

Formation of Fused 1,3-Benzothiaphosphole† from Fused 1,2,3-Benzothiadiphospholes by a Simple Phosphorus–Carbon Exchange

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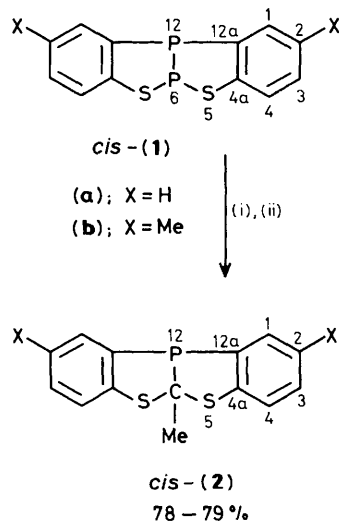
Treatment of fused 1,2,3-benzothiadiphospholes with acetyl chloride, in the presence of AlCl_3 , leads to fused 1,3-benzothiaphospholes, in which an unexpected phosphorus–carbon exchange has occurred; a single crystal X-ray diffraction of the dimethyl derivative of this new heterocycle confirmed its structure and showed the *cis*-configuration between the phosphorus lone pair and the 6-substituent.

We reported previously^{1,2} the highly stereoselective synthesis of *cis*-[1,2,3]benzothiadiphospholo[2,3-*b*][1,2,3]benzothiadiphosphole, a new fused heterocyclic system containing the S–P–P unit, formed by reaction of methyl phenyl sulphide with PCl_3 and AlCl_3 . During the study of the reactivity of this new compound we considered the possibility of exploiting it in order to synthesize other phosphorus and sulphur containing heterocycles. Exploring the reaction of (1) with acetyl chloride in the presence of AlCl_3 , we found the unexpected formation of (2) in good yields (Scheme 1). The peculiarity of the reaction should be noted; replacement of the phosphorus atom in the 6-position with the carbonylic carbon atom of acetyl chloride, in a simple one-pot reaction and under mild conditions. The reaction was monitored by t.l.c. (light petroleum as eluant) and g.l.c.–mass spectrometry. The product was separated by filtration on a Florisil column with cyclohexane/ CH_2Cl_2 9:1 as eluant. Compounds (2a) (R_F 0.13, m.p. 80–83°C) and (2b) (R_F 0.14, m.p. 160–163°C) were obtained as white crystals from light petroleum and CH_2Cl_2 in 78 and 79% yields, respectively. The structure of (2) was assigned essentially on the basis of ^1H , ^{13}C , and $^{31}\text{P}\{^1\text{H}\}$ n.m.r.‡ and mass spectrometry. In particular the mass

spectrum exhibits molecular ion peaks at m/z 274, 275, 276, 277 for (2a) and 302, 303, 304, 305 for (2b) with the isotopic distribution of two sulphur atoms, and a characteristic loss of 59 a.m.u. corresponding to a S–C–Me fragment is detected.

The ^1H n.m.r. spectrum shows a doublet at δ 2.2 (J_{HP} 16.4 Hz) which can be ascribed to the 6-methyl substituent. The ^{13}C n.m.r. data are in agreement with the proposed structure and in particular C(6) resonates at δ 71 with J_{CP} 23.6 Hz, and $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra show the phosphorus signals at 63 p.p.m.

The X-ray crystal structure determination§ of (2b) (Figure



Scheme 1. Reagents and conditions: (i), $\text{MeCOCl}/\text{AlCl}_3$, 1,2-dichloroethane, 5–10°C, (ii) room temp., 20 min.

† *cis*-6-Methyl[1,3]benzothiaphospholo[2,3-*b*][1,3]benzothiaphosphole.

‡ ^1H , ^{13}C , and $^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectra in CDCl_3 solutions were obtained with Me_4Si (internal) and 85% H_3PO_4 (external) as references: downfield shifts are positive. M.p.s. are uncorrected. Satisfactory elemental analyses were obtained for compounds (2).

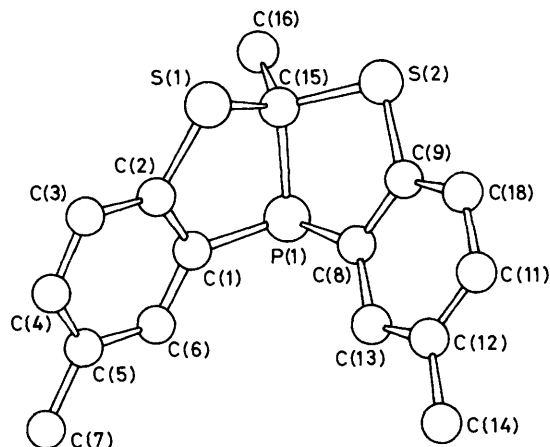


Figure 1. X-Ray structure of compound (2b). Selected bond lengths (Å) and angles (°): P(1)–C(15) 1.898(3); C(15)–S(2) 1.840(3); C(15)–S(1) 1.869(3); P(1)–C(8) 1.825(3); P(1)–C(1) 1.812(3); C(2)–S(1) 1.767(3); C(9)–S(2) 1.766(3); C(8)–P(1)–C(15) 93.9(1); C(15)–P(1)–C(1) 95.9(1); S(2)–C(15)–S(1) 108.1(2); P(1)–C(15)–S(2) 104.6(2); P(1)–C(15)–S(1) 106.7(1); C(15)–S(2)–C(9) 96.8(1); C(15)–S(1)–C(2) 97.7(1); S(1)–C(15)–C(16) 112.0(3); S(2)–C(15)–C(16) 110.1(2); P(1)–C(15)–C(16) 114.9(3).

§ *Crystal data* for (2b): $\text{C}_{16}\text{H}_{15}\text{PS}_2$; $M = 299.35$; monoclinic; space group $P2_1/c$; $a = 7.209(8)$; $b = 24.240(3)$; $c = 8.638(8)$ Å, $\beta = 92.00(3)^\circ$; $U = 1508.6$ Å³; $Z = 4$; $D_c = 1.32$ g cm⁻³; Mo- K_α radiation ($\lambda = 0.7107$ Å); $\mu = 3.9$ g cm⁻¹; $F(000) = 632$; $S = 1.26$; the intensity data were collected by a CAD4 diffractometer using $\omega/2\theta$ scan; range $2.5 \leq \theta \leq 25^\circ$. Of 2306 independent reflections, 735 having $I < 2.5\sigma(I)$ were considered unobserved. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centered reflections $7 \leq \theta \leq 13^\circ$. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares using the SHELX-76 program package (G. M. Sheldrick).³ The H atoms were calculated geometrically when they were not found in the ΔF syntheses but not refined. The final R value was 0.0364 and $R_w = 0.0417$ with $w = 5.1841/[\sigma^2(F_o) + 0.010 F_o^2]$. Programs XANADU⁴ and SCHAKAL⁵ used for geometrical calculations. 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.

1) has confirmed the assigned structure with the same 'butterfly' arrangement already observed for compound (1). However, the five-membered rings are somewhat puckered, with the deviations from planarity being more marked for the P(1)-S(2)-C(8)-C(9)-C(15)-ring than for the P(1)-S(1)-C(1)-C(2)-C(15) ring. The following distances are observed for the member atoms from least-squares planes: ring one P(1) 0.150, S(1) 0.151, C(1) -0.064, C(2) -0.057, C(15) -0.179; ring two P(1) -0.238, S(2) -0.221, C(8) 0.118, C(9) 0.062, C(15) 0.279 Å. The lone-pair of the phosphorus atom and the 6-substituent are in the *cis*-arrangement.

Since another isomer was detected only in trace amounts by g.l.c.-mass spectral analysis, we can affirm that the reaction of (1) with MeCOCl/AlCl₃ is also stereospecific with retention of configuration.

We thank the C.N.R. of Italy and Ministero della Pubblica Istruzione for financial support.

Received, 11th July 1988; Com. 8/02764A

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