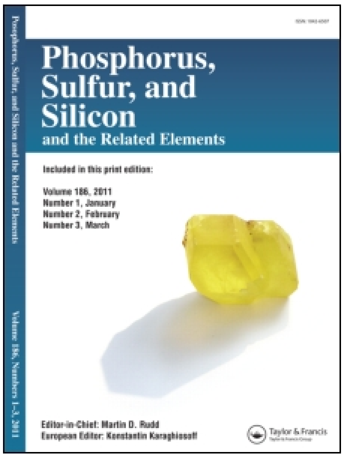

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE FIRST EXAMPLES OF BENZO-1,2,3-THIADIPHOSPHOLE SYSTEM

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To cite this Article Baccolini, Graziano , Mezzina, Elisabetta and Todesco, Paolo Edgardo(1989) 'THE FIRST EXAMPLES OF BENZO-1,2,3-THIADIPHOSPHOLE SYSTEM', Phosphorus, Sulfur, and Silicon and the Related Elements, 42: 1, 37 — 39

To link to this Article: DOI: 10.1080/10426508908054873

URL: http://dx.doi.org/10.1080/10426508908054873

Phosphorus, Sulfur, and Silicon, 1989, Vol. 42, pp. 37–39
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THE FIRST EXAMPLES OF BENZO-1,2,3-THIADIPHOSPHOLE SYSTEM

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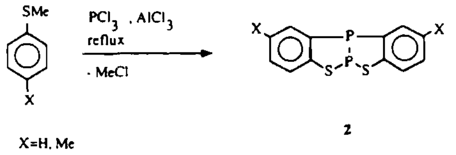
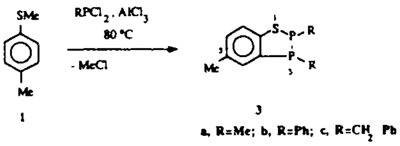
(Received June, 24, 1988)

The reactions of methyl p-tolyl sulfide with $RPCl_2/AlCl_3$ (R = Me, Ph, CH_2Ph) give the first examples of benzo-1,2,3-thiadiphosphole system by a one-pot procedure at 80°C.

In our efforts in order to realize the possibility of synthesizing new phosphorus and sulfur containing heterocycles by simple procedures we found a facile formation of fused benzo-1,2,3-thiadiphospholes starting from thioanisole, PCl_3 and $AlCl_3$.[1] This new heterocycle, consisting in two benzo-1,2,3-thiadiphospholes systems joined along the P—P bond, was the unexpected result of the construction of two new C—P, two P—S and one P—P bonds in a one-pot procedure. An X-ray crystal structure determination of **2** (X = Me) showed[1] the molecule in a "butterfly" arrangement in which the lone pairs of the phosphorus atoms were in cis position. No appreciable amounts of the other isomer was obtained. Now we wish to verify if this peculiar reactivity of $PCl_3/AlCl_3$ could be extended to the alkyl and aryl halogenophosphines in order to obtain benzo-1,2,3-thiadiphospholes, to our knowledge hitherto inaccessible heterocycles. For this purpose we carried out the reaction of *p*-tolyl methyl sufilde **1** with $RPCl_2$ (R = Me, Ph, CH_2Ph) in the presence of $AlCl_3$ and we found the suitable conditions to form the corresponding 2,3-disubstituted benzo-1,2,3-thiadiphospholes **3** in about 20% yield.



Scheme 1



Scheme 2

The course of the reaction was monitored by g.l.c.-m.s. analysis and the best results were obtained without solvent using a strong excess of $RPCl_2$ respect to **1** and $AlCl_3$. It should be noted that temperature is a determining factor of this synthesis. The formation of compounds **3** occurs at about 80°C: at higher or lower values they were obtained in very small amounts. The assignment of the structure for products **3** as benzo-1,2,3-thiadiphospholes is based on their spectroscopic data in analogy with our previous data for fused benzothiadiphospholes[1] and related compounds.[2] In particular in the $\{^1H\}^{31}P$-n.m.r. spectrum, the presence of two different phosphorus atoms is manifest in the multiplicity of spectral terms and coupling constants.

A typical procedure of the reaction is as follows; methyl *p*-tolyl sulfide **1** (30 mmol) is added dropwise to a solution of $AlCl_3$ (25 mmol) in $RPCl_2$ (80 mmol) ($R = Me, Ph, CH_2Ph$) and the mixture is heated at ~80°C in the case of $PhPCl_2$ and $PhCH_2PCl_2$, and at reflux (81°C) in the case of $MePCl_2$, for about 2–3 h under nitrogen atmosphere. After distillation under vacuo of the excess of $RPCl_2$ the products are isolated by a florisil column chromatography eluting with cyclohexane-CH_2Cl_2 (90:10) for **3a**, (80:20) for **3b** and (75:25) for **3c** in 13 and 20 and 25% yields respectively.

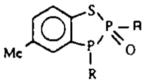
Compound **3a**: thick oil; R_f (light petroleum ether) = 0.26; M^+_{calcd} 214.01350, M^+_{found} 214.01386, *m/z* 214, 199 (base peak), 184, 121, 77, 63; ^1H-n.m.r. ($CDCl_3$) ∂ 1.22–1.38 (m, 6H, P-Me), 2.32 (s, 3H, Me), 7.06 (d, H-7, $J = 7.5$ Hz), 7.43 (d, H-6, $J = 7.5$), 7.59 (bd, H-4, $J = 7.5$ Hz); selected ^{13}C-n.m.r. ($CDCl_3$) ∂ 9.2 (dd, P-Me, $J_{CP} = 14.2$ Hz, $J_{CPP} = 8.3$ Hz), 13.3 (dd, P-Me, $J_{CP} = 24.3$ Hz, $J_{CPP} = 11.6$ Hz); $\{^1H\}^{31}P$-n.m.r. ($CDCl_3$) ∂ −0.9 (d, P-2), 2.5 (d, P-3), $J_{PP} = 223$ Hz.

Compound **3b**: white solid; R_f (light petroleum ehter) = 0.18; m.p. = 98–100°C; M^+_{calcd} 338.04479, M^+_{found} 338.04531, m/z 338 (M^+, 100%), 261, 231, 197, 183, 121, 77, 63; ^1H-n.m.r. ($CDCl_3$) ∂ 2.30 (s, 3H, Me), 7.12–7.71 (m, 13H arom); $\{^1H\}^{31}P$-n.m.r. ($CDCl_3$) ∂ 9.7 (d, P-2), 25.5 (d, P-3), $J_{PP} = 260$ Hz.

Compound **3c**: thick oil; R_f (light petroleum ether) = 0.14; M^+_{calcd} 366.07610, M^+_{found} 366.07625, m/z 366, 275, 211, 184, 121, 91 (base peak), 65, 63; ^1H-n.m.r. ($CDCl_3$) ∂ 2.25 (s, 3H, Me), 2.86–3.14 (m, 4H, P-CH_2), 6.94–7.32 (m, 12H, arom), 7.49 (d, H-4, $J = 7.8$ Hz); selected ^{13}C-n.m.r. ($CDCl_3$) ∂ 31.8 (dd, P-Me, $J_{CP} = 18.0$ Hz, $J_{CPP} = 9.0$ Hz), 35.2 (dd, P-Me, $J_{CP} = 29.1$ Hz, $J_{CPP} = 12.6$ Hz); $\{^1H\}^{31}P$-n.m.r. ($CDCl_3$) ∂ 8.0 (d, P-2), 16.1 (d, P-3), $J_{PP} = 251$ Hz.

Compound **3a** consists prevalently of one stereoisomer. About 10% of the other isomer was detectable by a signal at 2.31 ppm in the ^1H-n.m.r. spectrum (200 MHz) and by HPLC analysis. Attempts to separate them by chromatography were unsuccessful. The products **3b** and **3c** consist of only one diastereomer, there was no detectable amount of the other isomer by ^1H-n.m.r. spectroscopy. From these data it is not possible to give an exact assignment of the isomers, but on the basis of their J_{PP}, in analogy with the values reported for related fused compounds,[1] we tentatively attribute the cis configuration to the prevalent isomer.

During the work-up of the reaction, oxides of compounds **3** were detected in g.l.c.-m.s. analyses as by-products. In particular an oxide of compound **3b** was isolated and presumably has the structure **4** ($R = Ph$), deduced by its mass spectrum fragments.



4

R= Me, Ph, CH_2Ph

Scheme 3

Compound **4** (R = Ph): R_f (Ethyl ether) = 0.30; M^+_{calcd} 354.03971, M^+_{found} 354.04032, *m/z* 354 (M+, 100%), 307, 245, 197, 107, 63; ^{1}H-n.m.r. ($CDCl_3$) ∂ 2.32 (s, 3H, Me), 7.26–7.97 (m, 13H arom); {^{1}H}^{31}P-n.m.r. ($CDCl_3$) ∂ −26.4 (d), 69.8 (d), J_{PP} = 224 Hz; I.R. (CS_2) √1212 and 1196 cm^{-1} (P=O).

The relative oxides **4** (R = Me, CH_2Ph) were isolated in small amounts together with the respective compounds **3** and it could not be possible a further purification.

Satisfactory elemental analyses were obtained for all the isolated compounds.

ACKNOWLEDGEMENTS

We are grateful to Dr. Emilio Tagliavini for recording the ^{31}P-n.m.r. spectra. We wish to thank Italian C.N.R. for financial support.

REFERENCES

1. G. Baccolini, E. Mezzina, P. E. Todesco and E. Foresti, *J. Chem. Soc. Chem. Comm.*, 1988, 304.
2. (a) K. Jurkschat, C. Mugge, A. Tzaschach, W. Uhlig and A. Zschunke, *Tetrahedron Lett*, 1982, **23**, 1345. (b) A. Zschunke, C. Mugge, H. Meyer, A. Tzaschach and K. Jurkschat, *Org. Magn Res.*, 1983, **21**, 315.