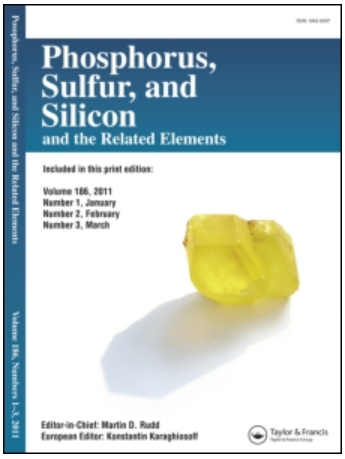

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SYNTHESIS OF PHOSPHORYLATED ALKYLCHLOROFORMOOXIMES

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SYNTHESIS OF PHOSPHORYLATED ALKYLCHLOROFORMOOXIMES

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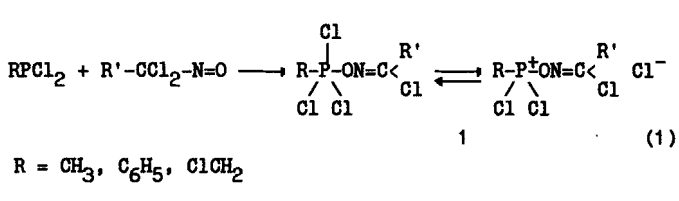
Various phosphorylated alkylchloroformooximes with —O—N=C(Alk)Cl group (hydroxamic acids chlorides) can be obtained in the one-pot synthesis with yields up to 73% from alcohols, α-dichloronitrosoalkanes and corresponding phosphorus(III) dichlorides. Reactions proceed through the formations of the corresponding diesters and esters of phosphorus(III).

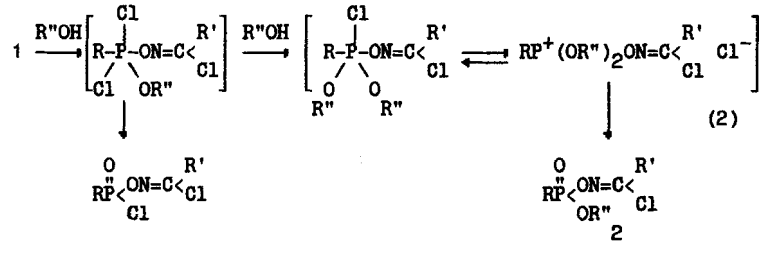
Key words: O-Alkyl-O-(methylchloroformoimino)methylphosphonates; O-alkyl-*S*-alkyl-O-(methylchloroformoimino)thiophosphates; O-alkyl-O-phenyl-O-(methylchloroformoimino)phosphates; O-alkyl-O-(2-ethoxyethyl)-O-(methylchloroformoimino)phosphates; O-alkyl-O-(2,2,3,3-tetrafluoropropyl)-O-(methylchloroformoimino)phosphates; *N,N*-diethylamido-O-alkyl-O-(methylchloroformoimino)-phosphates; O-alkyl-O-(methylchloroformoimino)morpholinoamidophosphates; O,O-dialkyl-O-(methylchloroformoimino)phosphates.

INTRODUCTION

Formerly we described[1] the synthesis of O-alkyl-O-(alkyl'chloroformoimino)phosphonates **2** with yields up to 40% when O-(alkylchloroformoimino)trichlorophosphoranes **1** were treated with alcohols (Equations 1–2):



(1)

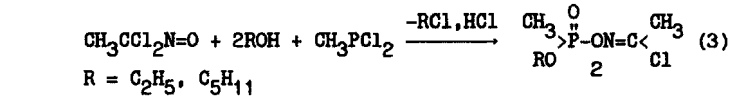


(2)

Here we report the optimization of this method (actually a reaction with its own pathway) and its application for obtaining of **2** and derivatives of **2** with R = alkylthio (**3**), phenoxy (**4**), 2-ethoxyethoxy (**5**), tetrafluoropropoxy (**6**), diethylamino (**7**), morpholino (**8**) and alkoxy (**9**).

RESULTS AND DISCUSSION

During optimization of obtaining of O-alkyl-O-(alkyl'chloroformoimino)phosphonates **2** the increase in yields of wanted products was found when the order of mixing of reagents was modified. Thus, when methyldichlorophosphine was added to the solution of α-dichloronitrosoethane in amyl alcohol, the yield of O-amyl-O-(methylchloroformoimino)methylphosphonate was 72% (Equation 3):

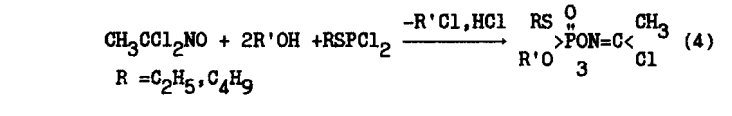


$$CH_3CCl_2N{=}O + 2ROH + CH_3PCl_2 \xrightarrow{-RCl,HCl} \underset{\mathbf{2}}{CH_3P(O)(OR)ON{=}C(CH_3)Cl} \quad (3)$$

$R = C_2H_5,\ C_5H_{11}$

In this case two reaction pathways were possible: first, through the primary formation of trichlorophosphoranes as in (Equation 2) and second, through the primary formation of phosphonous diesters and phosphinic esters. The special features of reaction (Equation 3) proceeding and some facts showed that in the case of reaction (Equation 3) the formation of trichlorophosphoranes **1** practically did not take place. First, the rates of the conversion of α-dichloronitrosoethane in (Equation 1) and (Equation 3) essentially differed. In (Equation 1) α-dichloronitrosoethane completely reacted with methyldichlorophosphine with the formation of **1** in some minutes, in (Equation 3) α-dichloronitrosoethane was completely conversed only when the reaction mixture was additionally kept 2 hours at a room temperature (the conversion level was checked by the disappearance of a blue colour of the starting nitrosocompound). Secondly, the ability of the compounds of trivalent phosphorus to interact with alcohols essentially exceeds the ability of the compounds of trivalent phosphorus to interact with α-dichloronitrosoalkanes: the exothermic reaction of alcohols with phosphorus trichloride is well-known, on the contrary when α-dichloronitrosoethane is kept under a room temperature with phosphorus trichloride the indications of interaction are lacking. Apparently mainly the reaction (Equation 3) proceeds with the intermediate formation of phosphonous diesters $RP(O)(OR)_2$ (which can react with α-dichloronitrosoalkanes at $-20°C$)[2] and phosphinic esters RP(O)(OR)H (which can react with α-dichloronitrosoalkanes at $+20°C$).[2]

O-Alkyl-S-alkyl-O-(methylchloroformoimino)thiophosphates **3** and O-alkyl-O-phenyl-O-(methylchloroformoimino)phosphates **4** are not attainable analogously to (Equation 2): trichlorophosphoranes of **1** type can not be obtained from $RSPCl_2$ and $C_6H_5OPCl_2$ because of the low nucleophilicity of dichlorophosphites in comparison with dichlorophosphines. Reaction of more active bromoderivative (namely $C_2H_5SPBr_2$) with α-dichloronitrosoalkanes proceeds slow even at a room temperature and has no practical significance. However the *in situ* conversion of dichlorophosphites in more nucleophilic alkoxyphosphites results in the formation of wanted products **3**,**4** (Equations 4–5, Tables I–II and V). Incidentally in reactions (Equations 4–5) alkyldichlorothiophosphites as more nucleophilic are a few more reactive than phenyldichlorophosphite.



$$CH_3CCl_2NO + 2R'OH + RSPCl_2 \xrightarrow{-R'Cl,HCl} \underset{\mathbf{3}}{RSP(O)(OR')ON{=}C(CH_3)Cl} \quad (4)$$

$R = C_2H_5, C_4H_9$

$$CH_3CCl_2NO + 2R'OH + C_6H_5OPCl_2 \xrightarrow{-R'Cl,HCl} C_6H_5O\underset{R'O}{\overset{O}{\underset{|}{\overset{\|}{P}}}}{>}PON=C\overset{CH_3}{\underset{Cl}{<}} \quad (5)$$

4

In the case of reaction with dichlorothiophosphites two different products can be obtained (Equation 6). As in the case[1] too at lesser temperatures the kinetically controlled products with a —O—N=C(Alk)Cl group are produced, at higher temperatures the more thermodynamically stable O,O-dialkyl-*S*-alkylthiophosphates are mainly produced. Better this is seen in the case of reactions with primary alcohols, reactions with secondary alcohols are less sensitive to temperature conditions.

TABLE I

Physical properties of O-alkyl-*S*-alkyl-O-(alkylchloroformoimino)thiophosphates **3**

	R	R'	Yield[a,b] (%)	B.p. (°C/mm Hg)	n_d^{20}
3a	C_2H_5	CH_3	2	91/0.04	1.5057
3b	C_2H_5	C_2H_5	13	102/0.05	1.4912
3c	C_2H_5	C_3H_7	32	110/0.05	1.4872
3d	C_2H_5	C_4H_9	15	128/0.05	1.4843
3e	C_4H_9	C_2H_5	23	122/0.05	1.4940
3f	C_4H_9	C_3H_7-i	38	124/0.05	1.4880
3g	C_4H_9	C_4H_9-i	14	137/0.05	1.4779
3h	C_4H_9	C_4H_9-sec	8	134/0.05	1.4908
3i	C_4H_9	C_4H_9	21	134/0.05	1.4795

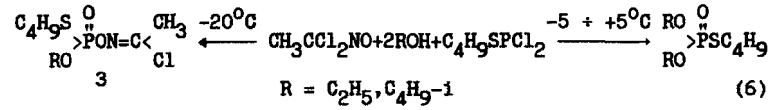
[a]Satisfactory microanalyses obtained: C±0.5 H±0.5 N±0.5
[b]Yield of isolated product

TABLE II

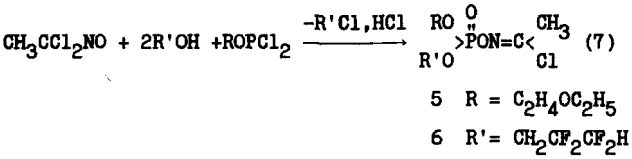
Physical properties of O-alkyl-O-phenyl-O-(alkylchloroformoimino)phosphates **4**

	R'	Yield[a,b] (%)	B.p. (°C/mm Hg)	n_d^{20}
4a	CH_3	9	115/0.04	1.5049
4b	C_2H_5	11	128/0.04	1.4972
4c	C_3H_7	11	129/0.04	1.5011
4d	C_4H_9	9	129/0.04	1.4902
4e	C_5H_{11}-i	23	132/0.04	1.4765

[a]Satisfactory microanalyses obtained: C±0.5 H±0.5 N±0.5
[b]Yield of isolated product



It was reported that alkoxyl groups with electronegative substituents are more stable than alkoxyl groups without electronegative substituents when P=O bond is formed from alkoxyl groups at a pentacoordinated phosphorus (for example see References 1 and 3). This allows to obtain O-alkyl''-O-alkyl'-O-(alkylchloroformoimino)phosphates with different alkyl groups, for example O-alkyl-O-(2-ethoxyethyl)-O-(methylchloroformoimino)phosphates **5** and O-alkyl-O-(2,2,3,3-tetrafluoropropyl)-O-(methylchloroformoimino)phosphates **6** (Equation 7, Tables III and V):



N,*N*-Dialkylamido-O-(alkylchloroformoimino)phosphates are not attainable through trichlorophosphoranes of **1** type because of easy elimination of nitrile oxides from the latter.[4] Probably in a general case π-donor substituents (C_6H_5-, AlkS-, R_2N-, see Reference 1 and 4) facilitate the elimination of nitrile oxides from phosphoranes with a —O—N=C(Alk)Cl group. Attempt to use the above-mentioned method (Equations 3–7) for synthesis of *N*,*N*-diethylamido-O-alkyl-O-(methylchloroformoimino)phosphates **7** also was ineffective. It is not surprising,

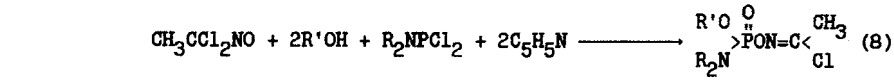
TABLE III

Physical properties of O-alkyl-O-(2-ethoxyethyl)-O-(methylchloroformoimino)phosphates **5** and O-alkyl-O-(2,2,3,3-tetrafluoropropyl)-O-(methylchloroformoimino)phosphates **6**

	R'	Yield[a,b] (%)	B.p. (°C/mm Hg)	n_d^{20}
5a	C_2H_5	7	116/0.05	1.4439
5b	C_4H_9	30	117/0.05	1.4509
5c	C_4H_9-1	45	113/0.05	1.4438
5d	C_5H_{11}-1)	30	126/0.05	1.4486
6a	C_2H_5	24	113/0.05	1.4081
6b	C_3H_7-1	73	113/0.05	1.4119
6c	C_4H_9	20	121/0.05	1.4272
6d	C_4H_9-1	24	124/0.05	1.4214
6e	C_5H_{11}-1	30	123/0.05	1.4302

[a]Satisfactory microanalyses obtained: C±0.5 H±0.5 N±0.5
[b]Yield of isolated product

the very acid reaction medium is favourable to breaking off P—N bond and the reaction proceeds with the elimination of amine hydrochloride (namely $(C_2H_5)_2NH \cdot HCl$ was isolated, ^1H NMR-spectrum, δ, ppm: 1.33 t 3H 8 Hz; 3.13 m 2H 8 Hz; 4.8 s) The modified method (Equation 8) yields the good results when the reaction medium is kept near to neutral by pyridine: the yields of *N,N*-diethylamido-O-alkyl-O-(methylchloroformoimino)phosphates **7** and morpholino-O-alkyl-O-(methylchloroformoimino)phosphates **8** are up to 73% (Tables IV–V).

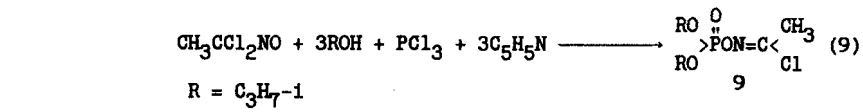


$$CH_3CCl_2NO + 2R'OH + R_2NPCl_2 + 2C_5H_5N \longrightarrow \begin{matrix} R'O & O & CH_3 \\ R_2N & >PON=C< & Cl \end{matrix} \quad (8)$$

7 $R_2N = (C_2H_5)_2N$

8 $R_2N = O(CH_2CH_2)_2N$

The latter method can be also used for obtaining of the derivatives of O,O-dialkyl'-O-(alkylchloroformoimino)phosphates **9** (Equation 9, yield 56%).



$$CH_3CCl_2NO + 3ROH + PCl_3 + 3C_5H_5N \longrightarrow \begin{matrix} RO & O & CH_3 \\ RO & >PON=C< & Cl \end{matrix} \quad (9)$$

$R = C_3H_7\text{-}i$ **9**

According to ^1H NMR-spectra the compounds **2–9** exist as mixture of (*Z*)-, (*E*)-isomers (signals at δ = 2.4). When in reactions a base is used the ratio of isomers is about 1:1, without base or in drastic conditions the ratio of isomers is about 5:95.

TABLE IV

Physical properties of *N,N*-diethylamido-O-alkyl-O-(methylchloroformoimino)phosphates **7** and morpholino-O-alkyl-O-(methylchloroformoimino)phosphates **8**

	R'	Yield[a,b] (%)	B.p. (C/mm Hg) ^{o}	n_d^{20}
7a	C_2H_5	73	113/0.05	1.4630
7b	$C_4H_9\text{-}i$	20	113/0.05	1.4600
7c	C_4H_9	49	121/0.05	1.4572
7d	$C_5H_{11}\text{-}i$	45	124/0.05	1.4571
8a	C_2H_5	21	131/0.05	1.4772
8b	$C_3H_7\text{-}i$	21	123/0.05	1.4706
8c	$C_4H_9\text{-}i$	17	131/0.05	1.4639
8d	C_4H_9	17	133/0.05	1.4592

[a]Satisfactory microanalyses obtained: C±0.5 H±0.5 N±0.5

[b]Yield of isolated product

TABLE V

NMR spectroscopic data of phosphorylated methylchloroformooximes

	δ ^{31}P	δ ^{1}H ($CDCl_3$/TMS; δ)
2a	33.9	1.33 t 3H 8 Hz; 1.56 d 3H 19 Hz; 2.4 s 3H; 4.11 m 2H
2b	33.3	0.93 m 3H; 1.36 m 4H; 1.56 d 3H 19 Hz; 1.66 m 2H; 2.39 s 3H; 4.02 m 2H
3a	34.0	1.42 m 3H; 2.40 s 3H; 3.0 m 2H; 3.89 m 3H
3b	33.1	1.38 m 6H 2.44 s 3H; 3.00 m 2H; 4.32 m 2H
3c	33.2	0.99 m 3H; 1.40 t 7 Hz 3H; 1.78 m 7 Hz 2H; 2.40 s 3H; 2.99 t 7 Hz 2H; 4.17 m 2H
3d	33.2	0.97 t 7 Hz 3H; 1.40 m 5H; 1.69 m 2H; 2.46 s 3H; 2.98 m 7 Hz 2H; 4.23 m 2H
3e	33.4	0.9 t 3H 8 Hz; 1.37 t 3H 8 Hz; 1.57–1.87 m 4H; 2.43 s 3H; 2.7 m 2H 8 Hz 2 Hz; 4.27 m 2H 8 Hz 2 Hz
3f	32.1	0.97 t 3H 8 Hz; 1.43 d 6H 8 Hz; 1.57–1.77 m 4H; 2.4 s 3H; 2.93 m 2H 8 Hz; 4.93 m H 8 Hz 3 Hz
3g	33.4	0.95 d 6H 7 Hz; 1.01 t 3H 7 Hz; 1.22–2.15 m 5H; 2.4 s 3H; 2.98 m 2H; 3.96 dd 2H 7 Hz
3h	32.1; 32.4	0.97 t 3H 6 Hz; 1.03 t 3H 6 Hz; 1.28–1.8 m 9H; 2.4 s 3H; 2.9 m 2H 7 Hz; 4.67 m H 7 Hz 3 Hz
3i	33.6	0.91 t 3H; 1.03 t 3H; 1.25–1.88 m 8H; 2.38 s 3H; 2.93 m 2H; 4.15 m 2H
4a	−5.0	2.38 s 3H; 3.98 d 3H 12 Hz; 7.28 m 5H
4b	−6.1	1.34 m 3H; 2.36 s 3H; 4.34 m 2H; 7.36 m 5H
4c	−6.0	0.98 t 3H 7 Hz; 1.76 m 2H 7 Hz; 2.38 s 3H; 4.26 m 2H; 7.28 m 5H
4d	−6.0	0.96 t 3H 7 Hz; 1.42 m 2H 7 Hz; 1.70 m 2H; 2.38 s 3H; 4.29 m 7 Hz 2H; 7.28 m 5H
4e	−5.7	0.9 d 6H 6 Hz; 1.27–1.6 m 3H; 2.37 s 3H; 4.1 m 2H 6 Hz; 7.23 s 5H
5a	−0.4	1.23 t 3H 7 Hz; 1.4 t 3H 7 Hz; 2.4 s 3H; 3.67 m 4H; 4.3 m 4H
5b	−0.3	0.93 t 3H 6 Hz; 1.2 t 3H 6 Hz; 1.4–1.87 m 4H; 2.37 s 3H; 3.6 m 4H; 4.23 4H
5c	−0.4 −0.5	0.97 d 6H 7 Hz; 1.2 t 3H 7 Hz; 2.0 m H 7 Hz; 2.37 s 3H; 3.6 m 4H; 3.93 t 7 Hz 2H; 4.23 m 2H
5d	−0.3	0.93 d 6H 6 Hz; 1.2 t 3H 6 Hz; 1.4–1.97 m 3H; 2.37 s 3H; 3.6 m 4H; 4.2 m 4H
6a	−0.2; −2.1	1.4 t 3H 7 Hz; 2.4 s 3H; 4.0–4.83 m 4H; 6.0 tt H 4 Hz 52 Hz
6b	−2.3	1.4 d 6H 8 Hz; 2.37 s 3H; 4.5 m 2H; 4.93 m H 8 Hz; 5.97 tt H 4 Hz 52 Hz
6c	−1.2; −0.4	0.97 m 3H; 1.23–1.87 m 5H; 2.37 s 3H; 4.0–4.73 m 3H; 5.97 tt H 4 Hz 52 Hz
6d	−1.3; −0.6	1.0 d 6H 6 Hz; 2.1 m H 6 Hz; 2.43 s 3H; 4.07 m 2H; 4.53 m 2H; 6.17 tt H 4 Hz 52 Hz
6e	−1.2; −0.4	0.97 d 6H 6 Hz; 1.3–2.06 m 3H; 2.4 s 3H; 3.9–4.83 m 4H; 6.07 tt H 4 Hz 52 Hz
7a	11.6	1.14 t 6H 7 Hz; 1.32 t 3H 7 Hz; 2.37 s 3H; 3.15 m 4H 7 Hz; 4.21 m 2H 7 Hz 2 Hz
7b	11.4	1.0 t 6H 8 Hz; 1.2 d 6H 8 Hz; 1.97 m H 8 Hz; 2.34 s 3H; 3.17 m 4H 8 Hz; 3.9 t 2H 8 Hz
7c	11.7	0.97 t 3H 8 Hz; 1.1 t 6H 8 Hz; 1.32–1.83 m 4H; 2.33 s 3H; 3.15 m 4H 8 Hz; 4.12 m 2H 8 Hz
7d	11.7; 11.5	0.97 d 6H 7 Hz; 1.12 t 6H 7 Hz; 1.3–1.93 m 3H; 2.33 s 3H; 3.15 m 4H 7 Hz; 4.08 m 2H 7 Hz
8a	8.6	1.37 t 3H 7 Hz; 2.4 s 3H; 3.25 m 4H 5 Hz; 3.63 m 4H 5 Hz; 4.2 m 2H 7 Hz
8b	8.0	1.38 d 6H 6 Hz; 2.4 s 3H; 3.23 m 4H 5 Hz; 3.63 m 4H 5 Hz; 4.77 m H 6 Hz
8c	8.9	0.95 d 6H 6 Hz; 1.95 m H 6 Hz; 2.38 s 3H; 3.23 m 4H 5 Hz; 3.65 m 4H 5 Hz; 3.92 t 2H 6 Hz
8d	9.0	0.94 t 3H 6 Hz; 1.2–1.83 m 4H; 2.38 s 3H; 3.25 m 4H 5 Hz; 3.65 m 4H 5 Hz; 4.1 m 7 Hz
9	−2.2	1.33 d 12H 7 Hz; 2.37 s 3H; 4.80 m 2H 7 Hz

EXPERIMENTAL

^{1}H-NMR and ^{31}P-NMR (ref. 85% H_3PO_4 ext, negative chemical shifts are upfield of the standard) spectra were recorded on a Bruker CXP-200 spectrometer and Tesla spectrometer.

Preparation (**3**) *of O-Alkyl-O-(methylchloroformoimino)methylphosphonates* **2**. The solution of α-dichloronitrosomethane (50 mmol) in ethyl alcohol (102 mmol) was stirred at −50°C while methyldichlorophosphine (50 mmol) was dropped to keep temperature below −30°C. The operations were carried out in an argon atmosphere. The stirred mixture was allowed to warm to a room temperature and then it was kept for 2 hour at a toom temperature. After distillation O-ethyl-O-(methylchloroformoimino)methylphosphonate **2a** was obtained (5.7 g, 29 mmol, 57%; b.p. 113°C/3 mm Hg; n_D^{20} 1.4580). By the same way O-amyl-O-(methylchloroformoimino)methylphosphonate **2b** (8.5 g, 36 mmol, 72%; b.p. 110°C/2 mm Hg; n_D^{20} 1.4538) was obtained. NMR-spectra of the compounds **2a,b** see in Table V.

Preparation (**4**) *of O-Alkyl-S-alkyl-O-(methylchloroformoimino)thiophosphates* **3**, *General Procedure*. The solution of α-dichloronitrosomethane (39 mmol) in a corresponding alcohol (98 mmol) was stirred at −35°C while dichloroalkylthiophosphite (39 mmol) was added. The stirred mixture was allowed to warm to a room temperature and after distillation **3** was obtained (Tables I and V).

Preparation (**5**) *of O-Alkyl-O-phenyl-O-(methylchloroformoimino)phosphates* **4**, *General Procedure*. The solution of α-dichloronitrosomethane (39 mmol) in a corresponding alcohol (117 mmol) was stirred at −10°C while dichlorophenylphosphite (7.6 g, 39 mmol) was added. The stirred mixture was allowed to warm to a room temperature and after distillation **4** was obtained (Tables II and V).

Preparation (**6**) *of O,O-Dialkyl-S-alkylthiophosphates*. The solution of α-dichloronitrosomethane (5 g, 39 mmol) in ethyl alcohol (3.6 g, 78 mmol) was stirred at −5–+5°C while dichlorobuthylthiophosphite (7.5 g, 39 mmol) was added. The stirred mixture was allowed to warm to a room temperature and then it was kept for 2 hour at a room temperature. After distillation O,O-diethyl-*S*-butylthiophosphate was obtained (2.5 g, 11 mmol, 28%; b.p. 85°C/0.05 mm Hg; n_D^{20} 1.4680; ^{31}P-NMR: 28.8; ^{1}H-NMR, δ: 0.9 t 3H 8 Hz; 1.37 t 6H 8 Hz; 1.40–1.73 m 4H; 2.7 m 2H 8 Hz; 4.17 m 4H 8 Hz). By the same way O,O-diisobutyl-*S*-butylthiophosphate (3.7 g, 13 mmol, 34%; b.p. 115°C/0.05 mm Hg; n_D^{20} 1.4602; ^{31}P-NMR, δ: 28.8; ^{1}H-NMR, δ: 0.97 d 12H 8 Hz; 1.03 t 3H 8 Hz; 1.3–2.26 m 6H; 2.84 m 2H 8 Hz; 3.9 dd 4H 8 Hz 8 Hz) was obtained.

Preparation (**7**) *of O-Alkyl-O-(2-ethoxyethyl)- and -(2,2,3,3-tetrafluoropropyl)-O-(methylchloroformoimino)phosphates* **5,6**, *General Procedure*. The solution of α-dichloronitrosomethane (5 g, 39 mmol) in a corresponding alcohol (98 mmol) was stirred at −10°C while a corresponding dichlorophosphite (39 mmol) was added. The stirred mixture was allowed to warm to a room temperature and then it was kept for 2 hour at a room temperature. After distillation the corresponding phosphate **5,6** was obtained (Tables III and V).

Preparation (**8**) *of N,N-Diethylamido- and morpholino-O-alkyl-O-(methylchloroformoimino)phosphates* **7,8** *General Procedure*. The solution of α-dichloronitrosomethane (5 g, 39 mmol) and a corresponding alcohol (98 mmol) in ether or tetrahydrofurane (100 ml) was stirred at −25°C while a corresponding amidophosphite (39 mmol) and pyridine (6.5 g, 82 mmol) were added. The stirred mixture was allowed to warm to a room temperature and after filtration of pyridine hydrochloride **7** or **8** was obtained by distillation (Tables IV and V).

Preparation (**9**) *of O,O-Diisopropyl-O-(methylchloroformoimino)phosphate* **9**. The solution of α-dichloronitrosomethane (7 g, 55 mmol) and isopropyl alcohol (10.2 g, 170 mmol) in ether (150 mmol) was stirred at −20°C while phosphorus trichloride (54 mmol) and pyridine (13.4 g, 170 mmol) were added. The stirred mixture was allowed to warm to a room temperature and after filtration of pyridine hydrochloride O,O-diisopropyl-O-(methylchloroformoimino)phosphate **9** (7.9 g, 31 mmol, 56%; b.p. 100°C/3 mm Hg; n_D^{20} 1.4415) was obtained by distillation. NMR-spectra see in Table V.

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