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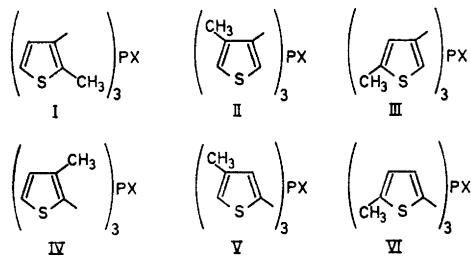
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## Preparation of Methyl-substituted Trithienylphosphines and Their Sulfides

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In connection with current studies of nuclear magnetic resonance spectra of aromatic and heteroaromatic phosphine derivatives<sup>1</sup> it was of interest to obtain information concerning the signs and magnitudes of the expected four-, five-, and six-bond methyl proton-ring phosphorus long-range spin-spin coupling constants in phosphorus substituted methylthiophenes. In this paper the preparations of the six hitherto unknown isomeric tri-(methylthienyl)-phosphines (Ia–VIa) and their sulfides (Ib–VIb) are described.



a: X=lone pair  
b: X=S

The phosphines were prepared in 28–66% yields from the corresponding methylthienyllithium derivatives, obtained either by low-temperature metal-halogen interconversion of the methylbromothiophenes (compounds Ia–IVa) or by direct metallation of the methylthiophenes (com-

pounds Va and VIa) with butyllithium, followed by reaction with phosphorus tri-bromide. The phosphines were converted to their sulfides in quantitative yields by reaction with elementary sulfur in solutions of methanol or chloroform. Structures and purities of the isolated compounds were checked by <sup>1</sup>H NMR spectroscopy, mass spectrometry, or by microanalyses. All compounds were obtained in a pure state, with the exception of the mixture of 4-methyl-2-thienyllithium (ca. 83%) and 3-methyl-2-thienyllithium (ca. 17%) resulting from metallation of 3-methylthiophene with butyllithium<sup>2</sup> which only allowed the isolation of tri-(4-methyl-2-thienyl)-phosphine (Va) as an oily mixture (ca. 54%) with some of the isomers di-(4-methyl-2-thienyl)-3-methyl-2-thienyl phosphine (ca. 40%) and di-(3-methyl-2-thienyl)-4-methyl-2-thienyl phosphine (ca. 6%) as deduced from <sup>1</sup>H NMR spectra. Separation by means of gas chromatography or thin layer chromatography could not be achieved. Attempts to prepare (Va) in a pure state by other synthetic routes were not carried out as the complete analysis of its <sup>1</sup>H NMR spectrum<sup>3</sup> could be performed on the mixture of isomers. However, the corresponding sulfide (Vb), prepared from the isomeric mixture, could easily be obtained in a pure crystalline state by fractional recrystallization. In the preparations of the phosphines (Ia–IIIa) low-boiling products, later shown<sup>4</sup> to result from a thiophene ring-opening reaction, were obtained.

*Experimental.* Boiling and melting points are uncorrected.

*Starting materials.* 2- and 3-Methylthiophene were commercially available (Schuchardt, Munich) and used without further purification. 2-Methyl-3-bromothiophene was prepared according to Gronowitz *et al.*<sup>5</sup> using dimethyl sulfate instead of methyl *p*-toluenesulfonate, b.p. 55°/9 mmHg (b.p. 56–58°/10 mmHg),<sup>5</sup> yield 88% (84%).<sup>5</sup> 4-Methyl-3-bromothiophene was obtained from 4-bromo-3-thienyllithium<sup>6</sup> and dimethyl sulfate, b.p. 58–60°/8–9 mmHg (b.p. 181–184°/770 mmHg),<sup>5</sup> yield 90%. 2-Methyl-4-bromothiophene was obtained from 4-bromo-2-thienyllithium<sup>6</sup> and dimethyl sulfate (at –70°) as an isomer-pure product (> 98%) which is inconsistent with the observations of Gronowitz and Frostling;<sup>7</sup> b.p. 58–59°/9 mmHg (b.p. 61–62°/11 mmHg),<sup>7</sup> yield 81%. 3-Methyl-2-bromothiophene was prepared by the method of Steinkopf and Jacob.<sup>8</sup>

*Tri-(2-methyl-3-thienyl)-phosphine (Ia)*. 2-Methyl-3-thienyllithium was prepared from 66.8 g (0.38 mol) of 2-methyl-3-bromothiophene in 125 ml of anhydrous ether and 370 ml of 0.95 N (0.35 mol) butyllithium at  $-70^{\circ}$ . 21.6 g (0.08 mol) of phosphorus tribromide in 50 ml of anhydrous ether were added dropwise to the reaction mixture at  $-70^{\circ}$  over 30 min. The reaction mixture was stirred overnight whilst the cooling bath was allowed to reach room temperature. After hydrolysis with a solution of ammonium chloride and dilute hydrochloric acid at  $0^{\circ}$  the organic layer was separated, washed with sodium bicarbonate solution, and dried. Fractionation *in vacuo* gave a fraction with b.p.  $50-65^{\circ}/0.15$  mmHg (14.5 g)<sup>4</sup> and the phosphine as a red, viscous oil with b.p.  $158-162^{\circ}/0.15$  mmHg, yield 16.5 g (64%). On standing overnight the oil crystallized; recrystallization from methanol gave fine, white crystals, m.p.  $81-83^{\circ}$ . (Found: C 55.82; H 4.64. Calc.: C 55.87; H 4.69).

*Tri-(2-methyl-3-thienyl)-phosphine sulfide (Ib)*. 1.5 g (4.65 mmol) of the phosphine (Ia) in 50 ml of methanol were refluxed overnight with a slight excess of sulfur. After removal of the solvent the crystals were dissolved in benzene and re-precipitated with petroleum ether in order to remove possible excess of sulfur. A final recrystallization from methanol gave white crystals in quantitative yield, m.p.  $117-119^{\circ}$ . (Found: C 50.99; H 4.37. Calc.: C 50.82; H 4.26).

*Tri-(4-methyl-3-thienyl)-phosphine (IIa)*, very viscous, orange-red oil, b.p.  $164-170^{\circ}/0.15$  mmHg, yield 54%. White crystals from methanol, m.p.  $91-93^{\circ}$ .

*Tri-(4-methyl-3-thienyl)-phosphine sulfide (IIb)*, white crystals, m.p.  $204-206^{\circ}$ , from benzene and petroleum ether.

*Tri-(5-methyl-3-thienyl)-phosphine (IIIa)*, very viscous, dark-red oil, b.p.  $165-185^{\circ}/0.15$  mmHg, yield 50%. Purification of the oil (900 mg) by preparative thin-layer chromatography (silica gel, 5% ether in petroleum ether) gave the pure phosphine as a light-yellow oil (810 mg). On prolonged standing at  $-20^{\circ}$  the pure phosphine crystallizes; however, the crystals melt at room temperature.

*Tri-(5-methyl-3-thienyl)-phosphine sulfide (IIIb)*, white needles, m.p.  $144-145^{\circ}$ , from benzene and petroleum ether.

*Tri-(3-methyl-2-thienyl)-phosphine (IVa)*. The light-yellow, viscous oil, b.p.  $170-180^{\circ}/0.2$  mmHg, isolated from the reaction mixture, consisted of about 70% of the phosphine (IVa) (yield 28%) and 30% of butyl di-(3-methyl-2-thienyl)-phosphine oxide (yield 13%); the

phosphine oxide was formed by air oxidation of butyl di-(3-methyl-2-thienyl)-phosphine resulting from incomplete consumption of butyllithium. Separation of the products by preparative thin-layer chromatography (silica gel, 5% ether in petroleum ether) gave the phosphine (IVa) as white crystals, m.p.  $75-77^{\circ}$ , and the phosphine oxide as a light-yellow oil in pure states.

*Tri-(3-methyl-2-thienyl)-phosphine sulfide (IVb)*, white crystals, m.p.  $133-135^{\circ}$ , from methanol.

*Tri-(4-methyl-2-thienyl)-phosphine (Va)*, light-yellow oil, b.p.  $172-180^{\circ}/0.15$  mmHg, yield 73%, contaminated with the isomers di-(4-methyl-2-thienyl)-3-methyl-2-thienyl phosphine (ca. 40%) and di-(3-methyl-2-thienyl)-4-methyl-2-thienyl phosphine (ca. 6%). Separation of the isomers was unsuccessful.

*Tri-(4-methyl-2-thienyl)-phosphine sulfide (Vb)*, obtained from the above mixture of isomers in a pure state after three re-precipitations from benzene with petroleum ether and finally recrystallization from ethanol. White crystals, m.p.  $170-172^{\circ}$ .

*Tri-(5-methyl-2-thienyl)-phosphine (VIa)*, dark-red oil, b.p.  $184-191^{\circ}/0.2$  mmHg, yield 66%. White crystals, m.p.  $48-49^{\circ}$ , from methanol.

*Tri-(5-methyl-2-thienyl)-phosphine sulfide (VIb)*, white crystals, m.p.  $136-137^{\circ}$ , from benzene and petroleum ether.

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