

42. Organic Phosphorus Compounds 59¹⁾

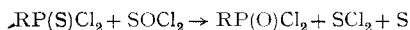
A New Method for the Synthesis of Phosphonic Dichlorides [1]

by **Ludwig Maier**

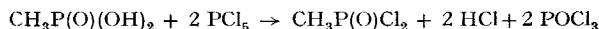
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Summary. Heating of thiophosphonic dichlorides, $\text{RP}(\text{S})\text{Cl}_2$, $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$, with a molar equivalent of SOCl_2 under pressure at 150° for 5 to 8 h yields phosphonic dichlorides in quantitative yield. In addition sulfur and sulfur dichloride is formed according to the equation:



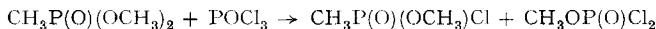
This method is particularly useful for the preparation of $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ since it was observed that chlorination of $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ with PCl_5 yields $\text{CH}_3\text{OP}(\text{O})\text{Cl}_2$ as a by-product which is difficult to separate from $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$. On the other hand chlorination of methylphosphonic acid with PCl_5 also gives pure $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$.



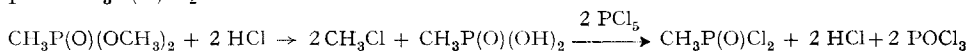
Several methods have been described in the literature for the preparation of phosphonic dichlorides [2]. One of the most widely used procedure consists in the conversion of phosphonates to phosphonic dichlorides by reaction with PCl_5 [2]. This reaction is, however, not as clean as given in the equation:



Often considerable amounts of ester-chlorides, $\text{RP}(\text{O})\text{Cl}(\text{OR})$ [3] and other compounds are formed which are difficult to separate from the dichlorides. For example, we observed that when dimethyl-methylphosphonate, $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ was treated with PCl_5 using POCl_3 as solvent, considerable amounts of $\text{CH}_3\text{OP}(\text{O})\text{Cl}_2$ were formed as by-products which could not be separated by fractional distillation from $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$.



We therefore hydrolyzed the phosphonates first to the acid and then chlorinated the acids with PCl_5 to the dichlorides as described in the literature [4]. In this way pure $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ was obtained.



Similarly, $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$ was also prepared in this way.

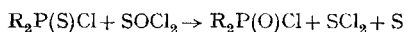
This procedure is, however, somewhat lengthy and troublesome and therefore a simpler method was sought.

Recently, methyl and ethyl-thiophosphonic dichlorides became commercially available²⁾. Therefore attempts were made to convert these thiophosphonic dichlorides in one step to phosphonic chlorides.

¹⁾ Part 58, sec [1].

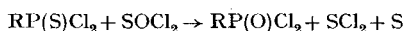
²⁾ Ethyl Corporation, Baton Rouge, La.

It is known from the literature [5] [6] that thiophosphinic chlorides may be converted to phosphinic chlorides by reaction with thionyl chloride at reflux temperature (80°). The method was, however, less successful in converting thiophosphonic dichlorides to the corresponding phosphonic dichlorides. Thus heating of PhP(S)Cl_2 with



SOCl_2 for 2 h to 80° (reflux) effected no reaction [6]. Also heating of PSCl_3 with SOCl_2 for 10 h to 80° caused no reaction. And on heating of PhP(S)Cl_2 with SOCl_2 for 10 h to 80° only at 24% conversion to PhP(O)Cl_2 was achieved [6]. We observed that $\text{CH}_3\text{P(S)Cl}_2$ remained unchanged when it was heated with SOCl_2 for 8 h to 80°.

It has now been found that heating of thiophosphonic dichlorides with SOCl_2 to 150° for 5 to 8 h under pressure effects a 100% conversion to the corresponding phosphonic dichlorides. In addition sulfur and sulfur dichloride is formed according to the equation:



Thus when a 1:1.2 mixture of $\text{CH}_3\text{P(S)Cl}_2$ and SOCl_2 was heated in a bomb tube to 150° for 2 h, a product was obtained which consisted of 92 mol-% $\text{CH}_3\text{P(O)Cl}_2$ and 8 mol-% $\text{CH}_3\text{P(S)Cl}_2$; further heating for 3 h at 150° changed the composition to 98.5 mol-% $\text{CH}_3\text{P(O)Cl}_2$ and 1.5 mol-% $\text{CH}_3\text{P(S)Cl}_2$; and finally heating for another 3 h effected a 100% conversion to $\text{CH}_3\text{P(O)Cl}_2$.

This reaction seems to be general. When $\text{C}_2\text{H}_5\text{P(S)Cl}_2$ and PhP(S)Cl_2 were heated with SOCl_2 in a bomb tube to 150° for 5 to 8 h a 100% conversion to the corresponding phosphonic dichlorides was observed.

Experimental. – 1. $\text{CH}_3\text{P(O)(OCH}_3)_2$ (I) and $\text{PCl}_5 \rightarrow \text{CH}_3\text{P(O)Cl}_2$ (II). $\text{CH}_3\text{P(O)(OCH}_3)_2$ was obtained in 85.3% yield from $(\text{CH}_3\text{O})_3\text{P}$ and a catalytic amount of NaI according to the literature [7], b.p. 70°/11 torr. $^1\text{H-NMR}$. (in CCl_4): PCH_3 1.33 ppm (d , J_{POCH} 17.7 Hz, 3H), OCH_3 3.62 ppm (d , J_{POCH} 11 Hz, 6H); ^{31}P - 31.5 ppm (in CCl_4) (Lit. [8] – 32.4 ppm).

A mixture of 116 g (0.93 mol) of $\text{CH}_3\text{P(O)(OCH}_3)_2$ in 120 ml POCl_3 and 131 g (0.955 mol) of PCl_5 was treated with Cl_2 and then heated to 80–90° as described in the literature [4, p. 388]. Distillation gave a product which contained

$\text{CH}_3\text{P(O)Cl}_2$:	^{31}P - 44.5 ppm; ^1H (in CCl_4): 2.48 ppm (J 16.5). Lit. [9] 2.57 ppm (J 16.1);
$\text{CH}_3\text{P(O)Cl(OCH}_3)$:	^{31}P - 31 ppm; ^1H : PCH_3 1.90 ppm (J 17.5); OCH_3 3.80 ppm (J 13.4). Lit. [9] PCH_3 2.03 ppm (J 17.4); OCH_3 3.82 ppm (J 13.4);
$(\text{CH}_3\text{O})_2\text{P(O)Cl}$:	^{31}P - 6.5 ppm; ^1H : 3.85 ppm (J 13.5). Lit. [9] 3.87 ppm (J 13.4);
$\text{CH}_3\text{OP(O)Cl}_2$:	^{31}P - 4.5 ppm; ^1H 4.0 ppm (J 16.4). Lit. [9] [10] 4.02 ppm (J 17.1).

Therefore the mixture was treated again with PCl_5 and heated for 2 h to 80°. Fractional distillation gave now a product, b.p. 47.5–50°/10 Torr (84.2 g) which consisted of 75.4 mol-% $\text{CH}_3\text{P(O)Cl}_2$ (^1H (in CCl_4): 2.45 ppm (J_{POCH} 17 Hz) and 24.6 mol-% $\text{CH}_3\text{OP(O)Cl}_2$ (^1H (in CCl_4): 3.98 ppm, J_{POCH} 16.5 Hz) (Lit. [10] 4.08 ppm (in CHCl_3), J_{POCH} 16.7 Hz). On standing $\text{CH}_3\text{P(O)Cl}_2$ crystallized out. It was filtered off and found to be pure, m.p. 32°.

2. $\text{CH}_3\text{P(O)(OH)}_2$ (III) and $\text{PCl}_5 \rightarrow \text{CH}_3\text{P(O)Cl}_2$ (II). Hydrolysis of I with conc. HCl at reflux for 14 h gave III in quantitative yield, eq. weight found: 100.12, calc. 96.02. Treatment of 80 g (0.83 mol) III with 430 g (2.07 mol) PCl_5 first at 65–75° then 9 h reflux gave on fractional distillation 238.5 g POCl_3 and 81.2 g (73.5%) $\text{CH}_3\text{P(O)Cl}_2$, b.p. 34–48°/10 Torr which crystallized on standing to the greater part. $^1\text{H-NMR}$. (in CCl_4) indicated that the product is pure II: CH_3 at 2.47 ppm (J_{POCH} 16.7 Hz); ^{31}P - 44.5 ppm (Lit. [8] ^{31}P - 44.5 ppm).

3. $\text{C}_2\text{H}_5\text{P(O)(OH)}_2$ (IV) and $\text{SOCl}_2 \rightarrow \text{C}_2\text{H}_5\text{P(O)Cl}_2$ (V). EtP(O)(OEt)_2 was prepared from $(\text{EtO})_3\text{P}$ and NaI [4], b.p. 75–77°/11 Torr; $^1\text{H-NMR}$. (in CCl_4): a) CH_3 1.28 ppm (t); b) PCH_2 0.94–1.95 ppm (m), a + b 10.9 Hz; OCH_2 4.0 ppm (J_{HH} 7, J_{POCH} 8.5 Hz, 4.06 Hz); ^{31}P - 32 ppm (neat).

Hydrolysis of ethylphosphonate with a 40% solution of HBr gave a quantitative yield of IV as an oily, viscous liquid. Treatment of 79.5 g (0.723 mol) IV with 190 g (1.53 mol) SOCl_2 at 70° for 3 h, then at 105° until evolution of HCl ceased, gave on distillation 55.5 g (52.8%) V, b.p. $60\text{--}61^\circ/10$ Torr; $^1\text{H-NMR}$. (in CCl_4): CH_3 at 1.38 ppm (2 t, J_{HH} 7, J_{PCH} 30 Hz, 2.99 H); CH_2 at 2.58 ppm (2 qu, J_{HH} 7, J_{PCH} 16 Hz, 2.01 H); ^{31}P - 53.5 ppm (neat) (Lit. [8] ^{31}P - 53 ppm).

4. $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ and SOCl_2 at 80° . A mixture of 14.9 g (0.1 mol) $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ and 1.46 g (0.12 mol) SOCl_2 was refluxed for 8 h at 80° . ^1H - and ^{31}P -NMR. indicated that after this period no reaction had occurred. $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ was quantitatively recovered by distillation, b.p. $39\text{--}43^\circ/0.1$ Torr, n_{D}^{20} 1.5470; ^1H (in CHCl_3): CH_3 at 2.78 ppm (J_{PCH} 14.5 Hz) (Lit. [11] 2.88 (J 14.6 Hz); ^{31}P -79.5 ppm (neat) (Lit. [8] ^{31}P - 79.4 ppm).

5. $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ and SOCl_2 at 150° . Three bomb-tubes were filled each with 10 g (0.067 mol) of $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ and 9.5 g (0.08 mol) of SOCl_2 and heated in a bomboven to 150° . Tube 1 was removed after 2 h at 150° . ^1H - and ^{31}P -NMR.-analysis indicated that its content consisted of 92 mol-% $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ [$^1\text{H-NMR}$. (in CDCl_3): CH_3 at 2.28 ppm (J_{PCH} 16.4 Hz), ^{31}P - 44 ppm] and 8 mol-% $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ [$^1\text{H-NMR}$. (in CDCl_3): CH_3 at 2.78 ppm (J_{PCH} 14.8 Hz) ^{31}P - 80 ppm].

In addition a trace of POCl_3 was seen in the ^{31}P -NMR. at -3.5 ppm.

Tube 2 was removed after 5 h at 150° . ^1H - and ^{31}P -NMR. analysis indicated that the solution consisted of 98.6 mol-% $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ and 1.4 mol-% $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$.

Tube 3 was removed after 8 h at 150° . ^1H - and ^{31}P -NMR.-analysis indicated that the solution consisted of a 100 mol-% $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$. Distillation of the contents of each tube gave $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ b.p. $53\text{--}54^\circ/10$ Torr, m.p. $30\text{--}32^\circ$ and SCL_2 ; in addition crystalline sulfur was isolated.

6. $\text{C}_2\text{H}_5\overset{\text{S}}{\underset{\text{||}}{\text{P}}}\text{Cl}_2 + \text{SOCl}_2$ at 150° . A bomb tube was filled with 20 g of $\text{C}_2\text{H}_5\text{P}(\text{S})\text{Cl}_2$ (0.123 mol) and 17.6 g (0.148 mol) of SOCl_2 and heated for 5 h to 150° . After this period a dark violet solution was present and crystalline sulfur had precipitated. ^1H - and ^{31}P -NMR.-analysis indicated that $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$ was formed in a 100% conversion. Distillation gave pure $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$ b.p. $33^\circ/3$ Torr, $75\text{--}78^\circ/50$ Torr. $^1\text{H-NMR}$. (in CDCl_3): CH_3 at 1.4 ppm (2 t, J_{HH} 7.5, J_{PCH} 30 Hz, 3H); CH_2 at 2.5 ppm (2 qu, J_{HH} 7.5, J_{PCH} 14.5 Hz, 2H), ^{31}P - 54 ppm (neat); contains a trace of $\text{P}(\text{O})\text{Cl}_3$ at -3.5 ppm (must have been formed by a P-C bond cleavage.)

7. $\text{C}_6\text{H}_5\overset{\text{S}}{\underset{\text{||}}{\text{P}}}\text{Cl}_2 + \text{SOCl}_2$ at 150° . A bomb tube was filled with 20 g (0.095 mol) $\text{PhP}(\text{S})\text{Cl}_2$ and 13.6 g (0.114 mol) SOCl_2 and heated in a bomb oven to 150° for 5 h. A yellow solution is obtained which consist, according to ^1H - and ^{31}P -NMR.-analysis, of 82 mol-% $\text{PhP}(\text{O})\text{Cl}_2$ (^{31}P - 34 ppm) and 18 mol-% $\text{PhP}(\text{S})\text{Cl}_2$ (^{31}P - 74.5 ppm) (Lit. [8] -34 ppm and -74.8 ppm, respectively).

Another tube filled with the same amounts of reagents was heated for 8 h to 150° . Thereby a quantitative conversion to $\text{PhP}(\text{O})\text{Cl}_2$ was effected. Distillation gave SCL_2 and $\text{PhP}(\text{O})\text{Cl}_2$, b.p. $104^\circ/4$ Torr; ^{31}P - 34 ppm (neat); $^1\text{H-NMR}$. (in CDCl_3): *m*- and *p*-CH 7.65 (*m*, 3H); *o*-CH 8.06 (*m*, 2H).

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