): s (q) [*C*H$_3$CH$_2$CH$_2$, $^1J_{HC}$ 124.4]; 1.51 d (d.q) (*C*H$_3$CH$_2$OP, $^3J_{PC}$ 8.4, $^1J_{HC}$ 127.4); 22.7 s (t) (CH$_3$*C*H$_2$CH$_2$, $^1J_{HC}$ 124.4); 27.1 s (t) (*C*H$_2$CH$_2$CH$_2$SP, $^1J_{HC}$ 121.4); 29.7 br.s (t) (C*C*H$_2$C, $^1J_{HC}$ 125.0]; 32.0 s (t) (CH$_3$CH$_2$*C*H$_2$, $^1J_{HC}$ 125.0); 38.2 d (t.d) (PSCH*C*H$_2$, $^1J_{HC}$ 128.2, $^3J_{PC}$ 4.0 from **IIIa**); 41.0 d (d.d) (PSCH$_2$*C*H$_2$CH$_2$, $^3J_{PC}$ 5.0 from **IIIb**); 41.3 d (d.d) (PS*C*H$_2$CH$_2$, $^3J_{PC}$ 5.1 from **IIIb**); 46.3 d (d.d) (PS*C*H $(CH_3)CH_2$, $^1J_{HC}$ 144.2, $^3J_{PC}$ 3.6 from **IIIa**); δ_1 63.68 two d (two t.d) [(CH$_3$*C*H$_2$O)$_2$P, $^1J_{HC}$ 147.8, $^3J_{PC}$ 4.8) and δ_2 63.72 two d (two t.d) [(CH$_3$*C*H$_2$O)$_2$P, $^1J_{HC}$ 147.8, $^3J_{PC}$ 5.4]. Mass spectrum (60 eV), *m/z* (I_{rel}, %): 410.3 $[M]^{+\cdot}$ (3). 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. *M* 410.3.

The IR spectra were recorded on a Bruker Vector 22 Fourier spectrometer (film, KBr). The ^{1}H and the ^{13}C NMR spectra were obtained on an Avance-600 spectrometer (600 and 100.6 MHz, respectively) in $CDCl_3$. The ^{31}P spectra were measured on a Bruker CXP-100 instrument (36.5 MHz) against external 85% H_3PO_4. The electron impact mass spectra were measured on a Finnigan MAT-212 instrument.

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