Notes

Sulfurization of Trivalent Phosphorus Compounds with 1,2-Dithiole-3-thione†

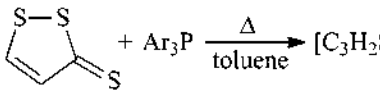
Józef Drabowicz,* Jerzy Łuczak, Piotr Łyżwa, Marian Mikołajczyk, and Carl Th. Pedersen‡

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Heteroorganic Chemistry, 90-363 Łódź, Sienkiewicza 112, Poland
‡Department of Chemistry, Odense University, DK-5230 Odense M, Denmark
Received May 18, 2004

Key Words : Sulfurization. Phosphine sulfide. Thionophosphate, Thione

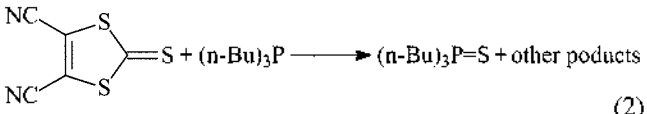
A few methods have been utilized for the preparation of tertiary phosphine sulfides. $R_3P{=}S$.[1] These include the reaction of organometallic reagents with halides of phosphorus thioacids,[2] the Fridel-Crafts reaction between thiophosphonyl (thiophosphoryl or thiophosphinic) chlorides and arenes[3] or between phosphorus trichloride and benzene in the presence of elemental sulfur.[4] The most convenient preparation of such phosphine sulfides constitutes still the direct sulfurization of the parent phosphines. Here again a few reagents have been applied including elemental sulfur,[5] sodium polysulfides[6] and cyclic organic sulfides.[7] Similarly, the addition of elemental sulfur to phosphites (or other trivalent analogues) constitutes the most common procedure for the preparation of the corresponding thionophosphates (or other thionoanalogues).

Earlier, one of us has reported[8] that the reaction of 1,2-dithiolane-3-thione **1** with triphenylphosphine **2a** afforded (beside the $[C_3H_2S_2]_n$ polymer terminated by Ph_3P substituent-**3**) almost quantitative yield of the corresponding triphenylphosphine sulfide **4a** (Eq. 1). This observation indicates a possibility of the use of the thione **1** as an alternative sulfurization agent for trivalent organophosphorus compounds.



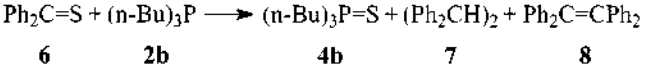
1 **2a** Ar=Ph **3** **4a** Ar=Ph (1)

In this context, it is interesting to note that in the chemical literature one can find only two papers describing the thionation type of the reaction between phosphorus compound and a thiocarbonyl component. The first paper reported[9] that the reaction of 4,5-dicyano-1,3-dithiole-2-thione **5** with tri-*n*-butylphosphine **2b** gave a mixture of products, one of which was identified as tri-*n*-butylphosphine sulfide **4b** (Eq. 2).



5 **2b** **4b** (2)

The second one described[10] the high temperature (100 °C) reaction of tri-*n*-butylphosphine **2b** with thiobenzophenone **6** which gave mainly tri-*n*-butylphosphine sulfide **4b** (89%), 1,1,2,2-tetraphenylethane **7** (65%) and tetraphenylethylene (28%) (Eq. 3). The intermediacy of carbene in the reaction was suggested.



6 **2b** **4b** **7** **8** (3)

Results and Discussion

To show a possibility of application of the thione **1** as a new sulfurizating reagent we have started our experiments with a few trialkyl phosphites **9**. We were glad to find that in this case sulfurization reaction is rapid and very clean giving at room temperature the corresponding thionophosphates **10** as a single reaction product (^{31}P-NMR assay) (Eq. 4). On the other hand, under the same reaction conditions triphenylphosphite **9d** (R=Ph) gave a complex mixture of phosphorus-containing products.

9 **10** (4)

In a sharp contrast to this when a few aromatic and aliphatic tertiary phosphines **2a-g** were allowed to react with the thione **1** in boiling benzene for a few hours the corresponding phosphine sulfides **4a-g** were formed cleanly although always accompanied by the traces of the corresponding phosphine oxides (^{31}P-NMR assay). They were isolated in a very high yield (Table 1) by a standard column chromatography of a crude reaction product.

If the reaction of P^{III} compounds with 1,2-dithiole-3-

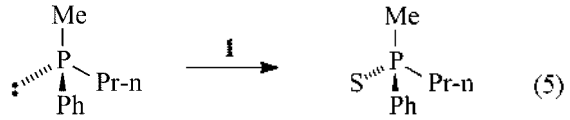
†Dedicated to Prof. Yong Hae Kim on the occasion of his retirement from the Korean Advanced Institute of Science and Technology [KAIST]
*Corresponding Author: e-mail: draj@bilbo.cbmm.lodz.pl

Table 1. Sulfurization of triaryl(alkyl)phosphines **2** with 1,2-Dithiole-3-thione-1

Substrate		Product		Yield [%][a]	Mp [°C]		^{31}P-NMR $CDCl_3$/85%H_3PO_4
No	R	No	R		found	reported	δ[ppm]
2a	Ph	**4a**	Ph	83	158-160	157-158[6]	+43.0
2b	*n*-Bu	**4b**	*n*-Bu	86	oil	134-136/0 mmHg[17]	+47.5
2c	*p*-Tol	**4c**	*p*-Tol	87	181-183	185-186[6,18]	+41.1
2d	*p*-Cl-C_6H_4	**4d**	*p*-Cl-C_6H_4	83	149-151	152-153[19]	+40.2
2e	*p*-F-C_6H_4	**4e**	*p*-F-C_6H_4	86	137-138	139-141[20]	+41.0
2f	*p*-MeO-C_6H_4	**4f**	*p*-MeO-C_6H_4	90	107-110	109-110[18]	+41.0

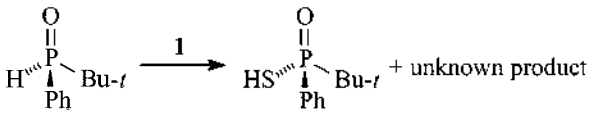
[a]isolated after column chromatography

thione **1** were found to be stereospecific, this thione would be the preferred reagent for thionation of chiral phosphines. With this in mind we have examined thionation of optically active (+)-(*S*)-methyl-*n*-propylphenyl phosphine **11**[11] and found that it resulted in the formation of the corresponding (+)-(*R*)-phosphine sulfide **12**[12] with stereoselectivity close to 70% and with retention of configuration at phosphorus (Eq. 5).



(+)-(*S*)-**11** (+)-(*R*)-**12** (5)

On the other hand, the reaction between the levorotatory phosphine oxide (−)-(*S*)-**13**[13] and the thione **1** gave after 33 days at room temperature the dextrorotatory enantiomer of *t*-butylphenylphosphinothioic acid (+)-(*R*)-**14**[14] with full retention of configuration at the stereogenic phosphorus atom (Eq. 6). However, a few unindentified phosphorus-containing products having chemical shifts around +70 ppm were observed in a crude reaction mixture (^{31}P-NMR assay).

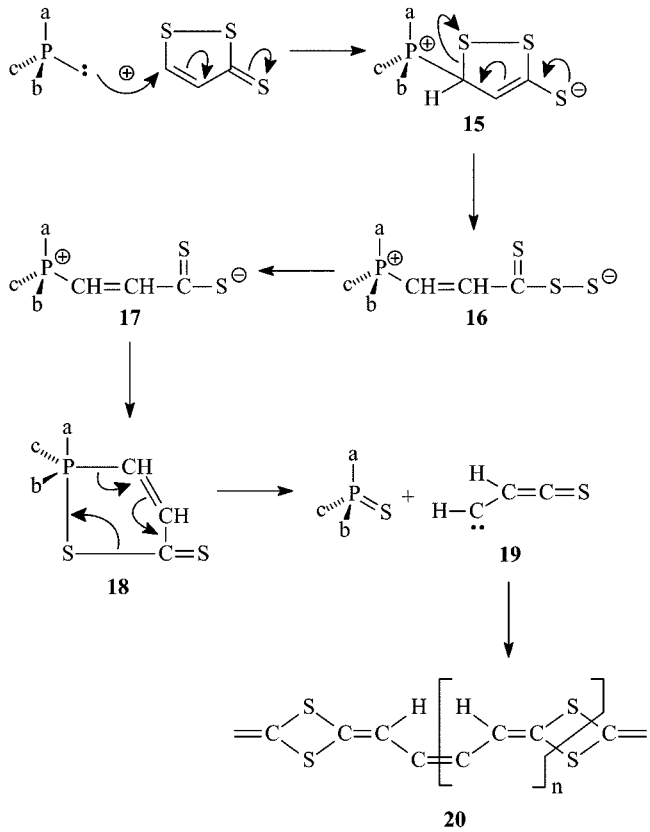


(-)-(*S*)-**13** (+)-(*R*)-**14** (6)

$[\alpha]_{589}$ = −32.5 ($CHCl_3$) $[\alpha]_{589}$ = +26.4 (MeOH)

ee = 88.4% ee = 88.4%

Retention at phosphorus observed in the above mentioned thionation reactions may be easily explained by the mechanistic sequence proposed in Scheme 1. It is reasonable to assume that the first step of the reaction between phosphines **2** or the trivalent tautomer of the phosphine oxide **13** and **1** is the nucleophilic attack of phosphorus at the 5-position of the thione as this position easily undergoes nucleophilic attack. This results in the formation of the "Zwitterion" **15**. It may then undergo internal opening to give subsequently the structures **16** and **17** which upon cyclization forms the intermediate phosphorane **18**, in which



Scheme 1

the five membered ring spans axial and equatorial positions. Such a structure should be the most convenient from the point of view of apicophilicity of substituents at phosphorus in trigonal-bipyramidal species.[15] Decomposition of the five-coordinate intermediate **18** gives the phosphine sulfide with retention of configuration at phosphorus and the carbene intermediate **19** from which polymer **20** could possibly be formed.[8] This proposal is in full agreement with the experimental observation that a black polymeric precipitate was always formed during the discussed thionation reaction.

Experimental Section

General. Melting points which are uncorrected were

determined in capillary tubes. ^{31}P NMR spectra were obtained on a Burker 200 MHz and JOEL 400 MHz spectrometer and the ^{31}P chemical shifts are reported as referenced to the external 85% H_3PO_4 with resonance deshielded from the reference as being reported as positive. Thin layer chromatograms for analytical purposes were run on alumina plates coated with a layer of silica gel GF_{254} (Merck). Column chromatography was done on silica gel (Merck, 60-200 mesh). Optical activity measurements were made with a Perkin-Elmer 241 MC photopolarimenter: concentrations of the solutions were about 1-2 g/100 mL.

Materials. All starting trialkyl(aryl) phosphates and triarylphosphines were commercially available products. 1,3-Dithiole-3-thione,[16] (+)-(*S*)-methyl-*n*-propylphenylphosphine[11] and (−)-(*S*)-*t*-butylphenylphosphine oxide **13a** were prepared according to the established procedure.

Reaction of 1,2-Dithiole-3-thione with Triarylphosphines. A solution of 1,3-dithiole-3-thione (0.536 g, 0.004 mol) and triarylphosphine **2** (0.004 mol) in 50 mL of dry benzene was refluxed and the reaction progress was monitored by TLC. After cooling, the black precipitate was filtered and washed with 50 mL of ether and 30 mL of benzene. Evaporation of the benzene and the solvent used to wash the precipitate gave brownish crystals, which were crude triarylphosphine sulfides. The crude phosphine sulfides were finally purified by column chromatography to give virtually pure products listed in Table 1.

Conversion of (+)-(*S*)-Methylphenyl-*n*-propylphosphine-11 to (+)-(*R*)-Phosphine Sulfide-12 by Means of 1,2-Dithiole-3-thione-1. A solution of **11** [448 mg (0.00024 mol), $[\alpha]_{589}$ = +18.3 (toluene), ee = 93.5%] and **1** [19 mg (0.00019 mol)] in benzene (2 mL) was stirred at room temperature for 0.5 hrs. After this time a black precipitate was filtered and washed with diethyl ether (3 × 20 mL). The organic phase was washed in a row with 5% aqueous solutions of H_2SO_4, 5% aqueous solution of K_2CO_3 and water and dried over dry $MgSO_4$. Evaporation of the solvent afforded a solid (39.8 mg 92%) which was purified by preparative TLC chromatography [ethyl ether-petroleum ether (1 : 1) as an eluent] to give virtually pure (+)-(R)-methylphenyl-*n*-propylphosphine sulfide **12** [21.8 mg (0.00011 mol), (46%), $[\alpha]_{589}$ = +14.4 (1.09 MeOH), ee = 63.4%, δ_{31P} = +41.48 (MeOH)].

Conversion of (−)-(*S*)-*t*-Butylphenylphophine Oxide-13 to (+)-(*R*)-*t*-Butylphenylthiophosphinic acid-14 by Means of 1,2-Dithiole-3-thione-1. A solution of **13** [0.184 g (0.001 mol), $[\alpha]_{589}$ = −32.5 (1.53 $CHCl_3$), ee = 88.4%] and **1** [80 mg (0.0006 mol)] in $CDCl_3$ (2 mL) was kept in a NMR tube at room temperature for 33 days and the reaction progress was followed by the ^{31}P NMR. After this time the black precipitate was filtered and washed with diethyl ether (3 × 20 mL). Evaporation of the $CDCl_3$ and the solvent used to wash the precipitate afforded a solid which was purified by column chromatography [ethyl ether-petroleum ether (1 : 1) as an eluent] to give (+)-(*R*)-*t*-butylphenylphosphinothioic acid **14** [0.092 g (48%). $[\alpha]_{589}$ = +26.4 (1.06 MeOH). ee = 88.4%, δ_{31P} = +98.6 ($CDCl_3$)].

Acknowledgements. Studies in Lodz were partially supported by the State Committee for Scientific Research (KBN-grant 4T09A 105 22 to J.D.)

References

1. (a) Heydt, H.; Regitz, M. In *Methoden der Organischen Chemie* (Houben-Weyl); Ed. Regitz, M., Ed.; Georg Thieme verlag: Stuttart-New York, 1982; Vol. E-2, pp 77-92.
2. (a) Screttas, C.; Isbell, A. F. *J. Org. Chem.* **1963**, *27*, 2573. (b) Harwood, H. J.; Pollart, K. A. *J. Org. Chem.* **1963**, *28*, 3430. (c) Maier, L. *Hel. Chim. Acta, Chem. Ber.* **1961**, *94*, 3043.
3. Maier, L. *Hel. Chim. Acta, Chem. Ber.* **1964**, *47*, 120.
4. Olah, G. A.; Hehemann, D. *J. Org. Chem.* **1977**, *42*, 2190.
5. Maier, L. In *Topics in Phosphorus Chemistry*; Gayson, M., Griffith, E. J., Eds.; Intrascience: New York, 1965; Vol. 2, p 43.
6. Miranda, R.; Salas, I.; Mondragon, J.; Valasco, L. *Synthetic Commun.* **1992**, *22*, 1077.
7. Young, D. P.; McEwen, W. E.; Valez, D. C.; Johnson, J. W.; Vander Werf, C. A. *Tetrahedron Lett.* **1964**, 359.
8. Pedersen, C. Th. *Sulfur Lett.* **1997**, *20*, 179.
9. Miles, M. M.; Wager, J. S.; Wilson, J. D.; Siedle, A. R. *J. Org. Chem.* **1975**, *40*, 2577.
10. Ogata, Y.; Yamashita, M.; Mizutani, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1721.
11. (a) Horner, L.; Balzer, W. D. *Tetrahedron Lett.* **1965**, 1175. (b) Zon, G.; De Bruin, K. E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023.
12. (a) Horner, L. *Pure Appl. Chem.* **1964**, *9*, 225. (b) Zon, G.; Mislow, K. *Top. Curr. Chem.* **1971**, *19*, 61.
13. (a) Drabowicz, J.; Łyżwa, P.; Omelańczuk, J.; Pietrusiewicz, K. M.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2757. (b) Wang, F.; Polavarapu, P. L.; Drabowicz, J.; Mikołajczyk, M. *J. Org. Chem.* **2000**, *65*, 7561.
14. (a) Michalski, J.; Skrzypczyński, Z. *J. Organomet. Chem.* **1975**, *97*, C31. (b) Wang, F.; Polavarapu, P. L.; Drabowicz, J.; Mikołajczyk, M. *J. Org. Chem.* **2001**, *66*, 9015.
15. Trippett, S. *Phosphorus Sulfur* **1976**, *1*, 89.
16. Meinetsberger, E.; Schöffer, A.; Behringer, H. *Synthesis* **1961**, 802.
17. Sherry, A. D.; Purcell, K. F. *J. Am. Chem. Soc.* **1972**, *94*, 1848.
18. Ballah, V.; Subbarayan, P. *J. Org. Chem.* **1960**, *25*, 1833.
19. Schimenz, G. P. *Chem. Ber.* **1966**, *99*, 504.
20. Schindlbauer, H. *Chem.Ber.* **1967**, *100*, 3432.