Mono- and bis[*N*-aryl(benzyl)]amides of phosphorylacetic acids. One-pot synthesis and extraction of actinides from nitric acid solutions

O. I. Artyushin,[a] E. V. Sharova,[a] I. L. Odinets,[a] K. A. Lyssenko,[a] D. G. Golovanov,[a] T. A. Mastryukova,[a] G. A. Pribylova,[b] I. G. Tananaev,[b] and G. V. Myasoedova[b]*

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5085. E-mail: odinets@ineos.ac.ru*
[b]*V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 ul. Kosygina, 119991 Moscow, Russian Federation*

A one-pot synthetic route to phosphorylacetic acid *N*-aryl(alkylaryl)amides, including those containing two phosphorylmethylcarbamoyl moieties attached to the arene framework, has been developed. The method is based on reactions of amines with the corresponding acid chlorides generated *in situ* with the use of phosphorus trichloride as a mild chlorinating agent. The compositions and structures of the compounds obtained and their extraction ability toward Am^{III} were determined. Suggestions were made about the compositions of the extracted complexes with phosphorylacetic acid *N*-aryl(alkylaryl)amides.

Key words: aromatic amines, phenylenediamines, xylylenediamines, phosphorylacetic acids, phosphorylacetic acid amides, carbamoylmethylphosphine oxides, actinides, americium, extraction.

Phosphorylacetic acid *N*,*N*-dialkylamides, in particular, derivatives containing the phosphine oxide moiety (carbamoylmethylphosphine oxides (CMPO)), are nowadays widely used as extractants for the processing of liquid radioactive wastes.[1—4] The application of these compounds makes it possible to concentrate actinides from highly active salt-containing wastes in a wide concentration range of nitric acid without their preliminary correction. Neutral organophosphorus complexing agents are well compatible with various solvents. Secondary phosphorylacetic acid *N*-alkylamides also proved to be efficient extractants for lanthanide ions.[5—8] The synthesis and the extraction properties of compounds containing the $NHC(O)CH_2P(O)Ph_2$ fragments attached to the upper rim of calix[4]- and calix[5]arenes,[5] to the C_3-symmetric triphenoxymethane framework,[6] or the carborane fragment[7] were documented.

Earlier, we have developed[8] a simple procedure for the preparation of the simplest representatives of this class of compounds, *viz.*, alkylamides $Ph_2P(O)CH_2C(O)NHAlk$ (**1**) (CMPO-NH, where Alk is alkyl C_2—C_{12}), based on direct amidation of commercially available ethyl diphenylphosphorylacetate with primary aliphatic amines (75—92% yields). An analogous approach can be used for the synthesis of phenyl(alkoxy)phosphorylacetic acid alkylamides $Ph(RO)P(O)CH_2C(O)NHAlk$ with proviso that the substituent R in the alkoxy group at the phosphorus atom contains at least eight carbon atoms. Study of extraction of transuranium ions from acidic media with amides **1** showed that the latter compounds are as good as *N*,*N*-dialkyl-substituted diphenyl(carbamoylmethyl)phosphine oxides for extraction of americium from nitric acid media, and the presence of the hydrogen atom at the nitrogen atom of the amide group increases hydrophilicity of organophosphorus complexation agents and changes the character of complexation compared to CMPO.[8,9] Unlike the latter, extraction of Am^{III} showed no pronounced dependence of the distribution coefficient D_{Am} on the structure of the complexation agent.

The above-described procedure for the preparation of secondary amides **1** has the following limitations: direct amidation of aromatic and aliphatic-aromatic primary amines cannot be performed, *i.e.*, carbamoylmethylphosphine oxides containing an aromatic or CH_2-aryl fragment at the nitrogen atom, as well as phosphinates, in which the substituent in the alkoxy group at the phosphorus atom contains less than eight carbon atoms, cannot be obtained.

The aim of the present study was to develop a new facile procedure for the synthesis of phosphorylacetic acid *N*-aryl(alkylaryl)amides based on the single organophosphorus substrate and commercially available amines and

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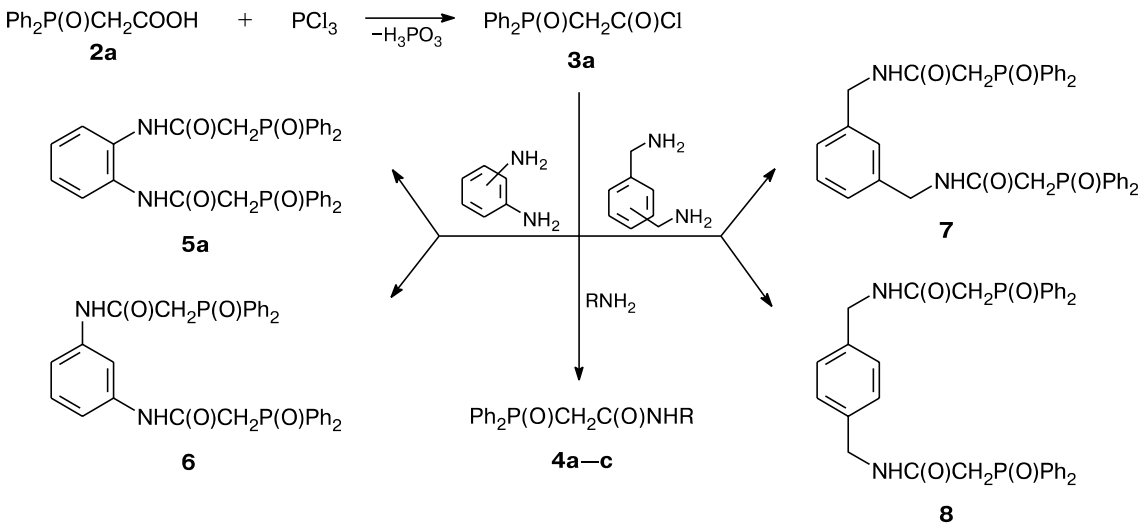
Scheme 1



R = Ph (**4a**), CH_2Ph (**4b**), CH_2CH_2Ph (**4c**)

investigate the extraction properties of the resulting compounds.

Results and Discussion

It seemed reasonable to use the reactions of the corresponding acid chlorides with amines as the simplest approach to the synthesis of phosphorylacetic acid *N*-aryl(benzyl)amides. This approach is widely used in synthetic organic chemistry.[10] Earlier,[11] we have employed the similar procedure for the preparation of *N*-alkyl- and *N*-dialkylamides from phosphorylcycloalkanecarboxylic acids with the use of thionyl chloride as the chlorinating agent. Oxalyl chloride[12] (C_6H_6, ~20 °C) and sulfuryl chloride (CH_2Cl_2, ~20 °C)[13] were used for the synthesis of monosubstituted phosphorylacetic acid chlorides. In the latter study, this chlorinating system was demonstrated to be efficient in preparing diethoxyphosphorylacetic acid chloride in nearly quantitative yield.

However, our attempts to reproduce this procedure[13] for chlorination of phosphorylacetic acids containing labile methylene hydrogens failed. The reactions with the use of thionyl or sulfuryl chloride produced diphenylphosphorylacetic acid chloride in a yield of at most 30—40% in spite of mild reaction conditions.

When studying the model reaction of diphenylphosphorylacetic acid **2a**, we found that phosphorus trichloride is a milder and more efficient chlorinating agent for the transformation of phosphorylacetic acids into the corresponding acid chlorides. The reaction with this agent proceeds at 0 °C and is not accompanied by side processes. Acid chloride **3a** was used in the further reactions with aniline and benzylamine without additional purification to give the corresponding amides **4a,b** in high yields. The analogous reactions with *o*- and *m*-phenylenediamines and *p*- and *m*-xylylenediamines produced compounds **5—8**, in which two diphenylphosphorylmethylcarbamoyl fragments are attached to different positions in the arene moiety (Scheme 1).

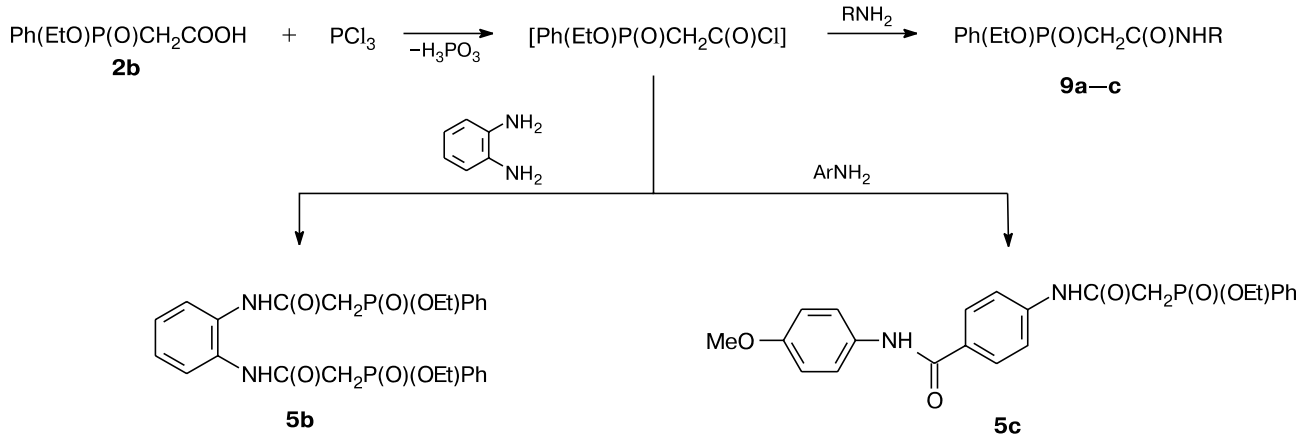
It appeared that this reaction has a general character and allows one to prepare not only the corresponding phosphine oxides but also phosphinates **5b,c** and **9a—c**. In this reaction, both aromatic and aliphatic amines can be used (Scheme 2).

After recrystallization from acetonitrile, chloroform, or (in the case of phosphinates **9a—c**) hexane followed by chromatographic purification, amides **4—9** were isolated as white crystalline compounds. Recrystallization of amide **5a** containing *ortho*-arranged complexing groups from MeCN afforded a stable solvate complex with one solvent molecule (MeCN) and one water molecule (m.p. 124—125 °C).* The structure of this complex was established by X-ray diffraction.

The compositions and structures of the reaction products were confirmed by elemental analysis (Table 1) and IR and NMR spectroscopy (Table 2). The IR spectra of amides **4—9** (KBr pellets) show characteristic absorption bands at 1663—1700 cm^{-1} (C=O) and 1167—1184 cm^{-1} (P=O). Absorption of the NH group appears as a broad band at 3188—3262 cm^{-1} (NH stretching vibrations) and bands at 1540—1556 cm^{-1} (combined frequencies of NH bending vibrations and C—N vibrations). The CH_2 bending vibrations are observed at 1436—1443 cm^{-1}, two

* The solvent molecules can be removed from complex **5a** · MeCN · H_2O upon prolonged keeping *in vacuo* at high temperature (110 °C, 1 Torr, 12 h).

Scheme 2



R = Bu^n (**9a**), *n*-C_6H_{13} (**9b**), *n*-C_8H_{17} (**9c**)

closely spaced absorption bands being observed for the compounds containing the N—Ar bond (**4a**, **5—c**, and **6**). The IR spectra of the resulting *N*-aryl- and *N*-(benzyl)amides are similar to each other and are comparable with the spectra of their *N*-alkyl analogs.[8]

The ^{31}P NMR spectra show singlets at δ 28.02—37.58 for compounds **4a,b**, **5a**, and **6—8** and at δ 38.43—38.46 for compounds **5b,c** and **9a—c**,, *i.e.*, these signals appear in the regions characteristic of this type of environment of the phosphorus atom. The ^{1}H NMR spectra are consistent with the structures of the resulting compounds and have, along with characteristic signals for the hydrogen atoms in the substituents at the phosphorus atom and the amide fragment, the characteristic doublet for the protons

Table 1. Yields, physicochemical constants, and elemental analysis data for the $PhRP(O)CH_2C(O)NHR'$ compounds

Compound	R	R′	Yield* (%)	M.p./°C (solvent)	Found / Calculated (%)			Molecular formula
					C	H	N	
4a	Ph	Ph	100 (68)	227—228 (MeCN)	71.21 / 71.63	5.41 / 5.41	4.11 / 4.18	$C_{20}H_{18}NO_2P$
4b	Ph	CH_2Ph	100 (65)	207 (MeCN)	71.17 / 71.20	5.68 / 5.77	3.99 / 4.01	$C_{21}H_{20}NO_2P$
5a	Ph	(*o*-C_6H_4)NHC(O)CH_2P(O)Ph_2	87 (54)	239—240 (MeCN)	68.96 / 68.92	5.09 / 5.10	4.61 / 4.73	$C_{34}H_{30}N_2O_4P_2$
5b	EtO	(*o*-C_6H_4)NHC(O)CH_2P(O)Ph(OEt)	91 (68)	194—195 (MeCN)	59.18 / 59.09	5.30 / 5.72	5.27 / 5.30	$C_{26}H_{30}N_2O_6P_2$
5c	EtO	(*p*-C_6H_4)C(O)NH(*p*-C_6H_4)OMe	100 (82)	217—218 (EtOAc)	63.36 / 63.71	5.68 / 5.57	6.01 / 6.19	$C_{24}H_{25}N_2O_5P$
6	Ph	(*m*-C_6H_4)NHC(O)CH_2P(O)Ph_2	100 (77)	294—295	68.81 / 68.92	5.07 / 5.10	4.69 / 4.73	$C_{34}H_{30}N_2O_4P_2$
7	Ph	CH_2(*m*-C_6H_4)CH_2NHC(O)CH_2P(O)Ph_2	100 (84)	217—218	69.53 / 69.67	5.38 / 5.52	4.39 / 4.51	$C_{36}H_{34}N_2O_4P_2$
8	Ph	CH_2(*p*-C_6H_4)CH_2NHC(O)CH_2P(O)Ph_2	100 (79)	314—315	69.31 / 69.67	5.37 / 5.52	4.16 / 4.51	$C_{36}H_{34}N_2O_4P_2$
9a	EtO	Bu^n	96 (58)	86—87	59.37 / 59.35	7.75 / 7.83	4.92 / 4.94	$C_{14}H_{22}NO_3P$
9b	EtO	*n*-C_6H_{13}	85 (50)	74—75	61.68 / 61.72	8.51 / 8.42	4.28 / 4.50	$C_{16}H_{26}NO_3P$
9c	EtO	*n*-C_8H_{17}	86 (42)	84—85	63.89 / 63.70	9.01 / 8.91	4.09 / 4.13	$C_{18}H_{30}NO_3P$

* The yield according to the ^{31}P NMR spectroscopic data of the reaction mixture; the yield of the isolated compound is given in parentheses.

Table 2. ^{31}P and ^{1}H NMR and IR spectroscopic data for compounds **4—9**

Compound	NMR ($CDCl_3$, δ, *J*/Hz)		IR, ν/cm^{-1}			
	^{31}P	^{1}H	C=O	CH_2	P=O	NH
4a	30.58	3.51 (d, 2 H, PCH_2, $^2J_{P,H}$ = 12.7); 7.00—7.04 (m, 1 H, H_p, NPh); 7.20—7.23 (m, 2 H, H_m, NPh); 7.53—7.57 (m, 2 H, H_o, NPh); 7.45—7.49 (m, 6 H, H_p, H_m, PPh); 7.72—7.77 (m, 4 H, H_o, PPh); 9.70 (br.s, 1 H, NH)	1684	1443, 1439	1184	3188, 3249
4b	29.81	3.35 (d, 2 H, PCH_2, $^2J_{P,H}$ = 12.8); 4.38 (d, 2 H, NCH_2Ph, $^3J_{H,H}$ = 5.9); 7.08—7.09 (m, 2 H, H_m, $C_6\underline{H}_5CH_2$); 7.18—7.20 (m, 3 H, H_o, H_p, $C_6\underline{H}_5CH_2$); 7.44—7.48 (m, 4 H, H_m, PPh); 7.53—7.56 (m, 2 H, H_p, PPh); 7.68—7.73 (m, 4 H, H_o, PPh); 7.77 (br.s, 1 H, NH)	1663	1438	1175	3252, 1556
5a	30.31	3.75 (d, 4 H, PCH_2, $^2J_{P,H}$ = 13.2); 7.10 (dd, 2 H, $C_{Ar}(4)H$, $C_{Ar}(5)H$, $^3J_{H,H}$ = 5.6, $^4J_{H,H}$ = 3.4); 7.31—7.41 (m, 8 H, H_m, PPh); 7.45—7.50 (m, 4 H, H_p, PPh); 7.59 (dd, 2 H, $C_{Ar}(3)H$, $C_{Ar}(6)H$, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 3.6); 7.64—7.71 (m, 8 H, H_o, PPh); 9.79 (br.s, 2 H, NH)	1700	1436, 1456	1167	3192, 1553
5b	39.08, 39.22	1.19—1.25 (m, 3 H, $C\underline{H}_3CH_2O$); 3.26—3.47 (m, 4 H, PCH_2); 3.97—4.11 (m, 4 H, $MeC\underline{H}_2O$); 6.87—6.91 (m, 1 H, Ar); 7.13—7.21 (m, 2 H, Ar); 7.44—7.51 (m, 4 H, H_m, PPh); 7.54—7.59 (m, 2 H, H_p, PPh); 7.69 (br.s, 1 H, Ar); 7.81—7.86 (m, 4 H, H_o, PPh); 10.07 (br.s, 2 H, NH)	1686	1428, 1439	1210	3270—3152 (br), 1553
5c	36.55	1.32 (t, 3 H, Me, $^3J_{H,H}$ = 7.0); 3.19—3.37 (m, 2 H, PCH_2); 3.80 (s, 3 H, OMe); 3.97—4.03, 4.10—4.18 (both m, 1 H each, $MeC\underline{H}_2O$); 6.88 (d, 2 H, Ar, $^3J_{H,H}$ = 9.0); 7.48—7.52, 7.58—7.63 (both m, 9 H, H_p, H_m, PPh, Ar); 7.78—7.83 (m, 2 H, H_p, Ph, Ar); 8.14, 10.03 (both br.s, 1 H each, NH)	1680	1439	1210	3260
6*	28.19	3.76 (d, 4 H, PCH_2, $^2J_{P,H}$ = 14.2); 7.17—7.18 (m, 3 H, $C_{Ar}(2)H$, $C_{Ar}(4)H$, $C_{Ar}(6)H$); 7.51—7.58 (m, 12 H, H_o, H_p, PPh); 7.79—7.85 (m, 9 H, H_m, PPh, $C_{Ar}(5)H$); 10.14 (s, 2 H, NH)	1685	1437, 1430	1174	1554
7	29.94	3.38 (d, 4 H, PCH_2, $^2J_{P,H}$ = 12.7); 4.30 (d, 4 H, $NHC\underline{H}_2(m\text{-}C_6H_4)C\underline{H}_2NH$, $^3J_{H,H}$ = 6.0); 6.93 (d, 2 H, $C_{Ar}(4)H$, $C_{Ar}(6)H$, $^3J_{H,H}$ = 7.2); 7.00 (br.s, 1 H, $C_{Ar}(2)H$); 7.05 (t, 1 H, $C_{Ar}(5)H$, $^3J_{H,H}$ = 7.3); 7.42—7.47 (m, 8 H, H_m, PPh); 7.52—7.56 (m, 4 H, H_p, PPh); 7.67—7.72 (m, 8 H, H_o, PPh); 7.77 (br.s, 2 H, NH)	1665	1437	1179	3262, 1540
8*	28.02	3.61 (d, 4 H, PCH_2, $^2J_{P,H}$ = 14.2); 4.18 (d, 4 H, $NHC\underline{H}_2(p\text{-}C_6H_4)C\underline{H}_2NH$, $^3J_{H,H}$ = 5.0); 6.99—7.13 (m, 3 H, $C_{Ar}(3)H$, $C_{Ar}(5)H$, $C_{Ar}(6)Hr$); 7.52—7.57 (m, 13 H, H_o, H_p, PPh, $C_{Ar}(2)H$); 7.79—7.84 (m, 8 H, H_m, PPh); 8.42 (br.s, 2 H, NH)	1667	1438	1179	3262, 1552
9a	38.46	0.90 (t, 3 H, Me, $^3J_{H,H}$ = 7.5); 1.29—1.31 (m, 3 H, $MeCH_2O$); 1.32—1.37 (m, 2 H, $NHCH_2CH_2C\underline{H}_2Me$); 1.43—1.50 (m, 2 H, $NHCH_2C\underline{H}_2CH_2Me$); 2.90—3.07 (m, 2 H, PCH_2); 3.23 (q, 2 H, NCH_2, $^3J_{H,H}$ = 6.5); 3.94—3.98, 4.07—4.14 (both m, 1 H each, $MeC\underline{H}_2O$); 7.06 (br.s, 1 H, NH); 7.47—7.57 (m, 3 H, H_p, H_m, PPh); 7.75—7.82 (m, 2 H, H_o, PPh)	1661	1439	1206	3295, 1541
9b	38.43	0.85 (t, 3,H, Me, $^3J_{H,H}$ = 6.4); 1.23—1.34 (m, 9 H, $C\underline{H}_3CH_2O$, $NHCH_2CH_2(C\underline{H}_2)_3Me$); 1.41—1.47 (m, 2 H, $NHCH_2C\underline{H}_2$); 2.88—3.05 (m, 2 H, PCH_2); 3.20 (q, 2 H, NCH_2, $^3J_{H,H}$ = 6.8); 3.89—3.96, 4.04—4.12 (both m, 1 H each, $MeC\underline{H}_2O$); 7.03 (br.s, 1 H, NH); 7.45—7.61 (m, 3 H, H_p, H_m, PPh); 7.73—7.81 (m, 2 H, H_o, PPh)	1662	1439	1205	3296, 1540
9c	38.43	0.86 (t, 3 H, Me, $^3J_{H,H}$ = 6.5); 1.25—1.32 (m, 13 H, $C\underline{H}_3CH_2O$, $NHCH_2CH_2(C\underline{H}_2)_5Me$); 1.44—1.48 (m, 2 H, $NHCH_2C\underline{H}_2$); 2.88—3.06 (m, 2 H, PCH_2); 3.21 (q, 2 H, NCH_2, $^3J_{H,H}$ = 6.6); 3.91—3.97, 4.07—4.13 (both m, 1 H each, $MeC\underline{H}_2O$); 7.00 (br.s, 1 H, NH); 7.48—7.58 (m, 3 H, H_p, H_m, PPh); 7.72—7.83 (m, 2 H, H_o, PPh)	1661	1439	1228, 1204	3290, 1540

* The ^{1}H and ^{31}P NMR spectra were recorded in DMSO-d_6.

of the PCH_2 group at δ 3.35—3.75 with the coupling constant of 12.7—14.2 Hz for phosphine oxides **4a,b**, **5a**, and **6—8**. In the spectra of phosphinates **5b,c** and **9a—c** containing the asymmetric phosphorus atom, this signal appears as an ABX system at δ 2.88—3.07.

To obtain additional data on the resulting neutral ligands, the molecular structures of diphenylphosphorylacetic acid phenylamide **4a** and the solvate of compound **5a**, in which two carbamoylmethylphosphoryl fragments are in the *ortho* positions of the benzene ring, were

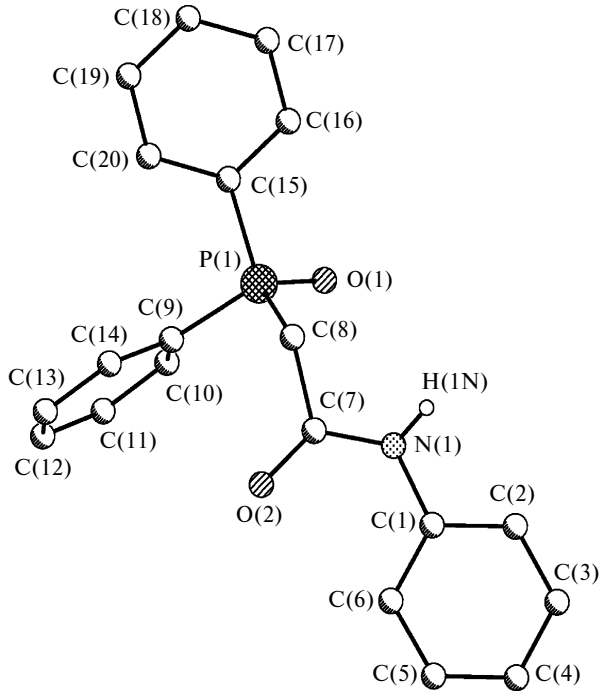


Fig. 1. General view of molecule **4a**.

established by X-ray diffraction. The general views of these compounds are shown in Figs 1 and 2, respectively. Selected bond lengths and bond angles are given in Table 3.

The introduction of the second phosphorus-containing group has no effect on the bond lengths in the carbamoylmethylphosphoryl fragments of compounds **4a** and **5a** (see Table 3). Moreover, a comparison of the mutual arrangement of the amide substituents in amides **4a** and **5a** indicates that the introduction of the second complexing fragment and the presence of the solvent water molecule do not lead to the change in the C(2)—C(1)—N(1)—C(7) torsion angle (in both structures, this angle is 171.1°). The observed stability of the antiperiplanar conformation of the C(2)C(1)N(1)C(2) fragment is evidently attributed to conjugation of the amide group with the aromatic ring. To the contrary, the amide group at the C(2) atom in molecule **5a** is anticlinal (C(1)—C(2)—N(1′)—C(7′) torsion angle is 115.1°), due apparently to steric repulsion between the amide groups.

The conformation of the phosphorylmethylcarbamoyl groups in molecules **4a** and **5a** also changes only slightly. In both compounds, the O(1)—P(1)—C(8)—C(7) and P(1)—C(8)—C(7)—N(1) torsion angles for the substituent at the C(1) atom are virtually equal (63.2, 99.8° and 62.9, 100° for **4a** and **5a**, respectively). The analogous parameters for the substituent at the C(2) atom in **5a** are 46.6 and 81.9°, respectively.

The solvent water molecule in the crystal structure of **5a** is located between two substituents and is held by the N(1′)—H(1N′)...O(1W) (N(1′)...O(1W), 2.865(3) Å) and O(1W)—H(1WB)...O(1) (O(1W)...O(1), 2.898(2) Å)

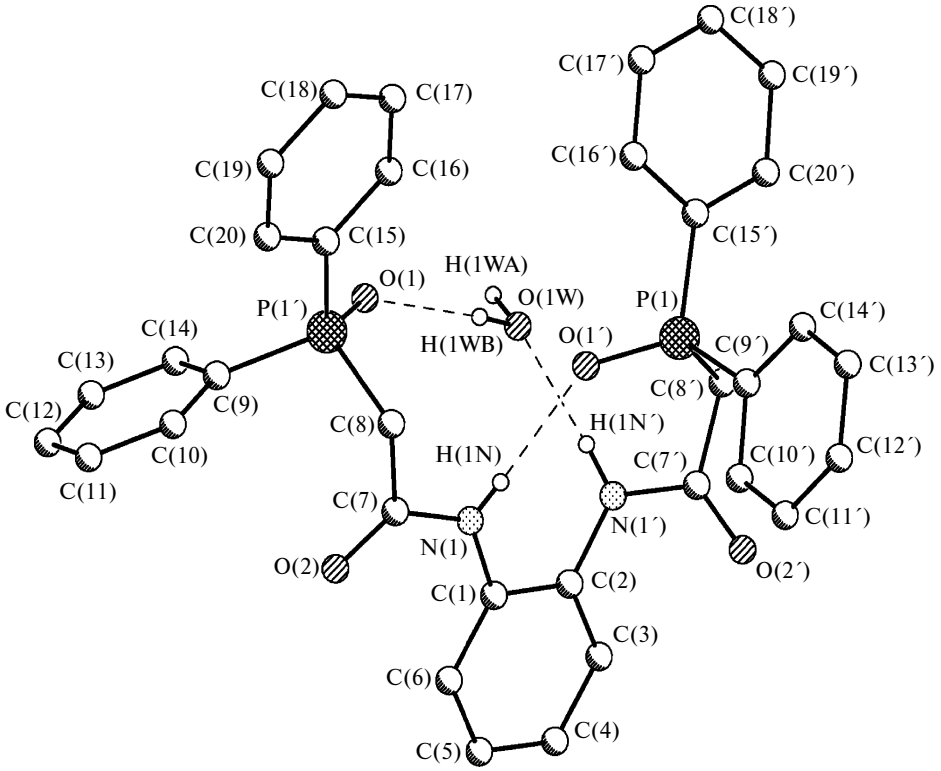


Fig. 2. General view of molecule **5a** · MeCN · H_2O.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecules **4a** and **5a**

Parameter	**4a**
Bond	*d*/Å
P(1)—O(1)	1.494(3)
P(1)—C(8)	1.805(3)
P(1)—C(9)	1.796(3)
P(1)—C(15)	1.812(4)
O(2)—C(7)	1.221(4)
N(1)—C(7)	1.353(4)
N(1)—C(1)	1.415(4)
C(1)—C(2)	1.392(5)
Angle	ω/deg
O(1)—P(1)—C(9)	113.0(1)
O(1)—P(1)—C(8)	111.3(2)
C(9)—P(1)—C(8)	106.6(1)
O(1)—P(1)—C(15)	112.9(1)
C(9)—P(1)—C(15)	108.3(2)
C(8)—P(1)—C(15)	104.1(2)
C(7)—N(1)—C(1)	127.6(3)
C(2)—C(1)—C(6)	119.2(3)
C(3)—C(2)—C(1)	120.1(4)

Parameter	**5a**
Bond	*d*/Å
P(1′)—O(2′)	1.492(2)
P(1′)—C(8′)	1.810(3)
P(1′)—C(9′)	1.797(3)
P(1′)—C(15′)	1.798(3)
O(1′)—C(7′)	1.213(3)
N(1)—C(7)	1.356(4)
N(1)—C(1)	1.412(4)
C(1)—C(2)	1.415(4)
Angle	ω/deg
O(1′)—P(1′)—C(15′)	113.3(1)
O(1′)—P(1′)—C(9′)	110.3(1)
C(15′)—P(1′)—C(9′)	108.0(1)
O(1′)—P(1′)—C(8′)	111.7(1)
C(15′)—P(1′)—C(8′)	105.2(1)
C(9′)—P(1′)—C(8′)	108.05(1)
C(7′)—N(1′)—C(2)	122.4(3)
C(6)—C(1)—C(2)	118.5(3)
C(3)—C(2)—C(1)	120.1(3)

Parameter	**5a**
Bond	*d*/Å
P(1)—O(2)	1.497(2)
P(1)—C(8)	1.804(3)
P(1)—C(9)	1.803(3)
P(1)—C(15)	1.788(3)
O(1)—C(7)	1.225(3)
N(1′)—C(7′)	1.365(4)
N(1′)—C(2)	1.420(4)
Angle	ω/deg
O(1)—P(1)—C(15)	111.9(1)
O(1)—P(1)—C(9)	111.3(1)
C(15)—P(1)—C(9)	109.1(1)
O(1)—P(1)—C(8)	112.3(1)
C(15)—P(1)—C(8)	104.0(1)
C(9)—P(1)—C(8)	107.8(1)
C(7)—N(1)—C(1)	127.7(3)

hydrogen bonds. In addition to these hydrogen bonds, there are also hydrogen bonds through which molecules **5a** in the crystal structure are linked to each other to form dimers, *viz.*, the intramolecular N(1)—H(1N)...O(1′) hydrogen bond (N(1)...O(1′), 2.929(3) Å) and the intermolecular O(1W)—H(1WA)...O(1) hydrogen bond ($1 - x$, $-y$, $-z$) (O(1W)...O(1), 2.801(3) Å). The solvent acetonitrile molecule is located between the H-bonded dimers and is not involved in strong intermolecular interactions.

In the crystal structures of both **4a** and **5a**, there are intermolecular bonds between the amide and phosphoryl groups (N(1)—H(1N)...O(1) (x, $1 - y$, $x + z$), N(1)...O(1), 2.803(2) Å) due to which phenylamide molecules **4a** are linked to each other to form chains along the crystallographic axis *c*. Therefore, in the case of competitive hydrogen bonding in the crystals of **4a** and **5a**, the hydrogen bonds with the phosphoryl groups are more favorable than those with the carbonyl groups.

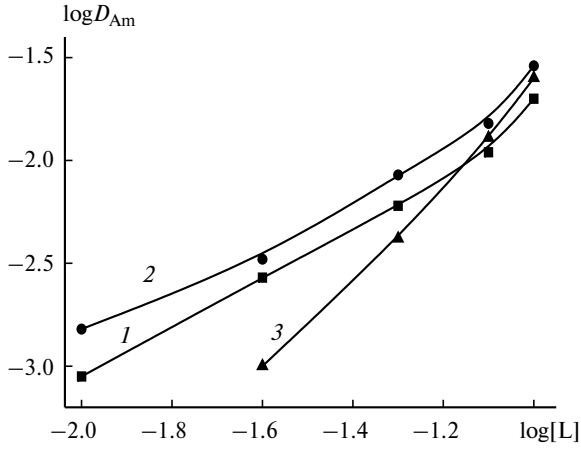


Fig. 3. Plots of the distribution coefficients of Am^{III} for extraction from 3 *M* HNO_3 *vs.* the concentration of the ligands containing different substituents at the nitrogen atom of the carbamoyl group in chloroform: **4a** (*1*), **4b** (*2*), and **4c** (*3*).

Study of the extraction ability of *N*-phosphorylacetic acid aryl(arylalkyl)amides of the general formula $Ph_2P(O)CH_2C(O)NHR$ (R = Ph (**4a**), CH_2Ph (**4b**), and CH_2CH_2Ph (**4c**)) toward Am^{III} demonstrated that complexes extracted by these ligands from 3 *M* HNO_3 solutions into an organic phase differ in composition. This fact is illustrated by the logarithmic dependence of the distribution coefficients of Am^{III} ($\log D_{Am}$) on the concentration of the complexing agent in chloroform (log[L]) shown in Fig. 3. For example, in the concentration range from 0.01 to 0.08 mol L^{-1}, compounds **4a** and **4b** containing the phenyl and benzyl substituents at the nitrogen atom extract Am^{III} as 1 : 1 complexes,* whereas Am^{III} is extracted as a 1 : 2 complex by amide **4c**. According to the data on extraction of trivalent actinides, the compositions of the complexes extracted by carbamoylmethylphosphoryl compounds are generally 1 : 2 or 1 : 3.[14] Presumably, the formation of 1 : 1 Am^{III} complexes with ligands **4a** and **4b** is attributed to steric hindrances due to the presence of the bulky Ph and CH_2Ph substituents, respectively, adjacent to the coordinated carbonyl group, thus hindering binding of the second ligand molecule to Am^{III}. A decrease in steric hindrance in amide **4c** leads to forma-

* A further increase in the concentration of **4a** and **4b** to 0.1 mol L^{-1} leads apparently to extraction of complexes of compositions 1 : 2 (**4a**) and 1 : 3 (**4b**).

tion of a complex of standard composition. The extraction ability of the Am^{III} complexes with the ligands under study differs only slightly. For example, $\log D_{Am}$ for extraction of Am^{III} by 0.05 *M* solutions of **4a**, **4b**, and **4c** in chloroform is −2.22, −2.07, and −2.38, respectively. The experimental data on extraction of Am^{III} show that the extraction ability of carbamoylmethylphosphine oxides containing an *N*-aryl or *N*-alkylaryl fragment is lower than that of analogs containing *N*,*N*-dialkyl or *N*-alkyl substituents studied earlier.[8,15] Apparently, this arises from steric hindrances and the electronic properties of the $-(CH_2)_nPh$ groups, which decrease the basicity and, as a consequence, the complexation and extraction properties of phosphorylacetic acid amides.[16]

To conclude, we developed a one-pot synthetic route to phosphorylacetic acid *N*-aryl(alkylaryl)amides based on the reactions of the corresponding amines and phosphorylacetic chlorides synthesized *in situ* with the use of phosphorus trichloride as a mild chlorinating agent. The obvious advantage of the above-described procedure for the synthesis of alkylamides CMPO-NH over direct amidation of ethyl phosphorylacetates[8] is the absence of limitations on the nature of amine or substituents at the phosphorus atom. The ability of phosphorylacetic acid *N*-aryl(alkylaryl)amides to form complexes with Am^{III} was examined by the extraction method. It was demonstrated that complexes of different composition are extracted into an organic phase depending on the length of the alkylene fragment between the nitrogen atom and the phenyl group.

Experimental

The ^1H and ^{31}P NMR spectra were recorded on Bruker AMX-400 (400.13 and 161.98 MHz, respectively) and Bruker AV-300 (300.09 and 121.49 MHz, respectively) instruments in $CDCl_3$ and DMSO-d_6 with the use of the signal of the residual protons of the deuterated solvent as the internal standard (^1H) and 85% H_3PO_4 as the external standard (^{31}P). The IR spectra were measured on a Magna-IR 750 Fourier-transform spectrometer (Nicolet), the resolution 2 cm^{-1}, the number of scans 128 (KBr pellets).

Starting phosphorylacetic acids **2a**[17] and **2b**[18] were synthesized by hydrolysis of ethyl esters of the corresponding acids according to a modified procedure.[17] Their physicochemical characteristics are identical to those published in the literature.

Phosphorylacetic acids *N*-arylamides (general procedure). Phosphorus trichloride (3.6 mmol) was added dropwise with stirring and cooling to 0 °C to a solution of phosphorylacetic acid (9 mmol) in anhydrous $CHCl_3$ (20 mL). Then cooling was stopped, and the mixture was stirred at 20 °C for 5 h and cooled to 0 °C. A solution of triethylamine (10 mmol) and the corresponding amine (9 mmol) or diamine (4.5 mmol) in anhydrous $CHCl_3$ (20 mL) was slowly added dropwise. The reaction mixture was stirred at 20 °C for 2 h and allowed to stand for ~14 h. Then water (20 mL) was added, the organic layer was separated, washed with water (50 mL), dried with Na_2SO_4, and filtered, the solvent was removed *in vacuo*, and the residue was purified by recrystallization and dried *in vacuo* over P_2O_5 to constant weight. In the case of compounds **6** and **8**, which are virtually insoluble in $CHCl_3$, the organic layer was filtered after washing with water. The resulting crystals were washed with several portions of $CHCl_3$ and dried *in vacuo* over P_2O_5 to constant weight. The yields, physicochemical characteristics, elemental analysis data, and spectroscopic parameters (^1H and ^{31}P NMR and IR) of the resulting compounds are given in Tables 1 and 2. The physicochemical characteristics of diphenylphosphorylacetic acid *N*-phenylethylamide **4c** synthesized according to this procedure are identical to those for compound **4c** prepared by direct amidation of ethyl diphenylacetate with phenylethylamine according to a procedure described earlier.[8]

Table 4. Principal crystallographic data and details of structure refinement for compounds **4a** and **5a**

Parameter	**4a**	**5a**
Molecular formula	$C_{20}H_{18}NO_2P$	$C_{34}H_{30}N_2O_4P_2 \cdot H_2O \cdot MeCN$
Diffractometer	«Syntex $P2_1$»	«Smart CCD»
Radiation	Mo-Kα	Mo-Kα
Scanning technique	θ/2θ	ω
T/K	173	120
Crystal system	Monoclinic	Triclinic
Space group	*Cc*	$P\bar{1}$
a/Å	19.347(6)	8.795(2)
b/Å	11.711(3)	12.832(2)
c/Å	8.102(1)	15.008(3)
α/deg	—	77.446(4)
β/deg	111.68(1)	84.892(5)
γ/deg	—	76.414(5)
V/Å^3	1706.0(7)	1605.9(5)
Z (*Z*′)	4 (1)	2 (1)
M	335.32	651.61
μ/cm^{-1}	1.73	1.84
F(000)	704	684
ρ_{calc}/g cm^{-3}	1.306	1.348
$2\theta_{max}$/deg	50	56
Number of measured reflections (R_{int})	1551 (0.0*)	14146 (0.0580)
Number of independent reflections	1551	7713
Number of observed reflections with $I > 2\sigma(I)$	1371	3832
Number of parameters	290	443
R_1 (based on observed reflections)	0.0335	0.0621
wR_2 (based on all reflections)	0.0840	0.1364
GOF	0.994	0.973
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.262/−0.291	0.582/−0.362

* The value $R_{int} = 0$ is attributed to the fact that the Friedel pairs of zero-layer reflections were in the region of forbidden χ angles due to the LT geometry of the attachement; the completeness of the data set was 99.8%.

X-ray diffraction study of compounds 4a and 5a. X-ray diffraction data sets for compounds **4a** and **5a** were collected on a four-circle Syntex $P2_1$ diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique) at 173 K and a three-circle SMART CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning technique) at 120 K, respectively. Principal crystallographic characteristics and details of structure refinement are given in Table 4. Semiempirical absorption corrections were applied based on equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were located in difference Fourier maps and refined isotropically. All calculations were performed with the use of the SHELXTL PLUS program package.[19]

Extraction was studied with the use of nitric acid solutions of $^{241}Am^{III}$ and nitric acid of special purity grade. Chloroform was used for dilution. Solutions of the complexing agents in dichloroethane were prepared using precisely weighed samples.

The extraction with the complexing agents was studied at 20±1 °C. Aliquots of $^{241}Am^{III}$ in 3 *M* nitric acid and a complexing agent in chloroform were placed in test tubes with ground stoppers. The phases were stirred for 3 min (this time was sufficient to achieve the equilibrium). After separation of the phases by centrifugation, the aliquots were withdrawn, and their γ activity was determined followed by calculations of the distribution coefficients of the elements (*D*). The distribution coefficients were determined as the ratio of the percentage of the element in the organic phase to its percentage in the aqueous phase.

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