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To the 100th Anniversary of A.N. Pudovik

α- and β-Diphenylphosphorylated Secondary Alkanols: I. General Method of Synthesis and Extraction Properties Towards *f*-Elements

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Abstract—A simple and effective general method of synthesis of α- and β-diphenylphosphorylated secondary alkanols by the reduction of the corresponding phosphorylalkanones with $NaBH_4$ was developed. The extraction properties of the resulting phosphorylalkanols $Ph_2P(O)(CR_2)_nCH_2CH(OH)Me$ (n = 0, 1; R = H, Me) were studied in the recovery of *f*-elements (La^{III}, Nd^{III}, Ho^{III}, Yb^{III}, U^{VI}, Th^{IV}) from nitric acid solutions into chloroform and compared with those of both related phosphorylketones and known extractants (n-$BuO)_3PO$, (n-$C_8H_{17})_3PO$, and $Ph_2P(O)CH_2C(O)N(n\text{-}Bu)_2$.

Keywords: *P,P*-diphenylphosphorylalkanones, sodium borohydride, secondary *P,P*-diphenylphosphorylalkanols, lanthanides, extraction

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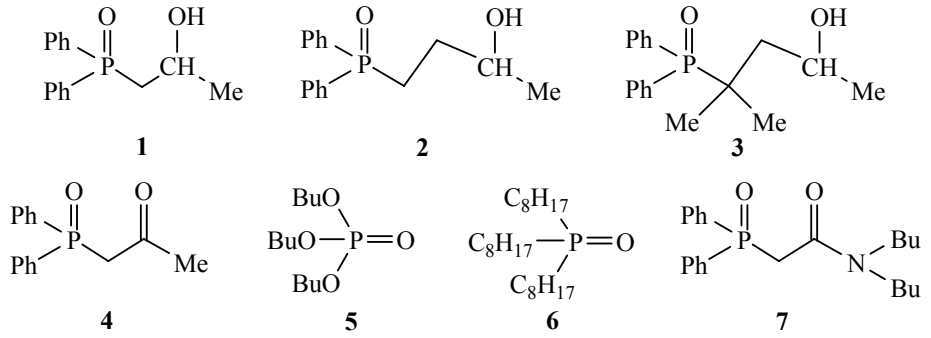
Solvent extraction is one of the methods most commonly used for the recovery and separation of elements with similar properties in hydrometallurgy and spent nuclear fuel reprocessing [1–4]. The most popular extractants in the industry are neutral organophosphorus compounds of diverse types [4–7]. The efficiency of extraction processes is known to be governed primarily by the choice of extractant that should fit to specific and fairly stringent requirements including high efficiency and selectivity in the extraction of target metals, low cost, chemical stability, easy stripping, etc. [1, 3–5].

Recently, acetyl-containing phosphine oxides were suggested as extractants for the separation of lanthanides. Compounds of this group $R_2P(O)–X–C(O)Me$ (R = Alk, cyclo-Alk, Ph; X – various linkers) were shown to be much more effective than the known extractants, e.g., tributyl phosphate $(BuO)_3PO$, trioctylphosphine oxide $(C_8H_{17})_3PO$, and carbamoylmethylphosphine oxide $Ph_2P(O)CH_2C(O)NBu_2$, in the extraction of heavy lanthanides from HNO_3 solutions into chloroform [8–10]. Also, the first data on the recovery of lanthanides from acidic media by micellar extraction with the use of the same acetyl-containing phosphine oxides as chelating agents [11] proved to be very interesting. One of the most effective phosphorylketones, $Ph_2P(O)CHMeCH_2C(O)Et$, was used in the development of extraction techniques for the recovery of lanthanides from low-margin mineral raw materials eudialyte [12] and phosphogypsum [13]. In complexing with lanthanide cations phosphorylketones typically exhibit P=O-monodentate coordination, but in the presence of C=O group in the molecule of the extractant its efficiency increases due presumably to the involvement of the carbonyl group[1] in additional

[1] The involvement is directly evidenced by high extraction capability towards lanthanides, exhibited by phosphorylketone $Ph_2P(O)CH_2CH_2C(O)Me$ compared to phosphine oxide $Ph_2P(O)Bu$-*n* [9].

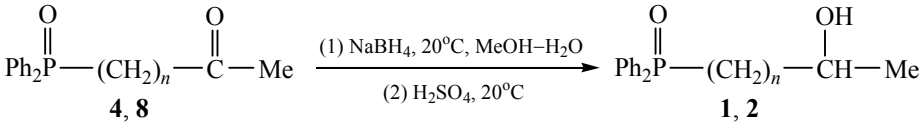
Scheme 1.



1 **2** **3**

4 **5** **6** **7**

Scheme 2.



4, **8** **1**, **2**

n = 1 (**1**, **4**), 2 (**2**, **8**).

weak interactions (hydrogen bonding, solvation, weak coordination bonding, etc.). Hence it can be expected that the modification of the structure of phosphine oxides by introducing another additional donor center which is not involved, or weakly involved, in coordination will also lead to more effective and selective extractants than unmodified prototypes. For example, in the structure of phosphorylalkanols, along with the phosphoryl group responsible for coordination, there is a center able to participate in weak interactions, OH group. In nonaqueous media phosphorylalkanols can form associates[2] $(L–OH)_n$ via intermolecular >P=O···HO– bonds. In this case, it can be expected that the extracted complexes will comprise not only the L–OH molecules but also associated $(L–OH)_n$ particles, whereby the extractability of the complexes will be enhanced. The molecules and associates in such complexes will form coordination bonds with *f*-element cations via P=O group, and the size (lipophilicity) of the coordinated ligand will increase due to intermolecular hydrogen bonding. Aggregation is well known to significantly improve the efficiency of extraction by acidic podands and acids of phosphorus [14–19].

Here, we synthesized a series of phosphorylalkanols **1–3** which are structurally related to the previously studied phosphorylketones [9], and this allowed us to subsequently assess most properly the influence of the structure modification on the extraction properties of ligands.

The extraction capabilities of phosphorylalkanols **1–3** towards *f*-elements were examined by analyzing how they are influenced by the structure of the linker between the P=O and CH(OH) groups. As references served phosphorylketone $Ph_2P(O)CH_2C(O)Me$ which is structurally related to alcohol **1**, as well as known organophosphorus extractants **5–7** (Scheme 1).

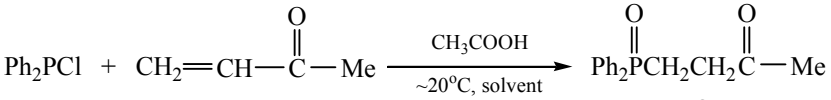
A number of α- and β-diphenylphosphorylated[3] secondary alkanols was described in the literature, but currently there exists no general simple, powerful, and technologically effective method for the synthesis of compounds of this type. It therefore seemed logical to develop a method for direct reduction of structurally similar phosphorylketones whose preparation methodology is fairly well established (see, e.g., [20]). This approach was tested on the synthesis of simplest α- and β-diphenylphosphorylalkanols **1** and **2**.

We found that the reduction of phosphorylated acetone **4** and 4-(diphenylphosphoryl)butan-2-one **8** by an excess of $NaBH_4$ in a water-methanol medium proceeds vigorously at room temperature with negligible formation of byproducts and gives target phosphorylalkanols **1** and **2** in nearly quantitative yields (Scheme 2).

[2] Along with associates, phosphorylalkanol molecules with intramolecular hydrogen bond can participate in the equilibrium.

[3] In this case, similarly to the previously studied phosphorylketones [9], compounds are considered in which the linker between the $Ph_2P(O)$ and CH(OH) moieties contains no more than two carbon atoms.

Scheme 3.



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Compound **1** obtained by this method is an air-stable white crystalline substance, mp 97.0–98.5°C. Although it exhibits unusually large differences in the physicochemical constants compared to those presented in various publications,[4] its structure was unambiguously confirmed by NMR and X-ray diffraction data.

As to alcohol **2**, the most efficient reported approach to its synthesis is based on the reaction of CH_2=CHCH(OH)CH_3 with diphenylphosphinous acid in a methanol-hexane medium at ~20°C in the presence of catalytic amounts of Et_3B, which affords only 80% yield of the target alcohol [24]. The preparation of alcohol **2** by the reduction of the corresponding ketone that we have developed proceeds under equally mild conditions but does not require the use of catalysts and allows isolation of the target product in a significantly higher yield.

We also explored the possibility of using a tw*o*-step one-pot process for preparation of β-diphenylphosphorylated secondary alkanols with the use of diphenylchlorophosphine as the initial organophosphorus compound. The first step of this process, conversion of Ph_2PCl to 4-(diphenylphosphoryl)butan-2-ones, could be based on the classical Conant reaction [25],[5] which is considered with good reason to be the best method for the synthesis of phosphorylketones [26]. Today the most efficient version of this reaction, which was implemented for the synthesis of simplest β-diphenylphosphorylated alkanone **8,** is the reaction of Ph_2PCl with the corresponding α,β-enone in anhydrous benzene at room temperature [27]. Unfortunately, a significant drawback of this method is a low reaction rate, with 42 h required for the reaction to go to completion. We believed that the use of a different solvent would significantly accelerate the process and so studied the reaction in diethyl ether, methylene chloride, and acetonitrile (Scheme 3).

Our experiments showed that in diethyl ether the reaction was complete after 5 days (67.5% yield). By contrast, the process was greatly accelerated when methylene chloride was used as the solvent (reaction time 8 h, 74.1% yield). In acetonitrile the reaction was complete within 3 h (75.3% yield). Thus, the use of MeCN significantly intensifies the synthesis of phosphorylketone **8**.[6]

Since both the synthesis of phosphorylketone **8** by the Conant reaction[7] and the reduction of this ketone by sodium borohydride proceed at room temperature at a fairly high rate without formation of any significant amounts of byproducts, we could reasonably expect that these processes might be effectively combined into a single one-pot process.

Indeed, elimination of the stage of isolation of ketone **8** as individual component in this case substantially simplifies the procedure of preparation of the target phosphoryl carbinol **2**, with its yield remaining very high, 90.9% (Scheme 4).

Further, a similar one-pot process (Scheme 4) we used equally successfully (87.6% yield) for obtaining a previously unknown phosphorylalkanol **3**, whose structure was confirmed by spectral and X-ray diffraction data.

Thus, we showed that the reduction of diphenylphosphorylalkanones with sodium borohydride in a water-methanol medium is a simple general powerful method for the synthesis of the corresponding α- and β-diphenylphosphorylated secondary alkanols, and this reaction is suitable in principle as the final stage of a technologically effective one-pot processes.

The extraction capabilities of phosphorylalkanols **1–3** towards *f*-elements were studied in the extraction of a group of lanthanides(III), as well as of uranium(VI) and thorium(IV) from nitric acid water solutions into chloroform at varied nitric acid con-

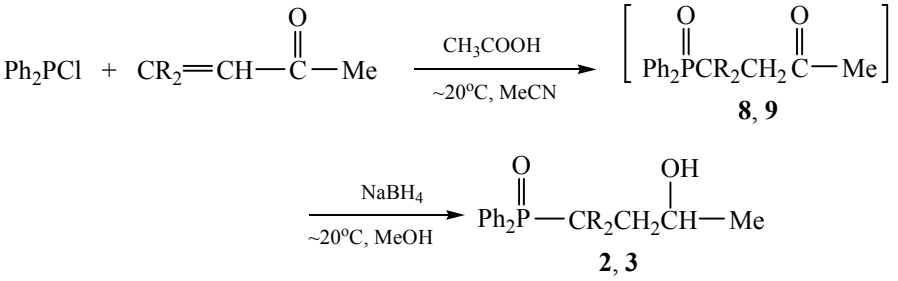
[4] For example, in [21], where its preparation was first mentioned, as well as in a later publication [22], alkanol **1** was isolated as a high-boiling liquid. In a recent study [23], by contrast, secondary alcohol **1** was obtained as a solid with mp 200–205°C (!).

[5] The reaction of Ph_2PCl with α,β-enone in the presence of glacial acetic acid.

[6] According to our preliminary results, this technique can also be successfully employed to improve the corresponding parameters of the reaction of diphenylchlorophosphine with other types of compounds containing the >C=CH–C(O)– moiety.

[7] The reaction is run in anhydrous acetonitrile.

Scheme 4.



R = H (**2**, **8**), Me (**3**, **9**).

centration and constant concentrations of the salt in the water phase and of the ligand in $CHCl_3$. When analyzing the distribution ratios (D_M) as dependent on the structure of phosphorylalkanols **1–3** we monitored the influence of the structure of the linker between the P(O) and CH(OH) moieties.

Structural data on metal complexes of phosphorylated alcohols are scarce. For example, in [28] the structure of lanthanide and alkaline earth metal complexes with alcohols $Alk_2P(O)CH_2CH(OH)Alk'$ and $AlkP(O)[CH_2CH(OH)Alk']_2$, patented as polymerization catalysts for carbonyl-containing or cyclic monomers, was described. According to the X-ray diffraction data [28], most of these complexes are alkoxides, and those involving the $AlkP(O)[CH_2CH·(O)Alk'][CH_2CH(OH)Alk']^-$ anion have the oxygen atom of the OH group directed towards the metal cation, suggesting a weak M→O(H) bond. The same patent [28] contains information on the complexes formed by the secondary alkanol $(t\text{-Bu})_2P(O)CH_2CH·(OH)Bu\text{-}t$ with chlorides of divalent metals (Mg, Zn, Sn), in which two alkanol molecules are coordinated to the cation by oxygen atoms of the P=O and OH groups. For example,[8] in the complex $[\{t\text{-}Bu_2P(O)·CH_2CH(OH)Bu\text{-}t\}_2(H_2O)Mg]Cl_2$ the Mg→O(H) bond length is 2.049 Å.

The involvement of the OH group in the coordination was also revealed for the crystalline complex $[Ni\{Ph_2P(O)CH_2CH_2OH\}_4]^{2+}·[NiCl_4]^{2-}$, in which, according to the X-ray diffraction data, all four molecules of the phosphorylated primary alcohol exhibit bidentate coordination via oxygen atoms of the P=O and OH groups, with the Ni→O(H) bond being fairly weak (bond length 2.576 Å) [29]. Thus, despite the presence of a strongly coordinating P=O center, the OH group of phosphorylalkanols can participate in weak coordination interactions, thereby modifying the extraction properties of the compound.

Studies of the solvent extraction of *f*-elements showed that alcohol **1** effectively extracts lanthanides(III), with D_{Ln} being 1.13–2.43 in the extraction from 4 M HNO_3 (Fig. 1). Under the same experimental conditions alcohols **2** and **3** show negligible extraction towards lanthanides(III), with D_{Ln} not exceeding 0.03 throughout the HNO_3 concentration range of 0.05–4 M and increasing only slightly to $D_{Ln} \leq 0.1$ in the extraction from 5 and 6 M HNO_3.

The NMR examination revealed the stability of the phosphorylalkanols during extraction from 4 M HNO_3 and their nearly equal solubilities in the water phase: $c \sim 2 \times 10^{-6}$ M in contact of 0.01 M solution of alkanol in chloroform with water (according to inductively coupled plasma atomic emission spectrometry data).

Unlike phosphorylalkanols **1–3**, their related phosphorylketones $Ph_2P(O)CH_2C(O)Me$ **4**, $Ph_2P(O)CH_2CH_2·C(O)Me$ **8**, and $Ph_2P(O)CMe_2CH_2C(O)Me$ **9** exhibit approximately equal extraction capabilities towards lanthanides [9].

The distribution ratios for lanthanides in the extraction by phosphorylalkanol **1** vary with the HNO_3 concentration in the water phase in nearly identical manner, exhibiting a growing trend (Fig. 1).

This pattern is exhibited by many extractants, including related diphenylphosphorylated ketones [9], with the main extractable species being presumably the cationic and neutral complexes $[Ln(L)_n(NO_3)_2]^+·(NO_3)^-$ and $[Ln(L)_n(NO_3)_3]^0$ ($n \leq 3$) occurring in equilibrium. With growing HNO_3 concentration the content of better extractable neutral complexes should increase, and so the distribution ratios tend to increase.

[8] Unfortunately, the X-ray diffraction data were stated in patent [28] very briefly and were not included in the Cambridge Crystallographic Database.

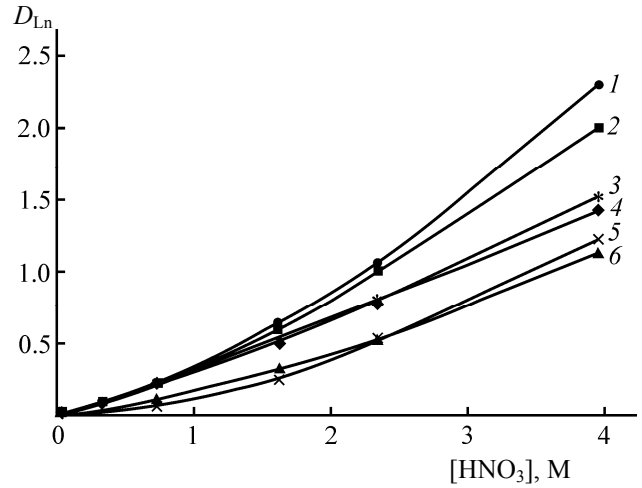


Fig. 1. Variation of the distribution ratios of lanthanides(III) with HNO_3 concentration in the extraction by ligand **1** (0.01 M solution in $CHCl_3$): (*1*) Gd, (*2*) Nd, (*3*) Pr, (*4*) La, (*5*) Yb, and (*6*) Ho.

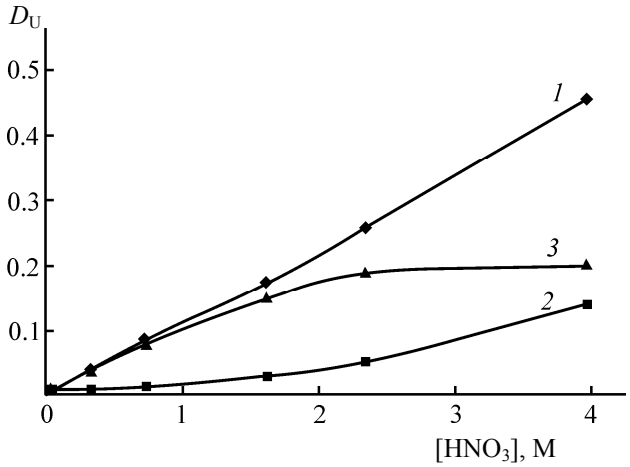


Fig. 2. Variation of the distribution ratio of uranium(VI) with HNO_3 concentration in the extraction by ligands **1–3** (0.01 M solutions in $CHCl_3$): (*1*) **1**, (*2*) **2**, and (*3*) **3**.

Our experiments revealed fairly poor extraction of U^{VI} (Fig. 2) and negligible extraction of Th^{IV} by all alkanols studied. The extraction capabilities of the most efficient alkanol **1** increase with increasing HNO_3 concentration (D_U 0.45 for 4 M HNO_3, Fig. 2), and those of ligands **2** and **3** are low (maximal D_U of 0.15 and 0.18, respectively), being nearly independent of the HNO_3 concentration in the 2–4 M range.

Thus, changes in the structure of the linker between the P=O and CH(OH) groups produce radical changes in the extraction properties of phosphorylated secondary alkanols. Reasons for this unusual effect are as yet unclear, but it can be presumed that the structure of alcohol **1**, by contrast to its homologs, is considerably more favorable for the participation of the OH group in additional interactions. For example, bidentate coordination of ligand **1,** similar to that described for phosphorylalkanols $Bu_2P(O)CH_2CH{\cdot}(OH)Bu\text{-}t$ [28] and $Ph_2P(O)CH_2CH_2OH$ [29], should cause an increase in the stability of the extracted complexes and, consequently, in the extraction efficiency. For alkanols **2** and **3** the possible bidentate coordination is less favorable, since it entails the formation of seven- rather than six-membered metal cycles. The bidentate coordination in the case of ligand **1** is more probable for lanthanides with large radii from the beginning of the series. Consequently, the efficiency of their extraction by phosphorylalkanol **1** should be higher than that of heavy lanthanides with smaller radii, which was indeed the case in our experiments (Fig. 1). Such bidentate coordination is also expected for ketone **4** in whose molecule both functional groups (in this specific case, phosphoryl and carbonyl groups), like in that of alkanol **1,** are separated by a methylene fragment, but the distribution ratios of ketone **4** differ only slightly from those of ketones **8** and **9** with the corresponding ethylene linker [9]. Therefore, the assumption of the inertness of phosphorylalkanols **2** and **3,** observed in the extraction experiments, as being due mainly to the different structures of the complexes extracted is not exhaustive. Presumably, the extraction properties of alkanols **1–3** are more strongly influenced by the difference in aggregation than in coordination properties.

Metal extraction is significantly affected by aggregation of ligands and their complexes in the organic phase [14–19]. For example, phosphoryl-containing acid podands and bisphosphonic acids differing in the structure of the bridge between the terminal groups form in organic solutions aggregates with different numbers of particles, and the degree of association in each group depends in a complicated manner on the bridge structure [14–19]. The effect of the aggregation state of compounds on the extraction of metals and the formation of hydrogen bonds in aggregates was examined earlier [14–19]. For example, for related podands the differences in the size and structure of the associates formed via hydrogen bonds are responsible for 3–70-fold changes in the distribution ratios of uranium(VI) and thorium(IV) [14, 30, 31]. At the same time for the phosphorylketones $Ph_2P(O)(CR^1R^2)_nCH_2C(O)Me$ (n = 0, 1; R^1, R^2 = H,

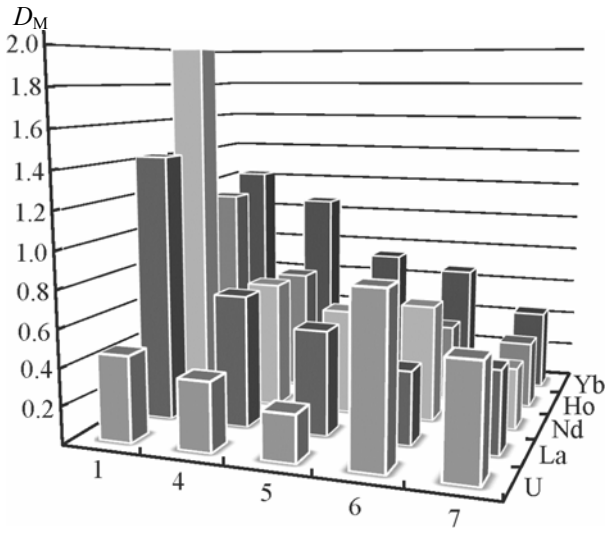


Fig. 3. Comparison of the distribution ratios of La^{III}, Nd^{III}, Ho^{III}, Yb^{III}, and U^{VI} in the extraction into chloroform by compounds **1** and **4–7** (0.01 M solutions in $CHCl_3$) from 3.96 M HNO_3; initial concentration of the lanthanide and uranyl nitrates in the water phase 2.5×10^{-4} M.

Me, Ar, Het) which are not prone to self-association D_{Ln} is weakly dependent on the structure of the linker between P(O) and C(O) groups.

Further research is required to verify these hypotheses, which is beyond the scope of this study.

The extraction properties of phosphorylated alcohol **1** were compared with those of related ketone **4** and known mono- and bidentate phosphoryl-containing extractants **5–7**, studied under identical experimental conditions. Figure 3 shows that alcohol **1** not only more effectively extracts lanthanides from nitric acid media than ketone **4** and known compounds **5–7** but also exhibits a fairly high selectivity towards pairs of heavy and light lanthanides. The separation factor for the neodymium–holmium pair is 1.8, and that for the gadolinium–holmium pair, 2.0. In the case of uranium, reference ligands **6** and **7** proved to be more powerful extractants, by contrast.

Thus, the transformation of phosphorylketone **4** into the corresponding alcohol **1** substantially improves the extraction properties of the ligand with respect to *f*-elements, particularly lanthanides. The distribution ratios achieved with alcohol **1** exceed 2–3-fold those with ketone **4** in the extraction of light lanthanides, and 1.2–1.7-fold in the extraction of heavy lanthanides and uranium.

As to significant difference in the extraction properties of phosphorylalkanols **1–3**, one of the main reasons for this is presumably the difference in their hydrophilic-lipophilic properties, leading, in particular, to higher aggregation states of both alcohol **1** and the complexes extracted.

EXPERIMENTAL

The NMR spectra of 0.1 M solutions in $CDCl_3$ were recorded on a Bruker AV-400 instrument [400.13 (^{1}H and ^{1}H–{^{31}P}), 100.61 (^{13}C), and 161.98 MHz (^{31}P)]. The residual proton signals of the deuterated solvent served as the internal reference for the ^{1}H and ^{1}H–{^{31}P} NMR spectra, and the signals from the carbon nuclei of the deuterated solvent, for the ^{13}C NMR spectra; 85% H_3PO_4 served as the external reference for the ^{31}P NMR spectra. The FTIR spectra were measured on a Bruker Tensor 37 FTIR spectrometer (KBr pellets). Elemental analysis was performed in the Laboratory of Microanalysis, Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences.

Diphenylchlorophosphine (98%, Acros) was purified by vacuum distillation just before the reaction; all the manipulations with this compound were performed under argon. Methyl vinyl ketone (95%, Acros) and mesityl oxide (99%, Aldrich) were distilled before the reaction at normal pressure over hydroquinone. Glacial acetic acid (reagent grade) was distilled just before use. Sodium borohydride (99%, Acros) was used without further purification. Basic Al_2O_3 Brockmann I (50–200 μm, Acros) and silica gel (130–270 μm, 60 Å, Aldrich) were used. Diphenylphosphorylated acetone **4** was synthesized and purified by the known procedure described in [32].

Acetonitrile (99.9%, Acros), methylene chloride (reagent grade), and diethyl ether (reagent grade) were dehydrated by standard procedures [33]. Other solvents [methyl *tert*-butyl ether (99.8%, Acros), hexane (reagent grade), methanol (reagent grade), and chloroform (reagent grade)] were used without further purification.

Model compounds tributyl phosphate (*n*-BuO)$_3$PO **5** (99%, Acros) and trioctylphosphine oxide (*n*-C_8H_{17})PO **6** (98%, Acros) were used without further purification; (*N*,*N*-dibutylcarbamoylmethyl)diphenylphosphine oxide $Ph_2P(O)CH_2C(O)N(Bu\text{-}n)_2$ **7** was synthesized and purified in accordance with the known technique from [34].

1-(Diphenylphosphoryl)propan-2-ol (1). To a solution of 2.0 g (7.74 mmol) of diphenylphosphorylated acetone **4** in 20 mL of methanol, a solution of 150 mg (3.94 mmol) of $NaBH_4$ in 4 mL of distilled water was added dropwise with stirring. The resulting mixture was stirred for 4 h at room temperature and left overnight, then diluted with an equal volume of distilled water, acidified to pH ≤ 3 with dilute (1 : 3) H_2SO_4, and extracted with chloroform (4 × 15 mL). The extract was washed successively with distilled water (3 × 10 mL) and saturated water solution of $NaHCO_3$ (2 × 5 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed in a vacuum, and the residue was washed successively with 11 mL of hexane–ether (10 : 1) mixture and 10 mL of hexane and then dried in a vacuum (~15 Torr) for 1 h at ~20°C. Yield 1.92 g (95%), mp 97.0–98.5°C.[9] IR spectrum, ν, cm^{-1}: 1169 (P=O), 3325 (OH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.27 d.d (3H, CH_3, $^3J_{HH}$ = 6.1, $^4J_{HP}$ = 1.4), 2.35 d.d.d (1H, $C\underline{H}_AH_B$, $^3J_{H^AH}$ = 2.2, $^2J_{H^AP}$ = 7.5, $^2J_{H^AH^B}$ = 14.9), 2.46 d.d.d (1H, $CH_A\underline{H}_B$, $^3J_{H^BH}$ = 9.9, $^2J_{H^BP}$ = 11.7, $^2J_{H^AH^B}$ = 14.9), 4.18–4.30 m [1H, $\underline{CH}$(OH)], 4.50 br.s (1H, OH), 7.42–7.57 m (6H, m,*p*-C_6H_5), 7.66–7.78 m (4H, *o*-C_6H_5). $^1H–\{^{31}P\}$ NMR spectrum, δ, ppm (*J*, Hz): 1.27 d (3H, CH_3, $^3J_{HH}$ = 6.1), 2.35 d.d (1H, $\underline{CH}_AH_B$, $^3J_{H^AH}$ = 2.1, $^2J_{H^AH^B}$ = 14.9), 2.46 d.d (1H, $CH_A\underline{H}_B$, $^3J_{H^BH}$ = 9.8, $^2J_{H^AH^B}$ = 14.9), 4.19–4.29 m [1H, $\underline{CH}$(OH)], 4.47 br.s (1H, OH), 7.43–7.57 m (6H, m,*p*-C_6H_5), 7.67–7.77 m (4H, *o*-C_6H_5). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 24.75 d (CH_3, $^3J_{CP}$ = 14.2), 37.94 d (CH_2, $^1J_{CP}$ = 71.2), 63.18 d (CH, $^2J_{CP}$ = 4.7), 128.68 d (*m*-C_6H_5, $^3J_{CP}$ = 11.5), 130.27 d (*o*-C_6H_5, $^2J_{CP}$ = 9.8), 130.83 d (*o*-C_6H_5, $^2J_{CP}$ = 9.4), 131.83 d (*ipso*-C_6H_5, $^1J_{CP}$ = 98.2), 131.92 d (*p*-C_6H_5, $^4J_{CP}$ = 2.7), 131.98 d (*p*-C_6H_5, $^4J_{CP}$ = 2.7), 133.16 d (*ipso*-C_6H_5, $^1J_{CP}$ = 99.6). ^{31}P NMR spectrum: δ_P 33.91 ppm. Found, %: C 69.28; H 6.65; P 11.88. $C_{15}H_{17}O_2P$. Calculated, %: C 69.22; H 6.58; P 11.90.

4-(Diphenylphosphoryl)butan-2-one (8).[10] To a solution of 0.44 g (6.3 mmol) of methyl vinyl ketone in 5 mL of anhydrous acetonitrile, a solution of 0.41 g (6.7 mmol) of glacial AcOH in 3 mL of anhydrous acetonitrile and a solution of 1.32 g (6 mmol) of Ph_2PCl in 3 mL of anhydrous acetonitrile were added sequentially dropwise. The resulting mixture was kept for 3 h at room temperature, and the solvent and other volatiles were removed under a water-jet pump (~10 Torr). The residue was kept in a vacuum (~1 Torr) for 2.5 h at ~55°C, then dissolved in 10 mL of CH_2Cl_2, and filtered sequentially through 1.3 g of basic Al_2O_3 and 1.3 g of silica gel; the carrier was washed with 6 mL of CH_2Cl_2 each time. The solvent was removed from the filtrate under vacuum, and the residue was recrystallized from methyl *tert*-butyl ether. Yield 1.27 g (77.8%), mp 98.5–100°C (mp 105–106°C [35]). IR spectrum, ν, cm^{-1}: 1185 (P=O), 1720 (C=O). ^1H NMR spectrum, δ, ppm: 2.09 s (3H, CH_3), 2.47–2.57 m (2H, CH_2P), 2.70–2.79 m [2H, $CH_2C(O)$], 7.40–7.54 m (6H, m,*p*-C_6H_5), 7.67–7.76 m (4H, *o*-C_6H_5). $^1H–\{^{31}P\}$ NMR spectrum, δ, ppm: 2.09 s (3H, CH_3), 2.47–2.56 m (2H, CH_2P), 2.70–2.78 m [2H, $CH_2C(O)$], 7.41–7.47 m (4H, *m*-C_6H_5), 7.48–7.53 m (2H, *p*-C_6H_5,), 7.71 d (4H, *o*-C_6H_5, $^3J_{HH}$ = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 23.16 d (CH_2P, $^1J_{CP}$ = 73.9), 29.61 s (CH_3), 35.08 d ($\underline{CH}_2CH_2P$, $^2J_{CP}$ = 2.4), 128.62 d (*m*-C_6H_5, $^3J_{CP}$ = 11.8), 130.59 d (*o*-C_6H_5, $^2J_{CP}$ = 9.1), 131.81 d (*p*-C_6H_5, $^4J_{CP}$ = 2.7), 132.28 d (*ipso*-C_6H_5, $^1J_{CP}$ = 99.6), 206.06 d (C=O, $^3J_{CP}$ = 13.5). ^{31}P NMR spectrum: δ_P 32.37 ppm. Found, %: C 70.68; H 6.39; P 11.49. $C_{16}H_{17}O_2P$. Calculated, %: C 70.58; H 6.29; P 11.38.

4-(Diphenylphosphoryl)butan-2-ol (2). *a*. To a solution of 1.0 g (3.67 mmol) of ketone **8** in 10 mL of methanol, a solution of 70 mg (1.86 mmol) of $NaBH_4$ in 2 mL of distilled water was added dropwise with stirring. The resulting mixture was stirred for 4 h at room temperature, left overnight, and then treated as described above for compound **1**. After removal of the solvent from the extract the residue was dried for 3 h at 50–60°C in a vacuum (~1 Torr). Yield 0.971 g (96.5%), mp 101.5–103.5°C (mp 101–102°C [36]). IR spectrum, ν, cm^{-1}: 1159, 1182 sh (P=O), 3500 sh, 3325, 3330 sh (OH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.19 d (3H, CH_3, $^3J_{HH}$ = 6.2), 1.69 d.d.d.d.d (1H, $C\underline{H}_AH_BCH$, $^2J_{H^AH^B}$ = 14.5, $^3J_{H^AH}$ = 8.2, $^3J_{H^AH^{A'}}$ = 8.2, $^3J_{H^AH^{B'}}$ = 6.6, $^3J_{H^AP}$ = 12.9), 1.85 d.d.d.d.d (1H, $CH_A\underline{H}_BCH$, $^2J_{H^BH^A}$ = 14.3, $^3J_{H^BH}$ = 3.3, $^3J_{H^BH^{A'}}$ = 6.5, $^3J_{H^BH^{B'}}$ = 8.5, $^3J_{H^BP}$ = 14.3), 2.41 d.d.d.d (1H, $PC\underline{H}_{A'}H_{B'}$, $^2J_{H^{A'}H^{B'}}$ = 15.2, $^3J_{H^{A'}H^A}$ = 8.3, $^3J_{H^{A'}H^B}$ = 6.5, $^2J_{H^{A'}P}$ = 11.5), 2.48 d.d.d.d (1H, $PCH_{A'}\underline{H}_{B'}$, $^2J_{H^{B'}H^{A'}}$ = 15.2, $^3J_{H^{B'}H^A}$ = 6.7, $^3J_{H^{B'}H^B}$ = 8.5, $^2J_{H^{B'}P}$ = = 11.4), 3.50–3.80 br.s (1H, OH), 3.90 d.d.q [1H, $\underline{CH}$(OH), $^3J_{HH}$ = 6.2, $^3J_{HH^A}$ = 8.4, $^3J_{HH^B}$ = 3.4], 7.44–7.50 m (4H, *m*-C_6H_5), 7.50–7.56 m (2H, *p*-C_6H_5), 7.72–7.79 m (4H, *o*-C_6H_5). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 23.32 s (CH_3), 26.45 d (CH_2P, $^1J_{CP}$ = 71.9), 31.24 d ($\underline{CH}_2CH_2P$, $^2J_{CP}$ =

[9] After recrystallization from the hexane–$CHCl_3$ mixture the melting point remains unchanged.

[10] The most powerful technique for the synthesis of **8** in an acetonitrile medium is presented.

3.7), 67.50 d (CH, $^3J_{CP}$ = 10.3), 128.71 d (*m*-C_6H_5, $^3J_{CP}$ = 11.7), 128.73 d (*m*-C_6H_5, $^3J_{CP}$ = 11.7), 130.80 d (*o*-C_6H_5, $^2J_{CP}$ = 9.5), 130.84 d (*o*-C_6H_5, $^2J_{CP}$ = 8.8), 131.81 d (*p*-C_6H_5, $^4J_{CP}$ = 2.9), 131.84 d (*p*-C_6H_5, $^4J_{CP}$ = 2.9), 132.54 d (*ipso*-C_6H_5, $^1J_{CP}$ = 99.0), 132.57 d (*ipso*-C_6H_5, $^1J_{CP}$ = 98.3). ^{31}P NMR spectrum: δ_P 34.54 ppm. Found, %: C 70.05; H 7.11; P 11.22. $C_{16}H_{19}O_2P$. Calculated, %: C 70.06; H 6.98; P 11.29.

b. To a solution of 1.802 g (25.7 mmol) of methyl vinyl ketone in 10 mL of anhydrous acetonitrile, a solution of 1.553 g (25.8 mmol) of glacial AcOH in 7 mL of anhydrous acetonitrile and a solution of 5.037 g (22.8 mmol) of Ph_2PCl in 7 mL of anhydrous acetonitrile were added sequentially dropwise. The reaction mixture was kept for 3 h at room temperature, and the solvent and other volatiles were removed under a water-jet pump (~10 Torr). The residue was kept under vacuum (~1 Torr) for 2.5 h at ~55°C and then dissolved in 30 mL of CH_2Cl_2. The resulting solution was filtered through 5.0 g of basic Al_2O_3, and the carrier was washed with 15 mL of CH_2Cl_2. The solvent was removed from the filtrate under a water-jet pump (~10 Torr), and the residue was kept under vacuum (~1 Torr) for 2 h at ~55°C. As a result, 5.983 g (~96%) of crystalline ketone **8** with ~99% purity according to the ^{31}P NMR data was obtained. The product was dissolved in 60 mL of methanol, and to the resulting solution a solution of 0.866 g (22.8 mmol) of $NaBH_4$ in 24 mL of distilled water was added dropwise. The mixture was stirred for 3 h at room temperature, left overnight, and then treated as described above for compound **1**. After removal of the solvent the residue was dried for 3 h at 50–60°C in a vacuum (~1 Torr), refluxed in 60 mL of hexane–ether (57 : 3) mixture, and then cooled to 0°C. The resulting precipitate was separated, washed with hexane–ether (57 : 3) mixture (2 × 30 mL) and air-dried. Yield 5.479 g (90.9%), mp 102–104°C. Found, %: C 70.05; H 7.07; P 11.24. $C_{16}H_{19}O_2P$. Calculated, %: C 70.06; H, 6.98; P 11.29. The spectral characteristics of the resulting compound were identical to those of the sample obtained by method *a*.

4-(Diphenylphosphoryl)-4-methylpentan-2-ol (3). To a solution of 2.522 g (25.7 mmol) of mesityl oxide in 10 mL of anhydrous acetonitrile, a solution of 1.553 g (25.8 mmol) of glacial AcOH in 7 mL of anhydrous acetonitrile and a solution of 5.037 g (22.8 mmol) of Ph_2PCl in 7 mL of anhydrous acetonitrile were added sequentially dropwise. The reaction mixture was kept for 24 h at room temperature, and the solvent and other volatiles were removed in a water-jet pump (~10 Torr). The residue was kept under vacuum (~1 Torr) for 2.5 h at ~55°C and then dissolved in 30 mL of CH_2Cl_2. The resulting solution was filtered through 5.0 g of basic Al_2O_3; the carrier was washed with 15 mL of CH_2Cl_2. The filtrate was evaporated in a vacuum (~10 Torr), and the residue was kept under vacuum (~1 Torr) for 2 h at ~55°C. As a result, 6.841 g (~100%) of crystalline 4-(diphenylphosphoryl)-4-methylpentan-2-one **9** with ~97% purity according to the ^{31}P NMR data was obtained. The product was dissolved in 60 mL of methanol, and to the resulting solution a solution of 0.866 g (22.8 mmol) of $NaBH_4$ in 24 mL of distilled water was added dropwise. The mixture was stirred for 3 h at room temperature, left overnight, and then treated as described above for compound **1.** After removal of the solvent the residue was dried for 3 h at 50–60°C in a vacuum (~1 Torr), refluxed in 60 mL of hexane–ether (57 : 3) mixture, and then cooled to 0°C. The resulting precipitate was separated, washed with hexane–ether (57 : 3) mixture (2 × 30 mL) and air-dried. Yield 6.038 g (87.6%), mp 126.5–127.5°C. IR spectrum, ν, cm^{-1}: 1159, 1182 (P=O), 3500 sh, 3390, 3330 sh (OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 d (3H, $\underline{CH_3}CH$, $^3J_{HH}$ = 6.2), 1.30 d (3H, $CH_3{}^ACP$, $^3J_{HP}$ = 15.6), 1.31 d (3H, $CH_3{}^BCP$, $^3J_{HP}$ = 14.7), 1.44 d.d (1H, $\underline{CH_A}H_B$, $^2J_{H^AH^B}$ = 15.2, $^3J_{H^AP}$ = 25.6), 1.93 d.d.d (1H, $CH_A\underline{H_B}$, $^2J_{H^BH^A}$ = 15.2, $^3J_{H^BP}$ = $^3J_{H^BH}$ = 10.0), 4.12 d.q (1H, CH, $^3J_{HH}$ = 6.2, $^3J_{HH^B}$ = 9.5), 5.64 br.s (1H, OH), 7.47–7.61 m (6H, *m*,*p*-C_6H_5), 7.93–8.05 m (4H, *o*-C_6H_5). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 22.13 s ($\underline{CH_3}{}^BCP$), 24.35 s ($\underline{CH_3}CH$), 26.76 d ($\underline{CH_3}{}^ACP$, $^2J_{CP}$ = 2.3), 37.17 d ($P\underline{C}Me_2$, $^1J_{CP}$ = 68.7), 49.97 s (CH_2), 62.90 d (CH, $^3J_{CP}$ = 1,5), 128.44 d (*m*-C_6H_5, $^3J_{CP}$ = 10.7), 128.52 d (*m*-C_6H_5, $^3J_{CP}$ = 10.7), 129.89 d (*ipso*-C_6H_5, $^1J_{CP}$ = 90.8), 130.12 d (*ipso*-C_6H_5, $^1J_{CP}$ = 93.1), 131.88 s (*p*-C_6H_5), 132.33 d (*o*-C_6H_5, $^2J_{CP}$ = 8.4), 132.51 (*o*-C_6H_5, $^2J_{CP}$ = 8.4). ^{31}P NMR spectrum: δ_P 42.80 ppm. Found, %: C 71.54; H 7.67; P 10.21. $C_{18}H_{23}O_2P$. Calculated, %: C 71.50; H 7.67; P 10.24.

Study of the extraction capabilities of compounds (1–7). For the preparation of solutions we used bidistilled water, $CHCl_3$ (reagent grade), arsenazo III (analytical grade), HNO_3 (high purity grade), $UO_2(NO_3)_2\cdot 6H_2O$ (reagent grade), $Th(NO_3)_4\cdot 4H_2O$ (reagent grade), $La(NO_3)_3\cdot 6H_2O$ (reagent grade), $Pr(NO_3)_3\cdot 6H_2O$ (reagent grade), $Nd(NO_3)_3\cdot 6H_2O$ (reagent grade), $Gd(NO_3)_3\cdot 6H_2O$ (pure grade), $Ho(NO_3)_3\cdot 6H_2O$ (pure grade), and $Yb(NO_3)_3\cdot 6H_2O$ (pure grade). The

solutions were prepared by the volumetric-gravimetric method. To prepare the solutions of actinide and lanthanide nitrates, weighted quantities of the corresponding nitrates were dissolved in 0.01 M HNO_3. The concentrations of the metal nitrate solutions were determined more precisely spectrophotometrically with the use of a Cary 50 Scan Varian spectrometer according to the technique described in [37]. The HNO_3 solution concentration was determined by potentiometric titration with 0.1 M NaOH using a Radelkis-125 pH/ion analyzer (OP-300 model).

The extraction experiments were performed in test tubes with ground-glass stoppers at a 1 : 1 water to organic phase volume ratio. To this end, 1.5 mL of nitric acid solution whose concentration was varied from 0.052 to 5.29 M and 0.5 mL of 1 mM solution of metal nitrate and 2 mL of 0.01 M solution of the ligand in $CHCl_3$ were introduced. The two-phase solution was stirred for 20 min in an RS-60 BioSan rotator at 80 rpm. The equilibrium time for the extraction was checked by increasing the phase contact time to 60 min; during that period the distribution ratios remained unchanged. The phase separation was achieved by centrifugation, after which the metal concentration in the water phase was determined by the spectrophotometric procedure from [37]. The distribution ratios ($D_M = [M]_{org}/[M]_{aq}$) were determined by calculating the concentration in the organic phase from the difference of the concentrations for the initial and equilibrium water phases. The D_M values were obtained at varied HNO_3 concentration and at constant concentrations of extractant (0.01 M in $CHCl_3$) and metal (0.25 mM in the water phase). For each HNO_3 concentration at least three independent experiments were performed. All experiments were run at the temperature of 20±1°C.

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