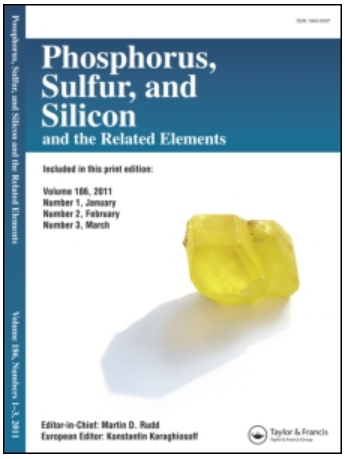

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CONVERSIONS OF THE ADDUCTS OF α-DICHLORONITROSOALKANES WITH DICHLOROPHOSPHINES

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CONVERSIONS OF THE ADDUCTS OF α-DICHLORONITROSOALKANES WITH DICHLOROPHOSPHINES

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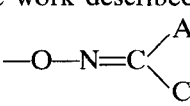
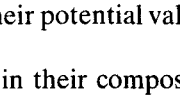
Structure, stability and some reactions of the obtained adducts of α-dichloronitrosoalkanes with dichlorophosphines are discussed. One-pot synthesis of O-(alkylchloroformoimino)phosphonic acid chlorides and esters is described.

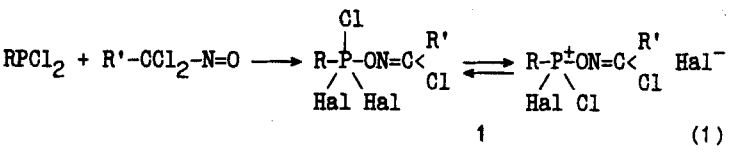
Key words: O-(alkylchloroformoimino)trichlorophosphoranes; O-(alkylchloroformoimino)chlorophosphonates; O-(alkylchloroformoimino)-O-alkylphosphonates; amides of O-(alkylchloroformoimino)-phenylphosphonic acids.

INTRODUCTION

During studies of the properties of α-dichloronitrosoalkanes the formation of not very stable intermediates with pentacoordinated phosphorus was assumed in reaction when phosphonates containing O-alkylchloroformoimino group were obtained.[1] It is known that in some cases similar phosphoranes having a —O—N=C< ligand can be stable.[2] In the work described here we tried to obtain a series of oxochlorophosphoranes with  ligand, to investigate some of their properties and to appreciate their potential value as possible precursors of biological active substances which have in their composition a  group.

RESULTS AND DISCUSSION

1:1 Adducts **1** were easily obtained with quantitative yield when α-dichloronitrosoalkanes were added to solutions of dichlorophosphines in inert solvents. The reaction completion was checked by disappearance of a blue colour of the starting nitrosocompound. The reaction rate depends on dichlorophosphine nucleophilicity and on the electronegativity of substituents at the α-carbon in nitrosoalkane, strongly increasing in the row $ClCH_2PCl_2 < C_6H_5PCl_2 < CH_3PCl_2$ and in going from 1,1-dichloro-1-nitrosoethane to 1,1,2-trichloro-1-nitrosoethane.



(1)

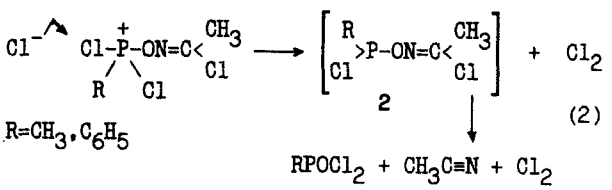
CH_3PCl_2, $C_6H_5PCl_2$, $ClCH_2PCl_2$, $BrCH_2PBr_2$, $(CH_3)_2C{=}CHPCl_2$

R'= CH_3, C_2H_5, C_3H_7, 1-C_3H_7, C_4H_9, CH_2Cl

It is known that practically all phosphorus compounds with a $XYPHal_3$ structure where Hal=Cl,Br are capable to exist both in ionic and in covalent form. In our case the chemical shifts of ^{31}P-NMR spectra of adduct solutions in toluene point out the presence of the pentacoordinated phosphorus in non-polar solvents. On the other hand the character of the solubility of the adducts (an agreeable solubility in the polar solvent SO_2Cl_2 and a low solubility in non-polar toluene, ether, hexane) shows that an ionic form of the adducts is available. It was reported[3] that CH_3PCl_4 in the solid state exists exclusively as $CH_3PCl_3^+Cl^-$; it is possible that in our case it is the same.

Isolated adducts **1** show high hygroscopicity, inherent in this type of compounds. Elemental analysis data indicate that adducts **1** suffer slow decomposition even under moisture free conditions. Only the adduct of 1,1-dichloro-1-nitrosoethane and dichloromethylphosphine turned out to be a bit more stable.

Heating to 100°C of the isolated adducts leads to decomposition of **1** which proceeds very vigorously to give the products corresponding to the scheme of halogenophilic interaction of chlorophosphonium cation with chloroanion.

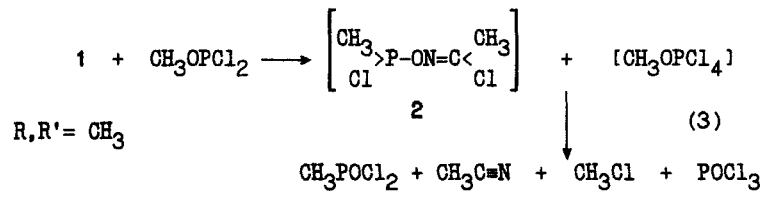


(2)

R=CH_3, C_6H_5

$RPOCl_2 + CH_3C{\equiv}N + Cl_2$

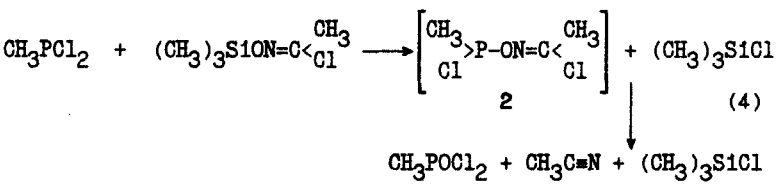
To define the existance of **2**, the reactions according to the Equations (3) (chlorophosphoranes reduction by methyldichlorophosphite)[4,5] and (4) were carried out. Both reactions demonstrate the extreme instability of structure **2**.



(3)

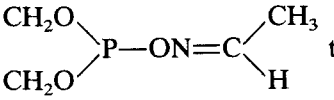
R,R'= CH_3

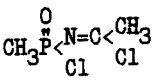
$CH_3POCl_2 + CH_3C{\equiv}N + CH_3Cl + POCl_3$



(4)

$CH_3POCl_2 + CH_3C{\equiv}N + (CH_3)_3SiCl$

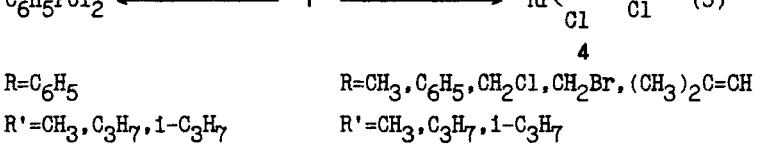
On the whole the behaviour of **2** is in conformity with the instability of similar imines which at temperature above 0°C are isomerised to alkylidenamides.[6,7] However in our case as in case[8] of  too the transformation of **2** goes further to nitrile elimination. Alkylidenamidophosphonate, **3**, formation was not ruled out.



3

Below we shall demonstrate that the low stability of isolated adducts **1** does not hinder their use as suitable intermediates for the synthesis of phosphorylated alkylchloroformoiminooximes when they are used in solution.

We discovered that, depending on conditions, the transformations of adducts **1** may proceed either with conservation or with splitting off of the chloroformoiminoyl fragment. Especially clearly is this revealed in the case of the interaction with sulphur dioxide (5). Indeed, the reaction of adducts **1** (R=C_6H_5; R'=CH_3, C_3H_7, i—C_3H_7) with SO_2 at 0–5°C brings about formation of phosphonic acid dichloride (yield up to 81%). However chlorides of oxoiminophosphonic acids (Tables I and II) turn out to be the ultimate products (yields up to 77%) if the reaction is carried out at −12°C. Thus practically complete change of reaction direction is possible.



(5)

4

R=C_6H_5 R'=CH_3, C_3H_7, 1-C_3H_7

R=CH_3, C_6H_5, CH_2Cl, CH_2Br, $(CH_3)_2C{=}CH$ R'=CH_3, C_3H_7, 1-C_3H_7

TABLE I

Physical properties of O-(Alkylchloroformoimino)chlorophosphonates

N	Compound[a]	Yield[b] (%)	B.p. (°C/mm Hg)	n_d^{20}	M.p. (°C)
4a	$C_6H_5P(O)(Cl)ON{=}CClCH_3$	71	115/0.03	1.5522	
4b	$C_6H_5P(O)(Cl)ON{=}CClC_3H_7$	39	153/0.08	1.5366	
4c	$C_6H_5P(O)(Cl)ON{=}CClC_3H_7$-1	66	140/0.08	1.5354	67
4d	$ClCH_2P(O)(Cl)ON{=}CClCH_3$	77	102/0.05	1.5099	
4e	$BrCH_2P(O)(Cl)ON{=}CClCH_3$	15	110/0.05	1.5344	
4f	$(CH_3)_2C{=}CHP(O)(Cl)ON{=}CClCH_3$	50	113/3	1.5018	

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

[b]Yield of isolated product

TABLE II

NMR spectroscopic data of O-(Alkylchloroformoimino)chlorophosphonates

N	^{31}P-NMR (δ, ppm)	^{1}H-NMR ($CDCl_3$/TMS, δ, ppm)
4a	33.7	2.38s 3H;7.59m 3H;7.96m 2H
4b	34.0	0.96t 3H 8Hz;1.71m 2H 8Hz;2.61t 2H 8Hz;7.59m 3H;7.96m2H
4c	33.8	1.22dd 6H 8Hz 2Hz;2.96m H 8Hz;7.59m 3H;7.96m 2H
4d	36.6	2.45s 3H;4.05d 2H 8Hz
4e	35.4	2.45s 3H;3.83d 2H 8Hz
4f	28.6	1.68d H 11Hz;2.03s 3H;2.21m 3H;2.46s 3H

To confirm the details of the process (5) the introduction of isotopic labelling and low temperature ^{31}P NMR spectrometry were used. The possibility of P—O bond breaking was revealed which is untypical for oxochlorophosphoranes which as a rule decay with P=O bond formation. When adduct **1** (R=C_6H_5, R'=CH_3) was treated with SO_2 enriched by ^{18}O isotope at 0–5°C the mass spectrometry testified inclusion of labelled oxygen into phenylphosphonic acid dichloride (Table VII) obtained together with O-(methylchloroformoimino)phenylphosphonic acid chloride in about the same molar quantity.

$$\underset{\text{R=}C_6H_5\ \text{R'=}CH_3}{\mathbf{1}} + \xrightarrow{S^{18}O_2,\,0^\circ\ -\ -5^\circ} C_6H_5\overset{\overset{18}{O}}{\overset{\|}{P}}Cl_2 + C_6H_5\overset{\overset{18}{O}}{\overset{\|}{P}}\!<\!\underset{Cl}{ON=C}\!<\!\underset{Cl}{\overset{CH_3}{}} \quad (6)$$

4

This fact favours slow transformation of **1** into tetrachlorophosphorane with elimination of nitrile oxide in accordance with Reference 9, (7).

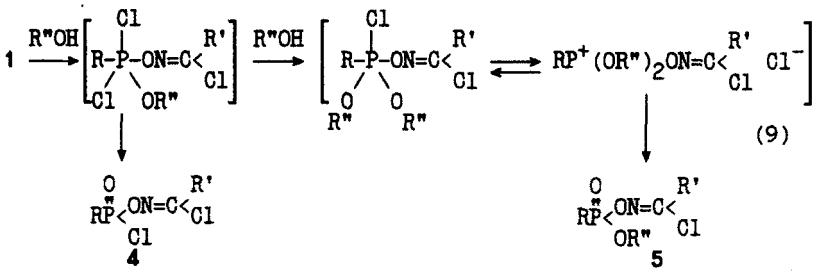
$$C_6H_5P(Cl)_3ON=C\!<\!\underset{Cl}{\overset{CH_3}{}} \longrightarrow C_6H_5PCl_4 + O\leftarrow N\equiv CCH_3 \quad (7)$$

Scheme (7) is confirmed too by ^{31}P NMR spectra of trichloro-O-(methylchloroformoimino)phenylphosphorane in toluene solution in which slow rise of the intensity of the signal at −42.4 ppm (literary data for $C_6H_5PCl_4$ − 43 ppm[4]) can be observed in accordance with increase of duration and temperature from −50°C to +10°C.

As it was expected, when in reaction (5) the adduct, obtained with bromomethyldibromphosphine, was used, the chloride of the corresponding acid was obtained. This is in conformity with the behaviour of bromoanion as a more active nucleophile then chloroanion.

$$\underset{\text{from } BrCH_2PBr_2,\,R'=CH_3}{\mathbf{1}} + \xrightarrow{SO_2,\ -\ 12^\circ} BrCH_2\overset{\overset{O}{}}{\overset{\|}{P}}\!<\!\underset{Cl}{ON=C}\!<\!\underset{Cl}{\overset{CH_3}{}} \quad (8)$$

Introduction of phosphoranes **1** into reaction with alcohols proved a convenient method for obtaining alkylesters of oxichloroformoimiinophosphonic acids (9) (Tables III and IV). The simultaneously formed small amounts of acid chlorides can be separated by distillation or transformed into other products. The reaction of **1** with alcohols proceeds as shown in Equation (9).



(9)

$CH_3PCl_2, C_6H_5PCl_2, ClCH_2PCl_2, BrCH_2PBr_2$

R'=$CH_3, C_2H_5, C_3H_7, 1\text{-}C_3H_7, C_4H_9, CH_2Cl$

R"=$CH_3, C_2H_5, C_3H_7, 1\text{-}C_3H_7, C_4H_9, 1\text{-}C_4H_9, C_5H_{11}, CH_2C{\equiv}CH$

TABLE III

Physical properties of O-(Alkylchloroformoimino)-O-alkylphosphonates

N	Compound[a]	Yield[b] (%)	B.p. (°C/mm Hg)	n_d^{20}
5a	$C_6H_5P(O)(OCH_3)ON{=}CClCH_3$	20	130/0.04	1.5355
5b	$C_6H_5P(O)(OC_2H_5)ON{=}CClCH_3$	40	135/0.05	1.5266
5c	$C_6H_5P(O)(OC_3H_7)ON{=}CClCH_3$	32	155/0.03	1.5200
5d	$C_6H_5P(O)(OC_3H_7\text{-}1)ON{=}CClCH_3$	30	140/0.03	1.5164
5e	$C_6H_5P(O)(OC_4H_9)ON{=}CClCH_3$	27	149/0.03	1.5150
5f	$C_6H_55P(O)(OC_4H_9\text{-}1)ON{=}CClCH_3$	28	153/0.03	1.5114
5g	$C_6H_5P(O)(OC_5H_{11})ON{=}CClCH_3$	21	152/0.03	1.5086
5h	$C_6H_5P(O)(OCH_3)ON{=}CClC_2H_5$	20	139/0.04	1.5185
5i	$C_6H_5P(O)(OC_2H_5)ON{=}CClC_2H_5$	31	135/0.04	1.5196
5j	$C_6H_5P(O)(OC_2H_5)ON{=}CClC_3H_7$	34	145/0.05	1.5146
5k	$C_6H_5P(O)(OCH_3)ON{=}CClC_3H_7\text{-}1$	15;28[c]	140/0.04	1.5206
5l	$C_6H_5P(O)(OC_2H_5)ON{=}CClC_3H_7\text{-}1$	9	135/0.04	1.5127
5m	$C_6H_5P(O)(OC_2H_5)ON{=}CClCH_2Cl$	26	158/0.04	1.5319
5n	$ClCH_2P(O)(OCH_3)ON{=}CClCH_3$	11;5[c]	90/0.05	1.4049

TABLE III (*Continued*)

N	Compound[a]	Yield[b] (%)	B.p. (^{o}C/mm Hg)	n_d^{20}
5o	$CH_3P(O)(OCH_2C{\equiv}CH)ON{=}CClCH_3$	10	98/0.03	1.4836
5p	$BrCH_2P(O)(OC_2H_5)ON{=}CClCH_3$	7	120/0.05	1.4946

[a]Satisfactory microanalyses obtained: C±0.5 H±0.5 N±0.5
[b]Yield of isolated product (obtained from phosphoranes)
[c]Yield of isolated product (obtained from acids chlorides)

TABLE IV
NMR spectroscopic data of O-(Alkylchloroformoimino)-O-alkylphosphonates

N	^{31}P-NMR (δ, ppm)	^{1}H-NMR ($CDCl_3$/TMS, δ, ppm)
5a	21.5	2.3s 3H;3.86d 3H 12Hz;7.48m 3H;7.8m 2H
5b	20.4	1.41t 3H 8Hz;2.29s 3H;4.26m 2H;7.47m 3H;7.77m 2H
5c	21.9	0.99t 3H 8Hz;1.8m 2H 8Hz;2.31s 3H;4.25m 2H 8Hz;7.5m 3H;7.9m 2H
5d	21.0	1.42dd 6H 8Hz 16Hz;2.31s 3H;5.0m H;7.5m 3H;7.88m 2H
5e	20.5	0.94t 3H 8Hz;1.44m 2H 8Hz;1.72m 2H 8Hz;2.26s 3H; 4.20m 2H 8Hz;7.46m 3H;7.8m 2H
5f	21.8	0.98d 6H 8Hz;2.04m H 8Hz;2.28s 3H;4.04t 2H 8Hz;7.48 m 3H;7.88m 2H
5g	21.9	0.9m 3H;1.36m 4H;1.76m 2H 8Hz;2.3s 3H;4.28m 2H 8Hz; 7.49m 3H;7.88m 2H
5h	21.6	1.18t 3H 8Hz;2.55m 2H 8Hz;3.85d 3H 12Hz; 7.46m 3H; 7.78m 2H;
5i	20.3	1.2t 3H 8Hz;1.41t 3H 8Hz;2.55m 2H 8Hz;4.24m 2H 8Hz; 7.45m 3H;7.8m 2H
5j	20.4	0.9t 3H 8Hz;1.39t 3H 8Hz;1.66m 2H 8Hz;2.48t 2H 8Hz; 4.25м 2H 8Гц;7.46м 3H;7.8м 2H
5k	21.6	1.21dd 6H 6Hz 1Hz;2.85m H 4Hz;3.9d 3H 11Hz; 7.44m 3H;7.79m 2H
5l	20.4	1.2dt 6H 8Hz 1Hz;1.42t 3H 8Hz;2.84m H 8Hz;4.26m 2H 8Hz;7.4m 3H;7.79m 2H
5m	21.3	1.41t 3H 8Hz;4.33m 4H;7.47m 3H;7.82m 2H

TABLE IV (*Continued*)

5n	24.5	2.4s 3H;3.77d 2H 10Hz;3.95d 2H 10Hz
5o	36.7	1.73d 3H 18Hz;2.39s 3H;2.65t H 3Hz;4.77m 2H
5p	23.3	1.39t 3H 8Hz;2.39s 3H;3.50 2H 10Hz;4.34m 2H

In this way many alkylesters of oxichloroformoiminophosphonic acids including functional ester **5p** were obtained. The conditions were not optimized. Therefore the yields of **5** are rather low.

The structure of the ultimate product is determined by the stability of the O-substituents on phosphorus. Thus in the case of the interaction of **1** (R,R'=CH_3) with $HOCH_2CH_2Cl$ the slow elimination of dichloroethane, in comparison with alkylchloride (the similar in Reference 10), produces mainly di(β-chlorethyl)methylphosphonate.

$$\underset{R=CH_3,R'=CH_3}{1} + ClCH_2CH_2OH \longrightarrow R\overset{O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2 \quad (10)$$

To determine the scope of this method of oxichloroformoiminophosphonic acids esters synthesis the interaction between adducts **1** and acetic acid was also investigated. In contrast to the interaction with alcohols this reaction produced chlorides **4** only.

$$\underset{R=CH_3,C_6H_5\ R'=CH_3}{1} + CH_3COOH \longrightarrow R\overset{O}{\overset{\|}{P}}\!<\!\underset{Cl}{ON=C}\!<\!\overset{R'}{Cl} \quad (11)$$

Because of the extreme facile elimination of acetyl chloride the introduction of a second acid molecule in reaction (11) is impossible, even at −87°C.

Reactions with propylene epoxide and acetic anhydride lead to the final product **4**.

The chlorides obtained according to (5), (9) and (11) can be utilized for obtaining esters (12), amides (13) (Tables V and VI) and others derivatives of chloroformoiminophosphonic acids.

$$\underset{\mathbf{4}}{R\overset{O}{\overset{\|}{P}}\!<\!\underset{Cl}{ON=C}\!<\!\overset{R'}{Cl}} + R''OH \xrightarrow{Py} \underset{\mathbf{5}}{R\overset{O}{\overset{\|}{P}}\!<\!\underset{OR''}{ON=C}\!<\!\overset{R'}{Cl}} \quad (12)$$

$$\underset{\mathbf{4}}{R\overset{O}{\overset{\|}{P}}\!<\!\underset{Cl}{ON=C}\!<\!\overset{R'}{Cl}} + NH_3 \longrightarrow \underset{\mathbf{9}}{R\overset{O}{\overset{\|}{P}}\!<\!\underset{NH_2}{ON=C}\!<\!\overset{R'}{Cl}} \quad (13)$$

$R=C_6H_5$

$R'=CH_3, C_3H_7, 1\text{-}C_3H_7$

TABLE V

Physical properties of the amides of O-(Alkylchloroformoimino)phosphonic acids

N	Compound[a]	Yield[b] (%)	M.p. (°C)
6a	$C_6H_5P(O)(NH_2)ON{=}CClCH_3$	24	126 - 127
6b	$C_6H_5P(O)(NH_2)ON{=}CClC_3H_7$	31	103 - 104
6c	$C_6H_5P(O)(NH_2)ON{=}CClC_3H_7$-1	37	102 - 103

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

TABLE VI

NMR spectroscopic data of the amides of O-(Alkylchloroformoimino)-phosphonic acids

N	^{31}P-NMR (δ, ppm)	^{1}H-NMR (D_2O, δ, ppm)
6a	27.8	2.3s 3H;2.1m;7.52m 3H;7.87m 2H
6b	28.5	0.78t 3H 8Hz;1.55m 2H 8Hz;2.49t 2H 8Hz;4.8m;5.43m; 7.51m 3H;7.76m 2H
6c	28.1	1.15d 6H 7Hz;2.87m H 8Hz;2.1m;7.51m 3H;7.9m 2H

Some of the synthetized compounds show fungicidal and plants growth regulating activity; however the comparatively high toxicity (LD_{50} about 50 mg/kg) makes their practical application questionable.

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, IR spectrum was recorded on a Specord IR-75 spectrometer, mass-spectrum was recorded on a Finnigan MS 4021 instrument. Dichlorophosphines and α-dichloronitrosoalkanes were prepared using literature methods. Experiments were conducted with careful exclusion of moisture.

Preparation of O-(Methylchloroformoimino)methyldichlorophosphonium Chloride. A solution of methyldichlorophosphine (2 g, 17 mmol) in ether (30 ml) was stirred at −30°C while a solution of 1,1-dichloro-1-nitrosoethane (2.4 g, 19 mmol) in ether (10 mmol) was added. The mixture was stirred at −20°C for 15 minutes. After filtration of the slurry of O-(methylchloroformoimino)methyldichlorophosphonium chloride and vacuum drying of the solid residue a white loose powder with melting point 53°C was obtained.

Anal.: Calcd. for $C_3H_6Cl_4NOP$: C 14.71; H 2.47; N 5.72. Found: C 14.21; H 2.51; N 5.61. All operations were carried out in a carefully dried apparatus under an argon atmosphere.

Preparation of O-(Alkylchloroformoimino)methyltrichlorophosphoranes, **1**. *General Procedure.* A solution of methyldichlorophosphine (5.8 g, 50 mmol) in toluene (50 ml) was stirred at −25 to −20°C while a solution of α-dichloronitrosoalkane (50 mmol) in toluene (8 ml) was added. Reaction completion was checked by disappearence of a blue colour of the starting nitrosocompound. ^{31}P-NMR spectra of the reaction mixture had one signal of −36.9 to −37.2 ppm [also due to CH_3POCl_2 (a hydrolysis product) one shift of 44.5 to 44.2 was present]. The product was used directly in the next step without isolation.

Preparation of O-(Alkylchloroformoimino)phenyltrichlorophosphoranes, **1**. *General Procedure.* A solution of phenyldichlorophosphine (5.4 g, 30 mmol) in toluene (35 ml) was stirred at −25 to −20°C while a solution of α-dichloronitrosoalkane (30 mmol) in toluene (5 ml) was added. Mixture was stirred at −10°C. Reaction completion was checked by disappearence of a blue colour of the starting nitrosocompound. ^{31}P-NMR spectra of the reaction mixture had a signal of −16.5 to −17.4 ppm [also due to a hydrolysis product 34.0 to 33.7 ppm and due to $C_6H_5PCl_4$ (decaying product) −42.4 to −42.6 ppm shifts were present]. The product was used directly in the next step without isolation.

Preparation of O-(Methylchloroformoimino)(chloromethyl)trichlorophosphorane, **1**. A solution of chloromethyldichlorophosphine (4.5 g, 30 mmol) in toluene (15 ml) was stirred at −20 to −10°C while 3.8 g (30 mmol) of 1,1-dichloro-1-nitrosoethane were added. The mixture was stirred at −7°C for 1.5 hour. The product was used directly in the next step without isolation.

Thermal Decomposition of Adducts of 1,1-Dichloro-1-nitrosoethane and Methyl (or phenyl) dichlorophosphines. From the solution of the adduct of 1,1-dichloro-1-nitrosoethane and dichlorophosphine in hexane the solvent was removed under vacuum. The evolved gas was collected in a dry ice trap while the reaction flask was warmed to 100°C until the solid residue became liquid. On distillation of the flask contents the corresponding phosphonic acid dichloride was obtained with quantitative yield. The flask and the trap on warming had the characteristic colour and odour of chlorine and gave a positive iodine starch test. Content of the trap had a ^{1}H-NMR chemical shift of 2.02 ppm (the same data for acetonitrile in reference books).

Interaction of the Adduct of 1,1-Dichloro-1-nitrosoethane and Dichloromethylphosphine with Dichloromethylphosphite. A solution of the adduct **1** (24.5 g, 100 mmol) in ether (150 ml) was stirred at 20°C while dichloromethylphosphite (13.3 g, 100 mmol) was added. The evolved gas was collected in a cooled trap at −40°C while the reaction mixture was stirred 1 hour at 30°C. The solution was rectified. The fraction with b.p. 25–30°C/200 mm Hg had a ^{1}H-NMR chemical shift of 1.98 ppm and addition of a $CH_3C{\equiv}N$ sample to the NMR ampoule led to an increase of the signal intensity. Also phosphorus oxychloride (7.3 g, 48 mmol) and methylphosphonic acid dichloride (9.8 g, 74 mmol) were separated in pure state by distillation. The evolved gas was identified as methyl chloride by gas chromatographic method in comparision with an authentic sample.

Interaction of Dichloromethylphosphine with O-(Trimethylsilyl)-methylchloroformooxime. To methyldichlorophosphine (3.5 g, 30 mmol) the O-(trimethylsilyl)methylchloroformooxime (5.0 g, 30 mmol) was added under cooling. The solution was rectified. Trimethylsilylchloride and methylphosphonic acid dichloride (1.5 g, 11 mmol) were isolated by rectification under vacuum. IR-spectrum of the gas collected in a cooled trap at −30° had a band at 2250 cm^{-1}, due to $CH_3C{\equiv}N$.

Interaction of Adducts of 1,1-Dichloro-1-nitrosoalkanes and Dichlorophosphines with SO_2:

Interaction terminating in dichlorophosphonate formation. The solution of the adduct of 1,1-dichloro-1-nitrosoethane (or butan or isobutan) and dichlorophenylphosphine (100 mmol) in toluene (200 ml) was stirred at 0–+5°C while SO_2 (15 g, 235 mmol) was added. Toluene was removed under vacuum. The residue was fractionated and gave 14.2 g (73 mmol) (or 9.9 g (51 mmol) or 15.9 g (81 mmol)) of phenylphosphonic acid dichloride with b.p. 74–79°C/0.03 mm Hg, n_D^{20} 1.5596, ^{31}P-NMR 36.2 ppm.

Interaction terminating in chlorophosphonate **4** *formation.* To a solution of dichlorophenylphosphine (8.9 g, 50 mmol) in ether (130 ml) at −30°C SO_2 (7.9 g, 123 mmol) was added. The mixture was stirred at −30 to −15°C while a solution of 1,1-dichloro-1-nitrosoethane (6.4 g, 50 mmol) in ether (17 ml) was added. The mixture was stirred at −10°C during 1.5 hour. The solvent was removed under vacuum and residue rectification gave O-(methylchloroformoimino)phenylphosphonic acid chloride (8.95 g, 35 mmol, 71%). By the same way chlorides of O-(propylchloroformoimino)phenylphosphonic acid, O-(isopropylchloroformoimino)phenylphosphonic acid, O-(methylchloroformoimino)isopropenylphosphonic acid, O-(methylchloroformoimino)chloromethylphosphonic acid and O-(methylchloroformoimino)brommethylphosphonic acid were obtained. (Tables I and II).

TABLE VII

Mass data of phenylphosphonic acid dichloride enriched with ^{18}O

ION	MASS	% RA	INTEN
PO^+	47	3.20	590
	49	0.69	127
$C_6H_5POCl^+$	159	100	18464
	161	67.94	12544
	163	8.58	1584
$C_6H_5POCl_2^+$	194	27.69	5112
	196	35.23	6504
	198	10.33	1908

Interaction terminating in chlorophosphonate and dichlorophosphonate formations. Solution of the adduct of 1,1-dichloro-1-nitrosoethane and dichlorophenylphosphine (28 mmol) in toluene (55 ml) was stirred at 0 to −5°C while SO_2 enriched with ^{18}O (2.6 g) was added. Toluene was removed under vacuum and residue rectification gave phenylphosphonic acid dichloride (1.6 g, 8 mmol, b.p. 74–79°C/0.03 mm Hg, n_D^{20} 1.5596) and O-(methylchloroformoiminophenylphosphonic acid chloride (2.8 g, 11 mmol, b.p. 123°C/0.03 mm Hg, n_D^{20} 1.5530). Phenylphosphonic acid dichloride mass-spectrum, see Table VII.

Preparation of O-(Alkylchloroformoimino)-O-alkylphosphonates **5.** *Preparation from phosphoranes.* The solution of the adduct of 1,1-dichloro-1-nitrosoalkane and dichlorophosphine (50 mmol) in toluene (40 ml) was stirred by cooling to −35°C while alcohol (66 mmol) was added to the solution. The temperature was kept below −25°C. The mixture was then allowed to warm to room temperature and toluene was removed under vacuum. After residue distillation the corresponding O-(alkylchloroformoimino)-O-alkylphosphonate was obtained. (Tables III and IV).

Preparation from acid chlorides. To a solution of O-(isopropylchloroformoimino)phenylphosphonic acid chloride (4.4 g, 16 mmol) in toluene (40 ml) the mixture from methanol (0.8 g, 25 mmol) and pyridine (1.4 g, 18 mmol) was added. The reaction mixture was boiled 2.5 hour at 100°C and then allowed to cool. After washing with water (3 × 20 ml) and drying with magnesium sulfate the toluene was removed under vacuum. By residue distillation 1.2 g (4 mmol, 27.71% yield) of O-(isopropyl-loroformoimino)-O-methylphenylphosphonate was obtained. The same product was obtained by preceding method with a yield of 15%.

Interaction of Adducts of 1,1-Dichloro-1-nitrosoethane and Dichloromethyl (or phenyl) phosphine with Acetic Acid. A solution of the adduct of 1,1-dichloro-1-nitrosoethane and dichloromethyl (or phenyl) phosphine (50 mmol) in toluene (60 ml) was stirred at a temperature lower than −35°C while a solution of acetic acid (6.9 g, 115 mmol) in toluene (3 ml) was added. The mixture was then allowed to warm to room temperature and toluene was removed under vacuum. By residue distillation 2.6 g (14 mmol) (or 4.2 g (17 mmol)) of the corresponding O-methylchloroformoiminophosphonic acid chloride was obtained with a yield of 27% (or 34%).

Preparation of O-(Alkylchloroformoimino)phenylphosphonic Acid Amides **6.** To a solution of O-(alkylchloroformoimino)phenylphosphonic acid chloride (20 mmol) in ether (120 ml) at −20°C ammonia (5 g, 294 mmol) was added. Solvent was removed under vacuum and after recrystallization from hot benzene/heptane the corresponding amide was obtained. (See Tables V and VI).

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REFERENCES

1. V. B. Sokolov, A. N. Ivanov, T. A. Epishina and I. V. Martynov, *Zhur. Obshchei Khim.*, **57,** 1659 (1987).
2. S. I. Malekin, V. I. Yakutin, M. A. Sokalskyi, Yu. L. Kruglyak and I. V. Martynov, *Zhur. Obshchei Khim.*, **42,** 807 (1972).
3. I. R. Beattie, K. Livingston and T. Gilson, *J. Chem. Soc., A*, 1 (1968).
4. L. Quin and C. Rolston, *J. Org. Chem.*, **23,** 1693 (1958).
5. M. I. Kabachnik and E. N. Tsvetkov, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1896 (1961).
6. Yu. L. Kruglyak, M. A. Landau, G. A. Leibovskaya, I. V. Martynov, L. I. Saltykova and M. A. Sokalskyi, *Zhur. Obshchei Khim.*, **39,** 215 (1969).
7. C. Brown, R. F. Hudson, A. Marov and K. A. F. Record, *J. Chem. Soc., Chem. Commun.*, **16,** 663 (1976).
8. M. P. Osipova, R. V. Volkova and I. A. Zlobina, *Zhur. Obshchei Khim.*, **55,** 697 (1985).
9. B. L. Dyatkin, E. D. Mochalina, Yu. S. Konstantinov, S. P. Sterlin and I. L. Knunyants, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, **10,** 2297 (1967).
10. P. Malatesta and B. D'Atri, *Farmaco [Pavia], Ediz. Sci.*, **8,** 398 (1953); *C. A.* **48,** 9312f (1954).