

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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>

### PHOSPHOROCHLORIDATE AND DICHLOROTHIOATE IONS: APROTIC ACCESS AND EVIDENCE FOR CHLORIDE ION RELEASE TO FORM METAPHOSPHATE TYPE INTERMEDIATES

Herbert Teichmann<sup>a</sup>; Joachim Schulz<sup>a</sup>

<sup>a</sup> Akademie der Wissenschaften der DDR, Zentralinstitut für Organische Chemie, Berlin, Adlershof

**To cite this Article** Teichmann, Herbert and Schulz, Joachim(1990) 'PHOSPHOROCHLORIDATE AND DICHLOROTHIOATE IONS: APROTIC ACCESS AND EVIDENCE FOR CHLORIDE ION RELEASE TO FORM METAPHOSPHATE TYPE INTERMEDIATES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 54: 1, 31 — 37

**To link to this Article:** DOI: 10.1080/10426509008042117

**URL:** <http://dx.doi.org/10.1080/10426509008042117>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# PHOSPHOROCHLORIDATE AND DICHLOROTHIOATE IONS: APROTIC ACCESS AND EVIDENCE FOR CHLORIDE ION RELEASE TO FORM METAPHOSPHATE TYPE INTERMEDIATES

HERBERT TEICHMANN and JOACHIM SCHULZ

*Akademie der Wissenschaften der DDR, Zentralinstitut für Organische Chemie,  
Rudower Chaussee 5, Berlin-Adlershof, DDR-1199*

*(Received January 30, 1990)*

Monomeric, non-coordinated salts of the dichlorophosphoric, dichlorophosphorothioic and dithioic acid are obtained in high yields by dealkylation of the corresponding methyl esters using quaternary ammonium or phosphonium halides. The mono and dithioate anions react under mild conditions with 4-dimethylaminopyridine as trapping agent to form the thiometaphosphate adducts **11b** and **11c**, respectively, whereas the dichlorophosphate anion merely yields condensation products. The capability of the title compounds to act as metaphosphate type precursors by chloride ion release may be compared with the analogous behaviour of phosphorochloroimidate and chlorosulfate anions.

**Key words:** phosphorodichloridate, phosphorodichloro(di)thioate ions; methyl phosphorodichloridate; methyl phosphorodichloro(di)thioate; chloro(di)thiometaphosphate; pyridinium thiophosphate betaines; 4-dimethylaminopyridine.

## INTRODUCTION

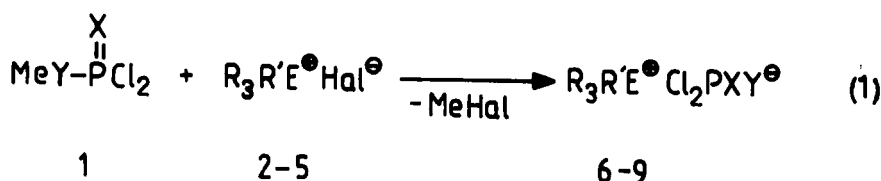
Definite salts of the dichlorophosphoric acid not existing in the state of coordination polymers were first obtained in 1939 by deoxygenative halogenation with  $\text{POCl}_3$  of phenylogous carboxamides.<sup>1</sup> The validity of the same principle in reactions generating Vilsmeier reagents with  $\text{POCl}_3$  was postulated by Wizinger<sup>2</sup> in 1945 and later proved by Martin and Martin<sup>3–5</sup>, who also demonstrated the analogous mode of formation of dichlorophosphorothioates and dithioates from  $\text{PSCl}_3$ .<sup>6</sup>

For preparative purposes, however, organic oxygen donors are not in use. Instead, hydrolytic processes in presence of bulky cations are employed to substitute one chlorine by anionic oxygen in  $\text{POCl}_3$ <sup>7,8</sup> and  $\text{PSCl}_3$ <sup>9,10</sup>, respectively. Though similar mechanisms of thiohydrolysis may work<sup>11</sup>, to obtain dichlorophosphorodithioates preformed  $\text{PS}_2$  moieties like  $\text{P}_4\text{S}_{10}$ <sup>12</sup> or the betaine  $\text{C}_5\text{H}_5\text{NPS}_2\text{Cl}$ <sup>13</sup> are used and subject to cleavage by hydrogen chloride. Since careful drying procedures may be required to obtain stable and analytically pure samples of dichlorophosphate and phosphorodichlorothioate salts from  $\text{P(X)Cl}_3$  hydrolysis, we report here a simple aprotic high yield preparation under remarkably mild conditions of such salts as well as of the corresponding dithioates.

## RESULTS AND DISCUSSION

During the study of betaine formation from  $\text{RY-P(X)Cl}_2$  ( $\text{X, Y} = \text{O, S}$ )<sup>14–16</sup> we observed, depending on the nature of the pyridine base used, some *N*-alkylation

competing with the main reaction of *N*-phosphorylation. In the case of  $\alpha$ -substituted pyridines *N*-methylation becomes strongly favoured for steric reasons. Thus, equimolar amounts of collidine and **1b** in  $\text{CH}_2\text{Cl}_2$  at room temperature form 74% of hygroscopic 1,2,4,6-tetramethylpyridinium dichlorophosphorothioate. An oily, hygroscopic salt also results from dealkylation of **1b** by  $\text{Et}_3\text{N}$ . However, dealkylation by quaternary ammonium or phosphonium halides **2-5** which form high yields of pure, non-hygroscopic salts **6-9** is to be preferred. Thiolester bonds as in **1c** or **1d** ( $\text{X} = \text{O}$ ,  $\text{Y} = \text{S}$ ) are likewise subject to  $\text{C}-\text{S}$  bond cleavage, whereby **1b** and **1d** yield identical salts.



| 1, 6-11 | X | Y | comp. | E | R  | R'                |
|---------|---|---|-------|---|----|-------------------|
| a       | O | O | 2, 6  | N | Et | PhCH <sub>2</sub> |
| b       | S | O | 3, 7  | P | Ph | Ph                |
| c       | S | S | 4, 8  | P | Ph | PhCH <sub>2</sub> |
|         |   |   | 5, 9  | P | Ph | Me                |

Hal : Cl (2-4),  
I (5)

Whilst on isolated, monomeric, non-coordinated dichlorophosphates and their thio analogues literature is scarce, in situ generated dichlorophosphate ions repeatedly are recommended to act as phosphorylating agents (see, e.g., lit.<sup>17-18</sup>, and references therein). It is difficult to imagine how anionic nucleophiles like  $\text{Cl}_2\text{PO}_2^-$  should be superior to neutral electrophiles of the acid chloride type in phosphorylation reactions unless one assumes the participation of a highly reactive chlorometaphosphate intermediate. There exists in fact some evidence for the formation of such transient species from  $\text{Cl}_2\text{PS}_2$  by chloride ion abstraction in the presence of a LEWIS acid, the substances isolated, however, are reorganisation products with a different structure.<sup>12</sup> To prove whether chloride ion expulsion also can occur in absence of any acceptor molecule, **6-8** were reacted in methylene chloride solution at ambient temperature with 4-dimethylaminopyridine as a trapping agent for the metaphosphate species.

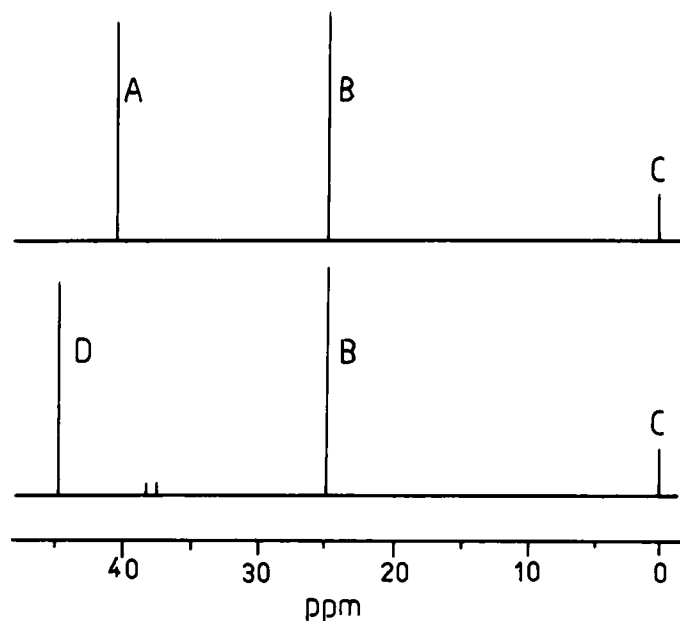
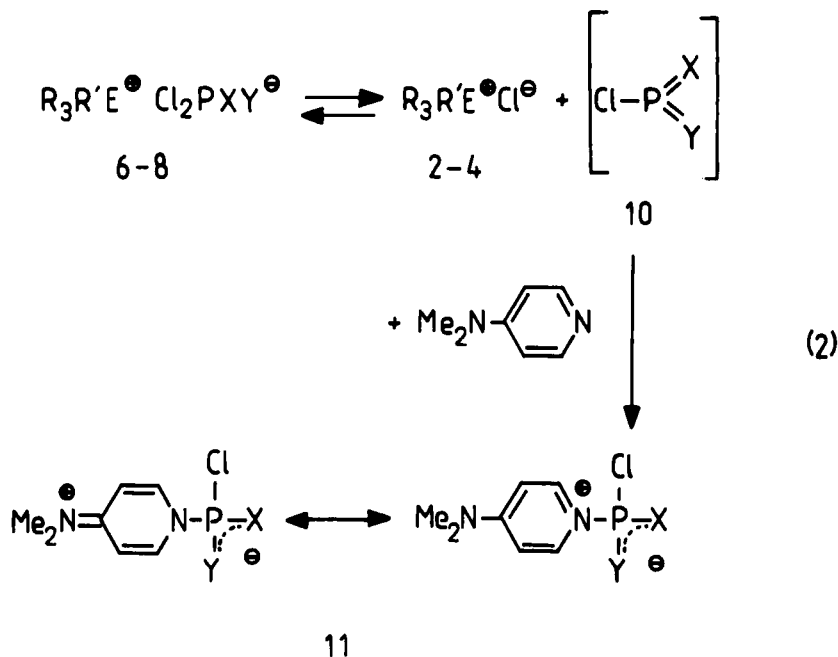


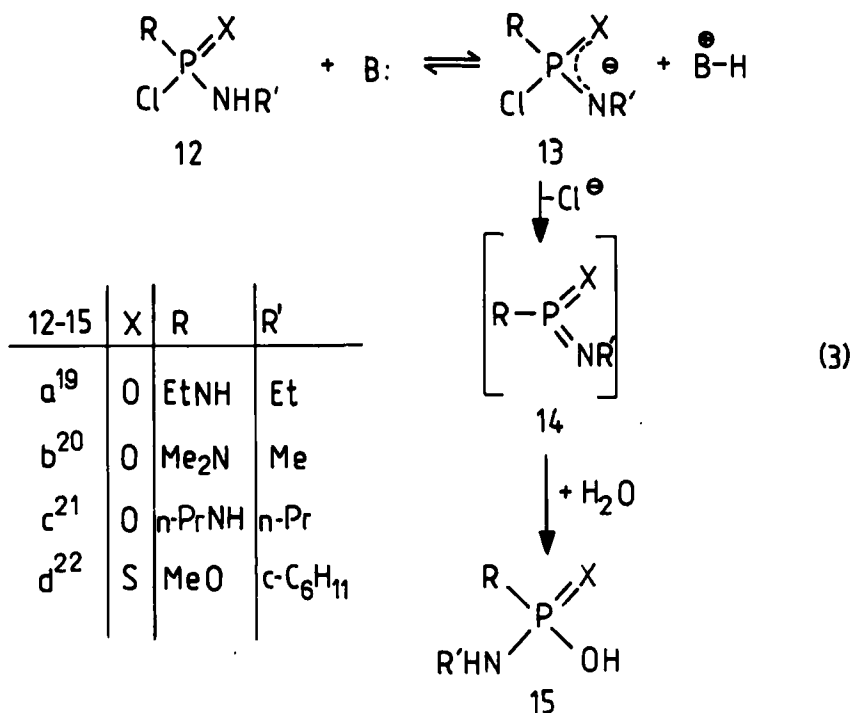
FIGURE 1  $^{31}\text{P}$ -NMR spectrum of **7b** (above) and its reaction product with 4-dimethylaminopyridine (below). A:  $\text{Cl}_2\text{PSO}^-$ ; B:  $\text{Ph}_3\text{P}^+$ ; C: standard ( $\text{H}_3\text{PO}_4$ ); D: betaine **11b**; solvent  $\text{MeNO}_2$ .



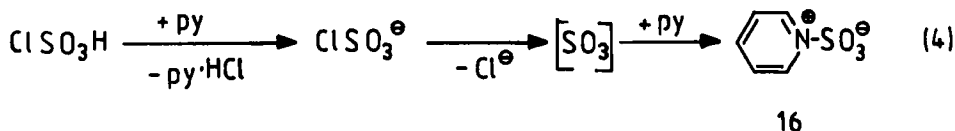
Results obtained with the dioxo salt **8a** are not conclusive, as  $^{31}\text{P}$ -NMR spectra indicate predominant formation of condensed phosphates (signals and groups of signals at  $-13.6$ ,  $-16.3$ ,  $-17$  and  $-20.5$  ppm) which occasionally are products, too, in preparations of betaine **11a** from **1a**.<sup>16</sup> Under the same conditions, however,

the monothio anion of **7b** ( $\delta 31_{\text{P}}$  41.3 ppm) completely disappears within one day while a new signal, similar in intensity to that of  $\text{Ph}_4\text{P}^+$  ( $\delta 31_{\text{P}}$  24.8 ppm, remaining unchanged), at 44.7 ppm is formed which is indicative of the betaine **15b**<sup>15</sup> (see, Figure 1). Similarly, the dithio anion of salt **6c** ( $\delta 31_{\text{P}}$  83.9 ppm) is converted to a large extent into a species of  $\delta 31_{\text{P}}$  93.9 ppm (as the dominant signal, along with some minor, in part unidentified ones), thus revealing the presence of betaine **11c**<sup>15</sup> as the main reaction product.

First order-type P—Cl bond cleavage in tetracoordinated phosphorus monoanions to form neutral tricoordinated species is not unprecedented and has since long been discussed for explaining the unusually large rates of alkaline hydrolysis in the *N*-monosubstituted phosphoric<sup>19-21</sup> and thiophosphoric amidochloridate series<sup>22</sup> by an elimination-addition mechanism. Chloroimidate ions **13**, thus arising from neutral amidates **12** by deprotonation, may be regarded as perfect analogues of the dichlorophosphate and phosphorothioate anions in **6-8**.

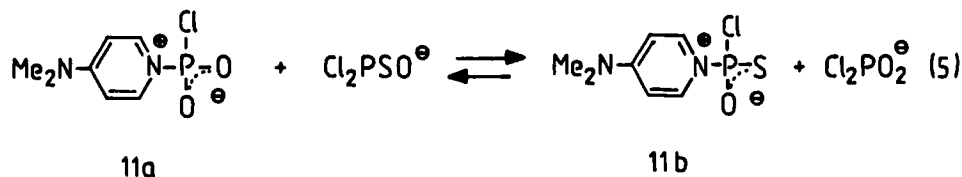


There exists even further analogy in the chlorosulfate series. It is known since more than a century that chlorosulfonic acid is not merely neutralized by pyridine to give the pyridinium salt but that the reaction proceeds to form the betaine **16**<sup>23,24</sup> which also can directly be obtained as a "pyridine-SO<sub>3</sub> adduct" from the components.<sup>24</sup>



Monomeric  $\text{SO}_3$  and monomeric metaphosphate species have in common that they strongly tend to increase their coordination number. In both instances pyridine bases act as excellent donors to stabilize the low-coordinated moieties by forming betaines of type **11** and **16**, respectively.

The aptitude for ready chloride ion release may suggest the anions in **6–8** to be regarded as a kind of donor-stabilized chloro(thio)metaphosphates, just the same way as are the betaines **11**, with the chloride ion being a poorer stabilizing donor than the pyridine base. In the pyridinium betaines **11** there is obviously some tendency to dissociate, yet, similar to that in the  $\text{SO}_3$ -adduct **16** which enables **16** to act as a sulfonating agent.<sup>25</sup> On mixing  $\text{MeNO}_2$  solutions of the monothio salt **6b** ( $\delta 31_{\text{P}}$  of the anion 41.4 ppm) and the dioxo betaine **11a** ( $\delta 31_{\text{P}}$  –8.6 ppm) after 6 hours at 60°C new signals arise at –7.8 and 45.3 ppm which unambiguously belong to the dichlorophosphate anion and the monothio betaine **11b**, respectively<sup>16</sup> (see, Figure 2).



## EXPERIMENTAL

Starting materials were either commercially available or prepared according to known literature procedures. All reactions were performed with carefully dried substances and solvents and protected against moisture by dry nitrogen gas. Melting points were estimated by using a Boetius apparatus.  $^{31}\text{P}$ -NMR spectra were obtained in  $\text{MeNO}_2$  solutions with a Bruker MSL 400 operating at 162 MHz<sup>26</sup>; 85%  $\text{H}_3\text{PO}_4$  was used as an external standard.

*Ammonium and phosphonium phosphorodichloridates and dichloro(di)thioates 6–9. General procedure.* To 5 mmol methylester **1** dissolved in 10 ml  $\text{CH}_2\text{Cl}_2$ , a solution of 5 mmol ammonium or phosphonium salt **2–5** in 15 ml  $\text{CH}_2\text{Cl}_2$  is added dropwise with stirring. Agitation at room temperature is then continued for 5 hours. After removal of the solvent at reduced pressure by rotary evaporation the residue is recrystallized from benzene/chloroform. Data see tables 1 and 2.

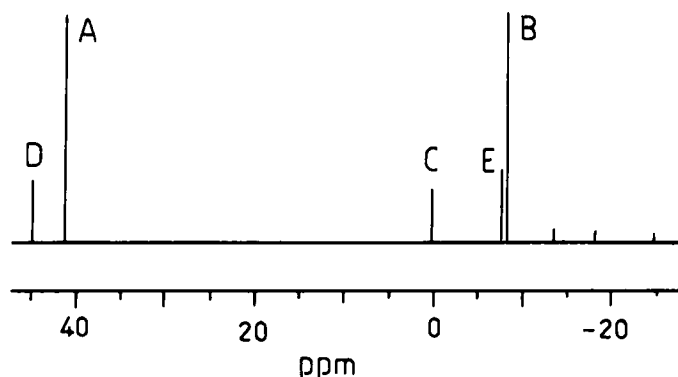


FIGURE 2  $^{31}\text{P}$ -NMR spectrum of a 1:1 mixture of **6b** and betaine **11a** after 6 h warming to 60°C in  $\text{MeNO}_2$ . A:  $\text{Cl}_2\text{PSO}^-$ ; B: betaine **11a**; C: standard ( $\text{H}_3\text{PO}_4$ ); D: betaine **11b**; E:  $\text{Cl}_2\text{PO}_2^-$ .

TABLE I  
Ammonium and phosphonium dichloridates and dichloro(di)thioates 6–9. Yields, melting points and elemental analyses

| Compd.          | Yield (%) | m.p. (°C) | Formula (mol. weight)  | Elemental analysis (calc./found) |              |                |
|-----------------|-----------|-----------|--|----------------------------------|--------------|----------------|
|                 |           |           |  | C                                | H            | Cl             |
| 6a <sup>a</sup> | 75        | 45–48     | C <sub>13</sub> H <sub>22</sub> Cl <sub>2</sub> NPO <sub>2</sub><br>(326.3)              | 47.84<br>47.62                   | 6.79<br>7.23 | 21.72<br>21.69 |
| 6b <sup>b</sup> | 90        | 49–51     | C <sub>13</sub> H <sub>22</sub> Cl <sub>2</sub> NPOS<br>(342.3)                          | 45.6<br>45.83                    | 6.47<br>6.73 | 20.71<br>20.54 |
| 6c <sup>c</sup> | 81        | 43–46     | C <sub>13</sub> H <sub>22</sub> Cl <sub>2</sub> NPS <sub>2</sub><br>(358.3)              | 43.57<br>44.22                   | 6.18<br>6.70 | 19.8<br>20.9   |
| 7a              | 90        | 223–225   | C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> P <sub>2</sub> O <sub>2</sub><br>(473.3) | 60.90<br>61.57                   | 4.25<br>4.37 | 14.98<br>14.81 |
| 7b <sup>d</sup> | 95        | 235–236   | C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> P <sub>2</sub> OS<br>(489.3)             | 58.9<br>58.9                     | 4.1<br>4.14  | 14.48<br>14.78 |
| 7c              | 75        | 125–128   | C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> P <sub>2</sub> S <sub>2</sub><br>(505.4) | 57.03<br>57.01                   | 3.98<br>4.57 | 14.03<br>14.96 |
| 8a <sup>e</sup> | 86        | 155–156   | C <sub>25</sub> H <sub>22</sub> Cl <sub>2</sub> P <sub>2</sub> O <sub>2</sub><br>(487.3) | 61.62<br>61.61                   | 4.55<br>4.58 | 14.55<br>14.33 |
| 8b <sup>f</sup> | 80        | 188–190   | C <sub>25</sub> H <sub>22</sub> Cl <sub>2</sub> P <sub>2</sub> OS<br>(503.3)             | 59.66<br>59.59                   | 4.37<br>4.37 | 14.08<br>14.63 |
| 9a              | 92        | 55–58     | C <sub>10</sub> H <sub>18</sub> Cl <sub>2</sub> P <sub>2</sub> O <sub>2</sub><br>(411.2) | 55.49<br>55.61                   | 4.41<br>4.70 | 17.24<br>15.5  |
| 9b              | 98        | 104–106   | C <sub>10</sub> H <sub>18</sub> Cl <sub>2</sub> P <sub>2</sub> OS<br>(427.3)             | 53.40<br>53.17                   | 4.24<br>4.24 | 16.59<br>16.79 |
| 9c              | 79        | 138–140   | C <sub>10</sub> H <sub>18</sub> Cl <sub>2</sub> P <sub>2</sub> S <sub>2</sub><br>(443.3) | 51.47<br>51.03                   | 4.09<br>4.09 | 15.99<br>15.02 |

<sup>a</sup> calc.: N 4.28; P 9.50; found: N 4.24; P 9.48

<sup>b</sup> calc.: N 4.1; P 9.05; found: N 4.21; P 9.13

<sup>c</sup> calc.: N 3.9; found: N 3.94

<sup>d</sup> calc.: P 12.65; found: P 12.35

<sup>e</sup> calc.: P 12.72; found: P 12.53

<sup>f</sup> calc.: P 12.31; found: P 12.30

TABLE II  
Observed chemical shifts of the anions in 6–9<sup>a</sup>

| Anion  | δ 31 <sub>P</sub> (ppm)         |   |
|--|---------------------------------|---|
|  | This paper (MeNO <sub>2</sub> ) | lit. <sup>2b</sup> (various solvents)   |
| Cl <sub>2</sub> PO <sub>2</sub> <sup>-</sup> | -7.8 . . . -8.3                 | -3.5 . . . -9 <sup>6</sup> ; -11 <sup>27</sup> ; -10.5 <sup>28</sup> ; -8.8 <sup>29</sup> |
| Cl <sub>2</sub> PSO <sup>-</sup>             | 41.0 . . . 41.4                 | 39.5 . . . 42.5 <sup>6</sup>  |
| Cl <sub>2</sub> PS <sub>2</sub> <sup>-</sup> | 83.7 . . . 84.0                 | 79.5 . . . 82.5 <sup>6</sup> ; 81.6 <sup>11</sup> ; 81.9 <sup>13</sup>                    |

<sup>a</sup> Chemical shifts of the cations: Ph<sub>4</sub>P<sup>+</sup> 24.8 . . . 24.9; Ph<sub>3</sub>PCH<sub>2</sub>Ph<sup>+</sup> 24.3 ppm.

*1,2,4,6-Tetramethylpyridinium phosphorodichlorothioate.* 3.23 g (26 mmol) 2,4,6-trimethylpyridine are dissolved in 10 ml CH<sub>2</sub>Cl<sub>2</sub> and cooled to -35°C. A solution of 4.4 g (26 mmol) 1b in 10 ml CH<sub>2</sub>Cl<sub>2</sub> is slowly added. The mixture is stirred for some hours and the solvent removed *i. vac.* next day. A hygroscopic oil remains which crystallizes over night, yield 5.5 g (74%), m.p. 60–63°C. Attempts to purify by recrystallization were unsuccessful. Anal. of the crude product: calc. for C<sub>9</sub>H<sub>14</sub>Cl<sub>2</sub>NOPS (271.9): C 37.77; H 4.93; Cl 24.77; N 4.91; found: C 36.70; H 4.93; Cl 23.82; N 4.76; δ 31<sub>P</sub>: 41.3 ppm.

*Reaction of phosphorodichloridates and phosphorodichloro(di)thioates with 4-dimethylaminopyridine.* To a solution of 1.1 g (9 mmol) 4-dimethylaminopyridine in 10 ml CH<sub>2</sub>Cl<sub>2</sub> at room temperature are added dropwise 4.5 mmol of 6c, 7b, or 8a, respectively, dissolved in 10 ml CH<sub>2</sub>Cl<sub>2</sub>. Stirring is continued

for 5 hours. The solution becomes gently cloudy and a white precipitation separates. After standing over night the solvent is removed in a rotary evaporator at a bath temperature of 30°C. The residue is dissolved in MeNO<sub>2</sub> and investigated by <sup>31</sup>P-NMR spectroscopy.

Reaction of **6b** with betaine **11a**. 320 mg **11a**, 500 mg **6b**, and 10 ml MeNO<sub>2</sub> are mixed and warmed to 60°C for 6 hours. A clear solution forms which is concentrated to about 40% by vol. and subject to <sup>31</sup>P-NMR investigation.

#### ACKNOWLEDGEMENT

We thank Dr. B. Costisella for support in NMR measurements.

#### REFERENCES

1. K. Gleu, S. Nitsche and A. Schubert, *Ber. Dt. Chem. Ges.* **72**, 1093 (1939).
2. H. Lorenz and R. Wizinger, *Helv. Chim. Acta* **28**, 600 (1945).
3. G. J. Martin and M. L. Martin, *Bull. Soc. Chim. France* 1963, 1637.
4. G. J. Martin and S. Poignant, *J. Chem. Soc., Perkin II* 1972, 1964.
5. M. L. Martin, G. Ricolleau, S. Poignant and G. J. Martin, *J. Chem. Soc., Perkin II* 1976, 182.
6. M. L. Martin, M. Helbert and S. Poignant, *J. Chem. Soc., Perkin II* 1977, 1243.
7. K. I. Askitipoulos, *Praktika Akad. Athenon* **18**, 146 (1943); *Chem. Zent.* 1953, 8303.
8. J. Goubeau and P. Schulz, *Z. Anorg. Allg. Chem.* **294**, 224 (1958).
9. H. Grunze and M. Meisel, *Z. Chem.* **8**, 301 (1963).
10. H. W. Roesky, *Chem. Ber.* **100**, 1447 (1967).
11. E. Fluck and B. Neumüller, *Z. Anorg. Allg. Chem.* **534**, 27 (1986).
12. U. Müller and A. T. Mohammed, *Z. Anorg. Allg. Chem.* **514**, 164 (1984).
13. M. Meisel and C. Donath, *Z. Anorg. Allg. Chem.* **500**, 73 (1983).
14. H. Teichmann, J. Schulz and D. Wilbrandt, *Z. Chem.*, **30**, 18 (1990).
15. H. Teichmann, D. Wilbrandt and J. Schulz, *Phosphorus, Sulfur and Silicon*, in press.
16. H. Teichmann, J. Schulz and B. Costisella, in preparation.
17. J. Smrt and J. Catlin, *Tetrahedron Letters* 1970, 5081.
18. M. T. Skoog and W. P. Jencks, *J. Amer. Chem. Soc.* **106**, 7597 (1984).
19. E. W. Crunden and R. F. Hudson, *Chem. and Ind.* **1958**, 1478.
20. D. Samuel and F. H. Westheimer, *Chem. and Ind.* **1959**, 51.
21. P. S. Traylor and F. H. Westheimer, *J. Amer. Chem. Soc.* **87**, 553 (1965).
22. A. F. Gerrard and N. K. Hamer, *J. Chem. Soc. B* **1968**, 539.
23. J. Wagner, *Ber. Dt. Chem. Ges.* **19**, 1157 (1886).
24. P. Baumgarten, *Ber. Dt. Chem. Ges.* **59**, 1166 (1926).
25. P. Baumgarten, *Angew. Chem.* **55**, 115 (1942).
26. Values of <sup>31</sup>P-NMR shifts reported here and measured at 162 MHz lie generally downfield of literature values which were usually taken at lower fields. This shift difference obviously caused by application of a stronger magnetic field exceeds that of solvent polarity influence and amounts up to 2–3 ppm in charged species (cations as well as anions and zwitter ions).
27. H. Eberwein and J. Weidlein, *Z. Anorg. Allg. Chem.* **420**, 229 (1976).
28. J.-R. Dormoy and B. Castro, *Tetrahedron Letters* **35**, 3321 (1979).
29. H. Teichmann, in *Khimia i primenenie fosfororganicheskikh soedinenii* (Papers of the 1977 conference, Kiev 1981), pp. 289–292.