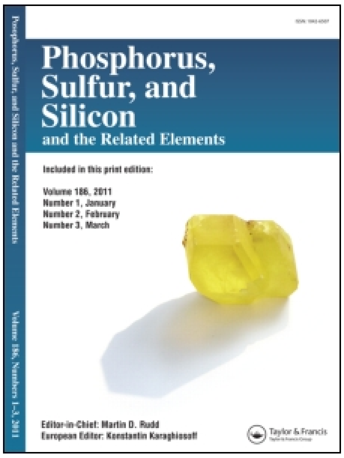


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SOME REACTIONS OF DICHLOROPHOSPHINO-METHANETHIOPHOSPHONIC DICHLORIDE

Manfred Fild[a]; Wolfgang Handke[a]
[a] Lehrstuhl B für Anorganische Chemie, Technische Universität, Braunschweig, FRG

To cite this Article Fild, Manfred and Handke, Wolfgang(1979) 'SOME REACTIONS OF DICHLOROPHOSPHINO-METHANETHIOPHOSPHONIC DICHLORIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 3, 337 — 340

To link to this Article: DOI: 10.1080/03086647908077735

URL: http://dx.doi.org/10.1080/03086647908077735

Phosphorus and Sulfur
1979, Vol. 5, pp. 337–340

SOME REACTIONS OF DICHLOROPHOSPHINO-METHANETHIOPHOSPHONIC DICHLORIDE

MANFRED FILD and WOLFGANG HANDKE

Lehrstuhl B für Anorganische Chemie, Technische Universität, D-3300 Braunschweig, FRG

(*Received July 25, 1978*)

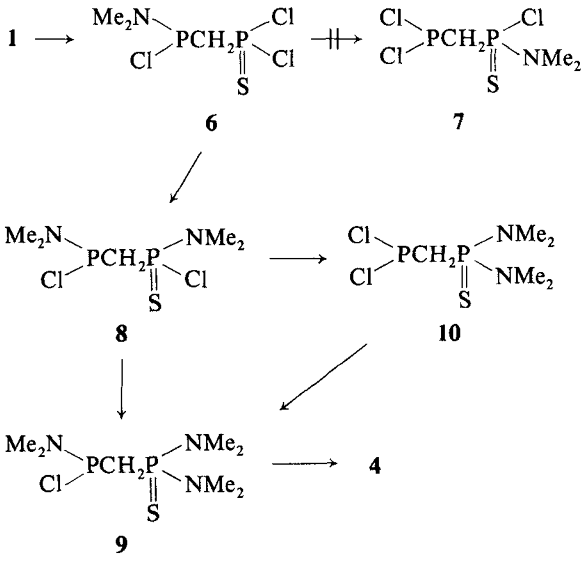
The synthesis of the thiophosphonic dichloride $Cl_2PCH_2P(S)Cl_2$ (**1**) is reported and some of its reactions are described. A detailed investigation of the aminolysis of **1** and the corresponding $F_2PCH_2P(S)F_2$ (**2**) reveals a stepwise substitution pattern.

Recently, we have reported the synthesis of methane-diphosphonous acid dichloride, $Cl_2PCH_2PCl_2$, from the corresponding sulfur derivative $Cl_2P(S)CH_2P(S)Cl_2$ by reduction with diphenylchlorophosphine.[1] Changing the molar ratio of chlorophosphine to $Cl_2P(S)CH_2P(S)Cl_2$ results in the formation of dichlorophosphinomethanethiophosphonic dichloride (**1**), $Cl_2PCH_2P(S)Cl_2$, in good yields. This compound has also been prepared by partial sulfurization of $Cl_2PCH_2PCl_2$ with $PSCl_3$ or sulfur.[2,3] Compound **1** may serve as a precursor for a series of derivatives containing phosphorus atoms in different oxidation states.

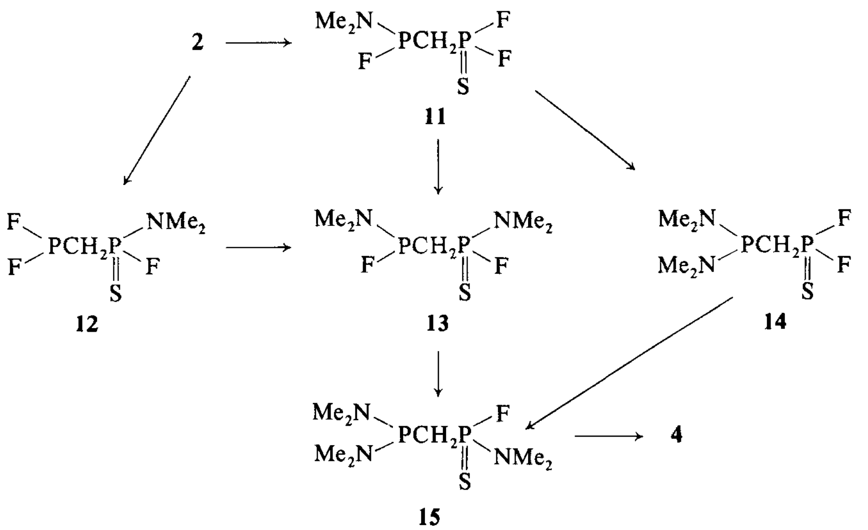
The fluorination of **1** with antimony trifluoride in N,N-dimethyl-aniline at room temperature leads to the fluoride $F_2PCH_2P(S)F_2$ (**2**) in good yields. At higher temperature and in the presence of excess SbF_3 **2** is converted to the phosphorane $F_4PCH_2P(S)F_2$.[3] Compound **2** can be handled in a vacuum-system without noticeable decomposition.

Solvolysis with methanol in the presence of a tertiary amine leads to an ester of the composition $(MeO)_2PCH_2P(S)(OMe)_2$ (**3**), in a similar way as has already been reported for the reaction with ethanol.[2] The substitution of chlorine by dialkylamino groups can be effected by dialkylamines or via a cleavage reaction with a dialkylaminotrimethylsilane and gives rise to, e.g., $(Me_2N)_2PCH_2P(S)(NMe_2)_2$ (**4**) and $(Et_2N)_2PCH_2P(S)(NEt_2)_2$ (**5**).

The presence of two phosphorus atoms in the same molecule in different oxidation states will influence the substitution pattern. Therefore, we have studied the aminolysis of **1** and **2** with Me_2NSiMe_3 in order to differentiate between the reactivity at phosphorus(III) and phosphorus(V). For the substitution reaction both molar ratio of aminosilane to phosphorus compound and temperature were varied. The results are presented in Schemes 1 and 2, and the nmr data are listed in Table I. Halosilane which is formed during the reaction has been omitted from the schemes. The compounds have not been isolated, since they decompose on attempted distillation at higher temperature. Their characterization by nmr is unambiguous.



SCHEME 1



SCHEME 2

TABLE I

^{19}F- and ^{31}P-chemical shifts and coupling constants

Compound		δP(III)	δP(V)	^{2}J(PP)	δF[P(III)]	δF[P(V)]	^{1}J(FP)[c]	^{1}J(FP)[d]
$Cl_2PCH_2P(S)Cl_2$	**(1)**	158.0	63.7	67.6				
$F_2PCH_2P(S)F_2$	**(2)**	208.5	86.0	39.5	−91.8	−36.5	1208	1169
$(MeO)_2PCH_2P(S)(OMe)_2$	**(3)**	168.5	93.4	56.6				
$(Me_2N)_2PCH_2P(S)(NMe_2)_2$[a]	**(4)**	83.7						
$(Et_2N)_2PCH_2P(S)(NEt_2)_2$	**(5)**	77.9	74.2	112.3				
$(Me_2N)ClPCH_2P(S)Cl_2$	**(6)**	124.4	72.3	83.5				
$(Me_2N)ClPCH_2P(S)Cl(NMe_2)$	**(8)**	130.9	84.8	75.3				
$(Me_2N)ClPCH_2P(S)(NMe_2)_2$	**(9)**	139.7	79.1	75.7				
$Cl_2PCH_2P(S)(NMe_2)_2$	**(10)**	162.6	76.0	56.8				
$(Me_2N)FPCH_2P(S)F_2$	**(11)**	150.5	98.0	56.7	−113.3	−39.6	945	1143
$F_2PCH_2P(S)F(NMe_2)$	**(12)**	219.5	85.3	45.6	−94.9	−46.8	1173	1045
$(Me_2N)FPCH_2P(S)F(NMe_2)$	**(13)**	156.4	94.0	68.8	−114.8	−48.6	938	1046
$(Me_2N)_2PCH_2P(S)F_2$	**(14)**	77.2	104.2	79.5		−42.5		1144
$(Me_2N)_2PCH_2P(S)F(NMe_2)$[b]	**(15)**	81.5	100.1	87.7		−51.1		1029

[a] AB-spectrum, outer lines not resolved. [b] ABX-spectrum. [c] P(III). [d] P(V).

For compound **1** the first step leads to species **6** with an amino group at the trivalent phosphorus atom. If a molar ratio of 1 : 1 is used the aminosilane is completely consumed at −35°C, no other phosphorus compound being detected. Compound **6** may be warmed up to 60°C for several hours without any noticeable decomposition or rearrangement reaction to **7**. A reaction of **1** with aminosilane conducted at 0°C (molar ratio 1 : 1) also gives rise to the formation of **6** but a small amount of compound **8** is found, in which the second amino substituent is bonded to phosphorus(V). Increasing the concentration of aminosilane to a molar ratio of 2 : 1 causes complete consumption of starting halide at temperatures between −35 to −25°C to yield compound **8** as the main product. A small amount of **6** is left, and a similar amount of **9** appears as a by-product.

A similar study has been performed on the nitrogen-bridged system $Cl_2PN(Me)P(O)Cl_2$.[4,5] In this case, the aminolysis of $Cl_2PN(Me)P(O)Cl_2$ with dimethylamino-trimethylsilane (molar ratio 1 : 1) yields $(Me_2N)ClPN(Me)P(O)Cl_2$ which rearranges rapidly at ambient temperature to $Cl_2PN(Me)$-$P(O)Cl(NMe_2)$. With a higher concentration of aminosilane, up to a molar ratio of 2 : 1, the compound $Cl_2PN(Me)P(O)(NMe_2)_2$ is formed at ambient temperature. It has been assumed that $(Me_2N)ClPN(Me)P(O)Cl(NMe_2)$ is the initial product in the reaction which then isomerizes.

In our case compound **8** rearranges very slowly at a temperature of 65 °C to the isomer **10** (Scheme 1). On increasing the amount of silane more of the triamino compound **9** is formed via **8** in the reaction at low temperature. On reaching the molar ratio of aminosilane to phosphorus compound of 4 : 1 it is shown that even at −30°C the triamine **9** is rapidly formed, and that the fully substituted product **4** is obtained at 0°C. These results show that the last step is a substitution at the phosphorus(III) center; the isomeric species of **9** of the composition $(Me_2N)_2PCH_2P(S)Cl(NMe_2)$ has not been observed.

In a similar way, the aminolysis of $F_2PCH_2P(S)F_2$ (**2**) was studied (Scheme 2). At low temperature (−70° C) and low concentration of aminosilane compound **11** is produced. If the sample is warmed up to room temperature quickly a small amount of **12** is observed which is formed from **2** before all of the aminosilane has been consumed. The composition of this mixture does not change on increasing the temperature to 65°C which excludes a rearrangement reaction of **11** to give **12**. On increasing the aminosilane concentration (molar ratio 1 : 1 to 2 : 1) the monosubstituted product **11** predominates, although two other species, **13** and **14** are observed depending on the temperature conditions used. It can be shown that **14** mainly forms in a low temperature reaction. On warming mixtures of **13** and **14** no rearrangement (**14** to **13**) is found.

Changing the molar ratio to 4 : 1, all of the starting material **2** reacts at −30°C to a mixture of compounds **13** and **14**, in which **13** is the main product. On warming this mixture to room temperature both compounds disappear to give only one product, compound **15** with the third aminoalkyl-substituent at the phosphorus(III) center. No reaction of **15** with the remaining aminosilane to yield **4** is observed up to a temperature of 80°C. At higher temperatures decomposition reactions take place, although the formation of **4** is indicated.

The results show a clear difference in reactivity of phosphorus(III) and phosphorus(V) depending on the halogen ligand which influences the substitution pattern. Furthermore, there seems to be a difference if compared with the nitrogen-bridged systems. The ease with which the partially substituted compounds mentioned above are rearranged contrasts with our observations for the methylene-bridged compounds.

EXPERIMENTAL

All operations were conducted under exclusion of moisture in a nitrogen atmosphere. Boiling and melting points are uncorrected. Solvents were carefully dried and distilled before use. ^{19}F and ^{31}P nmr spectra (in some cases also ^1H nmr spectra) were obtained on a Jeol C 60 HL spectrometer with proton decoupling facilities. All spectra were taken on neat liquids or on toluene solutions in 5 or 8 mm tubes. Chemical shifts are referenced to external $CFCl_3$ and H_3PO_4, respectively, and are positive when downfield from the standard. Mass spectra were measured on a AEI-MS 9 or a CH-4 spectrometer.

Dichlorophosphino-methanethiophosphonic dichloride (1)

A mixture of 26.0 g (92.2 mMol) $Cl_2P(S)CH_2P(S)Cl_2$ and 20.4 g (92.2 mMol) $(C_6H_5)_2PCl$ was heated to 135–140°C for about 3 h. The distillation of the reaction mixture gave, after a forerun of $Cl_2PCH_2PCl_2$, the product of bp 58–62°/0.1 mm (yield 45%). Anal. Calcd. for $CH_2Cl_4P_2S$: P, 24.79; Cl, 56.76. Found: P, 24.50; Cl, 56.63. The mass spectrum shows a molecular ion at 248. The viscous residue contains $(C_6H_5)_2P(S)Cl$ and a small amount of unreacted starting material as checked by nmr.

Fluorination of **1** Compound **1**, 7.0 g (28.0 mMol) was added to a suspension of 6.6 g (36.9 mMol) SbF_3 in 20 ml N,N-dimethylaniline. The reaction is exothermic and is completed after a few minutes. The product was distilled out of the mixture under reduced pressure and collected in a trap cooled with liquid nitrogen. The crude material was condensed onto NaF and fractionated on a vacuum-line with traps kept at −46, −86 and −196°C. The pure product was obtained at −86°C. The vapor pressure in the range −13,7 to 20°C can be expressed by the equation $\ln P = -4544.5/T + 18.97$ giving an extrapolated bp of 95.2°C. The yield was 63%. The mass spectrum gives the molecular ion at 184.

Alcoholysis of **1** To a mixture of 2.44 g (76.2 mMol) methanol and 6.02 g (76.1 mMol) pyridine in 50 ml anhydrous benzene was added dropwise under stirring 4.66 g (18.7 mMol) **1**, diluted with 20 ml benzene. The mixture was stirred for one hour after which the pyridine hydrochloride was removed by filtration. The solvent was stripped off and the residue dissolved in petroleum ether, filtered once more removing residual amounts of hydrochloride. The filtrate was fractionated to give $(MeO)_2PCH_2P(S)(OMe)_2$ with a bp of 92–94°/0.4 mm (yield 46%). Anal. Calcd. for $C_5H_{14}O_4P_2S$: C, 25.87; H 6.08. Found: C, 26.35; H, 6.05.

Aminolysis of **1** To a cooled solution of 3.75 g (15.0 mMol) **1** in 40 ml methylene chloride was added with stirring 8.18 g (69.8 mMol) dimethylaminotrimethylsilane. The mixture was warmed up and refluxed for 1 h. On stripping off the solvent and the chlorosilane at 10 mm the yellow residue was distilled to give $(Me_2N)_2PCH_2P(S)(NMe_2)_2$ of bp 100–103°/0.06 mm which solidifies on standing; mp 56–58°C (yield 73%). Anal. Calcd. for $C_9H_26N_4P_2S$: C, 38.02; H, 9.22. Found: C, 37.96; H, 9.08.

In a similar experiment using diethylamino-trimethylsilane $(Et_2N)_2PCH_2P(S)(NEt_2)_2$ was obtained as a viscous oil which did not crystallize (yield 75%). The mass spectrum shows the molecular ion at 396.

Aminolysis of **1** and **2**—*stepwise substitution* In a high-vacuum system a weighed amount of **2** was condensed into a nmr tube. Then a small amount of toluene was condensed to form a layer on compound **2**. Finally, the aminosilane was added and the tube was sealed. In the case of the less volatile **1** the phosphorus compound was placed into the nmr tube under atmospheric pressure and then attached to the vacuum line.

The molar ratios of aminosilane to **1** and **2**, respectively, were varied from 0.5 : 1, 1 : 1, 2 : 1, 3 : 1 to 4 : 1. The temperatures were varied between −70 and +80°C in steps of 10°C. In the case of **1** the stepwise substitution reaction was also studied by slow addition of aminosilane to **1** at several temperatures taking samples of the mixture at varying stages of addition. The nmr spectra were measured and the relative quantities determined by integration.

ACKNOWLEDGEMENTS

We are grateful to Deutsche Forschungsgemeinschaft for financial support. We are indebted to Chemische Fabrik Kalk, Germany and Mobil Chemical Company, Richmond, USA, for gifts of chemicals.

REFERENCES AND NOTES

1. M. Fild, J. Heinze and W. Krüger, *Chem. Ztg.* **101**, 259 (1977).
2. Z. S. Novikova, A. A. Prishchenko and I. F. Lutsenko, *Zhur. Obshch. Khim.* **47**, 775 (1977).
3. M. Fild and W. Handke, to be published.
4. R. Keat, *Phosphorus* **1**, 253 (1972).
5. R. Keat, *J.C.S. Dalton* **1974**, 876.