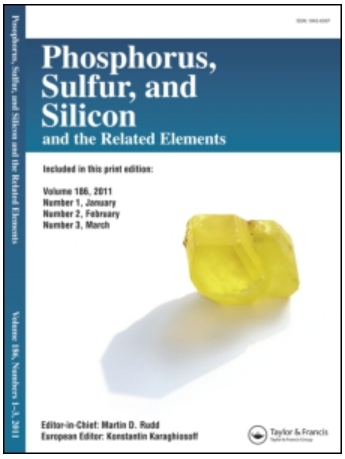

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Ludwig Maier[a]
[a] Agrochemicals Division, CIBA GEIGY A G, Basel, Switzerland

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ORGANIC PHOSPHORUS COMPOUNDS 90.[1] A CONVENIENT, ONE-STEP SYNTHESIS OF ALKYL- AND ARYLPHOSPHONYL DICHLORIDES

LUDWIG MAIER

CIBA-GEIGY AG, Agrochemicals Division, CH-4002 Basel, Switzerland

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N,N-Disubstituted formamides such as dimethylformamide, *N*-formylpyrrolidine, *N*-formylpiperidine etc. and also pyridine and hexamethylphosphonic acid triamide catalyze the chlorination of phosphonates with thionyl chloride to give phosphonyl dichlorides in high yield. Thus $RP(O)Cl_2$, $R = CH_3$, C_2H_5, $n\text{-}C_{12}H_{25}$, C_6H_5, have been isolated in better than 90 per cent yield. The procedure is less satisfactory for the production of 2-chloroethylphosphonyl dichloride. Only a 34 per cent yield was realized.

The chlorination proceeds very likely through the intermediate formation of the halfesters, RP(O)(OR)Cl since these could be isolated under favorable circumstances.

Key words: Chlorination of phosphonates; formamides as catalysts; phosphonyl dichlorides; phosphonyl ester chlorides.

INTRODUCTION

Several methods have been described in the literature for the preparation of phosphonyl dichlorides.[2,3] One of the most widely used procedure consists in the conversion of phosphonates which are readily available by the Michaelis–Arbuzov or Michaelis–Becker reaction, to phosphonyl dichlorides by reaction with PCl_5,[2,3] $SOCl_2$[2,4,5] or $COCl_2$.[2,6] However, this reaction is not as clean as given in the equation:

$$RP(O)(OR^1)_2 + 2\,PCl_5 \rightarrow RPCl_2 + 2\,POCl_3 + 2\,R^1Cl$$

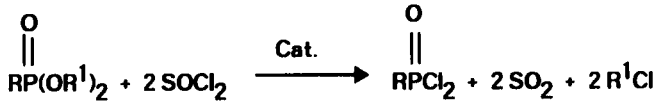
Often considerable amounts of ester-chlorides $RP(O)(OR^1)Cl$[7] and other compounds are formed which are difficult to separate from the dichlorides. For example, we observed that when $CH_3P(O)(OCH_3)_2$ was treated with PCl_5 using $POCl_3$ as solvent, considerable amounts of $CH_3OP(O)Cl_2$ were formed as by-products which could not be separated by fractional distillation from $CH_3P(O)Cl_2$.[8]

$$CH_3P(O)(OCH_3)_2 + PCl_5 \longrightarrow CH_3P(O)(OCH_3)Cl + CH_3OP(O)Cl_2$$

From the literature it is also known that 0,0-diisopropyl-methylphosphonate can be chlorinated with $SOCl_2$ at 130–200°C using a packed column. The yield of $CH_3P(O)Cl_2$ is only 80%.[4] According to another process $CH_2P(O)Cl_2$ is obtained in 98% yield if dimethyl–methylphosphonate is dropwise added very slowly to boiling $SOCl_2$ and after completion of the addition refluxing of the reaction mixture continued for about 15 hours.[5] The applicability of this process is limited, however, to the production of $CH_3P(O)Cl_2$, for even $C_2H_5P(O)Cl_2$ is obtained in a yield of only 72% of theory, whilst $ClCH_2CH_2P(O)Cl_2$ and n-$C_4H_9P(O)Cl_2$ cannot be produced at all in this manner. The production of $CH_3P(O)Cl_2$ too by this process is not, however, without problems, for on working according to the instructions given in Reference 5 we obtained $CH_3P(O)Cl_2$ in ten different runs in a yield of only 25 to 50% of theory.

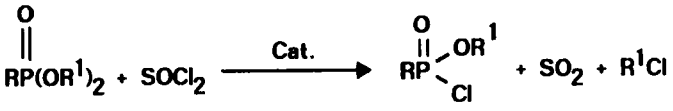
RESULTS AND DISCUSSION

We have now observed that the chlorination of phosphonates by $SOCl_2$ to give phosphonyl dichlorides can be catalyzed by *N,N*-disubstituted formamides such as dimethylformamide, *N*-formylpyrrolidine, *N*-formylpiperidine etc. and also by pyridine and hexamethylphosphonic acid triamide[9] (see Table I).



The results in Table I indicate that the highest yield of $CH_3P(O)Cl_2$ is obtained when the molar ratio of $SOCl_2$:DMMP† is 2.5:1, the amount of catalyst is between 1 and 5 mol% per mole of DMMP, the dropwise addition of DMMP plus catalyst to refluxing $SOCl_2$ is between 2 to 4 hr, and the subsequent refluxing time (after completion of the addition) is 7 to 19 hr. Under these conditions nearly quantitative yields of $CH_3P(O)Cl_2$ were isolated. Furthermore the application of these conditions to other phosphonates allowed the isolation of high yields of e.g. $C_2H_5P(O)Cl_2$, n-$C_{12}H_{25}P(O)Cl_2$ and $C_6H_5P(O)Cl_2$. The process was less satisfactory for the preparation of $ClCH_2CH_2P(O)Cl_2$ from $ClCH_2CH_2P(O)(OCH_2CH_2Cl)_2$. Only a 34% yield was realized.

The reaction proceeds stepwise and the half-esters are formed first as indicated by ^{1}H-NMR spectroscopy.

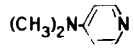


Attempt to isolate the half-esters resulted normally in great losses. Very likely this is due to the instability of the half-esters. They readily condense with

† DMMP = 0,0-Dimethyl-methylphosphonate.

Table 1. Conditions for the preparation of 1 according to:

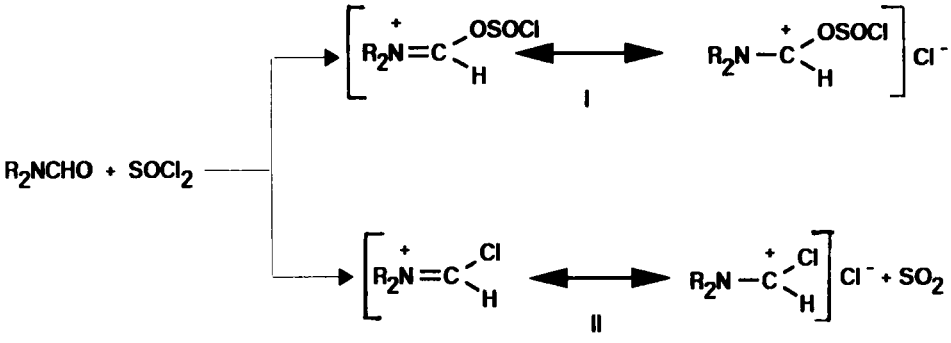
$$CH_3P(O)(OCH_3)_2 + 2\,SOCl_2 \xrightarrow{\text{cat.}} CH_3P(O)Cl_2 \bullet 2\,CH_3Cl \bullet 2\,SO_2$$

Molar ratio $SOCl_2$: DMMP[1)]	catalyst	mol % per mol of DMMP	Dropwise addition time in h of DMMP + cat. to refluxing $SOCl_2$	Subsequent refluxing time [h]	Final temperature (°C)	Yield of distilled product in %	Remarks
2.5 : 1	DMF	0	4	15	80	47.3	polymeric residue
2.5 :1	DMF	0	4	35	80	50	polymeric residue
2.1 : 1	DMF	0.1	1 1/3	1		24	
2.1 : 1	DMF	0.5	4	3	130	76.5	
2.1 : 1	DMF	1	1	4.5	130	68.5	
2.2 : 1	DMF	5	2	1.5	130	71	
2.2 : 1	DMF	10	2	1	140	58.7	
2.2 : 1	DMF	1	4	15	120	93	
2.5 : 1	DMF	1	2	7.5	120	94.4	
2.5 : 1	DMF	5	2	0	110	76.6	
2.5 : 1	DMF	0.5	2	10.5	110	91.4	
2.5 : 1	DMF	0.1	2	7	110	23.8	polymeric residue
2.3 : 1		1	2	9.5		91.3	
2.3 : 1	$[(CH_3)_2N]_3P{=}O$	1	2	11.5		92.9	
2.5 : 1	$(CH_3)_2NCHO$	1	2	7		95.9	
2.3 : 1		1	2	8		91.2	
2.3 : 1	$(C_2H_5)_3N$	1	2	11		83.5	
2.5 : 1		1	2	19		96	
2.5 : 1		1	2	19	120	99.2	
2.5 : 1		1	2	19		91	

1) DMMP = $CH_3P(O)(OCH_3)_2$

the formation of polymers.[5] 0-2-Chloroethyl-2-chloroethyl-phosphonyl chloride, however, was isolated in 82% yield. It would seem that this half-ester is more stable than others.

The role of the catalyst probably consists according to Zollinger *et al.*[10] in an activation of $SOCl_2$ through formation of the addition complex I or the amidechloride.



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EXPERIMENTAL

Phosphorus NMR-spectra were recorded using a Bruker WP 80 spectrometer at 32.28 MHz (Reference 85% H_3PO_4) and ^{1}H-NMR-spectra were recorded with a Varian EM 360 spectrometer at 60 MHZ or a Bruker WP 250/250 MHz spectrometer (Reference $(CH_3)_4Si$). The chemical shifts are reported in ppm, with negative values being upfield of the standard, and positive downfield.

1. Methylphosphonyl dichloride, **1**. A mixture of 124 g (1 mole) of 0,0-dimethyl-methylphosphonate and 0.73 g (0.01 mole) of dimethylformamide is added dropwise at reflux temperature, in the course of 2 hr, to 297.5 g (2.5 moles) of thionyl chloride. An intense gas-generation of sulfur dioxide and methyl chloride occurs during the dropwise addition. After completion of the addition, stirring is maintained for 7.5 hr at reflux temperature. Unreacted thionyl chloride is subsequently evaporated at 25°C in a rotavapor. As a residue is obtained 133.1 g (100.2%) of crude methylphosphonyl dichloride, which crystallizes completely on standing at room temperature and melts at 33°C. Distillation of the crude product yields 125 g (94.4% of theory) of pure **1**, b.p. 56–57°C/14 torr, m.p. 33°C (lit.[2] b.p. 57–58°C/14 torr, m.p. °).

^{1}H-NMR($CDCl_3$), $\delta = 2.5(d, J_{PCH}17, CH_3)$[ppm].

^{31}P-NMR($CDCl_3$)43.5 ppm (lit.[2] 43.5 to 44.5 ppm)

The results obtained under different conditions with various catalysts are summarized in Table I.

2. Ethylphosphonyl dichloride, **2**. A mixture of 166.1 g (1 mole) of 0,0-diethyl-ethylphosphonate and 1.46 g (0.02 mole) of dimethylformamide is added dropwise at reflux temperature, in the course of 5 hr, to 297.5 g (2.5 moles) of thionyl chloride. During the addition, there occurs an intense gas-generation of sulfur dioxide and ethyl chloride. As is shown by an ^{1}H-NMR spectroscopic examination, pure ethylphosphonyl ethyl ester chloride, $C_2H_5P(O)(OC_2H_5)Cl$, is present after completed addition of the diethyl-ethylphosphonate. The reaction mixture is subsequently stirred for 18 hr at reflux temperature, and is then freed in a rotavapor at 25°C from unreacted thionyl chloride to leave 147 g (100% of theory) of crude ethylphosphonyl dichloride. The crude product is purified by

vacuum distillation to yield 140.8 g (95.8%) of pure **2**, b.p. 67–68°C/13 torr (lit.[2] b.p. 69.5°C/13.5 torr).

^{1}H-NMR($CDCl_3$), δ = 1.5(2*t*, J_{PCH}29.5, J_{HH}7.5, CH_3); 2.7(2*qu*, J_{PCH}14, J_{HH}7.5, CH_2)[ppm].

^{31}P-NMR($CDCl_3$)52.6 ppm (lit.[2] 52.5 ppm).

$C_2H_5Cl_2OP$(146.94). Calc: C 16.35; H 3.43; Cl 48.26%. Found: C 15.8; H 3.4; Cl 48.0%.

3. O-(β-Chloroethyl)-β-chloroethylphosphonyl chloride, **3**. A mixture of 142.7 g (0.53 mole) of 0,0-(β-chloroethyl)-β-chlorethylphosphonate and 1.1 g (0.03 mole) of dimethylformamide is added dropwise at reflux temperature, in the course of 3 hr , to 148.7 g (1.25 moles) of thionyl chloride. After the addition is completed, the reaction mixture is kept at reflux temperature until the generation of sulfur dioxide ceases, which is the case after about 70 hr. Fractional distillation of the reaction mixture yields, after a forerun, 99 g (82.8%) of **3**, b.p. 157–162°C/0.5 torr, which after repeated distillation, boils at 109–110°C/0.15 torr.

^{1}H-NMR($CDCl_3$)δ = 2.8(*m*, CH_2P, 2H); 3.8(*m*, CH_2Cl, 4H); 4.5(*m*, OCH_2, 2H)[ppm]

^{31}P-NMR($CDCl_3$) 37.5 ppm

$C_4H_8Cl_3O_2P$ (225.44): Calc: C 21.31; H 3.58; P 13.74%. Found: C 21.10; H 3.85: P 13.54%.

4. β-Chloroethylphosphonyl dichloride, **4**. A mixture of 142.7 g (0.53 mole) of 0,0-(β-chloroethyl)-β-chloroethylphosphonate and 1.8 g (0.05 mole) of dimethylformamide is added dropwise at reflux temperature, in the course of 3 hr, to 148.7 g (1.25 moles) of thionyl chloride. After completion of the addition, the reaction mixture is firstly kept for 22 hr at reflux temperature and is then heated for 10 hr at 135°C in a bomb tube. Fractional distillation of the reaction mixture yields 33.7 g (34.6%) **4**, b.p. 111–115°C/15 torr. (lit.[2] b.p. 85–87°C/7 torr), and 11.2 g (5%) of 0-(β-chloroethyl)-β-chloroethylphosphonyl chloride.

^{1}H-NMR of **4** ($CDCl_3$) δ = 3.1(*m*, CH_2P); 3.9(*m*, $ClCH_2$)[ppm].

^{31}P-NMR($CDCl_3$) 42.9 ppm(lit.[2] 41.9 to 42.9 ppm).

5. O-Methyl-methylphosphonyl chloride, **5**. A mixture of 134.8 g (1 mole) of dimethyl-methylphosphonate and 0.73 g (0.01 mole) of dimethylformamide is added dropwise at reflux temperature, in the course of 2 hr, to 297.5 g (2.5 moles) of thionyl chloride. After completion of the addition, the reaction mixture is kept for a further half hour at reflux temperature. The ^{1}H-NMR spectrum ($CDCl_3$) indicates that after this period nearly pure **5** is present, δ = 1.9 (*d*, J_{PCH} 18, CH_3P, 3H) (impurity at 1.8 ppm); 3.9 (*d*, J_{POCH} 14, OCH_3, 3H)[ppm]. Subsequent vacuum distillation yields 38.5 g (30%) **5** b.p. 78–82°C/14 torr. The losses in yield occurring in purifying **5** are to be attributed to the fact that **5** polymerizes with splitting-off of methyl chloride to give an anhydrid.[5]

^{1}H-NMR($CDCl_3$) δ = 2.06(*d*, J_{PCH} 18, CH_3P, 3H); 3.92(*d*, J_{POCH} 14, OCH_3, 3H)[ppm].

6. n-Dodecylphosphonyl dichloride, A mixture of 52.8 g (0.172 mol) of diethyl *n*-dodecylphosphonate and 0.126 g (0.00172 mol) of dimethylformamide is added dropwise within 2 hr to 51.3 g (0.516 mol) of boiling thionyl chloride. The reaction mixture is maintained for a further 26.5 hr at boiling temperature and is subsequently fractionally distilled to yield 39.7 g (81%) of pure **6**, b.p. 128–130°C/0.3 torr (lit.[2] b.p. 161–168°C/5 torr). The product crystallizes when kept in the refrigerator.

^{1}H-NMR($CDCl_3$) δ = 0.7–2.0(*m*, $C_{11}H_{23}$); 2.5(*m*, CH_2P)[ppm].

$C_{12}H_{25}Cl_2OP$ (287.21). Calc: C 50.18; H 8.78%. Found: C 51.1; H 9.2%.

The experiment was repeated and the composition of the reaction mixture determined with ^{1}H-NMR spectroscopy after various refluxing periods. The following results were obtained:

refluxing time in hrs	composition (in mol%)	
	6	n-$C_{12}H_{25}P(O)(OC_2H_5)Cl$
6.5	31.6	68.4
21.5	75	25
26.5	92.9	7.1

7. Phenylphosphonyl dichloride, **7**. A mixture of 21.4 g (0.1 mol) of diethyl-phenylphosphonate and 0.113 g (0.001 mol) of *N*-formylpiperidine is added dropwise during 2 hr to 18.2 ml (0.25 mol) of boiling thionyl chloride. After completion of the addition, the reaction mixture is kept for a further 20 hr at reflux temperature and is subsequently fractionally distilled to yield 17.8 g (91.3%) of pure **7**, b.p. 132–136°C/18 torr (lit.[2] b.p. 138–139°C/17 torr).

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