Simple route to secondary amides of phosphorylacetic acids and their use for extraction and sorption of actinides from nitric acid solutions

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An efficient method for the synthesis of secondary alkylamides of phosphorylacetic acids (APA) was proposed. The method involves amidation of ethyl phosphorylacetates with primary aliphatic amines. The scope of reaction was determined. Reactions with ethylenediamine and 1,4-diaminobutane yield the corresponding bisamides; in the case of 1,3-diaminopropane, *N*-(3-aminopropyl)diphenylphosphorylacetamide or *N*,*N*′-propylenebis(diphenylphosphorylacetamide) was obtained, depending on the reaction conditions. The extraction of americium(III) complexes and the sorption of uranium(VI) by sorbents with physically sorbed APA from nitric acid solutions were studied. There is no correlation between the partition coefficient of americium(III) and the structure of APA; in the sorption of uranium(VI), the degree of extraction depends on the complexone structure.

Key words: amines, alkylenediamines, phosphorylacetates, ethyl diphenylphosphorylacetate, phosphorylacetamides, carbamoylmethylphosphine oxides, actinides, americium, uranium, extraction, sorption.

Development of nuclear industry and processing of accumulated liquid radioactive wastes necessitates selective extraction of long-lived isotopes (primarily, actinides). For this purpose, liquid-liquid extraction with neutral organophosphorus complexones, *e.g.*, *N*,*N*-dialkylphosphorylacetamides (so-called carbamoylmethylphosphine oxides (CMPO)), is widely used in current practice.[1,2] Their main advantages are that actinides can be quantitatively recovered from highly active salt-containing wastes (HAW) over a wide range of nitrogen acid concentrations without its preliminary correction and that CMPO are well compatible with various solvents. The so-called TRUEX process has been developed in the USA for fractionation of HAW with the use of *N*,*N*-diisobutylcarbamoylmethyl(octylphenyl)phosphine oxide.[2] Its versions were proposed in Japan and Italy. In Russia,[3] this technique was tested in processing of real wastes differing in origin and composition with *N*,*N*-dibutylcarbamoylmethyl(diphenyl)phosphine oxide.[4] At the same time, methods for sorption concentration of actinides from nitric acid media with sorbents (solid extractants) bearing selective complexone groups physisorbed on a polymer matrix are presently under intense development.[5,6] Use of CMPO in such sorbents makes it possible to extract actinides from nitric acid solutions with high partition coefficients.[7,8]

In recent years, CMPO containing the secondary amide fragment —C(O)NHR are of growing interest. The presence of the hydrogen atom at the N atom makes the CMPO molecule hydrophilic and can change the character of complexation with actinide ions and the sorption process as a whole. One can expect that the hydrophilic amide group in secondary alkylamides of phosphorylacetic acids (APA) will increase the hydrophilicity of sorbents bearing noncovalently fixed APA at the polymer matrix, thus promoting the sorption of actinides.

In particular, lanthanide and actinide ions were efficiently extracted from nitric acid media with compounds containing the fragments $NHC(O)CH_2P(O)Ph_2$ fixed on the upper rims of the calix[4]- and calix[5]arene rings,[9] the C_3-symmetrical triphenoxymethane framework,[10] and the carborane fragment.[11] However, such compounds are not easily accessible and no promising route to APA has been found to date. In addition, studies of the extraction and sorption of actinides by the aforesaid compounds containing alkyl substituents have not been documented.

During our investigations directed to syntheses of new types of CMPO and their complexation with *f* elements,[12]

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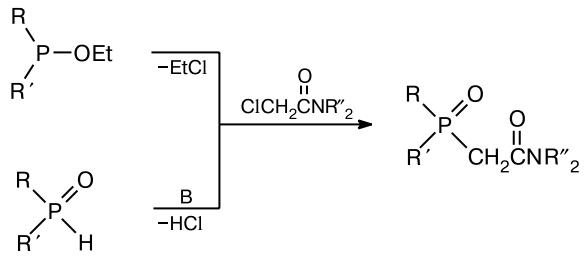
we proposed a simple and efficient method for the synthesis of APA containing the secondary amide fragment —C(O)NHR and estimated the possibility of using them for extraction and sorption concentration of actinides with Am^{III} and U^{VI} as examples.

Usually, phosphorylacetamides are prepared by the Arbuzov or Michaelis—Becker reaction of chloroacetamides with appropriate phosphorus(III) derivatives (Scheme 1).[1,13,14]

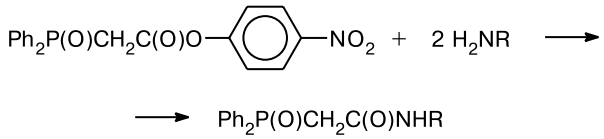
Scheme 1



B is the base

Earlier,[9,11,15] *p*-nitrophenyl diphenylphosphorylacetate was found to undergo amidation into secondary amides (Scheme 2). This method involves only one organophosphorus substrate. However, *p*-nitrophenyl phosphorylacetates are prepared in three steps from commercial ethyl esters, which substantially makes this method less advantageous.

Scheme 2



R = Pr^i, Bu^i, n-C_8H_{17}, $(CH_2)_5NH_2$

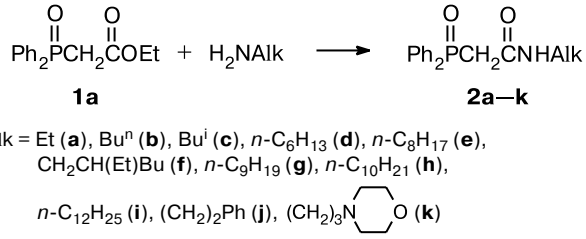
Use of commercially accessible phosphorus-containing reagents would make the synthesis cheaper and allow one to obtain a broad range of compounds at minimum costs.

We found that easily accessible ethyl diphenylphosphorylacetate (**1a**) can also undergo amidation in reactions with primary amines in ethanol (Scheme 3).

The yields of secondary amides (**2**) are nearly stoichiometric. The method is preparatively simple since a variety of secondary amides can be obtained from one organophosphorus reagent and a number of amines.

Although the amidation of carboxylates is well known, the study of the limits of its application showed that ester **1a** reacts in such a way only with primary amines containing an alkyl substituent at the N atom, while secondary, alkylaromatic, and aromatic amines cannot be involved in this reaction. However, when the heterocyclic or aromatic fragment and the N atom in an amine molecule are separated by at least two methylene groups, the reaction easily occurs to give the corresponding amides (**2j,k**).

Scheme 3



Alk = Et (**a**), Bu^n (**b**), Bu^i (**c**), n-C_6H_{13} (**d**), n-C_8H_{17} (**e**), $CH_2CH(Et)Bu$ (**f**), n-C_9H_{19} (**g**), n-$C_{10}H_{21}$ (**h**), n-$C_{12}H_{25}$ (**i**), $(CH_2)_2Ph$ (**j**), (**k**)

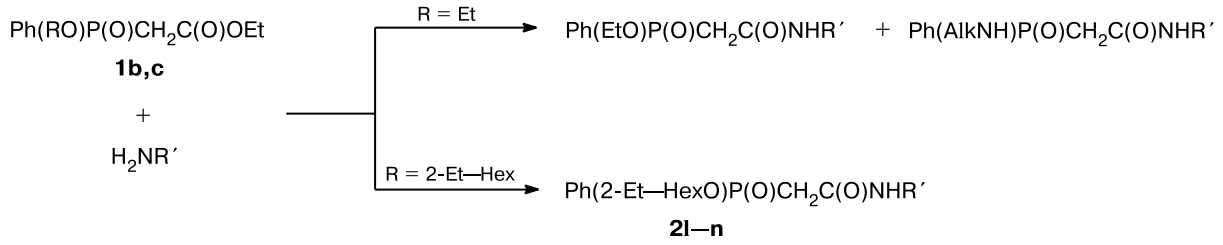
When the P atom in the starting ester bears at least one alkoxy group, the reaction is nonselective, yielding products with amide fragments at both C and P atoms. The ^{31}P NMR spectrum contains two signals of nearly equal intensity: the signal for the carbamide with the phenyl(alkoxy) group at the P atom is shifted downfield by ~4.5 ppm relative to the signal for the starting ethyl phosphorylacetate and the higher-field signal for the corresponding phosphinic acid amide. The amidation proceeds selectively only for sufficiently long radicals R in the alkoxy group RO at the phosphorus atom (Scheme 4).

The amidation of ethyl phosphorylacetates **1a—c** at 20 °C in ethanol was completed over ~10 days to give the target secondary amides **2a—n** in virtually stoichiometric yields. However, heating of a reaction mixture (in the presence of a small excess of the amine) in ethanol or without a solvent in a sealed tube at 100 °C for 8—10 h is more economical. The yields of analytically pure amides **2a—k** containing a phosphine oxide fragment were 68 to 92%. Phosphinates **2l—n** needed purification by chromatography, and their yields were reduced to 36—56%.

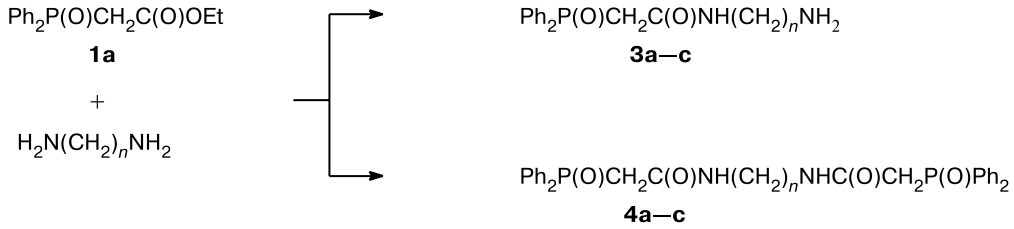
Reactions of alkylenediamines with ethyl diphenylphosphorylacetate **1a** involve either one or both N atoms, depending on the reaction conditions and the number of methylene groups *n* in the alkylene fragment (Scheme 5).

Monoamides (**3**) were prepared in dilute ethanol at room temperature; however, for even numbers *n*, the reaction is slow and the yields of monoamides (**3a**) and (**3c**) (from 1,2-ethylenediamine and 1,4-diaminobutane, respectively) was at most 8 to 9% even for prolonged reaction times. In contrast, amide **3b** was isolated in high yield (77%). An increase in the reaction temperature in EtOH leads to the nonselective formation of a mixture of amides **3** and **4**. With benzene as a solvent, bisamides **4** are the major products, irrespectively of the ratio between the starting reagents and the *n* value. Also, bisamides **4** are predominantly formed in hot concentrated ethanol over several hours. To obtain compounds **4a—c** in high yields,

Scheme 4



Scheme 5



n = 2 (**a**), 3 (**b**), 4 (**c**)

it is expedient to use the starting reagents in a stoichiometric ratio.

A distinctive feature of bisamides **4** is that these compounds with even and odd numbers *n* sharply differ in solubility. Products **4a,c** are poorly soluble in organic solvents; they can be recrystallized from DMF, while bisamide **4b** ($n = 3$) is well soluble in most organic solvents, except for benzene and diethyl ether.

The compositions and structures of products **2a—n**, **3**, and **4a—c** were confirmed by elemental analysis data (Table 1) and IR and NMR spectra (Table 2). Earlier,[16] *N*-ethyl(diphenylphosphoryl)acetamide **2a** was obtained in 63% yield by the Arbuzov reaction from *N*-ethylchloroacetamide and ethyl diphenylphosphinate; however, the spectroscopic data for this compound were missing.[16] Amides **2c,e** obtained earlier[11] from *p*-nitrophenyl diphenylphosphorylacetate were characterized only by IR and ^{1}H NMR spectra.

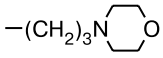
The IR spectra of alkylamides **2a—n**, **3**, and **4a—c** (KBr) show characteristic absorption bands at 1660—1680 (C=O) and 1180—1190 (P=O, **2a—k**) or 1205—1230 cm^{-1} (P=O, **2l—n**). The phosphoryl group in amides **2l—n** manifests itself as two peaks corresponding to the stretching vibrations of free and hydrogen-bound P=O fragments. The NH group absorbs at 3180—3260 (ν(NH), br) and 1540—1560 cm^{-1} (δ(NH) + and ν(C—N)). For the reported[11] amides **2c,e**, the latter band was erroneously assigned to the amide CO vibrations. On the whole, the IR spectra of the secondary amides obtained are similar, except for the vibrations of the corresponding alkyl groups in the substituent R.

The ^{31}P NMR spectra of compounds **2—4** show singlets at δ 30.08—34.72 for the corresponding phosphine oxides and at δ 38.29—38.34 for phosphinates **2l—n**, which are characteristic of this environment of the P atom. Usually, signals for amides **2—4** are shifted downfield compared to signals for the starting esters **1a—c**. Note that the chemical shifts for bisamides **4** are greater than those for compounds **3**. The structures of the compounds obtained were confirmed by ^{1}H NMR spectra containing, along with characteristic sets of signals for the corresponding substituents at the P and N atoms, signals for the PCH_2 protons at δ 3.29—3.71 as a doublet (J = 11.7—13.9 Hz) for compounds **2a—k**, **3**, and **4a—c** (magnetically equivalent) or as a multiplet for compounds **2l—n** with an asymmetric P atom (magnetically nonequivalent).

Thus, we demonstrated that ethyl diphenylphosphorylacetate can be easily and efficiently converted into the corresponding secondary amides by amidation with primary aliphatic amines.

Then, we studied extraction of americium(III) with 0.1 *M* solutions of APA **2b,c,e—h,i** in dichloroethane from nitric acid media. The results obtained are shown in Fig. 1. The highest partition coefficient of Am^{III} (D_{Am}) was attained at $[HNO_3]$ = 3 mol L^{-1} for all the compounds. APA **2b,e,g,h,i** with unbranched alkyl substituents are approximately equal in extraction ability toward Am^{III}. They are as effective as *N*,*N*-dialkylcarbamoylmethyl(diphenyl)phosphine oxides,[17,18] for which the partition coefficient also is insensitive to the structure of the substituent at the N atom.[18] However, APA **2c,f** with branched substituents are noticeably inferior to compounds with *n*-alkyl

Table 1. Yields and elemental analysis data for amides **2a—n**, **3b**, and **4a—c**

Compound	R	R′	Yield (%)	M.p./°C (benzene)	Found / Calculated (%)			Molecular formula
					C	H	N	
2a[a]	Ph	Et	89	163	—	—	—	—
2b	Ph	Bu^n	87	156—157	68.81 / 68.56	7.16 / 7.03	4.55 / 4.44	$C_{18}H_{22}NO_2P$
2c[b]	Ph	Bu^i	92	172—173	68.76 / 68.56	7.09 / 7.03	4.46 / 4.44	$C_{18}H_{22}NO_2P$
2d	Ph	*n*-C_6H_{13}	85	147—148	69.91 / 69.95	7.64 / 7.63	3.90 / 4.08	$C_{20}H_{26}NO_2P$
2e[b]	Ph	*n*-C_8H_{17}	72	149—150	71.28 / 71.14	8.19 / 8.14	3.71 / 3.77	$C_{22}H_{30}NO_2P$
2f	Ph	$Bu^nCH(Et)CH_2$—	74	147—148	70.96 / 71.14	8.14 / 8.14	3.81 / 3.77	$C_{22}H_{30}NO_2P$
2g	Ph	*n*-C_9H_{19}	68	141—142 (xylene)	71.70 / 71.66	8.49 / 8.37	3.60 / 3.63	$C_{23}H_{32}NO_2P$
2h	Ph	*n*-$C_{10}H_{21}$	70	146—147 (xylene)	72.09 / 72.15	8.68 / 8.58	3.57 / 3.51	$C_{24}H_{34}NO_2P$
2i	Ph	*n*-$C_{12}H_{25}$	75	134—135	73.18 / 73.21	8.97 / 8.74	3.18 / 3.28	$C_{26}H_{38}NO_2P$
2j	Ph	$-(CH_2)_2Ph$	78	214—215	72.95 / 72.71	6.04 / 6.10	3.79 / 3.85	$C_{22}H_{22}NO_2P$
2k	Ph		77	188—189	65.31 / 65.27	7.12 / 7.04	6.92 / 7.25	$C_{21}H_{27}N_2O_3P$
2l	$OCH_2CH(Et)Bu$	Bu^n	56	72—73 (hexane)	65.45 / 65.37	9.31 / 9.33	3.81 / 3.81	$C_{20}H_{34}NO_3P$
2m	$OCH_2CH(Et)Bu$	*n*-C_6H_{13}	42	84—85 (hexane)	66.71 / 66.81	9.74 / 9.68	3.54 / 3.54	$C_{22}H_{38}NO_3P$
2n	$OCH_2CH(Et)Bu$	*n*-C_8H_{17}	36	77—78 (hexane)	68.09 / 68.06	10.01 / 9.99	3.31 / 3.31	$C_{24}H_{42}NO_3P$
3b	Ph	$-(CH_2)_3NH_2$	77	134—135 (C_6H_6)	63.72 / 64.55	6.72 / 6.69	8.53 / 8.86	$C_{17}H_{21}N_2O_2P$
4a	Ph	$-(CH_2)_2NHC(O)CH_2P(O)Ph_2$	40	280—281 (DMF)	66.09 / 66.17	5.55 / 5.55	5.07 / 5.14	$C_{30}H_{30}N_2O_4P_2$
4b	Ph	$-(CH_2)_3NHC(O)CH_2P(O)Ph_2$	38	173 (EtOAc; C_6H_6; C_6H_6/CCl_4)	66.52 / 66.66	5.75 / 5.77	5.01 / 5.02	$C_{31}H_{32}N_2O_4P_2$
4c	Ph	$-(CH_2)_4NHC(O)CH_2P(O)Ph_2$	33	240—241 (DMF)	67.21 / 67.13	5.98 / 5.98	4.95 / 4.89	$C_{32}H_{34}N_2O_4P_2$

[a] Ref. 16: m.p. 161—162 °C.
[b] The IR and ^1H NMR spectra are reported in Ref. 11.

substituents in extraction ability toward Am^{III}. Earlier,[19] the negative effect on the extraction of actinides was reported for acidic and neutral organophosphorus extractants with branched alkyl substituents in the alkoxy group at the P atom.

The simplicity of the synthesis of APA with *n*-alkyl substituents makes them promising for extraction of actinides from nitric acid media.

In addition, we studied the sorption of uranium(VI) from nitric acid solutions by sorbents bearing noncovalently fixed APA **2a,b,d,e,g,h** as complexones with diphenylphosphoryl group at the P atom. The corresponding sorbents with [complexone] = 0.26 mmol L^{-1} g^{-1} were prepared by physisorption of APA at an Amberlite XAD-7™ macroporous acrylate matrix (particle size 0.2—0.5 mm).[20,21] Uranium(VI) was sorbed from 5 *M* HNO_3. The results obtained are shown in Fig. 2. It can be seen that the sorption of U^{VI} increases with the lengthening of the substituent at the N atom, reaching the maximum value for each compound upon a 2-h contact between the phases. For *N*-ethyl (**2a**), *N*-nonyl (**2g**), and *N*-decyl derivatives (**2h**), the sorption of U^{VI} over 24 h is lower than that reached in 2 h, which can be due to partial "washout" of the complexones from the polymer matrix to a nitric acid solution during their prolonged contact. For sorbents with physisorbed *N*-butyl (**2b**), *N*-hexyl (**2d**), and *N*-octyl APA (**2e**), the degree of sorption of U^{VI} reached over 2 h does not decline with time (24 h); this

Table 2. ^{31}P and ^{1}H NMR and IR spectra of amides **2a—n**, **3b**, and **4a—c** of the formula $PhRP(O)CH_2C(O)NHR'$

Compound	R	R´	NMR ($CDCl_3$)		IR, ν/cm^{-1}		
			δ_P	^{1}H NMR, δ, *J*/Hz	$\nu_{P=O}$	$\nu_{C=O}$	ν_{NH}
2a	Ph	Et	32.21	0.98 (t, 3 H, Me, $^{3}J_{H,H}$ = 7.3); 3.18 (br.s, 2 H, NCH_2); 3.44 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 12.8); 5.60 (br.s, 1 H, NH); 7.46—7.57 (m, 6 H, *p*- and *m*-C_6H_5P); 7.73—7.78 (m, 4 H, *o*-C_6H_5P)	1165	1670	3290, 1550
2b	Ph	Bu^n	31.26	0.80 (t, 3 H, Me, $^{3}J_{H,H}$ = 7.3); 1.17—1.24 (m, 2 H, $NHCH_2CH_2C\underline{H}_2Me$); 1.32—1.39 (m, 2 H, $NHCH_2C\underline{H}_2CH_2Me$); 3.18 (q*, 2 H, NCH_2, $^{3}J_{H,H} = {}^{3}J_{H,H}$ = 6.6); 3.29 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 12.4); 7.46—7.56 (m, 6 H, *p*- and *m*-C_6H_5P); 7.70—7.74 (m, 4 H, *o*-C_6H_5P); 7.35 (br.s, 1 H, NH)	1187	1662	3280, 1560
2c	Ph	Bu^i	33.25	0.77 (d, 6 H, Me, $^{3}J_{H,H}$ = 6.7); 1.62—1.68 (m, 1 H, CH); 3.00 (br.d, 2 H, NCH_2, $^{3}J_{H,H}$ = 5.5); 3.53 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 13.2); 7.48—7.58 (m, 6 H, *p*- and *m*-C_6H_5P); 7.75—7.80 (m, 4 H, *o*-C_6H_5P); 7.92 (br.s, 1 H, NH)	1170	1680	3310, 1545
2d	Ph	*n*-C_6H_{13}	34.72	0.83 (t, 3 H, Me, $^{3}J_{H,H}$ = 6.7); 1.17—1.23 (m, 6 H, $NHCH_2CH_2(C\underline{H}_2)_3Me$); 1.34—1.37 (m, 2 H, $NHCH_2C\underline{H}_2$); 3.14—3.17 (m, 2 H, NCH_2); 3.62 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 13.2); 7.49—7.59 (m, 6 H, *p*- and *m*-C_6H_5P); 7.77—7.82 (m, 4 H, *o*-C_6H_5P); 8.13 (br.s, 1 H, NH)	1180	1670	3290, 1545
2e	Ph	*n*-C_8H_{17}	34.07	0.86 (t, 3 H, Me, $^{3}J_{H,H}$ = 6.8); 1.17—1.26 (m, 10 H, $NHCH_2CH_2(C\underline{H}_2)_5Me$); 1.35—1.39 (m, 2 H, $NHCH_2C\underline{H}_2$); 3.13—3.17 (m, 2 H, NCH_2); 3.57 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 13.2); 7.49—7.59 (m, 6 H, *p*- and *m*-C_6H_5P); 7.76—7.81 (m, 4 H, *o*-C_6H_5P); 8.01 (br.s, 1 H, NH)	1175 1190	1670	3320 1555—1560
2f	Ph	$Bu^nCH(Et)CH_2$—	30.08	0.75 and 0.82 (both t, 6 H, Me, $^{3}J_{H,H}$ = 7.0); 1.15—1.33 (m, 9 H, $NHCH_2C\underline{H}(C\underline{H}_2CH_3)(C\underline{H}_2)_3Me$); 3.12—3.15 (m, 2 H, NCH_2); 3.30 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 12.2); 7.36 (br.s, 1 H, NH); 7.47—7.55 (m, 6 H, *p*- and *m*-C_6H_5P); 7.70—7.75 (m, 4 H, *o*-C_6H_5P)	1185	1660	3280, 1555
2g	Ph	*n*-C_9H_{19}	30.01	0.88 (t, 3 H, Me, $^{3}J_{H,H}$ = 6.7); 1.17—1.27 (m, 12 H, $NHCH_2CH_2(C\underline{H}_2)_6Me$); 1.37—1.38 (m, 2 H, $NHCH_2C\underline{H}_2$); 3.15—3.20 (m, 2 H, NCH_2); 3.29 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 12.3); 7.34 (br.s, 1 H, NH); 7.46—7.56 (m, 6 H, *p*- and *m*-C_6H_5P); 7.70—7.74 (m, 4 H, *o*-C_6H_5P)	1190	1660	3290, 1555
2h	Ph	*n*-$C_{10}H_{21}$	30.05	0.86 (t, 3 H, Me, $^{3}J_{H,H}$ = 6.8); 1.16—1.28 (m, 14 H, $NHCH_2CH_2(C\underline{H}_2)_7Me$); 1.36—1.37 (m, 2 H, $NHCH_2C\underline{H}_2$); 3.14—3.19 (m, 2 H, NCH_2); 3.29 (d, 2 H, PCH_2, $^{2}J_{P,H}$ = 12.4); 7.36 (br.s, 1 H, NH); 7.44—7.56 (m, 6 H, *p*- and *m*-C_6H_5P); 7.72—7.83 (m, 4 H, *o*-C_6H_5P)	1185	1660	3290, 1555

(*to be continued*)

Table 2 (*continued*)

Compound	R	R´	NMR ($CDCl_3$)		IR, ν/cm^{-1}		
			δ_P	^{1}H NMR, δ, *J*/Hz	$\nu_{P=O}$	$\nu_{C=O}$	ν_{NH}
2i	Ph	*n*-$C_{12}H_{25}$	30.11	0.87 (t, 3 H, Me, $^3J_{H,H}$ = 6.4); 1.12—1.28 (m, 14 H, $NHCH_2CH_2(C\underline{H}_2)_9Me$); 1.32—1.40 (m, 2 H, $NHCH_2C\underline{H}_2$); 3.14—3.19 (m, 2 H, NCH_2); 3.29 (d, 2 H, PCH_2, $^2J_{P,H}$ = 12.3); 7.35 (br.s, 1 H, NH); 7.48—7.56 (m, 6 H, *p*- and *m*-C_6H_5P); 7.69—7.74 (m, 4 H, *o*-C_6H_5P)	1190	1660	3290, 1545
2j	Ph	—$(CH_2)_2$Ph	31.07	2.60 (br.s, 1 H, NH); 2.67—2.71 (m, 2 H, $NHCH_2C\underline{H}_2$); 3.32 (d, 2 H, PCH_2, $^2J_{P,H}$ = 11.7); 3.43 (br.s, 2 H, NCH_2); 7.11—7.24 (m, 5 H, $NCH_2CH_2C_6\underline{H}_5$); 7.35—7.55 (m, 6 H, *p*- and *m*-C_6H_5P); 7.67—7.78 (m, 4 H, *o*-C_6H_5P)	1190	1660	3268, 1555
2k	Ph	—$(CH_2)_3$N⟨O⟩	30.60	1.78 (pentet, 2 H, $NCH_2C\underline{H}_2$, $^3J_{H,H}$ = 6.3); 3.85 (br.s, 4 H, —$C\underline{H}_2$—O—$C\underline{H}_2$—); 3.35 (d, 2 H, PCH_2, $^2J_{P,H}$ = 12.6); 3.28—3.33 (m, 2 H, NCH_2); 2.52—2.77 (two m, 6 H, —$C\underline{H}_2$—N—$(C\underline{H}_2)(C\underline{H}_2)$—); 7.46—7.49 (m, 6 H, *p*- and *m*-C_6H_5P); 7.69—7.81 (m, 4 H, *o*-C_6H_5P); 7.87 (br.s, 1 H, NH)	1185	1670	3290, 1550
2l	$OCH_2CH(Et)Bu$	Bu^n	38.34	0.80—0.90 (three t**, 9 H, Me); 1.14—1.54 (m, 13 H, *n*-$Me(C\underline{H}_2)_3C\underline{H}(C\underline{H}_2CH_3)CH_2O$—, $NHCH_2C\underline{H}_2C\underline{H}_2Me$); 2.87—3.06 (m, 2 H, PCH_2); 3.21 (q*, 2 H, NCH_2, $^3J_{H,H}$ = 4.8); 3.66—3.74 and 3.89—3.95 (two m, 2 H, $MeC\underline{H}_2O$); 7.07 (br.s, 1 H, NH); 7.46—7.59 (m, 3 H, *p*- and *m*-C_6H_5P); 7.72—7.77 (m, 2 H, *o*-C_6H_5P)	1210, 1230	1660	3280, 1554
2m	$OCH_2CH(Et)Bu$	*n*-C_6H_{13}	38.29	0.81—0.86 (three t***, 9 H, Me); 1.15—1.55 (m, 17 H, *n*-$Me(C\underline{H}_2)_3C\underline{H}(C\underline{H}_2CH_3)CH_2O$—, $NHCH_2C\underline{H}_2(C\underline{H}_2)_3Me$); 2.88—3.06 (m, 2 H, PCH_2); 3.18—3.24 (m, 2 H, NCH_2); 3.69—3.75 and 3.90—3.97 (two m, 2 H, $MeC\underline{H}_2O$); 7.05 (br.s, 1 H, NH); 7.47—7.60 (m, 3 H, *p*- and *m*-C_6H_5P); 7.73—7.78 (m, 2 H, *o*-C_6H_5P)	1205, 1225	1661	3276, 1555
2n	$OCH_2CH(Et)Bu$	*n*-C_8H_{17}	38.29	0.80—0.87 (three t***, 9 H, Me); 1.15—1.54 (m, 21 H, *n*-$Me(C\underline{H}_2)_3C\underline{H}(C\underline{H}_2CH_3)CH_2O$—, $NHCH_2C\underline{H}_2(C\underline{H}_2)_5Me$); 2.87—3.05 (m, 2 H, PCH_2); 3.17—3.23 (m, 2 H, NCH_2); 3.68—3.73 and 3.91—3.96 (two m, 2 H, $MeC\underline{H}_2O$); 7.06 (br.s, 1 H, NH); 7.48—7.61 (m, 3 H, *p*- and *m*-C_6H_5P); 7.72—7.79 (m, 2 H, *o*-C_6H_5P)	1205, 1225	1661	3274, 1555
3b	Ph	—$(CH_2)_3NH_2$	30.13	1.50 (quint, 2 H, $NHCH_2C\underline{H}_2CH_2NH_2$, $^3J_{H,H}$ = 6.6); 1.54—1.69 (m, 3 H, NH_2 + NH); 2.54 (t, 2 H, —$C\underline{H}_2NH_2$, $^3J_{H,H}$ = 6.8); 3.27 (q, 2 H, —$NHC\underline{H}_2$, $^3J_{H,H}$ = 6.2); 3.29 (d, 2 H, PCH_2, $^2J_{P,H}$ = 12.1); 7.47—7.55 (m, 6 H, *p*- and *m*-C_6H_5P); 7.70—7.73 (m, 4 H, *o*-C_6H_5P)	1185	1655	3242 br, 1562 br

(*to be continued*)

Table 2 (*continued*)

Compound	R	R´	NMR ($CDCl_3$)		IR, ν/cm^{-1}		
			δ_P	^{1}H NMR, δ, *J*/Hz	$\nu_{P=O}$	$\nu_{C=O}$	ν_{NH}
4a***	Ph	$-(CH_2)_2NHC(O)CH_2P(O)Ph_2$	29.39	3.15 (br.s, 4 H, NH(C<u>H</u>$_2$)$_2$NH); 3.71 (d, 4 H, PCH_2, $^2J_{P,H}$ = 13.9); 7.59—7.67 (m, 12 H, *p*- and *m*-C_6H_5P); 7.90—7.95 (m, 8 H, *o* -C_6H_5P); 8.41 (br.s, 2 H, NH)	1176	1662	3271, 1558
4b	Ph	$-(CH_2)_3NHC(O)CH_2P(O)Ph_2$	32.77	1.71 (quint, 2 H, $NHCH_2C\underline{H}_2CH_2NH$, $^3J_{H,H}$ = 6.8); 3.35 (q, 4 H, $NHC\underline{H}_2CH_2C\underline{H}_2NH$, $^3J_{H,H}$ = 5.4); 3.61 (d, 4 H, PCH_2, $^2J_{P,H}$ = 13.6); 7.32—7.37 (m, 8 H, *p*-C_6H_5P); 7.46—7.49 (m, 4 H, *m*-C_6H_5P); 7.62—7.66 (m, 8 H, *o*-C_6H_5P); 9.03 (br.s, 2 H, NH)	1173	1667	3258 br, 1541 br
4c***	Ph	$-(CH_2)_4NHC(O)CH_2P(O)Ph_2$	28.94	1.30 (br.s, 4 H, $NHCH_2(C\underline{H}_2)_2CH_2NH$); 3.05 (br.s, 4 H, $NHC\underline{H}_2(CH_2)_2C\underline{H}_2NH$); 3.69 (d, 4 H, PCH_2, $^2J_{P,H}$ = 13.1); 7.59—7.65 (m, 12 H, *p*- and *m*-C_6H_5P); 7.91—7.93 (m, 8 H, *o*-C_6H_5P); 8.19 (br.s, 2 H, NH)	1179	1663	3284 1547,

* The discernible quartet.
** The overlapping triplets.
*** The ^{1}H and ^{31}P NMR spectra were recorded in DMF-d_7.

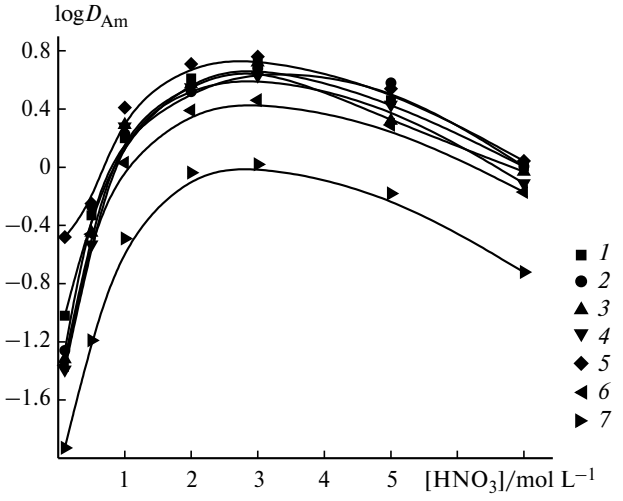


Fig. 1. Extraction curves of Am^{III} at different [HNO_3] values. The extractants are 0.1 *M* solutions of APA **2b,c,e—h,i** in dichloroethane: (*1*) Bu^n, (*2*) *n*-Oct, (*3*) *n*-Non, (*4*) *n*-Dec, (*5*) *n*-Dodec, (*6*) Bu^i, and (*7*) 2-EtHex.

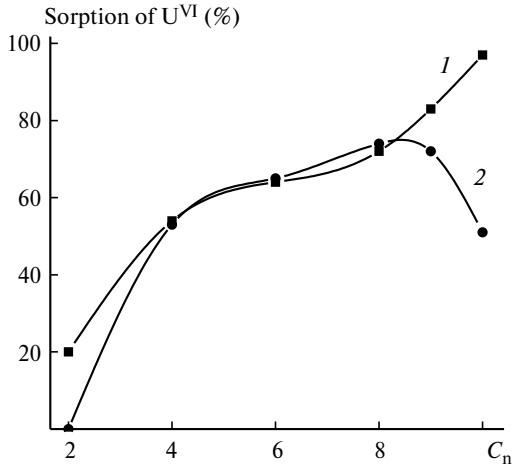


Fig. 2. Sorption of uranium(VI) (%) from 5 *M* HNO_3 by sorbents with physically sorbed *N*-alkylcarbamoylmethyl(diphenyl)phosphine oxides **2a,b,d,e,g,h** differing in the length of the alkyl radical at the N atom (R = *n*-C_2—C_{10}); static conditions, the initial concentration [UO_2^{2+}] = 10 mg L^{-1}, *V*/*m* = 500 mL g^{-1}; phase contact time was (*1*) 2 and (*2*) 24 h.

can probably be attributed to the low solubilities of these compounds in nitric acid. Apparently, the sorption equilibrium of U^{VI} between the contacting phases is established within the first two hours.

The data on the extraction of uranium and the rate at which the equilibrium is established suggest that the sorbent containing *N*-octyl APA **2e** as a complexone is best suitable for the sorption of actinides from nitric acid solutions.

Hence, we developed the simple and efficient method for the synthesis of *N*-alkylcarbamoylmethyl(diphenyl)phosphine oxides by amidation of ethyl diphenylphosphorylacetate. The compounds obtained are efficient

extractants for extraction of actinides from nitric acid solutions; APA with an unbranched substituent at the N atom are more efficient than their branched analogs. The compounds obtained can be used to prepare complexone-bearing sorbents (solid extractants) for extraction of uranium(VI) from nitric acid solutions. The most efficient sorbent was prepared by physisorption of *N*-*n*-octylcarbamoylmethyl(diphenyl)phosphine oxide at a XAD-7^{TM} matrix.

Experimental

NMR spectra were recorded on Bruker WP-200SY and Bruker AMX-400 instruments in $CDCl_3$ and DMF-d_7 with residual protons of the deuterated solvent as the internal standard (^{1}H, ^{13}C) and to 85% H_3PO_4 as the external standard (^{31}P). ^{13}C NMR spectra were recorded in the JMODECHO regime; signals for the C atoms bearing even and odd numbers of protons are of opposite polarity. IR spectra were recorded on a Magna-IR 750 FTIR-spectrometer (Nicolet Co., resolution 2 cm^{-1}, scan number 128, KBr pellets).

The starting phosphorylacetates **1a,b** were prepared according to a standard procedure by the Arbuzov rearrangement of ethyl esters of P^{III} acids with ethyl bromoacetate; the physicochemical constants of compounds **1a,b** agreed with the literature data.[22]

Ethyl 2-ethylhexyloxy(phenyl)phosphorylacetate (1c) was prepared by analogy with compounds **1a,b** from bis(2-ethylhexyl) phenylphosphonite and ethyl bromoacetate and purified by chromatography on silica gel (SiO_2 100/160 mesh, Aldrich) in hexane—acetone with a gradient from 100 : 1 to 100 : 30. The yield of compound **1c** was 85%, heavy oil. Found (%): C, 63.43; H, 8.37; P, 8.93. $C_{18}H_{29}O_4P$. Calculated (%): C, 63.51; H, 8.59; P, 9.10. ^{31}P NMR ($CDCl_3$), δ: 34.09. ^{1}H NMR ($CDCl_3$), δ: 0.81—0.87 (m, 6 H, Me); 1.13 (t, 3 H, C(O)OCH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 8.2 Hz); 1.20—1.45 (m, 8 H, *n*-CH$_3$(C$\underline{H}_2$)$_3$CH(C$\underline{H}_2$CH$_3$)CH$_2$O—); 1.53—1.58 (m, 1 H, *n*-CH$_3$(CH$_2$)$_3$C$\underline{H}$(CH$_2$CH$_3$)CH$_2$O); 3.11 (dq, 2 H, PCH$_2$, $^2J_{P,H}$ = 18.0 Hz and $^2J_{H,H}$ = 17.5 Hz); 3.82—3.74 and 3.96—4.02 (both m, 2 H each, POCH$_2$); 4.05 (q, 2 H, C(O)C$\underline{H}_2$, $^3J_{H,H}$ = 8.2 Hz); 7.44—7.84 (m, 5 H, C_6H_5P).

***N*-Alkylphosphorylacetamides 2a—n (general procedure).** A mixture of compound **1a,c** (2 mmol) and a primary amine (3 mmol) in 10 mL of anhydrous EtOH was heated in a sealed tube in a boiling water bath for 8 to 10 h. The tube was opened, the solvent was removed *in vacuo*, and the residue was recrystallized (**2a—k,m,n**) or purified by column chromatography on silica gel (**2l**) in hexane—acetone with a gradient from 100 : 1 to 100 : 30 followed by crystallization while triturating it with hexane. The yields, physicochemical constants, and elemental analysis data are given in Table 1. The parameters of the ^{1}H and ^{31}P NMR and IR spectra are presented in Table 2.

***N*-(3-Aminopropyl)diphenylphosphorylacetamide (3b).** A mixture of ester **1a** (0.576 g, 2 mmol) and 1,3-diaminopropane (0.128 g, 2 mmol) in 10 mL of anhydrous ethanol was stored at 20 °C until compound **1a** was consumed (monitoring by ^{31}P NMR). The solvent was removed *in vacuo* and the residue was recrystallized from benzene to give amide **3b** (0.49 g, 77%). The physicochemical constants and elemental analysis data are given in Table 1. The parameters of the ^{1}H and ^{31}P NMR and IR spectra are presented in Table 2. ^{13}C NMR ($CDCl_3$), δ: 32.45 (NH$_2$CH$_2$C$\underline{H}_2$); 37.07 (NH$_2$CH$_2$); 38.50 (d, PCH$_2$, $^1J_{P,C}$ = 60.0 Hz); 39.00 (NHCH$_2$); 128.63 (d, *m*-C, Ph, $^3J_{P,C}$ = 12.4 Hz); 130.50 (d, *o*-C, Ph, $^2J_{P,C}$ = 9.6 Hz); 131.34 (d, *ipso*-C, C_6H_5P, $^1J_{P,C}$ = 102.8 Hz); 132.17 (d, *p*-C, Ph, $^4J_{P,C}$ = 2.8 Hz); 164.49 (NHC(O), $^2J_{P,C}$ = 4.4 Hz).

1,3-Bis(diphenylphosphorylacetylamino)propane (4b). A mixture of ester **1a** (0.576 g, 2 mmol) and 1,3-diaminopropane (0.74 g, 1 mmol) in 10 mL of anhydrous benzene was stored at 20 °C until compound **1a** was consumed (monitoring by ^{31}P NMR). The solvent was removed *in vacuo* and the residue was recrystallized three times from ethyl acetate, C_6H_6, and C_6H_6/CCl_4 in succession. The yield of the target bisamide **4b** was 0.42 g (38%). The physicochemical constants and elemental analysis data are given in Table 1. The parameters of the ^{1}H and ^{31}P NMR and IR spectra are presented in Table 2. ^{13}C NMR ($CDCl_3$), δ: 27.85 (NH$_2$CH$_2$C$\underline{H}_2$); 38.74 (d, PCH$_2$, $^1J_{P,C}$ = 60.2 Hz); 39.50 (NHCH$_2$); 128.52 (d, *m*-C, Ph, $^3J_{P,C}$ = 12.4 Hz); 130.59 (d, *o*-C, Ph, $^2J_{P,C}$ = 9.7 Hz); 131.80 (d, *ipso*-C, C_6H_5P, $^1J_{P,C}$ = 103.2 Hz); 132.92 (d, *p*-C, Ph, $^4J_{P,C}$ = 2.8 Hz); 164.26 (NHC(O), $^2J_{P,C}$ = 6.4 Hz).

Bis(diphenylphosphorylacetylamino)alkanes (4a,c). A mixture of ester **1a** (0.576 g, 2 mmol) and an alkylenediamine (1 mmol) in 3 mL of anhydrous ethanol was heated in a sealed tube in a boiling water bath until compound **1a** was consumed (monitoring by the ^{31}P NMR method). The tube was opened, the solvent was removed *in vacuo*, and the residue was recrystallized from DMF. The recrystallized product was additionally washed with water (5 mL) and EtOH (5 mL). The yields, physicochemical constants, and elemental analysis data are given in Table 1. The parameters of the ^{1}H and ^{31}P NMR and IR spectra are presented in Table 2.

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