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SYNTHESIS OF NOVEL SULFUR CONTAINING SPIROCYCLIC PHOSPHORANES *

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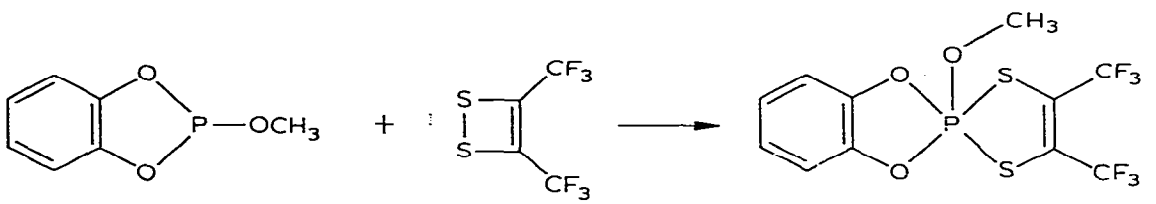
Summary

The synthesis of new spirocyclic phosphoranes containing both sulfur and oxygen hetero atoms bonded to phosphorus is described.

Introduction

The study of the chemistry and structure of cyclic phosphoranes has attracted increasing attention in recent years [1—4]. Much of the effort has been concerned with the assessment of factors which govern the reactivity and stereochemical properties of five-coordinate phosphorus compounds. For the most part, the studies involve carbon, nitrogen, and oxygen as the principal ring atoms directly attached to phosphorus.

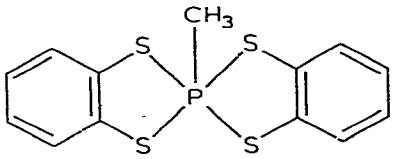
Partly because of the lower stability of sulfur derivatives, relatively few cyclic phosphoranes containing P—S bonds have been reported [5—10]. De'Ath and Denney [7] found that sulfur containing phosphoranes could be obtained in high yield by the reaction of small ring phosphines and phosphites with 3,4-bis-(trifluoromethyl)-1,2-dithieten I. For example, reaction of methyl catechol phosphite with I gave the spirocyclic II.



(I) (II)

* Dedicated to Professor H.C. Brown in recognition of his contributions to chemistry.

One derivative which has been reported whose X-ray structure is known [6] is the bis-dithiaphosphole III. The structure may be characterized as a mildly distorted rectangular pyramid [11].

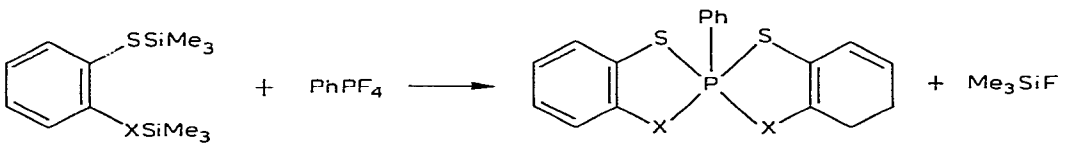


(III)

Because of the interesting structural consequences on pentacoordinate stereochemistry that arise on introducing directly bonded sulfur atoms, we undertook the investigation of synthetic routes leading to derivatives amenable to full characterization by X-ray analysis. Accordingly, we report here the synthesis of some new sulfur-containing spirophosphoranes.

Results and discussion

Reaction of $PhPF_4$ with the silane derivatives IV and V results in good yields (~60—70%) of the spirophosphoranes VI and VII, respectively. The bis-dithia-

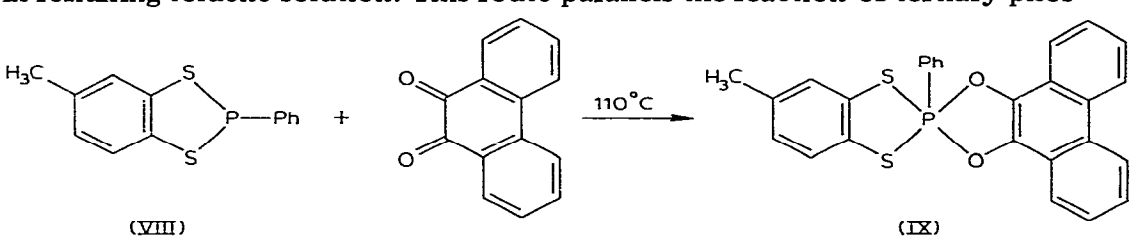


(IV) X = S
(V) X = O

(VI) X = S
(VII) X = O

phosphole VI has been reported [5,6] but details of the synthetic route are lacking. Our specific modifications are given in the experimental section. Both VI and VII are crystalline substances. Preliminary analysis by X-ray diffraction [12] reveals that they are intermediate in structure between the idealized trigonal bipyramid and rectangular pyramid *.

The mixed ligand containing spirophosphorane IX was obtained in 93% yield from the reaction of the dithiaphospholane VIII with 9,10-phenanthrenequinone in refluxing toluene solution. This route parallels the reaction of tertiary phos-



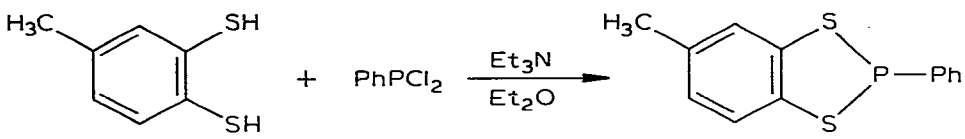
(VIII) (IX)

phines with *o*-quinones [13,14]. Recrystallization from benzene gave light brown crystals. The structure of IX from X-ray analysis is nearly rectangular

* For a discussion of the distortion coordinate followed by cyclic phosphoranes see ref. 11.

pyramidal [12], more so than that for III. This contrasts to VI and VII which have structures [12] less displaced from the trigonal bipyramid than that for III.

The dithiaphospholane VIII was prepared in 85% yield according to the following scheme:



(VIII)

The spirophosphoranes reported here are fairly stable at room temperature but undergo slow decomposition (as noted by their gradual color change) when stored in a desiccator for 2 to 3 months. As expected for the pentacoordinated structures VII and IX, the ^{31}P NMR spectrum shows a sharp single absorption at 18.2 and 29.5 ppm, respectively. The observed values lie near those reported for some sulfur-containing spirophosphoranes by De'Ath and Denney [7]. No ^{31}P NMR spectrum was obtained for VIII owing to its lack of solubility in methylene chloride at room temperature and its tendency to decompose in solvents in general at elevated temperatures.

With the newly synthesized starting materials V and VIII in addition to that already reported [5] for IV, the synthetic routes to other sulfur-containing cyclic phosphoranes may be advantageously explored. The detailed X-ray structural analysis of VI, VII, and IX will follow elsewhere.

Experimental

All reactions were carried out in a dry nitrogen atmosphere taking necessary precautions in handling air- and moisture-sensitive compounds.

^1H NMR spectra were recorded on $CDCl_3$ solutions with a Perkin—Elmer R12A instrument. Chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{31}P NMR spectra were recorded on a Varian HA-100 instrument. Chemical shifts are expressed in ppm relative to the external standard, 85% phosphoric acid. Upfield shifts are negative.

Materials

Phenyldichlorophosphine (Aldrich) was freshly distilled prior to use. Phenyltetrafluorophosphorane ($PhPF_4$) was prepared by the reaction of phenyldichlorophosphine with antimony trifluoride according to the procedure of Schmutzler [15]. Toluene-3,4-dithiol was obtained from Eastman Kodak Company. *o*-Mercaptophenol was made from *o*-aminophenol as described by Djerassi et al. [16]. Hydrocarbon solvents (benzene, toluene and hexane) were dried over calcium hydride. Methyl cyanide was distilled over phosphorus pentoxide. Triethylamine was purified by distillation over potassium hydroxide.

Preparation of o-phenyleneoxathiabis(trimethylsilane) ($C_6H_4(OSiMe_3)(SSiMe_3)$, V)

To a solution of *o*-mercaptophenol (12.6 g, 100 mmol) in anhydrous ethyl

ether (200 ml) triethylamine (20.2 g, 200 mmol) was added at 0°C. A flocculent precipitate immediately formed. Chlorotrimethylsilane (21.7 g, 200 mmol) was then added dropwise under vigorous stirring to this suspension over a period of 30 minutes. The resulting reaction mixture was heated under reflux for 3 h, filtered and the solvent evaporated *in vacuo*. Distillation of the viscous residue through a 15 cm Vigreux column gave the desired product, *o*-phenyleneoxathiabis(trimethylsilane) (V), as a clear liquid, b.p. 70—71°C/0.1 mmHg (yield 12.0 g, 86.6%). ^{1}H NMR ($CDCl_3$, TMS internal) δ 6.65—7.55 (m, 4H, C_6H_4), 0.30 (s, 9H, $OSiMe_3$), 0.25 (s, 9H, $SSiMe_3$) ppm.

Preparation of 2-phenyl-2,2'-spirobis(1,3,2-benzooxathiaphosphole) (VII)

A mixture of phenyltetrafluorophosphorane (3.68 g, 20 mmol) and *o*-phenyleneoxathiabis(trimethylsilane) (10.80 g, 40 mmol) in toluene (25 ml) was heated under reflux at 110°C (oil bath) for 20 h. The resulting reaction mixture was diluted with hexane (30 ml) and cooled at 0°C overnight in a refrigerator. The white lumpy crystals thus obtained were recrystallized from hexane at 0°C and yielded pure 2-phenyl-2,2'-spirobis(1,3,2-benzooxathiaphosphole) (VII), m.p. 116—117°C (yield 4.6 g, 64.3%). ^{1}H NMR ($CDCl_3$, TMS internal) δ 6.70—8.15 (m, aromatic protons) ppm. ^{31}P NMR (CH_2Cl_2) δ 18.2 ppm.

Anal. Found: C, 60.43; H, 3.77; P, 8.43. $C_{18}H_{13}S_2O_2P$ calcd.: C, 60.58; H, 3.65; P, 8.70%.

Preparation of 2-phenyl-2'-methyl-1,3,2-benzodithiaphospholane (VIII)

Triethylamine (13.10 g, 0.13 mol) was added to a solution of toluene-3,4-dithiol (10.00 g, 0.064 mol) in anhydrous diethyl ether (400 ml) cooled to 0°C. A flocculent light yellow precipitate immediately formed. To this well-stirred suspension a solution of phenyldichlorophosphine (11.5 g, 0.064 mol) was added dropwise over a period of 2 h. As the reaction progressed, the light yellow precipitate was replaced by a curdy white precipitate (triethylamine hydrochloride) and the ethereal solution turned light yellow. The resulting reaction mixture was stirred at 0°C for another 2 h and heated under reflux for 3 h. Ethylamine hydrochloride was filtered under suction in a dry nitrogen atmosphere and washed thrice with 100 ml portions of anhydrous ether. The original filtrate and the washings were combined. Evaporation of the solvent from the solution yielded a viscous liquid dispersed in a crystalline precipitate ($Et_3N \cdot HCl$). It was treated with benzene (75 ml) and shaken. The insoluble triethylamine hydrochloride precipitate was removed by filtration. The viscous residue, obtained after the evaporation of the benzene, solidified on cooling at 0°C in a refrigerator. The crude product was recrystallized from hexane at 0°C and yielded pure 2-phenyl-2'-methyl-1,3,2-benzodithiaphospholane (VIII), m.p. 59—60°C (yield 14.2 g, 84.7%). Compound VIII can also be obtained in pure form by subliming the crude material in vacuo (65°C/0.1 mmHg). ^{1}H NMR data in $CDCl_3$ at 60 MHz (TMS internal); δ 7.25 (m, 8 H, aromatic protons from C_6H_5 and C_6H_3), 2.20 (s, 3 H, CH_3) ppm. ^{31}P NMR (CH_2Cl_2), δ 50.0 (s) ppm.

Anal. Found: C, 60.04; H, 4.16; P, 11.96. $C_{13}H_{11}S_2P$ calcd.: C, 59.60; H, 4.19; P, 11.90%.

Preparation of 5-phenyl-2,3-phenanthro-7,8-(2'-methyl-5',6'-benzo)-1,4-dioxa-6,9-dithia-5-phospha(V)spiro[4.4]nona-2,7-diene (IX)

To a magnetically stirred suspension of 9,10-phenanthrenequinone (2.1 g,

10 mmol) in toluene (20 ml), a solution of 2-phenyl-2'-methyl-1,3,2-benzodithiaphospholane (VIII) (2.6 g, 10 mmol) was added at room temperature. The resulting reaction mixture was heated under reflux at 110°C (oil bath) for 2 h. On cooling the deep brown reaction mixture overnight at 0°C in a refrigerator, crystals of 5-phenyl-2,3-phenanthro-7,8-(2'-methyl-5',6'-benzo)-1,4-dioxa-6,9-dithia-5-phospha(V)spiro[4.4]nona-2,7-diene (IX) formed. The crude material was recrystallized from benzene and yielded light brown crystals of the spirophosphorane (IX), m.p. 222—223°C (yield 4.1 g, 91.5%). ^{1}H NMR ($CDCl_3$, TMS internal) δ 6.75—8.80 (m, 16 H, aromatic protons from C_6H_3, C_6H_5, $C_{14}H_8O_2$), 2.25 (s, 3 H, CH_3) ppm. ^{31}P NMR (CH_2Cl_2) δ 29.5 ppm.

Anal. Found: C, 69.96; H, 4.04; P, 6.65. $C_{27}H_{19}S_2O_2P$ calcd.: C, 69.00; H, 4.04; P. 6.59%.

Preparation of o-phenylenedithiobis(trimethylsilane) (IV)

o-Phenylenedithiobis(trimethylsilane) (IV) was prepared by the reaction of *o*-phenylenedithiol (prepared according to Hünig and Fleckenstein [17]) with chlorotrimethylsilane in the presence of triethylamine in diethyl ether as described by Eisenhut [5]. IV boils at 89°C/0.1 mmHg (yield 80%). ^{1}H NMR ($CDCl_3$, TMS internal) δ 6.6—7.5 (m, 4 H, C_6H_4), 0.28 (s, 18 H, $SSiMe_3$) ppm.

Preparation of 2-phenyl-2,2'-spirobis(1,3,2-benzodithiaphosphole) (VI)

Phenyltetrafluorophosphorane (5.52 g, 30 mmol) and benzene (20 ml) were added to a two-necked 100 ml round-bottomed flask equipped with an addition funnel, magnetic stirring bar, and reflux condenser. The top of the reflux condenser was connected to a tared trap cooled with a dry ice/acetone mixture and protected from moisture by connecting the open end to a bubbler (paraffin oil). *o*-Phenylenedithiobis(trimethylsilane) (IV) (17.16 g, 60 mmol) was added dropwise under vigorous stirring to this solution over a period of 45 minutes. The resulting yellow reaction mixture was heated under reflux at 100°C (oil bath) for 20 h. As the reaction progressed, the yellow color of the reaction mixture intensified. Removal of the solvent from the reaction mixture in vacuo yielded an orange-yellow solid. The solid was washed twice with hexane (20 ml) and recrystallized from benzene to yield yellow needle-shaped crystals of 2-phenyl-2,2'-spirobis(1,3,2-benzodithiaphosphole) (VI), m.p. 133—135°C (yield 5.88 g, 90%).

Anal. Found: C, 55.5; H, 3.4; P, 7.92. $C_{18}H_{13}S_4P$ calcd.: C, 55.6; H, 3.4; P, 8.0%.

Acknowledgements

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