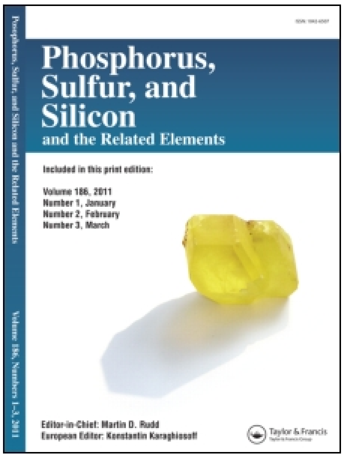

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REACTION OF TERVALENT PHOSPHORUS COMPOUNDS WITH STERICALLY HINDERED N-CHLOROAMINES

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REACTION OF TERVALENT PHOSPHORUS COMPOUNDS WITH STERICALLY HINDERED N-CHLOROAMINES

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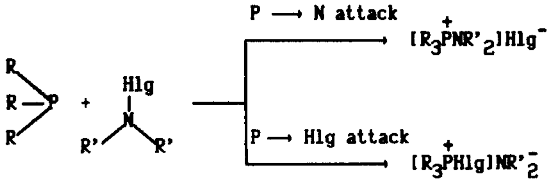
Reaction of tervalent phosphorus compounds with sterically hindered N-halogenoamines (**1**, **2**) proceeds via the formation of halogenophosphonium intermediates (**3**), containing an anion R_2N^-. Intermediates react with alcohols to afford alkoxyphosphonium salts (**6**), transform into halogenophosphonium salts (**4**) or P-halogenoylids (**10**). Sterical hindrances at the nitrogen atom of intermediates (**3**) favour the formation of P-halogenoylids. The P-chloroylid (**10**) exists in the chlorotropic equilibrium with the α-chloroalkylphosphine (**16**).

Key words: Sterical hindered N-halogenoamines, N-chlorodiisopropylamine, N-chloro-trimethylsilyl-*tert*-butylamine, alkoxyphosphonium salts, P-chloroylids, 1,2-CP-chlorotropy, positive halogen, NMR spectra, halogenophilic substitution.

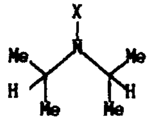
INTRODUCTION

Reaction of tervalent phosphorus compounds with compounds R'X, containing electropositive halogen atom (polyhalogenomethanes, α-halogenocarbonyle compounds, hypohalides, and generally R-X compounds (X = halogen) were R' is a good anionic group) are very important from theoretical and practical view points.[1,2] These reactions proceed through nucleophilic attack of the tervalent phosphorus atom on the halogen atom with formation of a halogenophosphonium intermediate, containing an anion R'^-: $R_3P + R' - X \rightarrow [R_3\overset{+}{P}X]\overset{-}{R}'$, which then undergoes easily various chemical transformations.

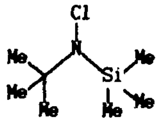
N-Halogenoamines possess electropositive halogen atoms.[2–4] However, according to the literature data, they react with tervalent phosphorus compounds to afford as a rule products, containing the phosphorus-nitrogen bond: aminophosphonium salts, iminophosphoranes, amides of phosphorus acids.[1–13] The authors suggested that this reaction proceeds via nucleophilic attack of the tervalent phosphorus atom on the nitrogen atom (P → N attack). Although N-halogenoamides, in particular the N-halogenosuccinimides, react with tervalent phosphorus compounds to yield, in some cases, products of the substitution at the halogen atom.[10,14,15] Therefore the halogenophilic attack of the tervalent phosphorus atom on the halogen atom (P → Hlg attack) in case of N-halogenoamines seems probable.



In this work we found that the sterical hindrances at the nitrogen atom of the N-halogenoamines (**1**, **2**) favour the nucleophilic attack of the tervalent phosphorus atom on the "positive" halogen atom with the formation of phosphorus halogenated products. The development of this reaction and its products indicate the formation of a halogenophosphonium intermediate, containing an anion NR_2^-. The reaction possesses interesting synthetical possibilities and is perspective for further studies.



1a,b



2b

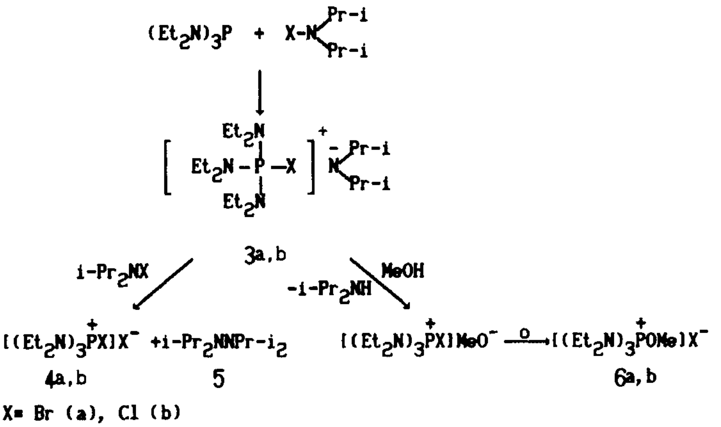
X=Br (a), Cl (b)

RESULTS AND DISCUSSION

The triphenylphosphine reacts with the N-chloroamine and with lowest N-chloroalkylamines to form aminotriphenylphosphonium salts.[5] The reaction proceeds probably via the P → N attack to afford products of the displacement on the saturated tricoordinate nitrogen atom. We have found that sterical hindrances at the nitrogen atom of N-halogenoamines favour the P → Hlg attack. Thus the reaction of N-chloro- and N-bromodiisopropylamines with tris(diethylamino) phosphine in diethyl ether proceeds in the ratio 2:1 of the initial reagents and results in tris(diethylamino)halogenophosphonium halides (**4**), which separated from the solution as a solid precipitate in high yields. In the mother solution the tetraisopropylhydrazine was found, however in low yield.[15]

The formation of these compounds may be explained by nucleophilic attack of the tervalent phosphorus atom on the "positive" halogen atom of N-chloroamine with the formation of the halogenophosphonium intermediate (**3**), containing an anion $i\text{-}Pr_2N^-$. Subsequent reaction of the anion $i\text{-}Pr_2N^-$ with the second molecule of N-halogenodiisopropylamine leads to the formation of tetraisopropylhydrazine and tris(diethylamino)phosphonium halides (**4**).

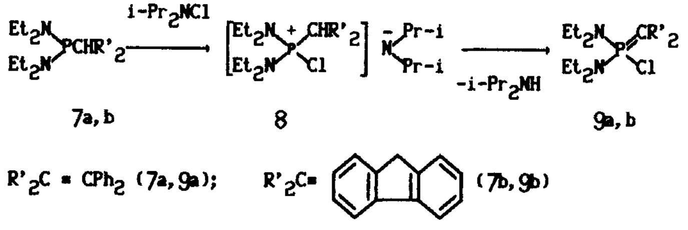
It is important to note that N-halogenoamines may also be, in certain conditions, halogenating reagents by a free radical mechanism. For instance, the Hoffman-Loffler reaction is an intramolecular chlorination of hydrocarbons involving protonated N-chloroamines.[16] In our opinion, this mechanism is improbable in case of tervalent phosphorus compounds. Thus the reaction of tris(diethylamino)phosphine with N-halogenodiisopropylamine is not depended on irradiation. Furthermore, the presence of the halogenophosphonium intermediate (**3**) was confirmed through the reaction with methyl alcohol which resulted in the formation of alcoxyphosphonium salt (**6a**, **b**) and diisopropylamine. In this case the anion $NPr\text{-}i_2^-$ deprotonates the methyl alcohol to give a salt, bearing an anion MeO^-, which then as a result of anion exchange converts into the alcoxyphosphonium salt (**6**) as shown in the Scheme I.



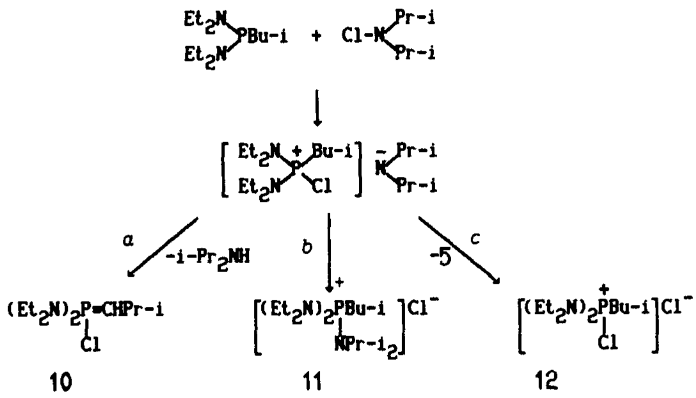
SCHEME I

Alcoxyphosphonium salts (**6a**, **b**) are stabilized by dissolution in water. Owing to the strong solvatation the salts (**6a**, **b**) are stable in the aqueous solution for 1–2 hours at room temperature and may be characterized by ^{31}P NMR spectroscopy, where the signal δ_P 39 ppm was found. Treatment of the salts (**6a**, **b**) by aqueous solution of $NaClO_4$ leads to exchange of the chlorine anion by the perchlorate anion to afford stable, easily crystallizable perchlorates (**6c**) for which correct results of elemental analyses were obtained.

The reaction between the alkylphosphines (**7**), containing the mobile hydrogen atom at the α-carbon atom and the N-chlorodiisopropylamine results in P-halogenoylids (**9a**, **b**) and proceeds evidently via the formation of chlorophosphonium intermediates (**8**). The increase of proton mobility at the α-carbon atom favours the deprotonation of the intermediates (**8**) by the anion NR_2^-. Therefore the reaction of tervalent phosphorus compounds (**7**), bearing diphenylmethyl or fluorenyl groups, with N-chlorodiisopropylamine occurs readily in ether or benzene at room temperature to afford the ylids (**9a**, **b**) and diisopropylamine in high yields. The ylids (**9a**, **b**) were isolated as stable orange crystalline solids and their structure was confirmed by NMR spectra and elemental analyses. The chemical shifts δ_P of the compounds (**9**) in the area of +60 ppm are typical for P-chloroylids.[17,18]

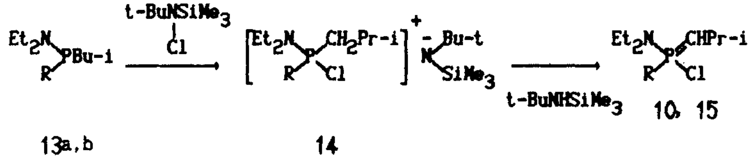


On the contrary the reaction of N-chlorodiisopropylamine with bis(diethylamino)isobutylphosphine, possessing low CH-acidity, affords the P-chloroylid (**10**) in poor yield. The ^{31}P NMR spectrum of the reaction mixture showed only a weak signal corresponding to the P-chloroylid (**10**) (δ_P 62 ppm). The main products of



SCHEME II

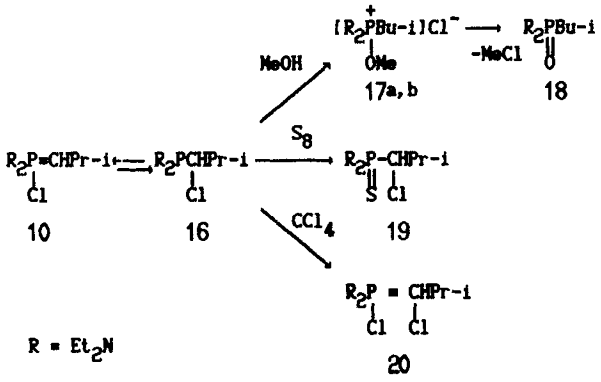
the reaction were bis(diethylamino)isobutylchlorophosphonium chloride (**11**) (δ_P 73 ppm) and bis(diethylamino)isobutylphosphonium chloride (**12a**) (δ_P 48 ppm). Probably because of the low mobility of the hydrogen atom at the α-carbon atom the anion NPr-i$_2^-$ can not deprotonate the intermediate (way a), but attacks the phosphonium cation to form the phosphonium salt (**11**) (way b), or reacts with the second molecule of N-chlorodiisopropylamine to result in the chlorophosphonium chloride (**12**) (way c) (Scheme II).



R= Et$_2$N (10, 13a), t-Bu (13b, 15)

Bulky substituents and sterical hindrances at the nitrogen atom prevent the attack of the anion NR$_2^-$ on the phosphonium cation and in this case it deprotonates the α-carbon atom of the halogenophosphonium intermediate (**14**). Therefore the reaction of phosphines (**13**), R = *i*-Bu, with the sterically hindered N-chloro-trimethylsilyl-*tert*-butylamine smoothly occurs in diethyl ether or benzene at 0– +20°C, to give P-chloroylids (**10**, **15**) in almost quantitative yield.

The ylid (**10**) is stable in a solution during several hours. By heating or by distillation in vacuum it easily rearrangements into the α-chloroalkylphosphine (**16**) to result in the tautomer mixture of two chlorotropic isomers (**10**) $\rightleftarrows$ (**16**) in the ratio 4:1.[17-19] The chlorotropic isomers were characterized by ^{31}P-NMR, where the signals δ_P 62 ppm [ylid form (**10**)] and 87.8 ppm [α-chloroaklylphosphine form (**16**)] were found. The ^{1}H NMR spectrum shows the presence of the signal δ_H 4.07, double doublet with constants J_{HH} 2.0 Hz and J_{HP} 3.4 Hz belonging to the CHCl group. The existence of the chlorotropic transformation (**10**) $\rightleftarrows$ (**16**) was showed also by chemical reactions. The ylid chlorotropic form (**10**) adds methyl alcohol to form the methoxyphosphonium salt (**17a**), X = Cl, which characterized ^{31}P NMR spectrum (δ_P 61 ppm). The salt converts then, in accordance with the Arbuzov



SCHEME III

reaction, into the (diethylamido)isobutylphosphonate (**18**). Treatment of the salt (**17a**) by aqueous solution of $NaClO_4$ yields the stable perchlorate (**17b**), X = ClO_4, as colorless crystalline solid. The α-chloroalkylphosphine chlorotropic form (**16**) adds the sulfur atom to form this bis(diethylamido) α-chloroisobutyl thiophosphonate (**19**). The mixture (**10**) ⇄ (**16**) reacts as well with carbon tetrachloride to afford the P-chloroylid (**20**), which was isolated by distillation in vacuum as a yellow liquid (Scheme III).

Sterically hindered N-chloroalkylamines react with tervalent phosphorus compounds similarly to carbon tetrachloride with the formation of P-chloroylids. At that time N-chloroalkylamines are more selective chlorinating reagents than the carbon tetrachloride. Thus, the reaction of bis(diethylamido)isobutylphosphonite (**13a**) with carbon tetrachloride in contrast to the reaction with N-chlorotrimethylsylil-*tert*-butylamine leads at once to the formation of the ylid (**20**) or, at a deficiency of carbon tetrachloride, gives a mixture of the compounds (**10a**), (**13a**), (**16a**) and (**20**).

In closing we wish to note that the N-chloro- and N-bromoamines (**1**, **2**) are accessible compounds and may be easily obtained by various methods. Thus, the reaction of diisopropylamines with bromine in the ratio 2:1 provides the N-bromodiisopropylamine. The reaction of dialkylamines with sodium hypochlorite or with *tert*-buytl-hypochlorite affords also N-chloroamines (**1**, **2**) in good yields (See experimental part). Sterically hindered N-halogenoamines are stable and not dangerous in the work. They can be distilled under reduced pressure without decomposition.

CONCLUSION

Sterically hindered N-halogenoalkylamines possess active halogenating properties and react with tervalent phosphorus compounds similarly to methane tetrahalides. Advantage of N-halogenoalkylamines over methane tetrahalides is their higher chemical selectivity. The potential for these selective chlorinating reagents is currently under investigation.

EXPERIMENTAL

Melting points were uncorrected. The NMR spectra were recorded on a "Bruker WP-200" spectrometer at 200 (^{1}H) and 81.1 MHz (^{31}P). All chemical shifts are expressed in δ (ppm). ^{1}H chemical shifts are expressed relative to Me_4Si as internal standard. ^{31}P NMR spectra are referenced to external 85% H_3PO_4. All manipulations were carried out under argon, solvents were also distilled under inert atmosphere from the following drying agents: diethyl ether, hexane, benzene, chloroform, carbon tetrachloride (P_2O_5), methanol, triethylamine (sodium). Column chromatography was performed by using Chemapol (Praha) silicagel L 100/160. *Tert*-butylhypochlorite was obtained according to known procedure.[20]

N-Bromodiisopropylamine (**1a**): To a solution of 10.2 g (0.1 mol) of diisopropylamine in 50 ml of the carbon tetrachloride cooled to −10°C was added dropwise with stirring a solution of 7.99 g (0.05 mol) of bromine in 10 ml of the same solvent. Then the temperature was raised to +20°C and the reaction mixture was stirred for 1 hour. The precipitate of diisopropylamine hydrobromide was filtered off and washed with 100 ml of ether. The filtrate was evaporated and the residue was distilled under reduced pressure.

Yield 40%. B.P. 55°C (15 mm Hg). Yellowish liquid.
Calcd. for $C_6H_{14}BrN$: Br 44.37. Found Br 43.8.

N-Chlorodiisopropylamine (**1b**): To a solution of 5.1 g (0.05 mol) of diisopropylamine in 50 ml of carbon tetrachloride cooled to −10°C was added dropwise 5.42 g (0.05 mol) of *tert*-butylhypochlorite under stirring. Then the temperature was raised to +20°C and the reaction mixture was stirred for 1 hour at this temperature. The solvent was evaporated under reduced pressure and the residue was distilled in vacuum.

Yield 60%. B.P. 50°C (15 mm Hg). Colorless liquid.
Calcd. for $C_6H_{14}ClN$: Cl 26.14. Found Cl 25.7.

N-Chloro-trimethylsilyl-tert-butylamine (**2**): To a solution of 7.26 g (0.05 mol) of trimethylsilyl-*tert*-butylamine in 100 ml of diethyl ether cooled in an ice-bad was added dropwise with stirring 5.4 g (0.05 mol) of *tert*-butylhypochlorite. Then the reaction mixture was stirred for 0.5 hour at room temperature. The solvent was evaporated and the residue was distilled under reduced pressure.

Yield 70%. B.P. 60°C (15 mm Hg).[21]
Calcd. for $C_7H_{18}ClNSi$: Cl 19.72. Found Cl 19.1.

The reaction of tris(diethylamino)phosphine with N-bromodiisopropylamine. Tris(diethylamino)bromo phosphonium bromide (**4a**): A solution of 3.77 g (0.021 mol) of N-bromodiisopropylamine in 5 ml of diethyl ether was added dropwise to a solution of 4.54 g (0.02 mol) of tris(diethylamino)phosphine in 10 ml of diethyl ether under stirring at −70°C. Then the temperature was raised to +20°C and the reaction mixture was stirred for 20 hours. The precipitate of tris-diethylamino)bromophosphonium bromide (**4a**) was filtered off and washed with 10 ml of ether.

Yield 75%.
NMR spectra (δ, ppm; J, Hz; $CDCl_3$):
δ_H: 1.148, t (J_{HH} 7.0, CH_3); 3.171 dq (J_{HH} 7.0, J_{HP} 8.0, CH_2N). δ_P 47.1.
Calcd. for $C_{12}H_{30}Br_2N_3P$: Br 39.25. Found Br 38.8.

In the mother solution the tetraisopropylhydrazine, the properties of which were identical to those reported in the literature,[15] was detected by means of gas chromatography. The polymer products have been also revealed.

The reaction of tris(diethylamino)phosphine with N-chlorodiisopropylamine. Tris(diethylamino)chlorophosphonium chloride (**4b**): To a solution of 5.94 g (0.02 mol) of tris(diethylamino)phosphine in 10 ml of diethyl ether was added a solution of 2.84 g (0.021 mol) of N-chlorodiisopropylamine in 5 ml of the same solvent at −70°C under stirring. Then the temperature was raised to +20°C and the reaction mixture was stirred for 2 hours. The oily layer of tris(diethylamino)chlorophosphonium chloride (**4b**) was separated and washed with 10 ml of ether. After standing for some time the oil solidified.

Yield 75%. M.P. 75°C. δ_P 53.1 ppm (lit.[22] M.P. 76–78°C, δ_P 53.8 ppm).

Tris(diethylamino)-methoxyphosphonium perchlorate (**6a**): To a solution of 5.94 g (0.02 mol) of tris(diethylamino)phosphine in 10 ml of diethyl ether was added dropwise a solution of 2.84 g (0.021 mol) of N-chlorodiisopropylamine and then 0.7 g (0.022 mol) of methyl alcohol under stirring at −70°C. The temperature of the reaction mixture was raised to 0°C and 5 ml of water was added with stirring to the reaction mixture and the aqueous layer was separated. Then the aqueous solution was cooled to +5°C and the aqueous solution of 1 g of $NaClO_4$ was added. The precipitate of the tris(diethylamino)methoxyphosphonium perchlorate was filtered off and recrystallized from ethanol-ether.

Yield 70%, B.P. 165–170°C. Colorless crystalline solid.
NMR spectra (δ, ppm; J, Hz; $CDCl_3$):
1.13 t (J_{HH} 7.0, CH_3); 3.08 dt (J_{HH} 6.0, J_{HP} 10.0, CH_2N); 3.89 d (J_{HP} 16.0, OCH_3). δ_P 39.0.
Calcd. for $C_{13}H_{33}ClN_3O_5P$: P 8.20; N 11.12. Found P 8.01; N 11.05.

Bis(diethylamino)chlorophosphonium diphenylmethylid (**9a**): Under stirring a solution of 2.7 g (0.02 mol) of N-chlorodiisopropylamine in 5 ml of diethyl ether was added dropwise to a solution of 6.84 g (0.02 mol) of bis(diethylamido) diphenylmethylphosphonite (**7a**) in 10 ml of ether at 0°C. The reaction mixture was allowed to stand for 1 hour at ambient temperature, the solvent was evaporated and the residue was crystallized from hexane.

Yield 90%, M.P. 98°C (lit.[23] M.P. 98°). Yellow-orange crystalline solid.
NMR spectra (δ, ppm; J, Hz; C_6D_6):
δ_H: 0.94 t (J_{HH} 7.2, CH_3); 3.0 m (CH_2N); 6.8–7.3 m (C_6H_5). δ_P 62.
Calcd. for $C_{21}H_{30}ClN_2P$: Cl 9.41; P 8.22. Found Cl 9.28; P 8.22.

Bis(diethylamino)chlorophosphonium fluorenylid (**9b**): A solution of 1.35 g (0.01 mol) of N-chlorodiisopropylamine was added with stirring to a solution of 1.71 g (0.005 mol) of bis(diethylamino) fluorenphosphonite in 25 ml of diethyl ether at −10°C and the temperature was raised to +20°C. An orange crystalline precipitate was filtered off and washed with 10 ml of ether.

Yield 70%, M.P. 122–124°C.
NMR spectra (δ, ppm; J, Hz; C_6D_6):
δ_H 1.32 t (J_{HH} 7, CH_3); 3.39 m (CH_2); 7.15–8.1 m (C_6H_4). δ_P 54.1.
Calcd. for $C_{21}H_{28}ClN_2P$: Cl 9.46; P 8.26. Found Cl 9.51; P 8.23.

Bis(diethylamino)-chlorophosphonium isobutylid (**10**): A solution of 5.37 g (0.03 mol) of N-chloro-*tert*-butyl-trimethylsilylamine was added dropwise to a solution of 4.6 g (0.025 mol) of bis(diethylamido)isobutylphosphonite in 15 ml of diethyl ether at −70°C under stirring. Then the temperature was raised to +20°C and the reaction mixture was left stand for 30 min. The NMR spectrum shows the quantitative yield of the ylid (**10**). The ylid (**10**) is stable for some time only in the solution.

NMR spectra (δ, ppm; J, Hz; C_6D_6):
0.933, t J_{HH} 7 (CH_3CH_2); the signal of P═CH coincides with the one of $C\underline{H}_3CH_2N$; 1.25 dd J_{HH} 6.6, J_{HP} 2 [$(CH_3)_2C$]; 1.45 m [$(CH_3)_2C$]; 2.97 dq J_{HH} 7, J_{HP} 12.3 (CH_2N). δ_P 62.

Diethylamino-tert-butyl-chlorophosphonium isobutylid (**15**): To a solution of 4.6 g (0.025 mol) of bis(diethylamido) isobutylphosphonite in 15 ml of diethyl ether a solution of 5.37 g (0.03 mol) of N-chloro-*tert*-butyltrimethylsilylamine was added dropwise at −70°C under stirring. Then the temperature was raised to +20°C and the reaction mixture was left for 30 min. The NMR spectrum (C_6D_6) shows the quantitative yield of the ylid (**10**), δ_P 94.45 ppm. The spectral data are identical with those reported in the literature.[24] The solvent was evaporated under reduced pressure.

Yield 95%. Colorless unstable liquid.
Calcd. for $C_{12}H_{27}ClNP$: Cl 14.08. Found Cl 13.70.

Bis(diethylamido) 1-chloro-2-methylpropylphosphonite (**16**): The solution of the bis(diethylamino)chlorophosphonium isobutylid (**10**), prepared as described above, was evaporated and the residue was distilled under reduced pressure.

Yield 70%. B.P. 85°C (0.05 mm Hg). Colorless liquid.
NMR spectra (δ, ppm; J, Hz; $CDCl_3$):
0.78 t (J_{HH} 7.2, $C\underline{H}_3CH_2'$); 0.91 t (J_{HH} 7.2, $C\underline{H}_3CH_2''$); 1.18 d [J_{HH} 6.5, $(C\underline{H}_3)_2CH'$]; 1.05 d [(J_{HH} 6.5, $(C\underline{H}_3)_2CH''$)]; 2.02 m [$(CH_3)_2C\underline{H}$]; 2.70 m (CH_2N); 2.90, m (CH_2N''); 4.07 dd (J_{HH} 2.0, J_{HP} 3.4, CHCl). δ_P 62 [ylid (**10**)] and 87.79 [phosphonite (**16**)] (a ratio 4:1).
Calcd. for $C_{12}H_{28}ClN_2P$: Cl 13.29. Found Cl 12.98.

Bis(diethylamino)-isobutylmethoxyphosphonium perchlorate (**17b**): To a solution of the bis(diethylamino)chlorophosphonium isobutylid (**11**), prepared as described above was added with stirring a solution of 1 g (0.031 mol) of methyl alcohol. The temperature was raised to 0°C, and 5 ml of water was added with stirring to the reaction mixture and the aqueous layer was separated. The ^{31}P NMR spectrum showed a single signal at δ_P 60 ppm for bis(diethylamino)isobutylmethoxyphosphonium chloride. Then the aqueous solution was cooled to +5°C and the solution of 1 g of $NaClO_4$ in 2–3 ml of water was added. The precipitate was filtered off and recrystallized from ethanol-ether.

Yield 95%, M.P. 165–168°C. Colorless crystalline solid.
NMR spectra (δ, ppm; J, Hz; $CDCl_3$):
1.07 dd (J_{HH} 6.6, J_{HH} 6.6, $(CH_3)_2CH$]; 1.55 t (J_{HH} 7.0, CH_3CH_3); 1.42 m (CHN); 2.3 dd (J_{HH} 6.6, J_{HP} 13.0, PCH_2); 3.13 dq (J_{HH} 7.0, J_{HP} 11.4, CH_2N); 3.85 d (J_{HP} 13.0, OCH_3); δ_P 60.3.
Calcd. for $C_{13}H_{32}ClN_2O_5P$: N 7.72; P 8.54. Found N 7.64; P 8.46.

Bis(diethylamido) isobutylphosphonate (**18**): To the solution of the bis(diethylamino)chlorophosphonium isobutylid (**10**), prepared as described above was added dropwise 1 g (0.031 mol) of methyl alcohol under stirring at 0°C. Then the solvent was evaporated and the residue was distilled under reduced pressure.

Yield 90%, B.P. 105°C (0.06 mm Hg). Colorless liquid.
NMR spectra (δ, ppm; J, Hz; $CDCl_3$):
1.0 d (J_{HH} 7.0, $(C\underline{H}_3)_2CH')$]; 1.022 t (J_{HH} 7.0, $C\underline{H}_3CH_2'$); 1.54 dd [J_{HH} 6.5, J_{HP} 13.5, PCH_2]; 1.93 spt [J_{HH} 6.0, $(CH_3)_2C\underline{H})$]; 3.0 dq (J_{HH} 7.0, J_{HP} 10.0, $\overline{C}H_2N$). δ_P 36.8.
Calcd. for $C_{12}H_{29}N_2OP$: N 11.28; P 12.47. Found N 11.17; P 12.35.

Bis(diethylamido) 1-chloro-2-methylpropylthiophosphonite (**19**): To the solution of the bis(diethylamido) 1-chloro-2-methylpropylphosphonite (**16**), prepared as described above was added 1 g of sulfur at room temperature. The reaction mixture was left for 2 hours, then the solvent was evaporated. The residue was chromatographed on a column of silica gel with benzene as eluent. After evaporation of the solvent under reduced pressure the product was distilled in vacuum.

Yield 50%, B.P. 135°C (0.05 mm Hg). Yellow liquid.
NMR spectra (δ, ppm; J, Hz; $CDCl_3$):
0.93 d [J_{HH} 6.6, $(C\underline{H}_3)_2CH$]; 0.99 d [J_{HH} 6.6, $(C\underline{H}_3)_2CH$]; 1.071 t (J_{HH} 7.2, $C\underline{H}_3CH_2$); 1.382 m [$(CH_3)_2C\underline{H}$]; 3.0 m (CH_2N); 4.053 dd (J_{HH} 2.0, J_{HP} 3.0, $C\overline{H}Cl$). δ_P 79.46.
Calcd. for $C_{12}H_{28}ClN_2PS$: P 10.36; S 10.73. Found P 10.05; S 10.31.

Bis(diethylamino)chlorophosphonium 1-chloro-2-methylpropylid (**20**): To the solution of the bis(diethylamino)chlorophosphonium isobutylid (**10**), prepared as described above was added dropwise 0.05 mole of carbon tetrachloride under stirring at −20°C. Then the mixture was stirred at ambient temperature for 20 min and the solvent was evaporated under reduced pressure. To the residue was added 15 ml of pentane under stirring, the dark oil was separated and the solvent was evaporated under reduced pressure. The residue was distilled in vacuum.

Yield 50%, b.p. 105°C (0.012 mm Hg).
NMR specrtra (δ, ppm; J, Hz; (C_6D_6):
0.88, t J_{HH} 7 ($C\underline{H}_3CH_2$); 1.18 dd J_{HH} 7, J_{HP} 1 [$CH(C\underline{H}_3)_2$]; 2.64 m [$C\underline{H}(CH_3)_2$]; 2.9 dq J_{HH} 7, J_{HP} 12.5 (CH_2N); δ_P 58 ppm.
Calcd. for the $C_{12}H_{27}Cl_2N_2P$: Cl 23.62; P 10.32. Found Cl 23.28; P 10.22.

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