

SHORT
COMMUNICATIONSThiophosphorylation of Commercial C₁₆–C₁₈ Olefins
with *O,O'*-(3,6-Dioxaoctane-1,8-diyl)
Bis(hydrogen 4-methoxyphenylphosphonodithioate)I. S. Nizamov^{a,b}, Ya. E. Popovich^b, I. D. Nizamov^c, G. T. Gabdullina^c, and R. A. Cherkasov^a^a Kazan State University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia
e-mail: Ilyas.Nizamov@ksu.ru; nizamov@iopc.knc.ru^b Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences,
ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia^c Tatar State Humanitarian Pedagogical University, ul. Tatarstana 2, Kazan, 420021 Tatarstan, Russia

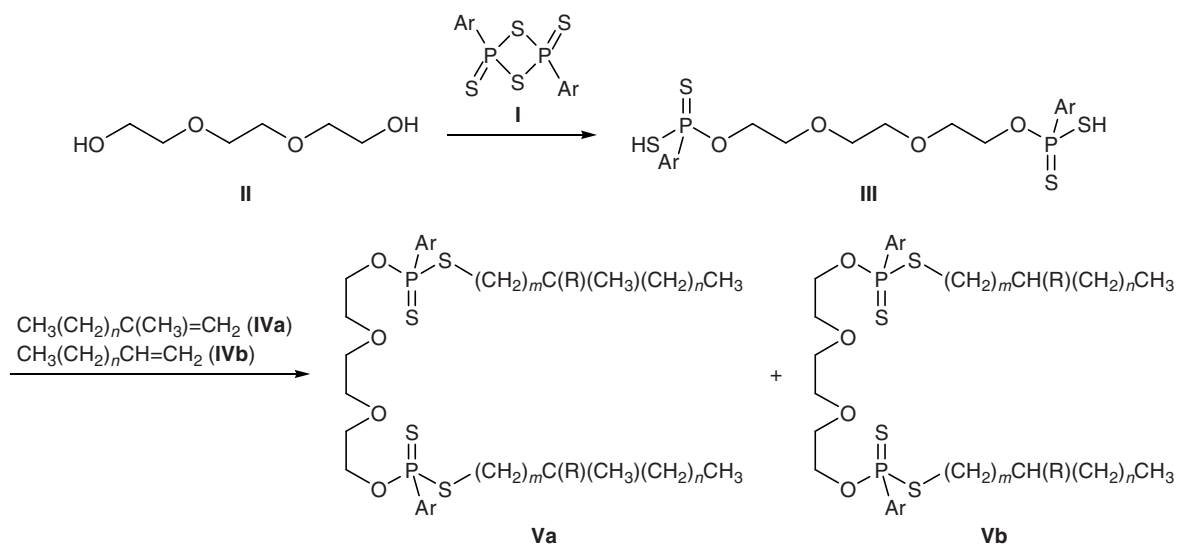
Received June 11, 2007

DOI: 10.1134/S1070428007120238

Phosphorus-and-sulfur-containing organic compounds having a C–P(=S)SR fragment (where R is a long-chain hydrocarbon radical) are used as lubricant additives, corrosion inhibitors, surfactants, detergents, emulgators, and pesticides [1–7]. Most procedures for the synthesis of these compounds are based on reactions of *O,O*-dialkyl phosphorodithioates with unactivated alkenes [2–7]. Unusual thiophosphorylating agents are bis-dithiophosphonic acids that are also capable of adding to alkenes. Bis(methylphosphonodithioic acids) were synthesized by reaction of 2,4-dimethyl-1,3,2λ⁵,4λ⁵-dithiadiphosphetane 2,4-disulfide with

glycols in diethyl ether [8]. However, attempts to synthesize pure bis-dithiophosphonic acids having an aryl group on the phosphorus were unsuccessful [9–11].

We have found that 2,4-bis(4-methoxyphenyl)-1,3,2λ⁵,4λ⁵-dithiadiphosphetane 2,4-disulfide (**I**, Lawesson's reagent) reacts with an equimolar amount of triethylene glycol (**II**) in anhydrous benzene at 50°C (reaction time 1 h) to give *O,O'*-(3,6-dioxaoctane-1,8-diyl) bis(hydrogen 4-methoxyphenylphosphonodithioate) (**III**). The latter adds to C₁₆–C₁₈ olefins **IVa–IVc** [a mixture of isomeric terminal olefins **IVa** having a methyl group in the 2-position, unbranched terminal

Ar = 4-MeOC₆H₄; **IV**, *n* = 12, 14 (**a**); 13, 15 (**b**); **V**, *n* = 13, 15 (**a**); 15, 17 (**b**); R = Me, *m* = 0; R = H, *m* = 1.

olefins **IVb**, and internal olefins **IVc** of the general formula CH₃(CH₂)_kCH=CH(CH₂)_mCH₃] in the presence of ZnCl₂ (60°C, 2 h), yielding the corresponding 1:2 adducts, *O,O'*-(3,6-dioxaoctane-1,8-diyl) *S,S'*-dialkyl bis(4-methoxyphenylphosphonodithioates) **Va** and **Vb**. Adducts **Va** and **Vb** were obtained as mixtures of homologs and isomers derived from isomeric terminal olefins **IVa** and **IVb** having C₁₆ and C₁₈ hydrocarbon chains both according and contrary to the Markovnikov rule. Almost no adducts corresponding to internal olefins **IVc** were formed in the reaction with bis-acid **III** under the above conditions.

***O,O'*-(3,6-Dioxaoctane-1,8-diyl) bis(hydrogen 4-methoxyphenylphosphonodithioate) (III)**. A suspension of 12.0 g (29.7 mmol) of Lawesson's reagent (**I**) and 4.4 g (29.7 mmol) of triethylene glycol (**II**) in 20 ml of benzene was stirred for 1 h at 50°C. The mixture was filtered, and the filtrate was evaporated at 40°C for 1 h at a residual pressure of 0.5 mm and for 1 h at a residual pressure of 0.06 mm. The residue was 10.0 g (61%) of compound **III**, *n*_D²⁰ = 1.5989. IR spectrum, *v*, cm⁻¹: 3050 (C–H_{arom}); 2941, 2884 (C–H_{aliph}); 2500 (SH, free); 2475 (SH, assoc.); 1595, 1569, 1501 (C=C_{arom}); 1259 (CH₂); 1116, 1026, 961 (C–O, C–O–C); 681, 663 (P=S); 620 (C–S); 534 (P–S). ¹H NMR spectrum, *δ*, ppm: 2.63 m (2H, PSH), 3.70 s (4H, COCH₂CH₂OC), 3.78 s (6H, CH₃O), 3.82 t (4H, OCH₂CH₂OP, ³J_{HH} = 7.8 Hz), 3.85 d.t (4H, CH₂OP, ³J_{HH} = 7.8, ³J_{PH} = 11.2 Hz), 6.98 d.d (4H, *m*-H, ³J_{HH} = 9.2, ⁴J_{PH} = 3.1 Hz), 7.93 d.d (4H, *o*-H, ³J_{HH} = 9.2, ³J_{PH} = 15.9 Hz). ³¹P NMR spectrum: *δ*_P 87.2 ppm. Found, %: C 43.24; H 5.15; P 11.35; S 23.29. C₂₀H₂₈O₆P₂S₄. Calculated, %: C 43.31; H 5.10; P 11.18; S 23.08.

***O,O'*-(3,6-Dioxaoctane-1,8-diyl) *S,S'*-dialkyl bis(4-methoxyphenylphosphonodithioates) Va and Vb**. A mixture of 5.3 g (9.6 mmol) of compound **III**, 4.6 g (19.3 mmol) of olefin mixture **IVa–IVc**, and 0.07 g (0.5 mmol, 1.3 wt %) of ZnCl₂ was heated for 2 h at 60°C under stirring. The mixture was diluted with 10 ml of diethyl ether and washed with water (3 × 10 ml), the organic phase was separated and dried over CaCl₂, the drying agent was filtered off, and the filtrate was evaporated at 40°C under reduced pressure (1 h at 0.5 mm and 1 h at 0.06 mm). The residue was 3.9 g (39%) of compounds **Va** and **Vb** (a mixture of homologs and isomers); a 2.6-g portion of the product was purified by column chromatography on silica gel using methylene chloride as eluent (*R*_f 0.84, CH₂Cl₂). IR spectrum, *v*, cm⁻¹: 3076 (C–H_{arom}); 2921, 2820 (C–H_{aliph}); 1596, 1501 (C=C_{arom}); 1464 (*δ*_{as}CH₃); 1257

(CH₂); 1114, 1031, 963 (C–O, C–O–C); 689, 663 (P=S); 534 (P–S). ¹H NMR spectrum, *δ*, ppm: 0.90 t (6H, CH₃, ³J_{HH} = 7.1 Hz), 1.28 m (CH₂), 1.38 d (6H, CH₃CHS, ³J_{HH} = 6.8 Hz), 1.52 m (4H, CH₃CH₂), 1.65 m (4H, CH₂CS), 2.63 m (4H, CH₂SP), 3.38 m (2H, CHS), 3.67 s (4H, COCH₂CH₂OC), 3.76 s (6H, CH₃O), 3.82 m (4H, OCH₂CH₂OP), 3.87 m (4H, CH₂OP), 6.96 m (4H, *m*-H), 7.92 m (4H, *o*-H). ³¹P NMR spectrum, *δ*, ppm: 90.5, 91.6 (1:1). Found, %: C 61.90; H 9.73; P 5.66; S 12.77. C₅₂H₉₂O₆P₂S₄, C₅₆H₁₀₀O₆P₂S₄. Calculated, %: C 62.23, 63.47; H 9.27, 9.54; P 6.18, 5.85; S 12.75, 12.08.

The IR spectra were recorded on a Bruker Vector 22 spectrometer with Fourier transform from films (neat) placed between KBr plates. The ¹H NMR spectra were measured on a Bruker Avance-600 spectrometer (600.13 MHz) from solutions in CDCl₃. The ³¹P NMR spectra were obtained on a Bruker CXP-100 instrument (36.5 MHz) from solutions in benzene-*d*₆ relative to 85% H₃PO₄.

REFERENCES

1. Corbridge, D.E., *Phosphorus. An Outline of Its Chemistry, Biochemistry, and Technology*, Amsterdam: Elsevier, 1980, 2nd ed.
2. Norman, G.R., LeSuer, W.M., and Mastin, T.W., *J. Am. Chem. Soc.*, 1952, vol. 74, p. 161.
3. Bacon, W.E. and LeSuer, W.M., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 670.
4. Norman, G.R., LeSuer, W.M., and Mastin, T.W., US Patent no. 2802856, 1957; *Chem. Abstr.*, 1958, vol. 52, p. 1201.
5. Bacon, W.E., Meinhardt, N.A., and LeSuer, W.M., *J. Org. Chem.*, 1960, vol. 25, p. 1993.
6. Loughran, G.A. and Hook, E.O., US Patent no. 2794821, 1953; *Ref. Zh., Khim.*, 1959, no. 16413P.
7. Pudovik, S.T., Sungatova, L.N., Kachalova, T.N., Kharlampidi, Kh.E., Surovtsev, A.A., Potanova, I.M., Safin, D.Kh., Khisaev, R.Sh., Ziyatdinov, A.Sh., and Ryzanov, Yu.I., Russian Patent no. 2194092, 2001.
8. Kutyrev, G.A., Korolev, O.S., Safiullina, N.R., Yarkova, E.G., Lebedeva, O.E., Cherkasov, R.A., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1986, vol. 56, p. 1227.
9. Shabana, R., Osman, F.H., and Atrees, S.S., *Tetrahedron*, 1993, vol. 49, p. 1271.
10. He, L.-N. Li, K., Luo, Y.-P., Liu, X.-P., Ding, M.-W., Zhuo, Q.-C., Wu, T.-J., and Cai, F., *Phosphorus, Sulfur Silicon Relat. Elem.*, 2000, vol. 156, p. 173.
11. Kutyrev, G.A., Korolev, O.S., Yarkova, E.G., Cherkasov, R.A., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1986, vol. 56, p. 1233.