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Synthesis of intermediate compounds with P-N bond from (thio)carbamates and chlorodioxaphospholanes and -phosphorinanes and their reactivity

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ABSTRACT

A variety of 2-(*N*-alkoxy(thio)carbonyl alkyl(aryl)amino)-1,3,2-dioxaphospholanes and phosphorinanes were prepared from chlorodioxaphospholanes and phosphorinanes. Their structures were determined by IR, Mass and NMR spectroscopy. These compounds were employed in direct reactions with elemental sulphur and methylester of chloroacetic acid giving potentially physiologically active *N*-phosphorylated carbamates with P(O)-N and P(S)N bonds.

1. Introduction

Synthesis of compounds with P-N bonds has been extensively discussed in the literature due to their physiological and catalytic properties. For example, synthesis of *N*-phosphorylated carbamates (Figure 1) is mainly driven by physiological properties of these compounds; those could be used as, for example, pesticides [1].

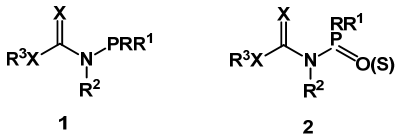

Figure 1. *N*-phosporylated carbamates, X stands for oxygen or sulphur.

An important property of such compounds is their selective toxicity. Carbamates with P-N bonds, derivatives of P(III), can have high reactivity, which gives an opportunity to synthesize corresponding derivatives of P(V) containing also sulphur. Synthesis of compounds **1** and **2** when R^2 is H, can be carried out through the route displayed in Scheme 1 [2]. Another synthetic option is the reaction of PCl_3 with *N*-chloroamides of carbonic acid ROC(O)NHCl or *N*-chloroaminoethers $(RO)_2C{=}NCl$ leading to $ROCON{=}PCl_3$ which can undergo hydrolysis to yield *N*-dichlorophosphoryl carbamates [3]. The range of synthetic methods was enlarged when it turned out that unsubstituted phosphorylated carbamates can be formed when phosphorylated isocyanates react with alcohols or mercaptanes [4]. This method can be applied for the synthesis of various types of phosphorylated carbamates. For example, bis(chlromethyl) phosphinoylisocyanate reacts easily with alcohols to give the corresponding phosphorylated carbamates $(ClCH_2)_2P(O)NHC(O)OR$ [5]. The methods discussed above allow, however, only the synthesis of unsubstituted phosphorylated carbamates. Substituted carbamates, in turn, can be obtained by several methods, including for example Arbuzov rearrangement (Scheme 2) [6].

Another method involves the reaction of chloroanhydrides of various phosphor containing acids with sodium carbamates [7]. Utilization of such preparative methods in industrial scale is challenging due to the need of using metallic sodium for synthesis of sodium carbamates, making the process unnecessarily complicated.

An alternative way is to form P-N bonds directly from a nitrogen compound containing an N-H bond. It is possible, for example, to react halogen containing compounds, such as chloroanhydrides of varios P(III) acids with amines giving a P(III)-N bond. In the work of Dutton and coworkers [8], chloro-2-dimethyl-5,5-dioxaphosporinane-1,3,2 was reacted with various amines, such as *tert*-butylamine resulting in the formation of several 1,3,2 dioxaphosporinanes. A similar approach was adopted by Browne *et al.* [9] where phosporochloridite was reacted with amines followed by reaction with elemental sulfur to obtain potential insecticides. Another example has been reported by de Vries [10], where ethylene chlorophosphite was allowed to react with diisopropylamine in dichloromethane giving the cyclic ethylene phosphite ester. This synthetic methodology became popular recently in connection with the synthesis of a library of chiral ligands based on monodentate phosphoramidites [11,12] when stoichiometric amounts of reagents such as chlorodioxa phospholane (**4**) and diacetylamines are put in contact in the presence of a HCl acceptor (triethylamine) giving finally phosphoramidites (**5**) (Scheme 3).

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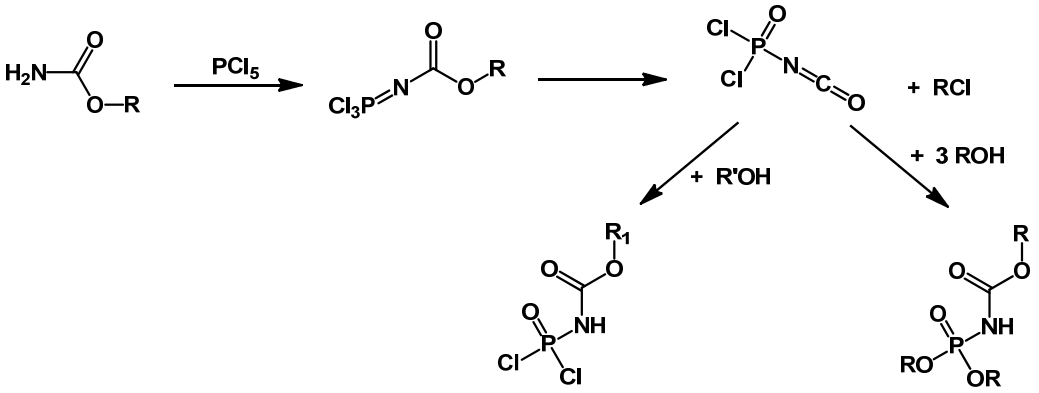
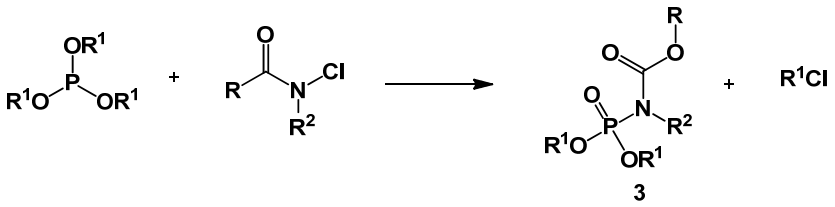
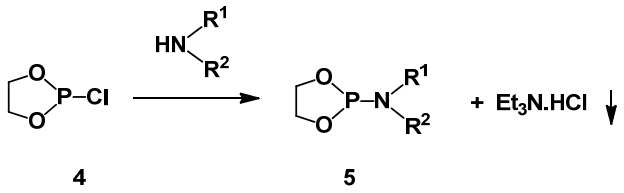


Scheme 1



Scheme 2



Scheme 3

The protocol was even automated by using a 96 well filter plate, as simple filtration of the precipitated HCl salt can be performed without further ligand purification. In fact, triethylamine started to be used rather long time ago as a HCl acceptor not only for reaction of phosphorochloridite with amines per se, but also for reactants with the -NH-C(O)- group, such as *N*-methylacetamide [13,14].

Alternatively ε-caprolactam can be used [15]. In the latter case [15] it is supposed that the reaction proceeds via intermediate formation of a five membered complex. Interestingly, in earlier work [13], also phosphorylated carbamates with P-N(R)-C(O)OR motifs were synthesized, including 2-(*N*-ethoxycarbonyl methylamino)-l,3,2-dioxaphospholane (**6**), diethyl *N*-ethoxycarbonyl-*N*-methylphosphoramidite (**7**) and 4,5-benzo-2-(*N*-ethoxycarbonymethylamino)-1,3,2-dioxaphospholane (**8**) (Figure 2). *N*-phosphorylated methylcarbamates, in turn, were shown to react with elemental sulfur [9,15]. The products possess insecticidal activity resulting, however, in burns of the leaves. Chloroanhydrides can also react with compound **7** [15].

The aim of the present work was to synthesize components with P-N bonds from (thio)carbamates and chlorodioxaphospholanes and -phosphorinanes and to study their reactivity in reactions with elemental sulphur and chloro anhydrides. The compounds obtained from these reactions could be potential insecticides and regulators of plant growth.

2. Experimental

2.1. Synthesis

In the current work, all synthesized phosphorylated carbamates were obtained by reactions of 2-chloro-1,3,2-dioxaphospholane/phosphorinane (**9**) with carbamates and thiocarbamates in the presence of HCl acceptor-triethylamine (Scheme 4). The synthesized compounds are presented in Table 1. It should be noted that among these compounds only compound **10b** was synthesized previously [13].

Synthesis of compounds **10a**-**10m** was performed under nitrogen atmosphere. To a solution of (thio)carbamate and triethylamine (1.5 fold mole excess) in 25 or 50 mL of dried dioxane an equimolar amount 2-chloro-1,3,2-dioxaphospholane or chloro-1,3,2-dioxaphosphorinane was added drop-wise. The quantities are given in Table 2. The mixture was stirred for 2 h at 55-60 °C. After filtering triethylamine salt and evaporating the solvent in vacuum (1-12 mm Hg) the residual was distilled at 0.1-0.2 mm Hg. The yields reported below are isolated yields.

Ethyl 1,3,2-dioxaphospholan-2-ylcarbamate (**10a**): IR (KBr, ν, cm^{-1}): 2990 (C-H), 1710 (C=O), 1230 (C-O-C), 1010 (P-O-C). ^{31}P NMR (36.43 MHz, 85%H_3PO_4, δ, ppm): 133. n_D^{20} = 1.4220 (Identical to the substrate).

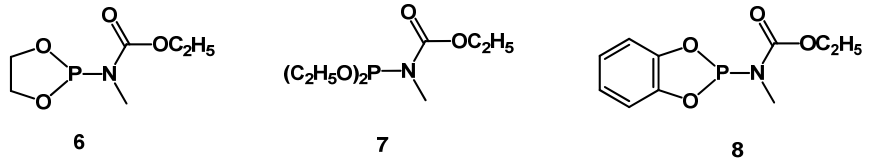
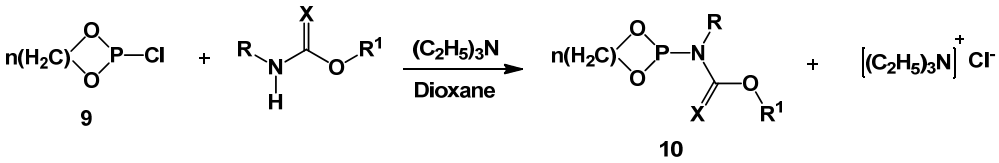


Figure 2. Phosphorylated carbamates with P-N(R)-C(O)OR motif.

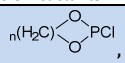


Scheme 4

Table 1. Structure of synthesized compound **10**.

Compound	n	X	R	R^1
10a	2	O	H	C_2H_5
10b			CH_3	C_2H_5
10c			C_6H_5	CH_3
10d			C_6H_5	*i*-C_3H_7
10e			C_6H_4Cl	*i*-C_3H_7
10f	2	S	CH_2-CH=CH_2	C_2H_5
10g			C_6H_5	CH_3
10h			C_6H_5	*i*-C_3H_7
10i			C_6H_5	C_4H_9
10j	3	O	H	C_2H_5
10k			C_6H_5	CH_3
10l			C_6H_5	*i*-C_3H_7
10m		S	H	CH_3

Table 2. Ratio of reactants.

Product/ Reactants	 mole	Carbamate, mole	Et_3N, mole	Volume of solvent, mL
10a	0.10	0.150	0.150	50
10b	0.10	0.150	0.150	50
10c	0.03	0.030	0.045	50
10d	0.03	0.030	0.045	50
10e	0.04	0.040	0.060	50
10f	0.03	0.030	0.045	25
10g	0.09	0.090	0.140	50
10h	0.03	0.030	0.045	50
10i	0.01	0.010	0.015	25
10j	0.05	0.075	0.050	50
10k	0.10	0.100	0.150	70
10l	0.05	0.050	0.075	50
10m	0.05	0.050	0.100	50

Ethyl 1,3,2-dioxaphospholan-2-yl(methyl)carbamate (**10b**): Yield: 32%. B.p.: 50 °C/0.1 mm Hg. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1710 (C=O), 1220 (C-O-C), 1010 (P-O-C). ^{31}P NMR (36.43 MHz, 85%H_3PO_4, δ, ppm):128.5 (128.8 in [12]). n_D^{20} = 1.4540.

Methyl 1,3,2-dioxaphospholan-2-yl(phenyl)carbamate (**10c**): Yield: 58%. B.p.: 85 °C/0.2 mm Hg. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1700 (C=O), 1600, 1500, 1450 (C_6H_5), 1000 (P-O-C). ^{31}P NMR (36.43 MHz, 85%H_3PO_4, δ, ppm): 130. MS (EI, *m/z* (%)): 241 (M^+, 0.55) M^+. n_D^{20} = 1.5268.

Isopropyl 1,3,2-dioxaphospholan-2-yl(phenyl)carbamate (**10d**): Color: White. Yield: 82%. M.p.: 80-81 °C. IR (KBr, ν, cm^{-1}): 1700 (C=O), 1600, 1530, 1440 (C_6H_5), 1220 (C-O-C), 995 (P-O-C).

Isopropyl (2-chlorophenyl)(1,3,2-dioxaphospholan-2-yl) carbamate (**10e**): Yield: 50%. B.p.: 95 °C/0.2 mm Hg. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1700 (C=O), 1600, 1530, 1440 (C_6H_5), 1220 (C-O-C), 990 (P-O-C). n_D^{20} = 1.5415.

O-ethyl allyl(1,3,2-dioxaphospholan-2-yl)carbamothioate (**10f**): B.p.: 65-68 °C/0.1 mm Hg. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1390 (C=S), 1620 (C=C), 1010 (P-O-C). MS (EI, *m/z* (%)): 235 (M^+, 190 $[(CH_2O)_2PN(CS)CH_2CH=CH_2]^+$, 149 $[(CH_2O)_2PN(CS)]^+$, 105 $[(CH_2O)_2PN]^+$. n_D^{20} = 1.5191.

O-methyl 1,3,2-dioxaphospholan-2-yl(phenyl)carbamo thioate (**10g**): Yield: 63%. B.p.: 85 °C/0.2 mm Hg. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1590, 1520, 1490 (C_6H_5), 1360 (C=S), 1010 (P-O-C). MS (EI, *m/z* (%)): 257(M^+, 1.1), 243 $[(CH_2O)_2PN(C_6H_5)CSOH]^+$, 4.19). n_D^{20} = 1.6150.

O-isopropyl 1,3,2-dioxaphospholan-2-yl(phenyl)carbamo thioate (**10h**): Color: White. Yield: 67%. M.p.: 84-85 °C. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1600, 1510, 1440 (C_6H_5), 1375 (C=S), 1250 (C-O-C), 990 (P-O-C).

O-butyl 1,3,2-dioxaphospholan-2-yl(phenyl)carbamothioate (**10i**): Color: White. Yield: 70%. M.p.: 68-70 °C. IR (KBr, ν, cm^{-1}): 2990 (C-H), 1600, 1520, 1450 (C_6H_5), 1360 (C=S). ^{31}P NMR (36.43 MHz, 85%H_3PO_4, δ, ppm): 112. MS (EI, *m/z* (%)): 299 (M^+, 0.11).

Ethyl 1,3,2-dioxaphosphinan-2-ylcarbamate (**10j**): IR (KBr, ν, cm^{-1}): 1790 (C=O), 1010 (P-O-C).

Methyl 1,3,2-dioxaphosphinan-2-yl(phenyl)carbamate (**10k**): Yield: 57%. B.p.: 115-120 °C/0.2 mmHg. IR (KBr, ν, cm^{-1}): 3000 (C-H), 1600, 1540, 1460 (C_6H_5), 1770 (C=O), 1020 (P-O-C), 1210 (C-O-C). MS (EI, *m/z* (%)): 255 (M^+).

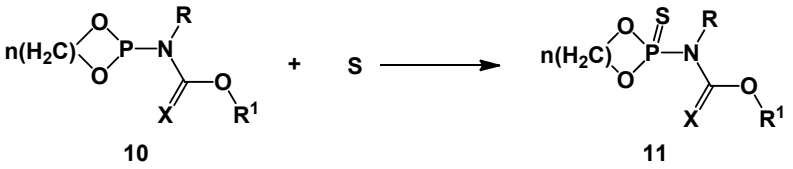
Isopropyl 1,3,2-dioxaphosphinan-2-yl(phenyl)carbamate (**10l**): Color: White. Yield: 64%. M.p.: 73-75 °C (crystallized in petroleum ether). IR (KBr, ν, cm^{-1}): 3000 (C-H), 1600, 1540, 1450 (C_6H_5), 1750 (C=O), 1040 (P-O-C). MS (EI, *m/z* (%)): 299 ($(M+O)^+$).

O-methyl 1,3,2-dioxaphosphinan-2-ylcarbamothioate (**10m**): Color: White. Yield: 52%. M.p.:90-91 °C. IR (KBr, ν, cm^{-1}): 3000 (C-H), 1600, 1500, 1450 (C_6H_5), 1370 (C=S), 1020 (P-O-C).

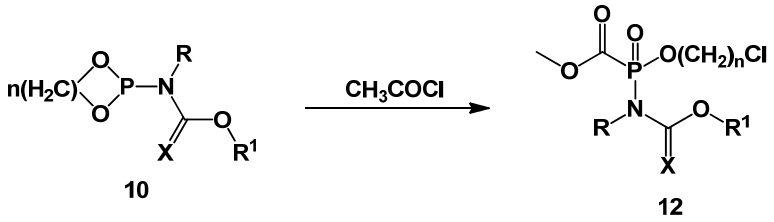
2.2. Reactions with elemental sulphur

For synthesis of phosphorylated carbamates with P=S bond corresponding reactants were put in contact with elemental sulphur in dioxane (Scheme 5). The list of synthesized compounds in displayed in Table 3. Few drops of the catalyst -triethylamine were added. The mixture was kept boiling for ca. 6 h. After evaporating the solvent, the products underwent crystallization by adding first toluene and then petroleum ether (**11a**) or hexane (**11c**, **11d**). Alternatively after solvent evaporation further distillation/treatment under vacuum (1 mm Hg) was performed (**11e**, **11f**) leading to viscosous oil. Compound **11b** was purified using TLC with eluent $CHCl_3$. Conditions of experiments are summarized in Table 4.

O-Isopropyl phenyl(2-sulfido-1,3,2-dioxaphospholan-2-yl) carbamate (**11a**): Color: White. Yield: 39%. M.p.: 96-98 °C. IR (KBr, ν, cm^{-1}): 1600, 1500, 1470 (C_6H_5), 1740 (C=O), 840 (P=S).



Scheme 5



Scheme 6

^{31}P NMR (36.43 MHz, 85%H_3PO_4, δ, ppm): 82.3. MS (EI, *m/z* (%)): 301 (15.47%) M^+. Anal. calcd. for $C_5H_{10}NO_3PS$: C, 47.77; H, 5.42; N, 4.70. Found: C, 47.80; H, 5.31; N, 5.22%.

O-Isopropyl 2-chlorophenyl(2-sulfido-1,3,2-dioxaphospholan-2-yl)carbamate (**11b**): Color: White. Yield: 20%. M.p.: 101-103 °C. IR (KBr, ν, cm^{-1}): 2990 (CH), 1595, 1530, 1440 (C_6H_5), 1730 (C=O), 1230 (C-O-C), 995 (P-O-C), 770, 690 (P=S).

O-methyl phenyl 2-sulfido- 1,3,2-dioxaphospholan-2-yl-carbamothioate (**11c**): Color: White. Yield: 27%. M.p.: 110-112 °C. IR (KBr, ν, cm^{-1}): 1590, 1530 (C_6H_5), 1730 (C=O), 1390 (C=S), 780 (P=S).

O-isopropyl phenyl 2-sulfido- 1,3,2-dioxaphospholan-2-yl carbamothioate (**11d**): Color: White. Yield: 34%. M.p.: 150-151 °C. IR (KBr, ν, cm^{-1}): 2980 (CH), 1595, 1530, 1440 (C_6H_5), 1380 (C=S), 990 (P-O-C), 690, 770, (P=S). MS (EI, *m/z* (%)): 139 ($(CH_2O)_2PSNH_2^+$, 8.65), 123 ($(CH_2O)_2PS^+$, (11.52)).

O-methyl phenyl(2-sulfido-1,3,2-dioxaphosphinan-2-yl) carbamate (**11e**): Yield: 59%. IR (KBr, ν, cm^{-1}): 1600, 1530, 1450 (C_6H_5), 1720 (C=O), 1220 cm^{-1}(C-O-C), 1020 (P-O-C), 690, 760, (P=S).

O-methyl phenyl 2-sulfido-1,3,2-dioxaphosphinan-2-yl carbamothioate (**11f**): Yield: 64%. IR (KBr, ν, cm^{-1}): 1590, 1490 (C_6H_5), 1380 (C=S), 1220 (C-O-C), 1030 (P-O-C), 680, 750, (P=S).

Table 3. Structure of synthesized compound **11**.

Compound	n	X	R	R¹
11a	2	O	C_6H_5	*i*-C_3H_7
11b			C_6H_4Cl	*i*-C_3H_7
11c	2	S	C_6H_5	CH_3
11d			C_6H_5	*i*-C_3H_7
11e	3	O	C_6H_5	CH_3
11f		S	C_6H_5	CH_3

Table 4. Ratio of reactants in reactions of carbamates with sulphur.

Product/ Reactants	Carbamate type	Carbamate amount, mole	S, mole	Volume of solvent
11a	10d	0.025	0.025	30
11b	10e	0.010	0.010	50
11c	10g	0.030	0.030	25
11d	10h	0.020	0.020	15
11e	10k	0.025	0.025	20
11f	10m	0.025	0.025	20

2.3. Reaction with methylchlorformate

Corresponding phosphorylated carbamates were put in contact with methyl chlorformate in dioxane (Scheme 6) and the synthesized compounds are presented in Table 5. Few drops of the catalyst - triethylamine were added. The mixture was kept boiling. After evaporating the solvent the products **12a**, **12b** slowly crystallized. Compound **12a** was purified using TLC with eluent $CHCl_3$. Compound **12c** is an oily compound which underwent vacuum treatment at 1 mm Hg. Alternatively after solvent evaporation subsequent distillation under vacuum (0.2 mm Hg) was performed (**12d**, **12e**, **12f**) leading to viscosous oils. Conditions of experiments are summarized in Table 6.

Table 5. Structure of synthesized compound **12**.

Compound	n	X	R	R¹
12a	2	O	H	C_2H_5
12b			C_6H_5	*i*-C_3H_7
12c			C_6H_4Cl	*i*-C_3H_7
12d	2	S	C_6H_5	CH_3
12e			C_6H_5	*i*-C_3H_7
12f	3	O	C_6H_5	CH_3

Table 6. Conditions in reactions of carbamates with methylchlorformiate.

Product/ Reactants	Carbamate type	Carbamate amount, mole	MCF, mL	Reaction time, h	Yield, %
12a	10a	0.05	40	6	79
12b	10d	0.04	30	4	83
12c	10e	0.04	30	4	79
12d	10g	0.01	30	11	80
12e	10h	0.01	30	11	74
12f	10k	0.03	25	8	67

Ethyl (2-chloroethoxy)(methoxy)phosphorylcarbamate (**12a**): Color: White. M.p.: 155-156 °C. IR (KBr, ν, cm^{-1}): 1730, 1780 (C=O), 1010 (P-O-C), 1270 (P=O).

Isopropyl (2-chloroethoxy)(methoxy)phosphoryl(phenyl) carbamate (**12b**): Color: White. M.p.: 109 °C. IR (KBr, ν, cm^{-1}): 1600, 1520, 1440 (C_6H_5), 1720, 1732 (C=O), 1210 (C-O-C), 1025, 1170 (P-O-C), 1275 (P=O). MS (EI, *m/z* (%)): 363 (M^+, 5.72), 328 ($(M-Cl)^+$, 1.34).

Isopropyl (2-chloroethoxy)(methoxy)phosphoryl(2-chloro phenyl)carbamate (**12c**): Color: Viscosous oil. IR (KBr, ν, cm^{-1}): 1600, 1510, 1440 (C_6H_5), 1717, 1740 (C=O), 1035 (P-O-C), 1270 (P=O). MS (EI, *m/z* (%)):397 (M^+, 1.24%).

O-methyl (2-chloroethoxy)(methoxy)phosphoryl(phenyl) carbamothioate (**12d**): B.p: 125 °C/0.2 mm Hg. n_D^{20} = 1.5510. IR (KBr, ν, cm^{-1}): 1590, 1530, 1440 (C_6H_5), 1750 (C=O), 1350 (C=S), 1210 (C-O-C), 1000 (P-O-C), 1300 (P=O).

O-isopropyl (2-chloroethoxy)(methoxy)phosphoryl(phenyl) carbamothioate (**12e**): B.p.: 120-122 °C/0.2 mm Hg, after that

the product crystallized. Color: White. M.p.: 125 °C. IR (KBr, ν, cm^{-1}): 1590, 1530, 1440 (C_6H_5), 1730 (C=O), 1390 (C=S), 1230 (C-O-C), 1000 (P-O-C), 1300 (P=O).

Ethyl (3-chloropropoxy)(methoxy)phosphoryl(phenyl) carbamate (**12f**): B.p: 96 °C/0.2 mm Hg. IR (KBr, ν, cm^{-1}): 1600, 1520, 1450 (C_6H_5), 1750, 1705 (C=O), 1200 (C-O-C), 1000 (P-O-C), 1300 (P=O). ^{31}P NMR (36.43 MHz, 85%H_3PO_4, δ, ppm): -13.9. MS (EI, *m/z* (%)): 290 (M-$COOCH_3$)$^+$, 5.72). n_D^{20} = 1.5510.

2.4. Instrumentation

Mass spectra were measured with Varian MAT CH-7A instrument, while Bruker HX-90E NMR spectrometer (36.43 MHz) with 85%H_3PO_4 as an external standard was used for ^{31}P NMR measurements. IR spectra were measured with IR spectrophotometer UR-20 either in CCl_4 or using KBr. The *'hot-stage'* apparatus was used to measure the melting point with a possibility to look at the sample through a microscope while its temperature is increased.

3. Results and discussion

3.1. Synthesis and characterization of phosphorylated carbamates

In IR spectra of components **10a**-**10e** and **10j**-**10l** there were characteristic peaks of carbonyl group in the range 1700-1720 cm^{-1} for **10a**-**10e** (1715 cm^{-1} as mentioned in [13]) and 1750-1790 for **10j**-**10l**. Presence of the C=S group resulted in peaks at 1360-1390 cm^{-1}. For the phospholane ring the characteristic peaks are in the region of 990-1100 cm^{-1}. The spectra also contain peaks of the phenyl ring (1450-1600 cm^{-1}), while components **10a** and **10j** have peaks corresponding to NH vibrations.

^{31}P NMP confirms formation of trivalent phosphor carbamates derivatives with signals at 122 ppm.

Mass spectra of some substances of type **10** contain molecular ions, such as for example component **10c**, where the amount of molecular ion is 0.55%, which is high for phosphor containing compounds at rather severe conditions (70 eV), being a sign of a strong P-N bond in phosphorylated carbamates. Calculations of the partial charge of P and N using extended Huckel method after structure optimization with MM2 (Chem 3D Pro) gave respectively the values 0.905374 and 0.164095, while P-N bond length is 1.773 Å. The values of ion fragments in the mass spectra of compound **10c** are given in Table 7.

Table 7. Mass spectra fragments for **10c**.

m/e	I/I_{max}	Ions
241	0.55	M^+
151	100%	$[C_6H_5NCOOCH_3]^+$
119	37.17	$[C_6H_5NCO]^+$
93	7.15	$[C_6H_5NH_2]^+$
92	28.37	$[C_6H_5NH]^+$
91	24.57	$[C_6H_5N]^+$
59	17.85	$[COOCH_3]^+$

The stability of the molecular ion depends on the number of carbon atoms in the chain, since for component **10k** with three carbon atoms in the cycle the relative amount of an ion with *m/e* 255 is 11.71%. The main fragmentation for compound **10k** path is [M+] ->$[(CH_2)_3OOP]^+$ (*m/e* 105; 88.77%) + $[NH(C_6H_5)COOCH_3]^+$ (*m/e* 151; 48.08%) although in the spectra also ions with the P-N bond are present. The main ions in the spectra of compound **10k** are given in Table 8.

In case of compound **10l** it could be expected that the molecular ion is not present, since the isopropyl group could be easily cleaved. On the other hand there is an ion with *m/e* 299, corresponding to compound **10l** with P=O. Moreover in mass spectra ions with *m/e* 105 (see Table 8) are absent, while there is an ion with *m/e* 121 ($CH_2(CH_2O)_2PO$) albeit with low intensity (5.64%). Oxidation of P(III) to P(V) during synthesis and work up also follows from NMR spectra.

Table 8. Mass spectra fragments for **10k**.

m/e	I/I_{max}	Ions
271	2.62	MO^+
255	11.71	M^+
196	1.53	$[M- CO- CH_3]^+$
185	30.55	$[HOPOHNC_6H_5COH]^+$
151	48.08	$[C_6H_5NCOOCH_3]^+$
139	22.12	$[POHNC_6H_5]^+$
120	11.52	$[C_6H_5NCOH]^+$
119	37.17	$[C_6H_5NCO]^+$
105	88.17	
93	7.15	$[C_6H_5NH_2]^+$
92	28.37	$[C_6H_5NH]^+$
91	24.57	$[C_6H_5N]^+$
77	25.3	$[C_6H_5]^+$
59	17.85	$[COOCH_3]^+$
41	100%	$[CH_2CH_2CH]^+$

Introduction of sulphur typically diminishes the stability of thiocarbamates under conditions of mass spectra measurements compared to carbamates. Thus the intensity of the molecular ion (*m/e* 257) in phosphorylated thiocarbamate **10g** is just 1.1%, while for compound **10i** it is even lower -0.11%. The P-N bond length calculated by extended Huckel method (Chem 3D Pro) after structure optimization for compound **10g** is marginally larger (1.775 Å) than for compound **10c**, while the partial charges for P and N get the values 1.06544 and 0.222732.

In the case of compound **10c** the ion with *m/e* 120 $[C_6H_5NHCO]^+$ is the main one, while intensity of ion with *m/e* 136 $[C_6H_5NHCS]^+$ is 14.06% which is typical for thiocarbamates with a long chain substituent in the ester part of the molecule. Mass spectrum of the same compound **10c** contains also ions with *m/e* 154 (16.04%) and 155 (5.5%) corresponding respectively to $[OPONC_6H_5]^+$ and $[OPONHC_6H_5]^+$. If a substituent at N is not phenyl, but for example allyl radical mass spectra are different, since then N-C bond is much less stable (N-C bond distances are respectively 1.316 and 1.470 Å for compound **10g** and **10f**). Thus mass spectrum of compound **10f** (Table 9) demonstrates presence of an ion of *m/e* 206 with intensity 1.37% as well the ion with *m/e* 149 (1.85%). The rupture of the dioxaphospholane cycle is hindered, which is confirmed by the presence of such ions as *m/e* 105 (2.01%) and *m/e* 91 (26.69%).

Table 9. Mass spectra fragments for **10f**.

m/e	I/I_{max}	Ions
255	1.05	M^+
206	1.3	$[(CH_2O)_2PN(CSO)CH_2CH=CH_2]^+$
190	3.28	$[(CH_2O)_2PN(CS)CH_2CH=CH_2]^+$
149	1.85	$[(CH_2O)_2PN(CS)]^+$
105	2.09	$[(CH_2O)_2PN]^+$
91	26.69	$[(CH_2O)_2P]^+$
58	19.38	$[NCS]^+$
45	30.29	$[OC_2H_5]^+$
41	36.65	$[CH_2CH=CH_2]^+$
28	100%	-

3.2. Reactivity

Reactions of phosphorylated carbamates with an effective electrophile, elemental sulphur (S_8) were conducted according to Scheme 5. Thin layer chromatography, IR, Mass and NMR spectra were used to identify the purity and structure of these not previously reported compounds.

In the IR spectra there are vibrations corresponding to the carbonyl group at 1720-1740 cm^{-1} (**11a**, **11b**, and **11e**) and C=S group at 1380-1390 cm^{-1} (**11c**, **11d**, and **11f**). In the region 1600-1470 cm^{-1} there are peaks corresponding to the phenyl ring and dioxaphospholane cycle. For P=S bonds typically there are two peaks in a rather range of 770-840 cm^{-1} and 600-700

cm^{-1} also seen for the compounds synthesized in the present work, where the peaks of P=S for compound **11d** were noticeable at 660 and 770 cm^{-1}.

In the mass spectrum of compound **11a** (Table 10) the intensity of the molecular ion is rather high (15.47%) confirming the strength of P-N bonds in the synthesized phosphorylated carbamates. Presence of $[M+2]^+$ also confirms the structure of compound **11a** since the signal is due to isotope S^{34}. In the mass spectrum of compound **11d** it could be expected that the intensity of molecular ion is low compared to compound **11a**, since thiocarbamates are not stable at the conditions of electron beam. Indeed the molecular ion is absent, while an ion $[(CH_2O)_2PS]^+$ with *m/e* 123 (11.53%) confirms addition of sulphur to the substrate **10h**. In the case of compound **11d** intensity of $[C_6H_5NCS]^+$ ion (*m/e* 135) is rather low (2.37%) in comparison with $[C_6H_5NCO]^+$, which is the main ion. The partial charges of P and N for compound **11a** (1.9673 and -0.0143) as well as the bond length (1.773 Å) differ from the corresponding thiocarbamate **11d** (Charges of P and N being 2.00269 and 0.17678, respectively, bond length 1.778 Å) in line with mass spectra.

Table 10. Mass spectra fragments for **11a**.

m/e	I/I_{max}	Ions
303	0.55	$[M+2]^+$
302	1.90	$[M+1]^+$
301	15.47	M^+
242	2.55	$[(CH_2O)_2PSNC_6H_5CO]^+$
215	19.25	$[(CH_2O)_2PSNHC_6H_5]^+$
214	1.82	$[(CH_2O)_2PSNC_6H_5]^+$
199	6.58	$[HOPSNC_6H_5CO]^+$
183	2.38	$[HPSNC_6H_5CO]^+$
182	5.25	$[PSNC_6H_5CO]^+$
172	6.39	$[HOPSNHC_6H_5]^+$
171	8.02	$[HOPSNC_6H_5]^+$
170	3.54	$[OPSNC_6H_5]^+$
155	8.0	$[PSNHC_6H_5]^+$
154	2.59	$[PSNC_6H_5]^+$
141	12.43	$[(CH_2O)_2PSHNH]^+$
140	16.1	$[(CH_2O)_2PSOH]^+$
138	2.59	$[(CH_2O)_2PSNH]^+$
124	1.88	$[(CH_2O)_2PSH]^+$
123	15.24	$[(CH_2O)_2PS]^+$
119	100	$[C_6H_5NCO]^+$
91	19.43	$[C_6H_5N]^+$
77	3.1	$[C_6H_5]^+$
43	49.11	$[C_3H_7]^+$

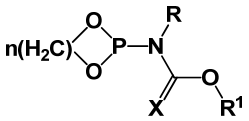
Reactivity of carbamates was also tested in the reaction with acetylchloride, which was taken in access (Scheme 6). Thin layer chromatography, IR, mass and NMR spectra were used to identify the purity and structure of these not previously reported compounds.

In the IR spectra there are peaks corresponding to C=O group for compound **12a** and **12c** (1700-1760 cm^{-1}), **12d** and **12e** (1730-1760 cm^{-1}) as well as P=O group (1210-1300 cm^{-1}) and the phenyl ring (1490-1600 cm^{-1}) for compounds **12b**-**12f**.

Intensity of molecular ions M^+ and $[M+2]^+$ was as high as 61.88% for compound **12f**, while it was only 5.72% for compound **12b** and 4.24 % for compound **12c**. Among other ions in the mass spectrum of compound **12f** the following ones should be mentioned corresponding to the removal of Cl $[M-Cl]^+$, (*m/e* 314, 1.38%), methoxycarbonyl group $[M-CH_3OC(O)]^+$ (*m/e* 290, 5.32%), as well as both of them $[M-Cl-CH_3OC(O)]^+$ (*m/e* 255, 4.21%).

4. Conclusions

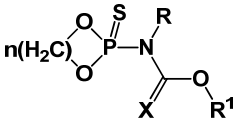
Several intermediates, derivatives of carbamates and cyclophosphoric acids with P-N bond and the following structure (Scheme 7) were synthesized from (thio)carbamates and chlorodioxa-phospholanes and -phosphorinanes using triethylamine as HCl acceptor. These compounds were identified using IR, mass spectroscopy and ^{31}P NMR.



n = 2, 3
R = H, $-CH_3$, $-CH_2-CH=CH_2$, C_6H_5, C_6H_4Cl
R^1 = CH_3, C_2H_5, *i*-C_3H_7, C_4H_9

Scheme 7

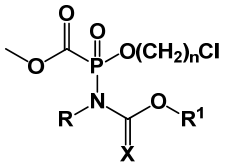
The reactivity of phosphorylated carbamates was investigated in the sulphur addition reaction giving the following previously not reported O-alkyl phenyl-2-sulfido-1,3,2-dioxaphospholan (or dioxaphospinan)-2-yl)-carbamates and -carbamothioates (Scheme 8). The structure was determined by IR, mass spectroscopy and ^{31}P NMR.



n = 2, 3
X = O, S
R = C_6H_5, C_6H_4Cl,
R^1 = CH_3, *i*-C_3H_7

Scheme 8

A possibility to synthesize for the first time alkyl (2-chloroethoxy or propoxy)(methoxy)phosphoryl(2-aryl) carbamates (or carbamothioates) (Scheme 9) through an Arbuzov type rearrangement was demonstrated by reacting corresponding intermediates containing P-N bonds and methyl formate.



n = 2, 3
X = O, S
R = H, C_6H_5, C_6H_4Cl
R^1 = CH_3, *i*-C_3H_7

Scheme 9

Detailed analysis of mass spectra of the intermediates and the products was performed and the main fragmentations pathways in mass spectra were discussed.

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