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2-Chloro-2-phenyl-2-(*p*-tolylthio)-1,3-diorgano-1,3,2λ^5-diazaphosphetidin-4-ones

Vasily A. Pinchuk[a], Ion Neda[a], Christian Müller[a], Axel Fischer[a], Peter G. Jones[a], Yuri G. Shermolovich[b], and Reinhard Schmutzler*[a]

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig[a], Postfach 3329, 38023 Braunschweig, Germany

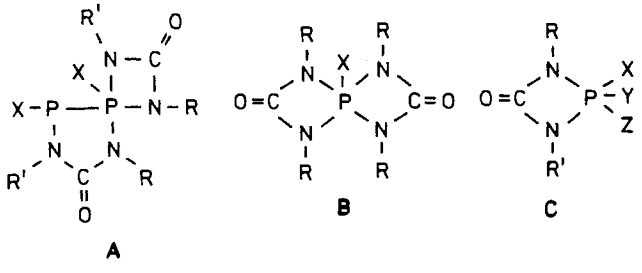
Institute of Organic Chemistry, Ukrainian Academy of Sciences[b], 253660 Kiev, Ukraine

Received December 27, 1993

Key Words: 1,3,2λ^5-Diazaphosphetidin-4-ones, 2-chloro-2-phenyl-2-(*p*-tolylthio)-1,3-diorgano- / Phosphorus, pentacoordinated

The reaction of *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea (**1**) or *N*-methyl-*N'*-phenyl-*N,N'*-bis(trimethylsilyl)urea (**2**) with *p*-toluenesulfenyl chloride furnished *N,N'*-dimethyl-*N*-(*p*-tolylthio)-*N'*-(trimethylsilyl)urea (**3**) and *N*-methyl-*N'*-phenyl-*N'*-(*p*-tolylthio)-*N*-(trimethylsilyl)urea (**4**), respectively. The reaction of $PhPCl_2$ with compounds **3** and **4** resulted in the formation of the title compounds **6** and **7**. Their identity and structure were established by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy and by a single-crystal X-ray structure analysis in the case of **7**, in which the geometry at phosphorus is that of a distorted trigonal bipyramid with the axial P–N bond significantly longer than in similar phosphoranes. The mechanism of formation of phosphoranes **6** and **7** is discussed.

N,N'-Disilyl derivatives of *N,N'*-diorgano-substituted ureas have been used successfully in the synthesis of different types of phosphoranes, involving nitrogen-containing groups. Phosphoranes of types **A**[1,2], **B**[3–7] and **C**[7,8], in which λ^5-phosphorus atoms are part of four-membered ring systems based on *N,N'*-disubstituted ureas, have been reported.

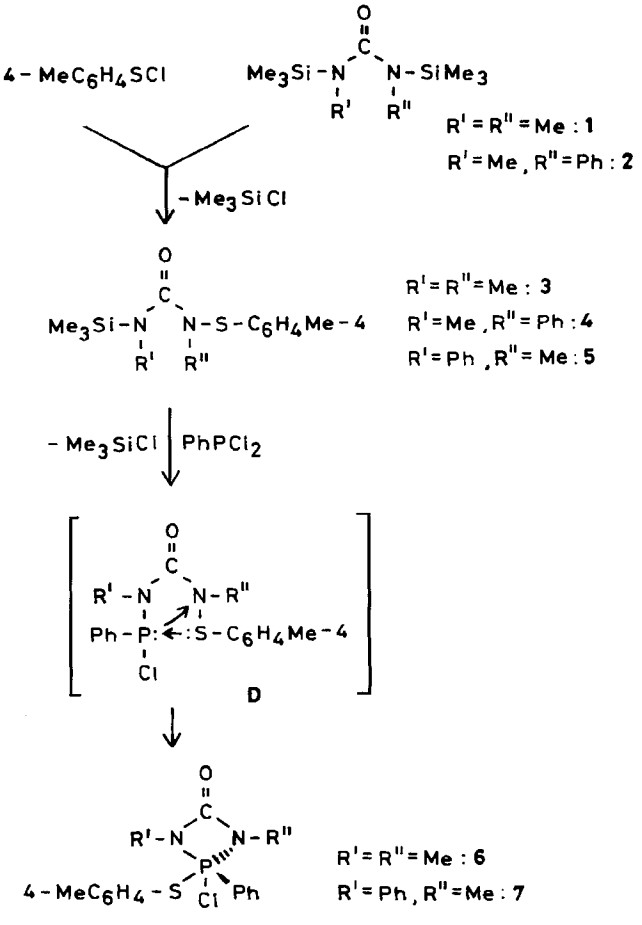


A **B** **C**

We have found a simple synthesis of four-membered cyclic thiophosphoranes by using the reaction of *N,N'*-dimethyl-*N*-(*p*-tolylthio)-*N'*-(trimethylsilyl)urea (**3**) and *N*-methyl-*N'*-phenyl-*N'*-(*p*-tolylthio)-*N*-(trimethylsilyl)urea (**4**) with $PhPCl_2$. Compounds **3** and **4** were prepared by the reaction of *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea (**1**) and *N*-methyl-*N'*-phenyl-*N,N'*-bis(trimethylsilyl)urea (**2**) with *p*-toluenesulfenyl chloride.

In the case of the *N*-methyl-*N'*-phenylurea derivative a mixture of **4** and *N*-methyl-*N'*-phenyl-*N*-(*p*-tolylthio)-*N'*-(trimethylsilyl)-urea (**5**) (^{1}H-NMR evidence) was formed and was used without separation. In the reaction of compound **3** with $PhPCl_2$ the phosphorane **6** was formed and in the reaction of the mixture of ureas **4** and **5** with $PhPCl_2$ the phosphorane **7**.

The 2-chloro-2-phenyl-2-(*p*-tolylthio)-1,3-diorgano-1,3,2λ^5-diazaphosphetidine-4-ones **6** and **7** are colourless crystalline substances, which are readily hydrolysed by moist air. Their δ(^{31}P)



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values lie in the region of −40 to −50, which is characteristic of compounds involving pentacoordinated phosphorus. A major difference in the δ(^{1}H) values of the CH_3 protons in the case of the 1,3-dimethyl derivative **6** is noteworthy because such substantial differences have not been observed for other known types of four-membered cyclic nitrogen-containing phosphoranes[1-8].

A single-crystal X-ray structure analysis of the phosphorane **7** was conducted (Figure 1). The geometry at the pentacoordinated phosphorus is that of a distorted trigonal bipyramid. Cl and N2 (phenyl-substituted) are axial, whereas S, N1 (methyl-substituted), and C2 occupy the equatorial positions [N2−P−Cl 166.22(6)°]. The equatorial angles vary from 117.01(7)° (C2−P−S) to 124.07(7)° (N1−P−S). The distortion towards a rectangular pyramid (with C2 at the apical position) is not as marked as that displayed by phosphoranes of a similar type[7,8]. The axial P−N bond is significantly longer than in related phosphoranes[7,8], whereas the equatorial P−N bond length corresponds well to literature values. The four-membered ring is, as in refs.[7,8], essentially planar (mean deviation is less than 0.1 pm). The phenyl group at N2 and the *p*-tolyl group subtend a dihedral angle of 21.8°.

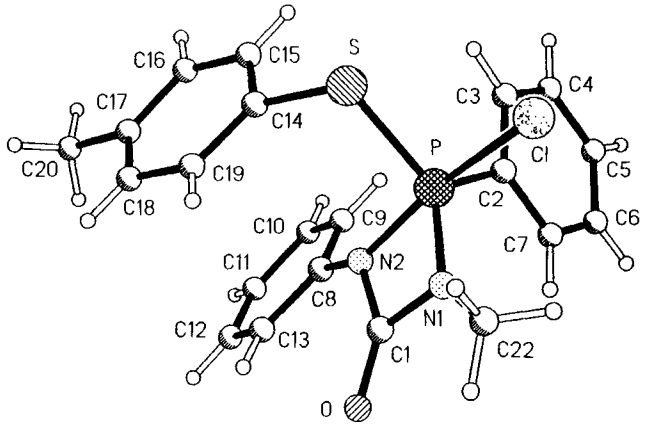
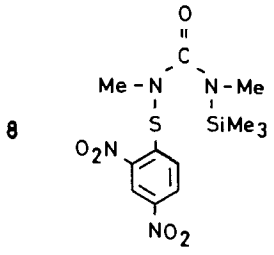


Figure 1. A molecule of **7** in the crystal. Radii are arbitrary. Bond lengths [pm] and angles [°]: P−N(1) 167.1(2), P−N(2) 181.1(2), P−Cl 221.80(8), P−C(2) 179.8(2), P−S 208.34(8), S−C(14) 177.6(2); N(1)−P−C(2) 118.86(9), C(2)−P−N(2) 98.05(8), C(2)−P−S 117.01(7), N(1)−P−Cl 92.26(6), N(2)−P−Cl 166.22(6), N(1)−P−N(2) 74.19(8), N(1)−P−S 124.07(7), N(2)−P−S 100.72(6), C(2)−P−Cl 90.65(6), S−P−Cl 84.61(3), C(22)−N(1)−P 136.9(2), C(1)−N(2)−P 91.17(2)

In solution these phosphoranes apparently undergo permutational isomerisation implied by the observation that the broad signals of the CH_3 protons in the case of compound **6** become sharp doublets only at −40°C.

The formation of compounds **6** and **7** can be explained by migration of an arylthio group from nitrogen to phosphorus in an initially formed aminophosphane **D**. The formation of compounds with pentacoordinated phosphorus in the reactions of phosphanes with sulfenamides has been discussed, and reactions of this type were successfully used in peptide synthesis[9]. Intramolecular interaction between phosphorus and other elements, including P, As and Sn, in related substituted urea systems was reported previously[10-12]. In confirmation of the proposed scheme, it may be noted that in the reaction of $PhPCl_2$ with the urea **8**, where the electron-donating properties of sulfur are reduced by the influence of two NO_2 groups, the formation of a phosphorane does not take place[16]. No product was isolated but in the ^{31}P-NMR spectra a signal in the region of δ = 120 was observed, which indicates that the reaction finishes at the stage of substitution, and no migration of arylthio group occurs.



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The authors thank Prof. *L. N. Markovskii* for useful discussions. The *Deutsche Forschungsgemeinschaft* is thanked for financial support. I. N. is indebted to the *Bundesanstalt für Arbeit* for ABM support. *BASF-Aktiengesellschaft*, *Bayer AG*, and *Hoechst AG* are thanked for generous gifts of chemicals. Prof. *L. Ernst* of this Institute has helped with the interpretation of NMR spectra. The support of *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

All experiments were carried out with exclusion of air and moisture, solvents were purified and dried according to the usual methods[13]. − NMR: Bruker AC 200 (^{1}H at 200.1 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.3 MHz); reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C) and 85% H_3PO_4 ext. (^{31}P); high-field shifts are given negative, low-field shifts positive signs. − Materials: *N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)urea (**1**), *N*-methyl-*N'*-phenyl-*N,N'*-bis(trimethylsilyl)urea (**2**)[14], and *p*-toluenesulfenyl chloride[15] were synthesized according to procedures described in the literature. "In vacuo" (i.v.) refers to a pressure of 0.1 Torr, unless otherwise stated.

N,N'-Dimethyl-N-(p-tolylthio)-N'-(trimethylsilyl)urea (**3**): A solution of *p*-toluenesulfenyl chloride (5.0 g, 32 mmol) in 20 ml of dichloromethane was added dropwise with stirring over 15 min at 0°C to a solution of **1** (7.35 g, 32 mmol) in 20 ml of dichloromethane. Dichloromethane was removed in vacuo and the oily residue distilled in vacuo (0.3 Torr); colourless liquid, b.p. 126−129°C (0.3 Torr); yield 4.85 g (66%). − ^{1}H NMR ($CDCl_3$): δ = 0.25 [s, $Si(CH_3)_3$], 2.31 (s, $H_3CC_6H_4$), 2.85 (s, *N'*-CH_3), 3.06 (s, *N*-CH_3), 7.01−7.21 (m, C_6H_4). − ^{13}C NMR ($CDCl_3$): δ = −0.25 [s, $Si(CH_3)_3$], 20.94 (s, $H_3CC_6H_4$), 33.84 (s, *N'*-CH_3), 41.35 (s, *N*-CH_3), 124.03−137.22 (m, C_6H_4), 167.44 (s, C=O). − $C_{13}H_{22}N_2OSSi$ (282.5): calcd. C 55.27, H 7.85, N 9.92; found C 55.37, H 7.43, N 10.18.

N-Methyl-N'-phenyl-N'-(p-tolylthio)-N-(trimethylsilyl)urea (**4**): A solution of *p*-toluenesulfenyl chloride (2.5 g, 16 mmol) in 10 ml of dichloromethane was added dropwise with stirring during 15 min at 0°C to a solution of **2** (4.65 g, 16 mmol). The solvent was removed in vacuo, and the oily residue was used in the subsequent reaction with $PhPCl_2$ without further purification. − ^{1}H NMR ($CDCl_3$): δ = 0.27 [s, $(CH_3)_3Si$], 0.29* [s, $(CH_3)_3Si$], 2.28 (s, $H_3CC_6H_4$), 2.32* (s, $H_3CC_6H_4$), 2.55 (s, *N*-CH_3), 3.17* (s, $H_3CC_6H_4SNCH_3$), 7.05−7.33 (m, Ar). (* Signals of the isomeric urea **5**. The integral intensity ratio was approximately 8:1). − $C_{18}H_{24}N_2OSSi$ (344.5): calcd. C 62.74, H 7.02, N 8.13; found C 62.53, H 7.12, N 7.95.

2-Chloro-1,3-dimethyl-2-phenyl-2-(p-tolylthio)-1,3,2λ^5-diazaphosphetidin-4-one (**6**): A solution of $PhPCl_2$ (0.92 g, 5.1 mmol) in 10 ml of dichloromethane was added dropwise with stirring during 15 min at 0°C to a solution of **3** (1.45 g, 5.1 mol) in 10 ml of dichloromethane. The solvent was removed in vacuo and the prod-

uct recrystallised from dichloromethane/diethyl ether (1:3) resulting in a colourless crystalline substance; yield 1.64 g (91%), m.p. 102–104°C. – ^{1}H NMR (+23°C, $CDCl_3$): δ = 1.46 (broad s, 1-CH_3), 2.29 [d, J(HP) = 4.0 Hz, $H_3CC_6H_4$], 3.15 [broad d, ^3J(HP) = 18.4 Hz, 3-CH_3], 7.07–7.85 (m, Ar). – ^{1}H NMR (–40°C, $CDCl_3$): δ = 1.46 [d, ^3J(HP) = 8.1 Hz, 1-CH_3], 2.29 [d, J(HP) = 4.0 Hz, $H_3CC_6H_4$], 3.15 [d, ^3J(HP) = 18.4 Hz, 3-CH_3], 7.07–7.85 (m, Ar). – ^{13}C NMR (+23°C, $CDCl_3$): δ = 21.37 [d, J(CP) = 2.1 Hz, $H_3CC_6H_4$], 27.6 (broad s, NCH_3), 28.0 (broad s, NCH_3), 130.1–144.3 (m, Ar), 156.06 [d, ^2J(CP) = 10.74 Hz, C=O]. – ^{31}P NMR: δ = –43.82. – $C_{16}H_{18}ClN_2OPS$ (352.8): calcd. C 54.47, H 5.14, N 7.94; found C 54.49, H 5.31, N 8.01.

2-Chloro-1-methyl-2,3-diphenyl-2-(p-tolylthio)-1,3,2λ^5-diazaphospheti din-4-one (**7**): A solution of $PhPCl_2$ (2.26 g, 13 mmol) in 10 ml of dichloromethane was added dropwise with stirring during 15 min at 0°C to a solution of a mixture of **4** and **5** in 10 ml of dichloromethane. The solvent was removed in vacuo and the product recrystallised from dichloromethane/diethyl ether (1:3) resulting in a colourless crystalline substance; yield 4.71 g (90%), m.p. 118–122°C. – ^{1}H NMR ($CDCl_3$): δ = 2.22 [d, J(HP) = 4.4 Hz, $H_3CC_6H_4$], 3.27 [d, ^3J(HP) = 17.8 Hz, $PNCH_3$], 6.60–7.90 (m, Ar). – ^{13}C NMR ($CDCl_3$): δ = 21.19 [d, J(CP) = 2.1 Hz, $H_3CC_6H_4$], 27.81 (s, NCH_3), 118.3–142.85 (m, Ar), 153.08 [d, ^2J(CP) = 12.08 Hz, C=O]. – ^{31}P NMR: δ = –48.68. – $C_{21}H_{20}ClN_2OPS$ (414.9): calcd. C 60.94, H 4.86, N 6.75; found C 60.85, H 4.35, N 6.83.

N-(1,3-Dinitrophenylthio)-N,N'-dimethyl-N'-(trimethylsilyl)urea (**8**): A solution of 1,3-dinitrobenzenesulfenyl chloride (1.6 g, 6.8 mmol) in 10 ml of dichloromethane was added dropwise with stirring during 15 min at room temp. to a solution of **1** (1.5 g, 6.8 mmol) in 10 ml of dichloromethane, and the reaction mixture was stirred at room temp. for 1 h. Dichloromethane was removed in vacuo and the product recrystallised from 10 ml of diethyl ether resulting in a yellow crystalline substance; yield 2.0 g (82%), m.p. 132–133°C. – ^{1}H NMR ($CDCl_3$): δ = 0.24 [s, $Si(CH_3)_3$], 2.82 (s, N'-CH_3), 3.21 (s, N-CH_3), 7.62–9.15 (m, C_6H_3). – $C_{12}H_{18}N_4O_5SSi$ (358.4): calcd. C 40.21, H 5.06, N 15.63; found C 40.54, H 5.21, N 15.46.

Single-Crystal X-Ray Structure Determination of Compound **7**: *Crystal data:* M = 414.87, monoclinic, $P2_1/c$, a = 1291.0(3), b = 1442.7(3), c = 1068.7(2) pm, β = 90.96(3)°, U = 1.9902(7) nm^3, Z = 4, D_x = 1.385 Mg m^{-3}, λ(Mo-K_α) = 71.073 pm, μ = 0.39 mm^{-1}, F(000) = 864, T = 143 K. – *Data collection and reduction:* A colourless prism 1.0 × 0.7 × 0.5 mm was mounted in inert oil (type RS 3000, donated by Fa. Riedel de Haen) on a glass fibre and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low-temperature attachment). Cell constants were refined from ±ω angles of 62 reflections in the 2Θ range 20–23°. 4884 Intensities in the 2Θ range 6–55° were collected (4584 unique, R_{int} 0.038). – *Structure solution and refinement:* The structure was solved by direct methods and refined anisotropically on F^2 using the program SHELXL-93 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$. The final $wR(F^2)$ was 0.109, with a conventional $R(F)$ of 0.040. 246 Parameters, S = 1.1; max. Δ/σ = 0.001; max. Δ = 336 e · nm^{-3}. – Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD-400833.

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