Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1996, **6(2)**, 48–50

Mendeleev Communications

Intramolecular alkylation of 3- and 4-halogenoalkyldiphenylphosphine sulfides. Ring-chain halogenotropic tautomerism of 2,2-diphenyl-1,2λ^4-thiaphospholanium and 2,2-diphenyl-1,2λ^4-thiaphosphorinanium iodides

Inga M. Aladzheva,* Olga V. Bykhovskaya, Dmitrii I. Lobanov, Konstantine A. Lyssenko, Oleg V. Shishkin, Mikhail Yu. Antipin, Yurii T. Struchkov, Tatyana A. Mastryukova and Martin I. Kabachnik

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085

Heating of 3- and 4-chloroalkyldiphenylphosphine sulfides **1a**,**b** with sodium iodide in acetone leads to 2,2-diphenyl-1,2λ^4-thiaphospholanium iodide **2a** and 2,2-diphenyl-1,2λ^4-thiaphosphorinanium iodide **2b**; relatively uncommon ring-chain halogenotropic tautomerism is observed in solutions of these compounds.

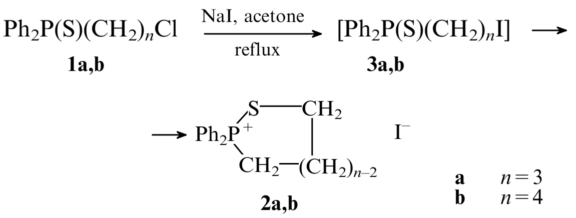
Tertiary phosphine sulfides are known[1,2] to react with alkyl halides to yield alkylthiophosphonium salts, reaction (1).

$$R_3P{=}S + AlkX \longrightarrow R_3P^+SAlk\ \ X^- \qquad (1)$$

The phosphonium structure of the alkylation product obtained from trimethylphosphine sulfide and methyl iodide was confirmed by X-ray analysis.[3] We have found that by refluxing 3- and 4-chloroalkyldiphenylphosphine sulfides **1a,b**[4] with sodium iodide in acetone, previously unknown cyclic thiaphosphonium salts **2a,b** are produced. These compounds might result from the intramolecular alkylation of intermediate iodides **3a,b**.

The salts **2a,b** are stable crystalline compounds;[†] their structures were confirmed by X-ray analysis.[‡]

In the crystal structure of **2a** (Figure 1) the five-membered heterocycle has an envelope conformation with a deviation of the C(2) atom from the plane of the four other atoms of the ring by 0.6224 A. The six-membered ring in the structure of **2b** (Figure 2) has a chair-like conformation with torsion angles PSC(1)C(2) –55.8(1)°, SC(1)C(2)C(3) 67.4(2)°, C(1)C(2)C(3)C(4) –68.1(3)° and SPC(4)C(3) –54.9(1)°. The phosphorus atoms have a slightly distorted tetrahedral configuration. Bond lengths P–S (2.068 A in **2a**, 2.051 A in **2b**) are typical of a single bond P–S,[3] which may point to a phosphonium structure of the salts investigated. The bond lengths S–C(1), P–C(3) and P–S in the structure of **2a** are larger than those in the structure of **2b**, where these bonds have the expected values [C_{sp^3}–S–$X_{(aver)}$ 1.833 A and C_{sp^3}–$P(4)^+_{(aver)}$ 1.800 A].[6]



The reason for the elongation of the P–C, S–C and P–S bond lengths in **2a** is probably related to the intermolecular contacts of the sulfur atoms with the halogen: S···I⁻ (O + *x*, 0.5–*y*, –0.5 + *z*) 3.633(2) A in the structure of **2a** and S···I⁻ 3.825(2) A in **2b**.

The intermolecular contact in **2b**, according to the classification in ref. 7, represents a shortened contact, and in **2a** represents a strongly contracted one. According to Zefirov[7] only strongly-contracted contacts lead to changes in the molecular geometry, as observed in structures **2a** and **2b**. The difference in strength of contacts in **2a** and **2b** is probably connected with the different packing of molecules in the crystals.

Taking the contact with the counterion into account, the sulfur atoms have a trigonal planar coordination. Atoms S, P, C(1) and I are coplanar within an accuracy of 0.042 A in the structure of **2a** and 0.003 A in **2b**. Torsion angles SPC(4)C(5), SPC(10)C(11) in the structure **2a** and SPC(5)C(10), SPC(11)C(12) in **2b** are equal to 117.1(3)°, 9.4(4)° and 168.5(3)°, 61.2(2)°, respectively.

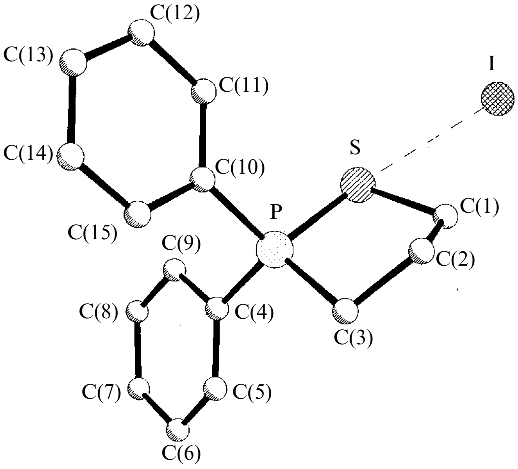


Figure 1 Molecular structure of **2a**. The main bond lengths /A and angles /°: P–S 2.068(1), P–C(3) 1.805(4), P–C(4) 1.786(4), P–C(10) 1.800(3), S–C(1) 1.850(6), C(2)–C(3) 1.530(6), C(1)–C(2) 1.518(7); S–P–C(3) 100.1(1), S–P–C(4) 111.8(1), C(3)–P–C(4) 113.7(2), S–P–C(10) 110.2(1), C(3)–P–C(10) 112.7(2), C(4)–P–C(10) 108.2(2), P–S–C(1) 93.0(2), P–C(3)–C(2) 104.0(3), C(1)–C(2)–C(3) 109.9(4), S–C(1)–C(2) 110.5(3).

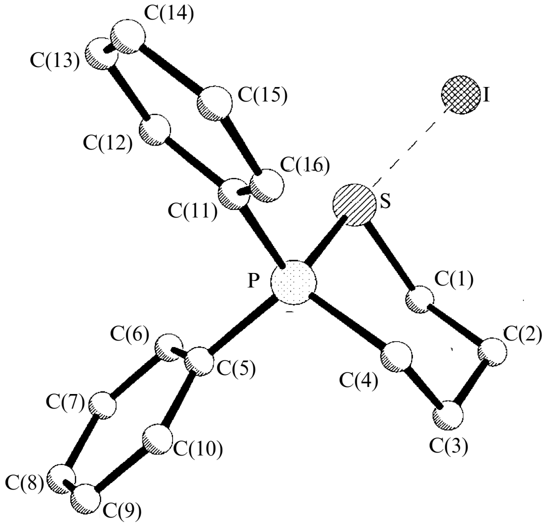


Figure 2 Molecular structure of **2b**. The main bond lengths /A and angles /°: S–P 2.051(2), S–C(1) 1.837(5), P–C(4) 1.778(5), P–C(5) 1.785(5), P–C(11) 1.793(3), C(1)–C(2) 1.510(8), C(2)–C(3) 1.522(6), C(3)–C(4) 1.532(6); P–S–C(1) 97.1(2), S–P–C(4) 108.2(1), S–P–C(5) 107.3(2), C(4)–P–C(5) 111.1(2), S–P–C(11) 110.7(1), C(4)–P–C(11) 109.2(2), C(5)–P–C(11) 110.3(2), S–C(1)–C(2) 114.4(3), C(1)–C(2)–C(3) 114.7(4), C(2)–C(3)–C(4) 114.0(4), P–C(4)–C(3) 110.0(3).

The behaviour of the compounds **2a,b** in solution is of particular interest because of tautomeric equilibria. There are two tautomeric forms: the ring 1,2λ^4-thiaphospholane **2a** (or 1,2λ^4-thiaphosphorinane **2b**) form and the open phosphine sulfide form **3a** (or **3b**). This is a new type of ring-chain anionotropic tautomerism,[8] hitherto poorly investigated.

The ring form **2** is characterized by ^{31}P NMR chemical shifts in the region of 72 ppm (**2a**) and 38 ppm (**2b**); and for the open forms **3** in the region 41–42 ppm (Table 1).[§]

The presence of the open form **3** in solution is also confirmed by the ^{1}H NMR spectrum of **2a** in $CDCl_3$. Along with other signals a triplet with a chemical shift 3.17 ppm ($^3J_{HH}$ 6 Hz) is observed. The latter is typical of methylene

---

[†] For **2a**: yield 77%; mp 203–204.5 °C (MeCN-ethyl acetate). For **2b**: yield 65%; mp 205–206 °C (MeCN). Both of these compounds gave satisfactory elemental analyses.

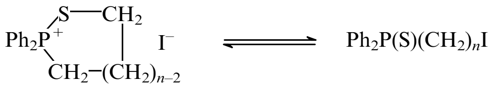
[‡] *Crystallographic data for* **2a,b**: **2a,** $C_{15}H_{16}IPS$, $M = 386.25$, monoclinic crystals, space group $P2_1/c$ at –120 °C, $a = 12.204(4)$ A, $b = 12.049(4)$ A, $c = 11.483(4)$ A, $\beta = 114.96(3)°$, $V = 1530(2)$ A , $z = 4$, $D_{calc} = 1.582$ g cm^{-3}, μ(MoKα) = 23.1 cm^{-1}, $F(000) = 760$. Intensities of 5028 reflections were measured on Siemens P3/PC diffractometer at –120 °C (MoKα radiation, $\theta/2\theta$, $2\theta < 60°$) and 4021 observed independent ones with $I > 2\sigma(I)$ were used in calculations and refinement. **2b**, $C_{16}H_{18}IPS$, $M = 400.28$, monoclinic crystals, space group $P2_1/c$ at –86 °C, $a = 12.143(4)$ A, $b = 12.346(4)$ A, $c = 12.169(4)$ A, $\beta = 117.16(3)°$, $V = 1623(1)$ A , $z = 4$, $D_{calc} = 1.638$ g cm^{-3}, μ(MoKα) = 21.57 cm^{-1}, $F(000) = 793$. Intensities of 3024 reflections were measured on a Syntex-P2$_1$ diffractometer at –86 °C (MoKα radiation, $\theta/2\theta$, $2\theta < 60°$) and 2492 observed independent ones with $I > 2\sigma(I)$ were used in calculations and refinement. The structures were solved by direct methods and refined by a least-squares method with anisotropic-isotropic (H atoms) approximation. Absorption correction was applied to all data sets using the DIFABS program.[5] The final discrepancy factors were $R = 3.25$, $wR = 4.0$, GOF = 1.71 (for **2a**) and $R = 2.8$, $wR = 3.0$, GOF = 1.03 (for **2b**). All calculations were performed using the program SHELXTL PLUS on an IBM PC/AT. Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Notice to authors, *Mendeleev Commun.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1135/1.

protons of the $(CH_2)CH_2(Hlg)$ group (*cf.* ref. 4). The tautomeric equilibrium (**2a**,**b**$\rightleftharpoons$**3a**,**b**) is established only slowly (within a few days at 20 °C). The equilibrium position depends on the solvent used and the ring size. According to the ^{31}P NMR spectra 30% of the open form **3a** is present in a CH_2Cl_2 solution of **2a** and 13% in $CHCl_3$.

Table 1 ^{31}P NMR spectral data for **2** and **3** in various solvents (δ, ppm).

Solvent	2a	3a	2b	3b
CH_2Cl_2	72.2	41.4	37.6	42.2
$CHCl_3$	72.2	41.1	37.8	42.5
MeCN	73.3	–	38.1	–

At the same time the equilibrium is completely shifted to the ring form **2a** in MeCN; *i.e.* the content of the less polar ring-opened form **3a** in a tautomeric mixture decreases with increasing solvent polarity. The relative amounts of the open form **3** also decreases in the case of **2a** compared to **2b** which possesses a less strained six-membered 1,2λ⁴-thiaphosphorinane ring. There is 15% of the open form **3b** in CH_2Cl_2 solution of **2b** and 8% in $CHCl_3$. In MeCN solution, as in the case of **2a**, the equilibrium is completely shifted to the ring form **2b**.



2a,**b** **3a**,**b**

$n = 3,4$

This work was financially supported by the Russian Foundation for Basic Research (grant nos. 93-03-04351 and 94-03-08338).

References

1 A. Hantzsch and H. Hibbert, *Ber. Dtsch. Ges.*, 1907, **40**, 1508.
2 R. K. Haynes and C. Indorato, *Aust. J. Chem.*, 1984, **37**, 1183.
3 R. Minkwitz, G. Medger, R. Greth and H. Preut, *Z. Naturforsch.*, 1992, **47b**, 1654.
4 I. M. Aladzheva, O. V. Bykhovskaya, D. I. Lobanov, P. V. Petrovskii, T. A. Mastryukova and M. I. Kabachnik, *Zh. Obshch. Khim.*, 1995, **65**, 1586 (in Russian).
5 N. Walker and D. Stuart, *Acta Crystallogr.*, 1983, **39**, 158.
6 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2,* 1987, 20.
7 Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.,* 1989, **58**, 713 *(Russ. Chem. Rev.,* 1989, **58**, 421).
8 R. E. Valters and W. Flitsch, *Ring-chain tautomerism,* Plenum Press, New York, London, 1985.
9 I. M. Aladzheva, I. L. Odinets, P. V. Petrovskii, T. A. Mastryukova and M. I. Kabachnik. *Zh. Obshch. Khim.*, 1993, **63**, 611 (*Russ. J. Gen. Chem.,* 1993, **63**, 431).

Received: Moscow, 15th December 1995
Cambridge, 22nd January 1996; Com. 5/08222F

[§] For comparison: δ_P (CH_2Cl_2) for 3- and 4-chloroalkyldiphenylphosphine sulfides **1a**,**b** 41.2 and 42.7 ppm, respectively;[4] δ_P for $Ph_2P(S)Bu$ 42.8 ppm.[9]