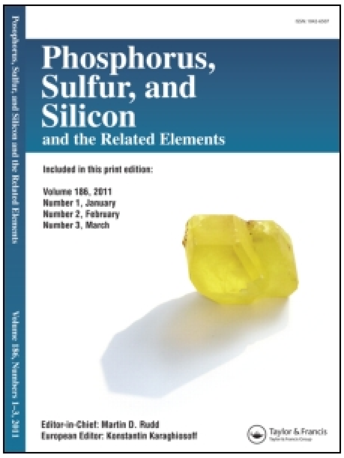


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A SIMPLE ROUTE TO 1,4-DIHYDRO-1δ^5,4δ^5- DIPHOSPHORINES

To cite this Article (1992) 'A SIMPLE ROUTE TO 1,4-DIHYDRO-1δ^5,4δ^5- DIPHOSPHORINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 71: 1, 245 — 248

To link to this Article: DOI: 10.1080/10426509208034517

URL: http://dx.doi.org/10.1080/10426509208034517

Phosphorus, Sulfur, and Silicon, 1992, Vol. 71, pp. 245–248
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

A SIMPLE ROUTE TO 1,4-DIHYDRO-1λ^5,4λ^5-DIPHOSPHORINES

EKKEHARD FLUCK*
Gmelin-Institut für Anorganische Chemie der Max-Planck Gesellschaft, Varrentrappstraße 40-42, D-6000 Frankfurt am Main 90, Germany

and

KLAUS BIEGER and GERNOT HECKMANN
Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Germany

and

FRANK WELLER
Fachbereich Chemie der Universität Marburg, Hans Meerweinstraße, D-3550 Marburg/Lahn, Germany

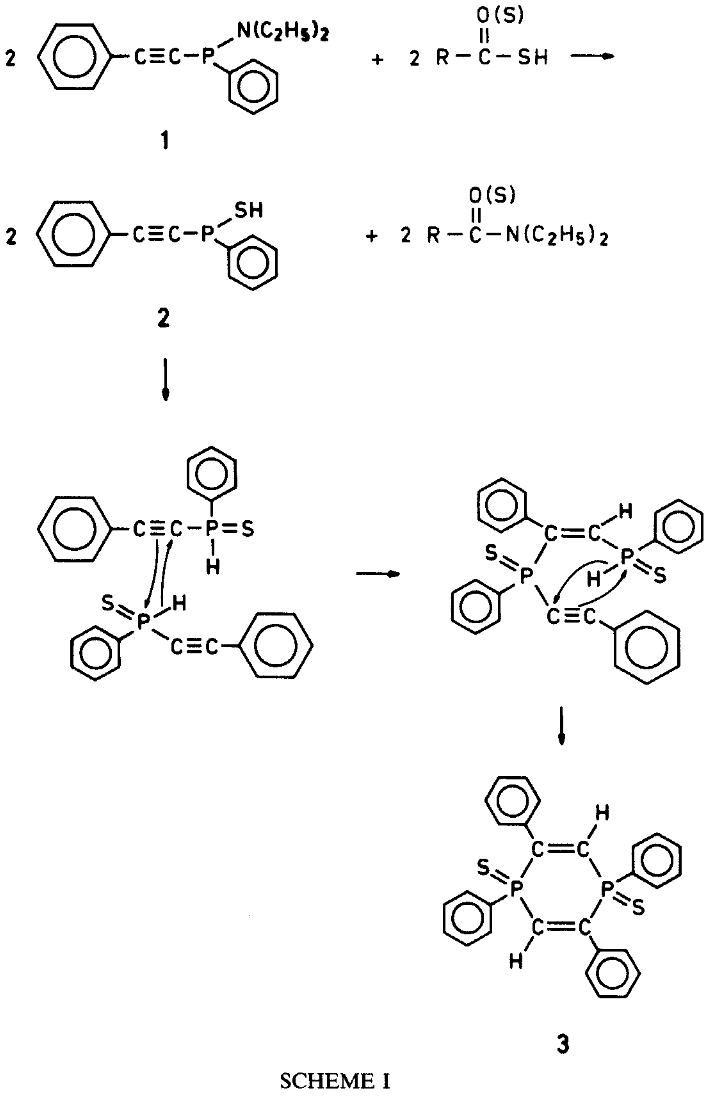
(Received June 4, 1992)

Reaction between ethynylaminophosphanes with thiobenzoic acid or 3-oxobutanedithioic acid yield 1,4-dihydro-1λ^5,4λ^5-diphosphorine 1,4-disulfides. The NMR data and the results of the x-ray structure determination of 1,4-dihydro-1,2,4,5-tetraphenyl-1λ^5,4λ^5-diphosphorine 1,4-disulfide are described.

Key words: Dihydro-diphosphorine disulfides; crystal structure; NMR.

INTRODUCTION AND RESULTS

Compounds of the monocyclic 1,4-dihydro-1λ^5,4λ^5-diphosphorine (or 1λ^5,4λ^5-diphosphadihydrobenzene) class are almost unknown. The first representatives of this class were described by Märkl in 1975.[1] In this paper we describe a simple route to compounds of this type based on the reaction of ethynylaminophosphanes with thiobenzoic acid or 3-oxobutanedithioic acid, $CH_3C(O)CH_2C(S)SH$. Reaction of the latter with phenyl(phenylethynyl)diethylaminophosphane **1** (Scheme I), for example, gives 1,4-dihydro-1,2,4,5-tetraphenyl-1λ^5,4λ^5-diphosphorine 1,4-disulfide **3**, isolated after recrystallization from chloroform in the form of a colorless crystalline solvate that decomposes rapidly in air with loss of chloroform. We assume that the reaction proceeds via phenyl(phenylethynyl)mercaptophosphane **2**, which then rearranges to phenyl(phenylethynyl)phosphane sulfide. Two successive additions (one inter-, the other intramolecular) of P—H to the triple bond result in the formation of **3**.[2]



SCHEME I

Crystals of **3** recrystallized from 1,2-dichloroethane are solvent-free. They melt at 287°C. In the $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 85% H_3PO_4 reference) of **3**, the chemical shift is at 17.0 ppm. The $^{13}C\{^1H, ^{31}P\}$ NMR spectrum (C_6D_6, TMS reference) of **3** shows chemical shifts for the endocyclic carbon atoms at 134.6 ppm (methyne C) and 144.6 ppm. The associated $^1J(PC)$ values of 77.8 Hz and 73.0 Hz and the $^3J(PP)$ value of 44.1 Hz were extracted from the ^{13}C satellites in the $^{31}P\{^1H\}$ NMR spectrum, which comprises the AB portion of an ABX spin system.[3] The $^1H\{^{31}P\}$ NMR spectrum (C_6D_6, TMS reference) of **3** shows a broad singlet for the olefinic hydrogen atoms with a chemical shift of 6.75 ppm.

The NMR data, together with the results of the X-ray structure determination (see Figure 1), confirm the structure of **3**.

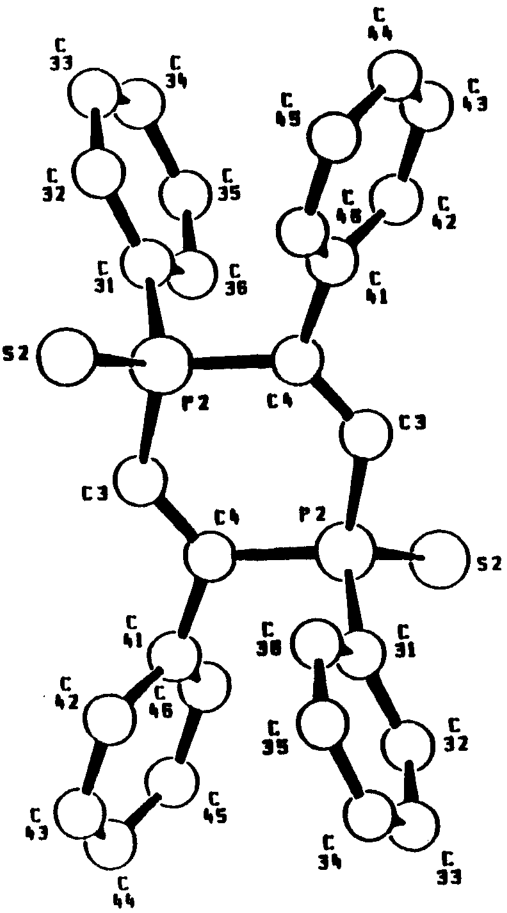


FIGURE 1 Molecular structure of **3**. Only one of the two crystallographically independent but very similar molecules is shown. The H atoms have been omitted for clarity. The ring atoms are approximately planar; the average and the maximum deviations of the "best" plane in each molecule are 1.7 and 1.9 pm or 2.2 and 2.4 pm, respectively. The corresponding distances (pm) and angles (°) are almost identical: P2—C4 179.1(5), P2—C3 179.8(5), C3—C4 134.4(6), P2—S2 194.5(2); P2—C4—C3 124.1(4), P2—C3—C4 127.9, C3—P2—C4 107.8(2).

EXPERIMENTAL

A solution of 10 mmol phenyl phenylethinyl diethylamino phosphane in 10 ml of chloroform was cooled to −30°C and treated dropwise with stirring with a solution of 2.4 ml thiobenzoic acid in 10 mL of chloroform. When the reaction mixture was kept in a refrigerator at 3°C for several days a colorless solid precipitated, which after cooling of the mixture to −30°C is separated by filtration. By recrystallization from chloroform **3** was obtained in the form of a colorless crystalline solvate that decomposed in air with release of chloroform. Crystals of **3** from 1,2-dichlororoethane, however, were solvent free. Yield, 1,0 g (20%).

Crystal Data. —$C_{28}H_{22}P_2S_2$, $M = 484.5$, triclinic, $P\bar{1}$; $Z = 2$; $a = 940.2(2)$, $b = 1139.2(2)$, $c = 1263.9(3)$ pm; $\alpha = 104.32(2)$, $\beta = 98.48(2)$, $\gamma = 102.32(2)°$; $D_c = 1.29$ g/cm^3 at 20°C; four circle diffractometer CAD 4 (graphite monochromator, scintillation counter, CuK_α); Ω-scans in the region $2° < \theta < 65°$; 4217 symmetry independent reflections, 869 with $F_o < 4\sigma < (F_o)$; empirical absorption correction with Ψ-scans; structure solution with direct methods in $P\bar{1}$; refinements with full matrix least squares, $R = 0.057$; after anisotropic refinement of the P, S, and C atoms, the H atoms were localized by differential Fourier synthesis. The calculations were done with SHELXTL,[4] PLATON,[5] and SCHAKAL.[6] Atomic coordinates, bond lengths, bond angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.

REFERENCES

1. G. Märkl, D. Matthes, A. Donaubauer and H. Baier, *Tetrahedron Lett.*, 1975, 3171; see also: G. Märkl, W. Weber and W. Weiss, *Chem. Ber.*, **118,** 2365 (1985).
2. We thank Dr. Arlen W. Frank, correspondent member of Gmelin-Institut staff, for suggesting this reaction path.
3. G. Heckmann, E. Fluck and K. Bieger, *Magn. Reson. Chem.*, in preparation.
4. G. M. Sheldrick, SHELXTL-Plus, Release 4.0 for Siemens R3 Crystallographic Research Systems. Siemens Analytical X-Ray Instruments, Inc., Madison, WI, USA, 1989.
5. A. L. Spek, PLATON-89, University of Utrecht, 1989.
6. E. Keller, SCHAKAL-86, a FORTRAN Program for the Graphical Representation of Molecular and Crystallographic Models, Freiburg, 1986.