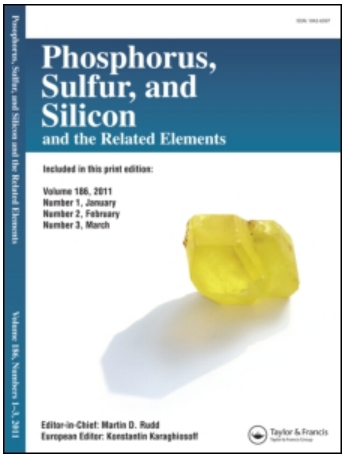


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTION OF *o*-BENZENEDITHIOLS AND DERIVATIVES WITH PHOSPHORUS PENTACHLORIDE

Donald B. Denney[a]; Dorothy Z. Denney[a]; Lun-Tsu Liu[a]
[a] Department of Chemistry, Rutgers-The State University of New Jersey, New Brunswick, New Jersey

To cite this Article Denney, Donald B. , Denney, Dorothy Z. and Liu, Lun-Tsu(1982) 'REACTION OF *o*-BENZENEDITHIOLS AND DERIVATIVES WITH PHOSPHORUS PENTACHLORIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 13: 2, 243 — 248
To link to this Article: DOI: 10.1080/03086648208081181
URL: http://dx.doi.org/10.1080/03086648208081181

Phosphorus and Sulfur, 1982, Vol. 13, pp. 243–248
0308-664X/82/1302-0243/$06.50/0

REACTION OF *o*-BENZENEDITHIOLS AND DERIVATIVES WITH PHOSPHORUS PENTACHLORIDE

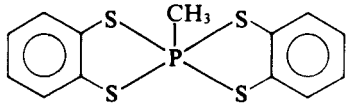
DONALD B. DENNEY,* DOROTHY Z. DENNEY and LUN-TSU LIU

Department of Chemistry, Rutgers—The State University of New Jersey, New Brunswick, New Jersey 08903

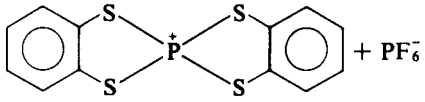
(*Received February 1, 1982; in final form March 6, 1982*)

Reaction of phosphorus pentachloride with thiocatechol, 4-methyl-1,2-benzenedithiol and their trimethyl-silylated derivatives under a variety of conditions produced chlorodithiophosphites in which a 5-membered ring with two sulfurs is bonded to phosphorus. The other product of this reaction is probably an oligomeric disulfide derived from the original dithiol.

Although the chemistry of phosphoranes has received much attention over the past two decades, there remain a number of interesting problems which require solution. Much of the information which is currently available on these systems stems from studies of phosphoranes with alkoxy groups or fluorines bonded to phosphorus.[1] Considerably less information is available concerning the structure and stabilities of phosphoranes containing other heteroatoms bonded to phosphorus. In particular few studies of phosphoranes containing sulfur bonded to phosphorus have been made.[2] The interesting compound **1** has been prepared and its structure has been shown to be intermediate between that of a trigonal bipyramid and a square pyramid. When the trimethylsilyl ether of *o*-benzenedithiol was allowed to react with phosphorus pentafluoride the interesting ion pair, **2**, was formed.[2b]



1



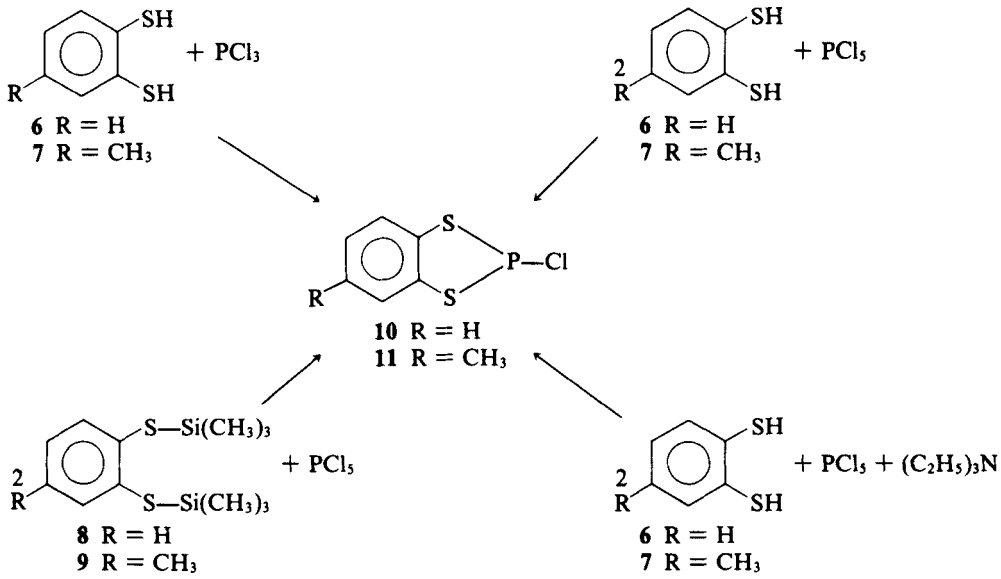
2

Recently attempts to prepare pentaperfluorophenylthiophosphorane, **3**, by a variety of reactions led always to the thiophosphite **4** and the disulfide, **5**. It was concluded that **3** was probably formed and then decomposed rapidly to **4** and **5**.[3] Such decompositions are not uncommon and they have been found with a variety of compounds derived from various metaloids.[4] The mechanism of these decompositions has not received extensive study. In two cases it has been concluded that the decompositions are concerted, and thus a reverse biphilic insertion mechanism is implied.[4a,b]

$$\underset{\mathbf{3}}{(C_6F_5S)_5P} \rightarrow \underset{\mathbf{4}}{(C_6F_5S)_3P} + \underset{\mathbf{5}}{(C_6F_5S)_2}$$

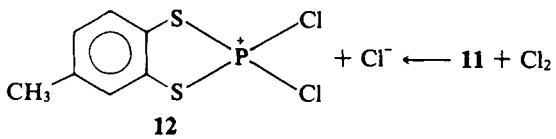
* Author to whom all correspondence should be addressed.

The stabilization of oxyphosphoranes by five-membered rings is well-known. The preparation of **1** indicates that the same effect may be operating when sulfur is substituted for oxygen. An investigation of the reactions of *o*-benzenedithiol and some of its derivatives with phosphorus pentachloride was undertaken as a potential route to a variety of phosphoranes containing sulfur bonded to phosphorus. In fact none of these reactions produced stable phosphoranes. The overall course of the reactions is illustrated in Scheme 1. Reaction of two moles of **6** or **7** in the presence or absence of triethylamine led to the dithiohalophosphites **10** or **11**. These materials were independently prepared by allowing **6** or **7** to react with phosphorus trichloride. When two moles of the trimethylsilylated derivatives **8** or **9** were allowed to react with phosphorus pentachloride, **10** or **11** was the product.



Scheme 1

When **7** was allowed to react with one mole of phosphorus pentachloride at reduced temperature, a solution was obtained which had a single resonance in its ^{31}P NMR spectrum at δ 213.8. This resonance is not that of **11** which is found in the region δ 153–156 depending on conditions. When another mole of **7** was added to this reaction mixture, and it was allowed to stand overnight conversion to **11** was observed. The resonance at 213.8 is assigned to the ions **12**.



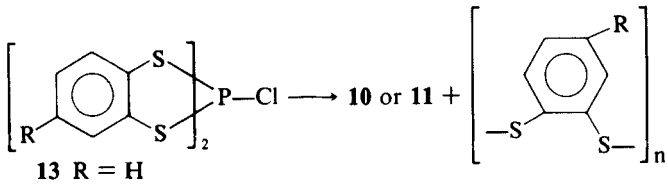
12

This structural assignment is supported by the observation that **11** reacts with chlorine to give a solution which has a single resonance at δ 214.1.

The fate of the second mole of dithiol has not been determined totally. A reaction mixture from two moles of **7** and one of phosphorus pentachloride was hydrolyzed

with aqueous sodium hydroxide. The aqueous layer had a resonance in its ^{31}P NMR spectrum at δ −0.8. The methylene chloride soluble material was treated with triphenylphosphine in the presence of water. Triphenylphosphine oxide and **7** were formed. The above described conditions are those used to convert disulfides into thiols.

The results of these experiments suggest that the phosphoranes **13** and **14** are formed and that they are unstable with respect to loss of what is probably oligomeric disulfide. It is not clear just why **13** and **14** are so unstable. Sau and Holmes[2c] have prepared the phenyl analog of **1** by heating the trimethylsilylated benzenedithiol with phenyltetrafluorophosphorane in refluxing benzene for 20 hr. They did remark that the phosphorane was somewhat unstable in hot solvents.



13 R = H
14 R = CH_3

Ionization of **13** and **14** is probably not facile because there is no acceptor for the chloride ion as was the case with the formation of **2**. Compounds **13** and **14** are probably less stable than **1** and the phenyl analog because the rings force the chlorine into an unfavorable position i.e., equatorial if the structure is trigonal bipyramidal or apical if it is square pyramidal.

EXPERIMENTAL SECTION

^1H NMR spectra were recorded with Varian Models T-60 and A-60A spectrometers. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. ^{13}C and ^{31}P spectra were recorded with a Varian Model FT-80 spectrometer equipped with a variable-temperature broad band probe. In all cases nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift. ^{13}C NMR spectra were obtained by using full proton decoupling, a 45° flip angle and a 2-s repetition rate with no pulse delay. All ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{31}P NMR spectra were acquired using a 45° flip angle, a 1-s repetition rate with no pulse delay and with full proton decoupling. Chemical shifts are reported relative to external phosphoric acid (85%).

All manipulations were carried out under an atmosphere of nitrogen. All solvents were freshly distilled and scrupulously dried.

Reaction of o-Benzenedithiol, **6**, *and Phosphorus Pentachloride*

To a solution of *o*-benzenedithiol,[5] **6**, (0.57 g, 0.004 mol) in benzene (5 mL) was added, with stirring at 25°, phosphorus pentachloride (0.42 g, 0.002 mol). The reaction mixture was heated, while being stirred, to 70° for 2 hrs. The solvent was removed at reduced pressure and the residual oil was dissolved in chloroform-d; ^{31}P NMR δ 158.4; ^1H NMR δ 6.9–7.8.

Reaction of o-*Benzenedithiol,* **6**, *with Phosphorus Pentachloride in the Presence of Triethylamine*

To a solution of *o*-benzenedithiol, **6**, (0.38 g, 0.0026 mol) in dichloromethane (5 mL) was added, with stirring, at −40°, triethylamine (0.53 g, 0.0052 mol). To this mixture was then added phosphorus pentachloride (0.278 g, 0.0013 mol). The reaction mixture was allowed to warm to room temp and the solid was removed by filtration. The ^{31}P NMR spectrum of the filtrate showed one absorption at δ 156.0 (external lock).

Preparation of **8**

To a stirred solution of *o*-benzenedithiol, **6**, (0.81 g, 0.0057 mol) in ether (30 mL) at −10° was added triethylamine (1.2 g, 0.012 mol). Chlorotrimethylsilane (1.24 g, 0.012 mol) was then added in a dropwise fashion. The reaction mixture was then heated under reflux for three hrs. The solid was removed by filtration and the filtrate was concentrated at reduced pressure. The residual oil was molecularly distilled (65°, 0.05 mm) to yield 1.18 g (72.4%) of **8**; ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 18 H), δ 6.9–7.6 (m, 4 H).

Reaction of **8** *with Phosphorus Pentachloride*

A mixture of **8** (1.18 g, 0.004 mol), phosphorus pentachloride (0.42 g, 0.002 mol) and benzene (10 mL) was heated under reflux for three hrs. The ^{31}P NMR spectrum of this solution showed one resonance at δ 156.5 (external lock).

Preparation of **10**

Compound **10** was prepared by the method of Bauder *et al.*,[6] ^{31}P NMR δ 156.8 (external lock) (lit[6] δ 157).

Reaction of Toluene-3,4-dithiol, **7**, *and Phosphorus Pentachloride*

To a solution of toluene-3,4-dithiol, **7**, (0.95 g, 0.006 mol) in benzene (15 mL) was added, with stirring, phosphorus pentachloride (0.63 g, 0.003 mol). The reaction mixture was heated to 70° for two hrs. After removing the solvent at reduced pressure the residual oil was dissolved in chloroform-d; ^{31}P NMR δ 152.8.

Reaction of Toluene-3,4-dithiol, **7**, *and Phosphorus Pentachloride in the Presence of Triethylamine*

To a stirred solution of toluene-3,4-dithiol, **7**, (0.76 g, 0.0048 mol) in ether (15 mL) at 0° was added triethylamine (0.98 g, 0.0097 mol). To this mixture was then added phosphorus pentachloride (0.51 g, 0.0024 mol). The reaction mixture was allowed to warm to room temp. and it was stirred for an additional 2 hrs. The solid was removed by filtration. The filtrate showed one resonance in its ^{31}P NMR spectrum δ 156.1 (external block).

Preparation of **9**

To a stirred solution of toluene-3,4-dithiol, **7**, (2.5 g, 0.016 mol) in ether (50 mL) was added, at −20°, triethylamine (3.23 g, 0.032 mol). To this mixture was then added, dropwise, chlorotrimethylsilane (3.48 g, 0.032 mol). The reaction mixture was heated under reflux for 3 hrs. After having removed the solid by filtration the solvent was removed under reduced pressure and the residual oil was molecularly distilled (95°, 0.05 mm) to yield 3.08 g (64.2%) of **9**; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 18 H), δ 2.28 (s, 3 H), δ 6.8–7.6 (m, 3 H).

Reaction of **9** *with Phosphorus Pentachloride*

A mixture of **9** (1.2 g, 0.004 mol), phosphorus pentachloride (0.42 g, 0.002 mol) and toluene (20 mL) was heated under reflux for 10 hrs. The ^{31}P NMR spectrum of this solution showed one resonance at δ 156.5 (external lock).

Preparation of **11**

To a stirred solution of toluene-3,4-dithiol, **7**, (0.9 g, 0.0058 mol) in benzene (3 mL) was added at 25° phosphorus trichloride (0.79 g, 0.0058 mol). The mixture was heated under reflux for 2 hrs. The solvent was removed at reduced pressure and the residual oil was molecularly distilled (75°, 0.25 mm); ^{31}P NMR ($CDCl_3$) δ 160.7; ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3 H), δ 6.9–7.6 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.44 (s), δ 126.07 (d, J_{CCSP} = 5.5 Hz), δ 126.88 (d, J_{CCSP} = 5.6 Hz), δ 128.42 (s), δ 134.89 (d, J_{CSP} = 3.4 Hz), δ 137.59 (s), δ 138.36 (d, J_{CSP} = 3.2 Hz).

Anal. Calcd. for $C_7H_6ClPS_2$: C, 38.10; H, 2.70. found: C, 38.45; H, 2.64.

Reaction of the Products with Triphenylphosphine

To a solution of toluene-3,4-dithiol, **7**, (1.28 g, 0.0082 mol) in dichloromethane (5 mL) was added phosphorus pentachloride (0.86 g, 0.0042 mol). The reaction mixture was heated under reflux for two hrs. The solution was cooled to room temp. and to this was added, with stirring, sodium hydroxide (0.8 g, 0.02 mol) in water (5 mL). This mixture was stirred for one hr. and then the layers were separated. The ^{31}P NMR spectrum of the aqueous layer showed one resonance at $\delta - 0.8$, the organic layer showed no resonances.

To the dichloromethane solution was added triphenylphosphine (1.0 g, 0.004 mol) and a drop of water. This mixture was heated under reflux for 1 hr. After having been dried with magnesium sulfate the reaction mixture was concentrated at reduced pressure. The ^{31}P NMR spectrum of the residual oil showed a single absorption at δ 29.3 ($CDCl_3$). The product was molecularly distilled (50°, 0.25 mm) to yield material which was identical in all respect to toluene-3,4-dithiole, **7**; ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H), δ 3.6 (s, 2 H), δ 6.6–7.3 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.3, δ 127.1, δ 128.1, δ 131.8, δ 132.1, δ 132.4, δ 137.5.

Reaction of Toluene-3,4-dithiol, **7**, *with One and then a Second Equivalent of Phosphorus Pentachloride*

To a stirred solution of toluene-3,4-dithiol, **7**, (0.31 g, 0.002 mol) in dichloromethane (3 mL) at −10° was added phosphorus pentachloride (0.41 g, 0.002 mol). The ^{31}P NMR spectrum of the reaction mixture at −10° showed one resonance at δ 213.8 (external lock). To this mixture was then added, at −10°, another equivalent of toluene-3,4-dithiol, **7**, (0.31 g, 0.002 mol). There appeared to be no reaction at this temp. as evidenced by the lack of change in the ^{31}P NMR spectrum at −10°. The reaction mixture was allowed to warm to room temp. for 5 min and it was then returned to the −10° probe. The ^{31}P NMR spectrum of this mixture showed two absorptions at, δ 213.8 and δ 155.1 in a ratio of about 10:1. The reaction mixture was allowed to stand at room temp. for 16 hrs, the ^{31}P NMR spectrum then showed only one resonance at δ 155.1.

Reaction of **11** *with Chlorine*

To a stirred solution of toluene-3,4-dithiol, **7**, (0.65 g, 0.0042 mol) in dichloromethane (5 mL) was added phosphorus pentachloride (0.44 g, 0.0021 mol). The reaction mixture was heated under reflux for 2 hrs. After having been cooled, this solution was added to chlorine (0.3 g, 0.0042 mol) dissolved in dichloromethane (2 mL) at −20°. This mixture was allowed to warm to room temp. and the ^{31}P NMR spectrum was taken. There was only one resonance at δ 214.1 (external lock).

ACKNOWLEDGMENTS

This research has been supported by The National Science Foundation and by the Public Health Research Grant GM26428. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of NMR equipment. L. T. L. wishes to thank the Peoples Republic of China for financial support.

REFERENCES

1. (a) J. Emsley and C. D. Hall, "The Chemistry of Phosphorus," John Wiley and Sons, New York, N.Y., 1976.
   (b) W. S. Sheldrick, *Top. Curr. Chem.*, **73**, 1–49 (1978).
   (c) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements," G. Theime; Stuttgart, 1973.
2. (a) S. A. Bone, S. Tripett and P. J. Whittle, *J. C. S. Perkin I*, 80 (1977).
   (b) M. Eisenhut, R. Schmutzler and W. S. Sheldrick, *Chem. Commun.*, 143 (1973).
   (c) A. C. Sau and R. R. Holmes, *J. Organmet, Chem.*, **156**, 253 (1978).
   (d) R. R. Holmes and J. A. Dieters, *J. Amer. Chem. Soc.*, **99**, 3318 (1977).
   (e) B. C. Burros, N. J. De'Ath, D. B. Denney, D. Z. Denney and I. J. Kipnis, *J. Amer. Chem. Soc.*, **100**, 7300 (1978).

3. D. B. Denney, D. Z. Denney and Lun-tsu Liu, *Phosphorus and Sulfur,* in press.
4. (a) S. A. Glover, *J. C. S. Perkin I,* 1338 (1980).
   (b) D. B. Denney, D. Z. Denney and D. M. Gavriolovic, *Phosphorus and Sulfur,* **11,** 1 (1981).
   (c) A. F. Janzen, O. C. Vaidza and C. J. Willis, *J. Inorg. Nucl. Chem.,* **43,** 1469 (1981).
   (d) M. E. Peach, *Can. J. Chem.,* **46,** 2699 (1968).
   (e) M. E. Peach and H. G. Spinney, *Can. J. Chem.,* **49,** 644 (1971).
5. A. Ferretti, *Org. Syn., Coll. Vol.,* **5,** 419 (1973).
6. M. Bauder, A. Moog, K. Glinka and U. Kelsch, *Zeit. fur Natur., Teil B,* **28,** 363 (1973).