Facile Synthesis of Fused Benzo-1,2,3-thiadiphospholes,† a New Heterocyclic System

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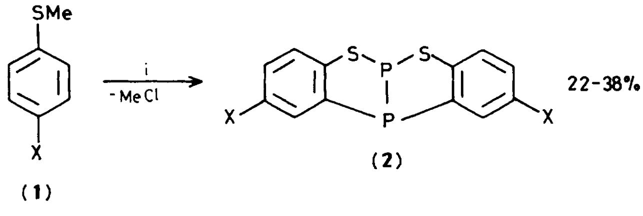
The reaction of thioanisole with PCl_3 and $AlCl_3$ leads to the title compound; its structural characterization is based on spectroscopic studies and confirmed by a single crystal *X*-ray diffraction of its dimethyl derivative.

The Friedel–Crafts reaction of aromatic compounds with PCl_3–$AlCl_3$ is a well known[1,2] method for preparing aryl phosphorus derivatives in which new C–P bonds are formed.

During our recent studies[3] on the reactivity and use of PCl_3 in organic synthesis we have found the surprising result that fused benzo-1,2,3-thiadiphospholes (**2**) are formed by reaction of (**1**) with PCl_3 and $AlCl_3$ (see Scheme 1). In this synthesis the breaking of the S–Me bond and the concomitant formation of two C–P, two S–P, and one P–P bonds occur in a



(**1**)

(**2**)

a; X = H
b; X = Me

Scheme 1. *Reagents and conditions*: i, $3PCl_3$, 3/4 $AlCl_3$, reflux.

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† [1,2,3]Benzothiadiphospholo[2,3-*b*][1,2,3]benzothiadiphosphole.

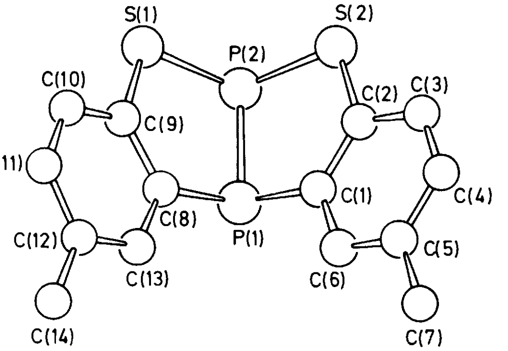

Figure 1. *X*-Ray structure of compound (**2b**). Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.234(2); P(2)–S(2) 2.135(2); P(2)–S(1) 2.123(2); P(1)–C(8) 1.825(6); P(1)–C(1) 1.835(6); C(2)–S(2) 1.779(6); C(9)–S(1) 1.773(6); C(8)–P(1)–P(2) 98.1(2); P(2)–P(1)–C(1) 97.6(2); S(1)–P(2)–S(2) 107.0(1); P(1)–P(2)–S(1) 96.6(1); P(1)–P(2)–S(2) 97.0(1); P(2)–S(1)–C(9) 102.7(2); P(2)–S(2)–C(2) 102.2(2).

one-pot reaction. A typical procedure is as follows. Thioanisole (**1a** or **b**) (20 mmol) was added dropwise to a suspension of $AlCl_3$ (15 mmol) in PCl_3 (60 mmol) and the mixture was heated under reflux for about 2 h. The reaction was monitored by t.l.c. (light petroleum as eluant) and g.l.c.–mass spectrometry. After evaporation of the excess of PCl_3 *in vacuo*, the crude product was purified by simple filtration on a Florisil column with cyclohexane–CH_2Cl_2 (8:2) as eluant. Compounds (**2a**) (R_F 0.15, m.p. 92—94 °C) and (**2b**) (R_F 0.16, m.p. 157—159 °C) were obtained as white crystals from light petroleum ether and CH_2Cl_2 in 22 and 38% yields, respectively. The yields are highly dependent on the molar ratios of the reagents. When the reaction was carried out using benzenethiol, only a trace amount of compound (**2a**) was obtained. The structures of (**2**) were assigned on the basis of analytical[‡] and spectroscopic[§] data. The mass spectrum exhibits molecular ion peaks at *m/z* 278, 279, 280, 281 for (**2a**) and *m/z* 306, 307, 308, 309 for (**2b**) with the isotopic distribution of two sulphur atoms. In addition, peaks at *m/z* 215 ($M-63$, 100%) 183, 139, 107, 77, 63 for (**2a**) and *m/z* 243 ($M-63$, 100%) 211, 153, 121, 77, 63 for (**2b**) are detected.

In the $^{31}P\{^1H\}$ n.m.r. spectrum the pattern expected for an AB spin system is observed: for (**2a**), δ (p.p.m.) (P^1) +85.1 δ (P^2) +65.7; $J_{P(1)P(2)}$ 212 Hz; for (**2b**), δ (p.p.m. (P^1) +88.3 δ (P^2) +65.4, $J_{P(1)P(2)}$ 212 Hz. Analogous assignments have been reported[4] for related compounds. The ^1H n.m.r. spectrum is in agreement with the proposed structure and in particular shows the following signals: for (**2a**), δ (CH=CP) 7.63, 't', $J_{HH'} \simeq J_{HP} \simeq 8.0$ Hz; δ (CH=CS) 7.36, d, $J_{HH'}$ 7.5 Hz; for (**2b**), δ (CH=CP) 7.41, d, J_{HP} 8.0 Hz, δ (CH=CS) 7.25, d, J_{HH} 7.5 Hz.

An *X*-ray crystal structure determination[¶] of (**2b**) was undertaken in order to confirm its structure unambiguously. Compound (**2b**) exhibits a 'butterfly' arrangement of two benzothiadiphosphole systems joined along the P–P bond (see Figure 1).

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[‡] Satisfactory elemental analyses were obtained for compounds (**2**). Mass spectrum, M^+, calc. for $C_{12}H_8P_2S_2$ *m/z* 277.9543, found 277.9546; calc. for $C_{14}H_{12}P_2S_2$ *m/z* 305.9855, found 305.9857; M.p.s are uncorrected.

[§] ^{31}P and ^1H n.m.r. spectra were obtained at 121.5 and 300 MHz, respectively, on a Brucher CXP 300, with 85% H_3PO_4 (external) and Me_4Si (internal) as references; downfield shifts are positive.

[¶] *Crystal data* for (**2b**): $C_{14}H_{12}P_2S_2$; triclinic; space group $P\bar{1}$; a = 9.117(2); b = 10.683(4); c = 7.506(7) Å; α = 95.80(6); β = 93.77(5); γ = 75.06(2)°; U = 702.2 Å^3; Z = 2; D_c = 1.45 g cm^{-3}; Mo-K_α radiation (λ = 0.7107 Å); μ = 5.2 g cm^{-1}; $F(000)$ = 316.0; the intensity data were collected by a CAD4 diffractometer using ω/2θ scan; range 2.5° $\leqslant \theta \leqslant$ 25°. Of 1540 indedependent reflections, 122 having $I < 2.5\,\sigma(I)$ were considered unobserved. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares using the SHELX-76 program package (G. M. Sheldrick). The H atoms were calculated geometrically, but not refined. The final R value was 0.051. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.