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Reaction of P(III) Chlorides with Aldehydes: III.[1] Reaction of Primary Intermediates with Oxidants and Chlorinating Agents

M. B. Gazizov, R. A. Khairullin, and R. F. Karimova

Kazan National Research Technological University, ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia
e-mail: mukattisg@mail.ru

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Abstract—Primary intermediates of P(III) chlorides reaction with aldehydes have been converted into the corresponding phosphates by treating with oxidants: dimethylsulfoxide and *tert*-butyl hypochlorite. In reactions of the intermediates with chlorinating agents (PCl_5 and Cl_2) the oxidation products are formed (due to the ligand exchange at quasiphosphonium center) along with the expected P(IV) acid chlorides.

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Oxidation has used as an efficient chemical method to elucidate the structure of primary reaction intermediates. In [2] we have demonstrated phosphorus atom of compounds **I** bears the substituents exhibiting different donor-acceptor properties. Therefore, it is necessary to find the suitable agents capable of oxidizing both the electrophilic and nucleophilic P(III) derivatives.

The following compounds have been known to oxidize various P(III) derivatives: oxygen [3–8], ozone [9, 10], alkyl- [11], and dialkyl peroxides [12–16], tertiary amine oxides [17–19], dimethylsulfoxide [20, 21], and alkyl hypochlorites [17, 22–25]. Analysis of the above-listed reference has suggested that dimethylsulfoxide **II** and *tert*-butyl hypochlorite **III** are suitable candidates to oxidize the primary intermediates. Both **II** and **III** are readily available, easy and safe in handling, and oxidation can be performed under the conditions of stability of **I**. Electrophilic as well as nucleophilic P(III) derivatives can likely be oxidized with these reagents.

The experiments confirmed that both oxidants were efficient oxidizers of the primary intermediates. The oxidation was carried out under mild conditions: in the solution and upon cooling. In all the cases, the stable oxidation products **IV** were isolated. The mixture of intermediates **Ic** with paraldehyde (could not be separated by distillation) was also subjected to oxidation. The oxidation product **IVc** had significantly higher boiling point than that of paraldehyde and thus could be isolated by vacuum distillation. The intermediates **Ik**, and **Il** (obtained by treating of compound **Ie** with alcohols in the presence of tertiary base) were oxidized in heavily diluted ether solution right after removing the amine salt. Physical parameters and elemental analysis data of compounds **IV** are given in the Experimental section. The compounds structures were confirmed by ^1H and ^{31}P NMR spectroscopy (see the table).

Scheme of the intermediates oxidation could be presented as follows.

$$\underset{\mathbf{I}}{R^1R^2POCHClR^3} + Me_2SO \rightarrow \underset{\mathbf{II}}{R^1R^2P(O)OCHClR^3} + \underset{\mathbf{IV}}{Me_2S},$$

$R^1 + R^2 = C_6H_4O_2$, R^3 = Me (**a**), Pr (**b**); $R^1 = R^2$ = Cl, R^3 = Me (**c**), CCl_3 (**d**), *i*-Pr (**e**); $R^1 = R^2 = CCl_3CH_2O$, R^3 = *i*-Pr (**f**); R^1 = Cl, R^2 = MeCHClO, R^3 = Me (**g**); R = CCl_3CH_2O, R^2 = MeCHClO, R^3 = Me (**h**), R^2 = *i*-PrCHClO, R^3 = *i*-Pr (**i**).

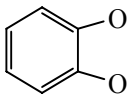
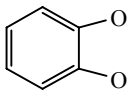
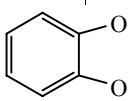
$$\underset{\mathbf{I}}{R^1R^2POCHClR^3} + \textit{t}\text{-BuOCl} \rightarrow \underset{\mathbf{III}}{R^1R^2P(O)OCHClR^3} + \underset{\mathbf{IV}}{\textit{t}\text{-BuCl}},$$

$R^1 = R^2$ = Cl, R^3 = Me (**c**), Pr (**j**); $R^1 = R^2$ = MeO, R^3 = *i*-Pr (**k**); $R^1 = R^2$ = EtO, R^3 = *i*-Pr (**l**).

It should be noted that *tert*-butyl hypochlorite oxidized the intermediates **Ic** and **Ij** (with phosphorus atom being an electrophile) under mild conditions. In

[1] For communication II, see [1].

^{1}H and ^{31}P NMR parameters of phosphates $R^1R^2P(O)OCHClR^3$

Comp. no.	R^1	R^2	R^3	δ, ppm (J_{HH} and J_{PH}, Hz)	δ_P, ppm
IVa			Me	1.5 d (3H, Me, J_{HH} 5.0), 6.12 d.q (1H, POCH, J_{PH} 9.0, J_{HH} 5.0), 6.92–7.09 m (4H, Ar)	11.0
IVb			Pr	0.93 t (3H, $CH_2CH_2\underline{CH_3}$, J_{HH} 6.5), 1.37–1.63 m (2H, $CH_2\underline{CH_2}CH_3$), 1.78–2.02 m (2H, $\underline{CH_2}CH_2CH_3$), 6.23 d.t (1H, POCH, J_{PH} 8.0, J_{HH} 5.5), 6.90–7.10 m (4H, Ar)	11.0
IVc	Cl	Cl	Me	1.80 d (3H, Me, J_{HH} 5.0), 6.30 sextet (1H, POCH, J_{PH} 10.0, J_{HH} 5.0)	5.0
IVd	Cl	Cl	CCl_3	6.52 d (1H, POCH, J_{PH} 11.3)	8.0
IVe	Cl	Cl	$CHMe_2$	0.95 d (6H, Me, J_{HH} 5.0), 1.78–2.00 m (1H, CH), 6.30 d.t (1H, POCH, J_{PH} 10.0, J_{HH} 5.0)	6.0
IVf	CCl_3CH_2O	CCl_3CH_2O	$CHMe_2$	0.99 d (6H, Me, J_{HH} 6.3), 2.0–2.3 m (1H, $\underline{CH}Me_2$), 4.55 d (4H, CH_2OP, J_{PH} 5.0), 5.92 d.d (1H, POCH, J_{PH} 9.0, J_{HH} 5.0)	–6.0
IVg	Cl	$OCHClCH_3$	Me	1.79 d (6H, Me, J_{HH} 7.0), 6.13–6.43 m (2H, CH)	2.42, 1.2, 0.7
IVj	Cl	Cl	Pr	0.90 t (3H, $CH_2CH_2\underline{CH_3}$, J_{HH} 6.3), 1.38 sextet (2H, $CH_2\underline{CH_2}CH_3$, J_{HH} 6.3), 1.88 d.t (2H, $\underline{CH_2}CH_2CH_3$, J_{PH} 5.0, J_{HH} 6.3), 6.25 d.t (1H, POCH, J_{PH} 5.0, J_{HH} 6.3)	6.0
IVk	MeO	MeO	$CHMe_2$	0.99 d (6H, Me, J_{HH} 6.3), 1.93–2.20 m (1H, $\underline{CH}Me_2$), 3.70 d and 3.74 d (6H, OMe, J_{PH} 12.5), 5.83 d.d (1H, POCH, J_{PH} 8.8, J_{HH} 5.0)	0
IVl	EtO	EtO	$CHMe_2$	1.42 d (6H, $CH\underline{Me_2}$, J_{HH} 6.3), 1.2 t (6H, $OCH_2\underline{CH_3}$, J_{HH} 7.5), 1.9–2.2 m (1H, $\underline{CH}Me_2$), 4.00–4.04 m (4H, $O\underline{CH_2}CH_3$), 5.85 d.q (1H, POCH, J_{PH} 9.0, J_{HH} 6.3)	–3.0
IVm			$CHMe_2$	0.98 d (6H, Me, J_{HH} 6.0), 1.85–2.25 m (1H, $\underline{CH}Me_2$), 6.12 d.d (1H, POCH, J_{PH} 8.0, J_{HH} 5.0), 0.85–7.12 m (4H, Ar)	10.6
IVn	MeO	CH_3CHClO	Me	1.50–1.72 m (6H, Me), 3.61 d and 3.63 d (3H, OMe, J_{PH} 12.0, J_{PH} 15.0), 5.90–6.16 m (2H, POCH)	–3.89, –4.86, –5.14
IVo	MeO	MeO	Me	1.42 d (6H, Me, J_{HH} 6.3), 5.85 d.q (1H, POCH, J_{PH} 9.0, J_{HH} 6.3), 3.40 d and 3.44 d (6H, OMe, J_{PH} 12.0)	–1

order to demonstrate that the reaction was common for the electrophilic P(III) derivatives, we performed the oxidation of PCl_3 and ethyl phosphorodichloridite as well; the reaction gave the corresponding phosphates with good yields under mild conditions.

Some of the compounds **IV** were synthesized by other methods. For example, compounds **IVn** and **IVo** were prepared via the reaction of the products of oxidation of **Ic** and **Ig** with methanol in the presence of tertiary amine.

$$\underset{\textbf{IVc, IVg}}{Cl(MeCHClO)P(O)X} + n\,MeOH \xrightarrow[-n\,Et_3N\cdot HCl]{n\,Et_3N} \underset{\textbf{IVn, IVo}}{MeO(MeCHClO)P(O)Y},$$

X = Cl (**c**), MeCHClO (**g**); Y = MeCHClO (**n**), MeO (**o**).

In order to extend the knowledge on chemical properties of the primary intermediates **I**, we studied the reactions of compounds **Ia** and **Im** with PCl_5 and gaseous Cl_2. The structures of (**Ia** and **Ib**) and (**Im** and **In**) intermediates were those of trisubstituted phosphite. Trialkyl phosphites are known to react with halogens, in particular, with chlorine, to form dialkyl chlorophosphates [17, 24]. Phosphorus pentachloride may act as source of chlorine.

$$(RO)_3P + Cl_2 \rightarrow [(RO)_3PCl_2 \rightleftarrows (RO)_3\overset{+}{P}Cl\ Cl^-]$$
$$\rightarrow (RO)_2P(O)Cl + RCl.$$

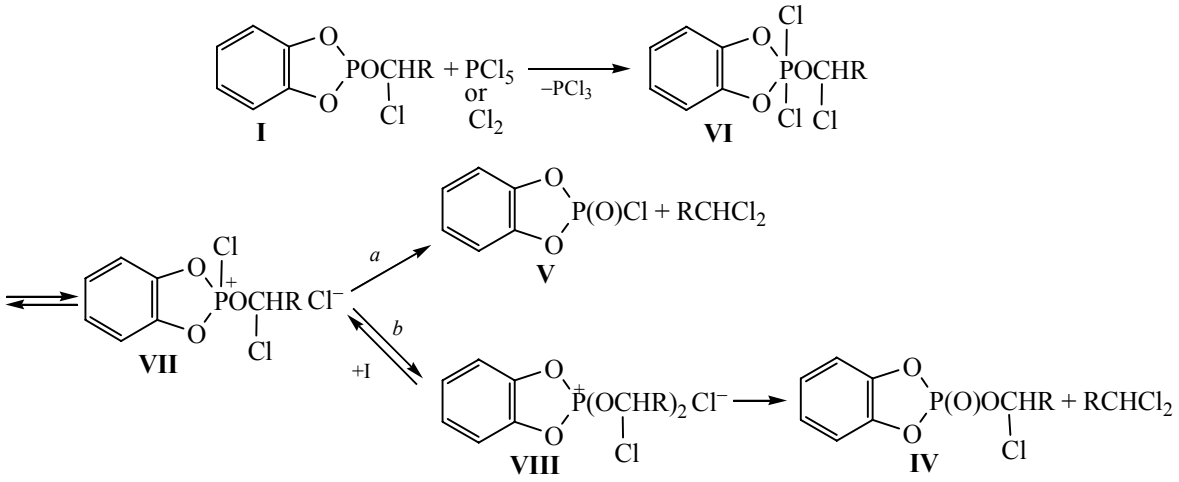
It reacts with trialkyl phosphites to give PCl_3, and the second major reaction product being dialkyl chlorophosphate [26, 27].

$$(RO)_3P + PCl_5 \rightarrow (RO)_2P(O)Cl + PCl_3 + RCl.$$

In the excess of trialkyl phosphite, it can disproportionate via interaction with PCl_3 [27].

$$3P(OR)_3 + PCl_5 \xrightarrow[-RCl]{} PCl_3 + (RO)_2P(O)Cl + 2P(OR)_3$$
$$\rightarrow (RO)_2P(O)Cl + 3(RO)_2PCl.$$

We proposed that the intermediates **Ia** and **Ib** should react with PCl_5 and Cl_2 similarly to trialkyl phosphites, to give chlorophosphate **V** (pathway *a*).



R = Me (**a**), *i*-Pr (**m**).

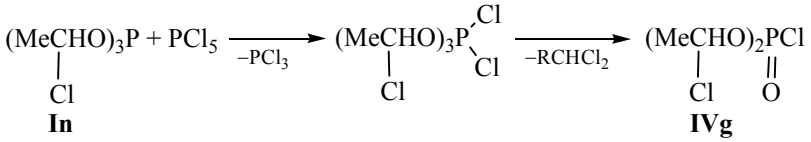
However, chlorophosphate **V** was not the only phosphorus-containing reaction product; trisubstituted phosphates **IV** (the products of oxidation of intermediates **I**) were formed as well (pathway *b*). The ratio of the products **IV** and **V** depended on the order of mixing of reagents. In view of that, using PCl_5 seemed more convenient. When the intermediate **Im** was added dropwise to the benzene solution of PCl_5, chlorophosphate **V** was the only product. With the reversed mixing order, both **IV** and **V** were obtained with 1 : 1 ratio. ^{31}P NMR spectrum of reaction mixture after evaporating all the volatile products contained two singlets of equal intensity at δ_P 19 and 10.5 ppm. The first fraction of the first vacuum distillation contained chlorophosphate **V** (δ_P 19 ppm). Slow distillation of the third fraction (containing **V** and **IVm** in the 1 : 4 ratio) gave the pure compound **IVm**.

In the course of chlorination with gaseous chlorine, the reversed reagents mixing order could not be carried out. Therefore, in all the cases the chlorine gas was passed through the solution of intermediate **Im** in methylene chloride. The major reaction product was chlorophosphate **V**, the ratio of δ_P 19 and 10.5 ppm signals being of 10 : 1. By distillation with reflux condenser, compound **V** was isolated in pure form in 78% yield. Chlorination of the intermediate **Ia** in toluene the major fraction contained the products **V** and **IVa** in the 1 : 3 ratio. Repeated distillation of that fraction with reflux condenser gave the mixture majorly containing the trisubstituted phosphate **IVa** (**V** : **IVa** ratio of 1 : 10). In the ^1H NMR spectrum of that fraction, all the characteristic signals of **IVa** were observed. Hence, the reactions of intermediates **I** with PCl_5 and Cl_2 proceeded via different path-

ways: chlorination and oxidation took place simultaneously.

We propose that the intermediates **I** first reduced PCl_5 to PCl_3, being simultaneously chlorinated to give the quasiphosphonium compound **VII** via the phosphorane intermediate **VI**. Then, the quasiphosphonium compound **VII** was subjected to ligand exchange with the initial trisubstituted phosphite **I** to give the quasiphosphonium compound **VIII** that was further dealkylated to give the oxidation product **IV**. Noteworthily, such ligand exchange at quasiphosphonium center is a well known organophosphorus compounds reaction [17, 29, 30].

Reaction with PCl_5 was also used for confirmation of tris(1-chloroethyl) phosphite **In** structure. The reaction product was bis(1-chloroethyl) chlorophosphate **IVg** that could be prepared as well by oxidation of phosphoromonochloridite **Ig** with DMSO, as discussed above. The spectral properties of compound **IVd** obtained by different methods were identical.



In **IVg**

EXPERIMENTAL

^1H (300 MHz), ^{13}C (75.5 MHz), and ^{31}P (121.5 MHz) NMR spectra were registered with 7.0 T IBM/Bruker AF 300 spectrometer. ^1H (100 MHz) NMR spectra were recorded with Tesla BS-567A device, and ^{31}P (162 MHz) NMR spectra were recorded with Bruker MSL-400 spectrometer. Chemical shifts of hydrogen and carbon are given with reference to TMS. Chemical shifts of phosphorus are given with reference to 85% phosphoric acid.

1-Chloroethyl dichlorophosphate IVc. 2.79 g (0.036 mol) of DMSO in benzene was added dropwise at 0–5°C to solution of 6.47 g (0.036 mol) of 1-chloroethyl phosphorodichloridite **Ic** (containing admixture of paraldehyde) in benzene. Vacuum distillation gave 2.13 g (30%) of dichlorophosphate **IVc**, bp 30°C (0.04 mm Hg), n_D^{20} 1.4531, d_4^{20} 1.4854. Found, %: C 11.92; H 1.92; Cl 53.80; P 15.63. $C_2H_4Cl_3O_2P$. Calculated, %: C 12.15; H 2.02; Cl 53.92; P 15.69.

1-Chlorobutyl dichlorophosphate IVj. Reaction of 5.48 g (0.026 mol) of 1-chlorobutyl dichlorophosphite **Ij** and 2.04 g (0.026 mol) of DMSO yielded 2 g (31%) of dichlorophosphate **IVj**, bp 40°C (0.025 mm Hg), n_D^{20} 1.4561. Found, %: C 21.09; H 3.24; Cl 47.11, P 13.72. $C_4H_8Cl_3O_2P$. Calculated, %: C 21.29; H 3.54; l 47.18; P 13.74.

2-Methyl-1-chloropropyl dichlorophosphate IVe. Similar reaction of 51 g (0.206 mol) of 2-methyl-1-chloropropyl phosphorodichloridite **Ie** with 16.09 g (0.206 mol) of DMSO gave 28 g (52%) of dichlorophosphate **IVe**, bp 43°C (0.01 mm Hg). Found, %: C 21.01; H 3.50; Cl 47.15; P 13.68. $C_4H_8Cl_3O_2P$. Calculated, %: C 21.29; H 3.54; Cl 47.18; P 13.74.

Pyrocatechol(1-chloroethyl) phosphate IVa. Similar reaction of 33 g (0.151 mol) of pyrocatechol(1-chloroethyl) phosphite **Ia** and 11.8 g (0.151 mol) of DMSO gave 13.11 g (38%) of phosphate **IVa**, bp 95–98°C (0.03 mm Hg), n_D^{20} 1.4985, d_4^{20} 1.3005. Found, %: C 40.86; H 3.32; Cl 15.10; P 13.15. $C_8H_8ClO_4P$. Calculated, %: C 40.94; H 3.41; Cl 15.13; P 13.20.

Pyrocatechol(1-chlorobutyl) phosphate IVb. Similar reaction of 33.56 g (0.136 mol) of pyrocatechol(1-chlorobutyl) phosphite **Ib** and 10.64 g (0.136 mol) of DMSO gave 14 g (53%) of phosphate **IVb,** bp 98–100°C (0.02 mm Hg), n_D^{20} 1.5022; d_4^{20} 1.2999. Found, %: C 45.35; H 4.46; Cl 13.48; P 11.45. $C_{10}H_{12}ClO_4P$. Calculated, %: C 45.71; H 4.57; Cl 13.52; P 11.79.

1,2,2,2-Tetrachloroethyl dichlorophosphate IVd. Solution of 9.2 g (0.118 mol) of DMSO in diethyl ether was added dropwise at 0–3°C to solution of 33.6 g (0.118 mol) of crude 1,2,2,2-tetrachloroethyl dichlorophosphite **Id** in diethyl ether**.** Vacuum distillation gave 20.5 g (58%) of phosphate **IVd**, bp 106–108°C (0.01 mm Hg). Found, %: C 7.89; H 0.38; Cl 70.69; P 10.17. C_2HCl_6PO. Calculated, %: C 7.27; H 0.33; Cl 70.76; P 10.29.

Di(1-chloroehyl) chlorophosphate IVg. DMSO, 3.12 g (0.04 mol), was slowly added dropwise to the solution of 9.02 g (0.01 mol) of crude di(1-chloroethyl)-phosphorodichloridite **Id** in 15 mL of methylene chloride. Vacuum distillation gave 4.1 g (42%) of chlorophosphate **IVg**, bp 67–69°C (0.1 mm Hg).

Found, %: C 19.76; H 3.26; Cl 43.94; P 12.85. $C_4H_8Cl_3O_3P$. Calculated, %: C 19.87; H 3.31; Cl 44.10, P.12.84.

Di(2-methyl-1-chloropropyl)-2,2,2-trichloroethyl phosphate IVi. Solution of 2.34 g (0.03 mol) of DMSO in 8 mL of benzene was added dropwise to solution of 13.85 g (0.03 mol) of crude phosphite **Ii** in 30 mL of benzene at 0–10°C. Vacuum distillation gave 5.32 g (37%) of phosphate **IVi**, bp 131°C (0.03 mm Hg). Found, %: C 29.01; H 4.42; Cl 43.11; P 7.44. $C_{10}H_{18}Cl_5O_4P$. Calculated, %: C 29.23; H 4.38; Cl 43.24; P 7.55.

(2-Methyl-1-chloropropyl)bis(2,2,2-trichloroethyl) phosphate IVf. Solution of 3.2 g (0.04 mol) of DMSO in 5 mL of diethyl ether was added dropwise at 0–10°C to a solution of 18.1 g (0.041 mol) of crude phosphite **If** in 70 mL of diethyl ether. Vacuum distillation gave 7.9 g (43%) of phosphate **IVf**, bp 132–135°C (0.02 mm Hg), n_D^{20} 1.5022, d_4^{20} 1.2999. Found, %: C 21.13; H 2.58; Cl 54.87; P 6.67. $C_8H_{12}Cl_7O_4P$. Calculated, %: C 21.26; H 2.65; Cl 55.03; P 6.17.

Di(1-chloroethyl)-2,2,2-trichloroethyl phosphate IVh. Similar reaction of 28.19 g (0.08 mol) of crude phosphite **Ih** and 6.5 g (0.08 mol) of DMSO gave 11.62 g (41%) of phosphate **IVh**, bp 119°C (0.03 mm Hg). Found, %: C 20.23; H 2.79; Cl 49.97; P 8.67. $C_6H_{10}Cl_5O_4P$. Calculated, %: C 20.31; H 2.82; Cl 50.07; P 8.74.

1-Chloroethyl dichlorophosphate IVc. 12.47 g (0.115 mol) of *tert*-butyl hypochlorite was added dropwise at 0–2°C to solution of 20.84 g (0.115 mol) of chloroethyl phosphorodichloridite **Ic** in 50 mL of carbon tetrachloride. Vacuum distillation gave 6.13 g of phosphate **IVc**, bp 30°C (0.04 mm Hg). n_D^{20} 1.4529, d_4^{20} 1.4858. Found, %: C 12.01; H 1.97; Cl 53.08; P 15.53. $C_2H_4Cl_3O_2P$. Calculated, %: C 12.15; H 2.02; Cl 53.92; P 15.69.

1-Chlorobutyl dichlorophosphate IVj. Similar reaction of 9.84 g (0.047 mol) of phosphorodichloridite **Ij** and 5.1 g (0.047 mol) of *tert*-butyl hypochlorite gave 2.65 g (25%) of phosphate **IVj**, bp 40°C (0.025 mm Hg). Found, %: C 21.19; H 3.44; Cl 46.96; P 13.67. $C_4H_8Cl_3O_2P$. Calculated, %: C 21.29; H 3.54; Cl 47.18; P 13.74.

Dimethyl(2-methyl-1-chloropropyl) phosphate IVk. Solution of 9.76 g (0.0116 mol) of 2-methyl-1-chloropropyl phosphorodichloridite **Ie** in diethyl ether was added dropwise at –10°C to solution of 2.98 g (0.093 mol) of methanol and 13.93 g (0.093 mol) of *N,N*-diethylaniline in 100 mL of anhydrous diethyl ether. The reaction mixture was stirred at that temperature during 2.5 h. The precipitate formed was filtered off, and 5.06 g (0.0116 mol) of *tert*-butyl hypochlorite was added dropwise at –5 to –10°C to the mixture obtained. Vacuum distillation gave 5.38 g (53%) of phosphate **IVk**, bp 49–50°C (0.04 mm Hg), n_D^{20} 1.4312, d_4^{20} 1.1950. Found, %: C 33.05; H 6.34; Cl 15.98; P 13.93. $C_6H_{14}ClO_4P$. Calculated, %: C 33.25; H 6.47; Cl 16.40; P 14.30.

Diethyl(2-methyl-1-chloropropyl) phosphate IVl. Similar reaction of 3.64 g (0.079 mol) of ethanol, 11.82 g (0.079 mol) of *N,N*-diethylaniline, 8.3 g (0.0396 mol) of phosphorodichloridite **Ie**, and 4.3 g (0.039 mol) of *tert*-butyl hypochlorite gave 4.64 g (48%) of phosphate **IVl**, bp 75–77°C (0.04 mm Hg), n_D^{20} 1.4462, d_4^{20} 1.1534. Found, %: C 38.96; H 7.27; Cl 14.18; P 12.13. $C_8H_{18}ClO_4P$. Calculated, %: C 39.29; H 7.36; Cl 14.49; P 12.67.

Phosphorus trichloroxide. 10 g (0.092 mol) of *tert*-butyl hypochlorite was added dropwise to 4 g (0.092 mol) of PCl_3 at 10–15°C. Distillation of reaction mixture gave 2 g of *tert*-butyl chloride, bp 50–53°C (reported data 51–52°C [31]) and 2.53 g (57%) of phosphorus trichloroxide, bp 103-105°C.

Ethyl dichlorophosphate. *tert*-Butyl hypochlorite, 3.8 g (0.035 mol), was added dropwise at 10–15°C to 4.25 g (0.029 mol) of ethyl phosphorodichloridite. Distillation of the reaction mixture gave 1.63 g of *tert*-butyl chloride (bp 49–50°C) and 0.9 g of ethyl dichlorophosphate, bp 52–54°C (10 mm Hg), n_D^{20} 1.4445 (reported data bp 92°C (65 mm Hg) [32]).

Methyldi(1-chloroethyl) phosphate IVn. Chlorophosphate **IVg**, 6.25 g (0.027 mol), was added dropwise to solution of 0.864 g (0.027 mol) of methanol and 2.73 g (0.027 mol) of triethylamine in diethyl ether. The reaction mixture was stirred during 2 h at room temperature, and triethylamine hydrochloride was filtered off. Vacuum distillation gave 3.1 g (50%) of phosphate **IVn**, bp 83–84°C (0.1 mm Hg). Found, %: C 25.31; H 4.60; Cl 29.81; P 13.18. $C_5H_{11}Cl_2O_4P$. Calculated, %: C 25.31; H 4.64; Cl 29.96; P 13.08.

Dimethyl(1-chloroethyl) phosphate IVo. 1-Chloroethyl dichlorophosphate **IVc**, 4.68 g (0.024 mol), was added dropwise at 0–3°C to a solution of 1.51 g (0.047 mol) of methanol and 4.8 g (0.047 mol) of triethylamine in 50 mL of diethyl ether. Reaction

mixture was stirred during 1 h at that temperature, and the obtained precipitate was filtered off. Distillation of the filtrate in vacuum gave 1.58 g (35%) of phosphate **IVo**, bp 73–75°C (10 mm Hg), n_D^{20} 1.4373, d_4^{20} 1.2018.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphite Im with phosphorus pentachloride. *a*. Compound **Im**, 15.61 g (0.063 mol), was added dropwise to a solution of 13.12 g (0.063 mol) of PCl_5 in 50 mL of CH_2Cl_2 upon cooling with cold water. Distillation of the reaction mixture gave 8.1 g (70%) of pyrocatechol chlorophosphate **VI**, bp 82–83°C (0.03 mm Hg). ^{1}H NMR spectrum (δ, ppm): 6.8 m (C_6H_4); ^{31}P NMR spectrum (δ_P, ppm): 19.

b. Solution of 39.2 g (0.187 mol) of PCl_5 in 15 mL of benzene was added dropwise to solution of 57.8 g (0.234 mol) of compound **Im** in 120 mL of benzene upon cooling with cold water. Distillation of the reaction mixture in vacuum gave three fractions.

The first fraction contained pyrocatechol chlorophosphate (δ_P 19 ppm). According to ^{31}P NMR data, the second fraction consisted of compounds **IVm** and **V** in the 1 : 3 ratio. In the third fraction, the same compounds were found in 4 : 1 ratio. Distillation of the third fraction with reflux condenser gave 22 g (36%) of (2-methyl-1-chloropropyl)pyrocatechol phosphate **IVm**, bp 104°C (0.02 mm Hg), n_D^{20} 1.0525, d_4^{20} 1.3024. Found, %: C 45.23; H 4.33; Cl 13.30; P 11.90. $C_{10}H_{12}ClO_4P$. Calculated, %: C 45.71; H 4.57; Cl 13.50; P 11.79.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphite Im with chlorine. The calculated amount of chlorine was passed at 10°C through solution of 48.5 g (0.196 mol) of compound **Im** in methylene chloride. After removing the volatile products under vacuum, ^{31}P NMR spectrum of the residue contained two signals at δ_P 19 and 11 ppm in the 10:1 ratio. By distillation with reflux condenser, 27.1 g (73%) of chlorophosphate **V** was isolated, bp 83–84°C (0.02 mm Hg).

Reaction of (1-chloroethyl)pyrocatechol phosphite Ia with chlorine. The calculated amount of chlorine was passed at 10°C through solution of 30 g (0.165 mol) of compound **Ia** in anhydrous toluene. By vacuum distillation, the major fraction with bp 100–118°C (0.015 mm Hg) was isolated. Its ^{31}P NMR spectrum contained two signals at δ_P 19 and 11 ppm in the 1:3 ratio. Repeated distillation of that fraction with reflux condenser gave two fractions. In ^{31}P NMR spectrum of the first one [bp 80–86°C (0.02 mm Hg)] the ratio of the δ_P 19 and 10 ppm signals was of 3 : 1; in the spectrum of the second fraction [bp 100–104°C (0.02 mm Hg)] those signals were observed in the 1 : 10 ratio. Thus, the main component of the second fraction was the oxidation product **IVa**.

Reaction of tris(1-chloroehyl)phosphite In with phosphorus pentachloride. Acetaldehyde, 17.4 g (0.396 mol), was slowly added dropwise to a mixture of 12.0 g (0.088 mol) of phosphorus trichloride and 0.656 g (0.0011 mol) of *N,N*-diethylaniline at 0 to –3°C upon vigorous intense stirring. The reaction mixture was allowed to stand for 24 h at –1°C, and the volatile products were removed upon cooling in high vacuum. The residue, crude intermediate **Ip**, was dissolved in 15 mL of cold benzene, and that solution was added dropwise to solution of 17.72 g (0.088 mol) of PCl_5 in 60 mL of benzene. Reaction mixture was slowly heated to 45°C. Distillation in vacuum gave 10.1 g (47%) of di(1-chloroethyl) chlorophosphate **Ig**.

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