

TABLE 1. Oxides of Dialkyl(diaryl)(dialkylcarbamoylmethyl)phosphines

Comp- pound	R ¹	R ²	R ³	Yield, %	bp, °C (p, mm Hg) mp, °C (solvent)	n _D ²⁰	Found/Calculated, %				Molecular mass, found/ calculated
							C	H	P	N	
(I)	Ph	Ph	Bu	70	210-244 (4) 81-82 (benzene:ether)	1,5625	70,9 71,1	7,9 8,1	8,3 8,3	4,0 3,8	C ₂₂ H ₃₀ O ₂ NP 371 371
(II)	Ph	Ph	Et	87,6	164-165 (benzene:alcohol)		68,3 68,6	7,1 7,0	9,8 9,8	4,8 4,4	C ₁₈ H ₂₂ O ₂ NP 315 315
(III)	c-C ₆ H ₁₁	c-C ₆ H ₁₁	Et	52,3	198-200 (1) 62-64 (hexane)				9,2 9,5	4,0 4,3	C ₁₈ H ₂₄ O ₂ NP 327 327
(IV) *	Bu	Bu	Et	74,0	168-170 (0,5)	1,4788	60,6 61,0	11,3 10,8	11,0 11,3		C ₁₄ H ₂₀ O ₂ NP 275 275
(V)	Ph	Et	Et	74,3	178-180 (0,5) 33-34	1,5392	62,5 62,9	8,4 8,2	11,6 11,6		C ₁₄ H ₂₂ O ₂ NP 267 267
(VI)	BuO	BuO	Et	62,6	170-172 (3)	1,4558			10,0 10,1		C ₁₄ H ₂₀ O ₄ NP 307 307

* d₄²⁰ 0.9814. Found MR 79.10; calculated MR 79.35.

TABLE 2. Complexes of RR¹PCH₂CNR₂² (L) of Composition L:M = 1:1 with Uranyl Nitrate (M)

L in complex	Yield, %	mp, °C	Found/calculated		ν, cm ⁻¹		ν _{as} UO ₂ , cm ⁻¹	νNO ₃ ⁻ , cm ⁻¹				δ ³¹ P, ppm (-30° C, DMFA)
			P	N	P=O	C=O		ν _s NO ₂ ν ₁	N-O ν ₂	ν _{as} ONO ₂ ν ₄	NO ₂ ⁻ A=ν ₁ -ν ₄	
(I) L-M	73,2	222-223	4,1 4,1	5,4 5,4	1195 1145	1650 1605	985	1270, 1288	1030	1525	1385	25,4 45,7
(II) L-M	62,3	250-252	4,4 4,4	6,8 7,3	1208 1145	1630 1605	986	1275, 1290	1030	1530	1385	25,8 45,6
(III) L-M	54	179-181	5,2 4,3	6,0 5,8	1175 1105	1640 1595	982	1285	1035	1520	1385	47,9 70,3
(IV) L-M	44,9	200-201	4,7 4,6	6,8 6,3	1175 1105	1635 1595	988	1275, 1290	1105	1530	1385	43,7 68,9
(V) L-M	61,1	185-186	4,7 4,7	6,8 6,4	1195 1140	1640 1600	988	1275, 1300	1035	1530	1385	36,8 58,9
(VI) L-M	50,9	64-65	4,5 4,4	6,0 6,0	1265 1175 1195	1650 1610	940	1275, 1295	1040	1530	1385	22,2 * 28,5 *

* In CH₂Cl₂.

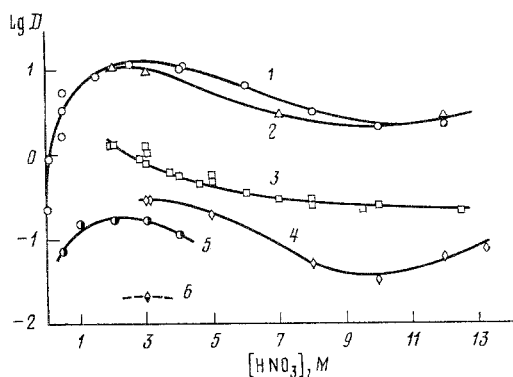
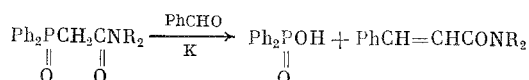
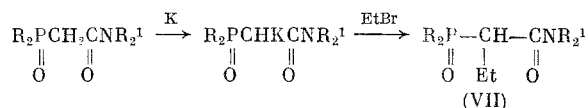


Fig. 1. Extraction curve (log D) for Am(III) by 0.1 M solutions of reagents (I)-(VI) in dichloroethane as a function of HNO₃ concentration. Numbers of curves correspond to compounds.

This method of synthesis did not preclude the possibility of occurrence of the Perkov reaction with the formation of α -aminovinylphosphinates (B). The structure of the product (A) which we accepted was confirmed by its chemical properties. Thus, these compounds are capable of entering into the Horner reaction



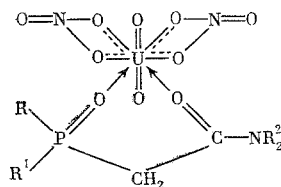
We alkylated the methyl group



Properties of the products are given in Table 1. For comparison of the properties of the phosphines (I)-(V) obtained with those of the phosphonates described earlier, the phosphonate (BuO)₂P(O)CH₂C(O)NEt₂ (VI) [1-3] was synthesized. Its properties differed sharply from those of (IV).

Compounds (I)-(VI) form yellow powdery complexes of composition L:M = 1:1 with uranyl nitrate (Table 2).

Shift of the $\nu_{\text{P}=\text{O}}$ and $\nu_{\text{C}=\text{O}}$ valence vibrations to the region of lower frequencies (see Table 2) is observed in the IR spectra of the complexes, which confirms the participation of two coordination centers of the ligand in coordination with uranyl nitrate. The large values of shifts provide evidence of the high stability of the complexes formed. The NO₃⁻ group appears to be one of the ligands the coordination of which can appear in the spectra upon change of symmetry. For all complexes obtained, bands are observed in the spectra which are attributed to covalently bonded nitrate groups. In [6], the difference Δ is proposed for acceptance as a measure of the covalent character of the bond of the NO₃⁻ group with the metal. For the complexes synthesized, Δ varies within the interval 235-255 cm⁻¹, which provides evidence of the bidentate coordination of the NO₃ group. It can be assumed that the structures of these complexes are analogous to that for the dioxide of tetraphenylmethylenediphosphine [7]:



The compounds synthesized were studied as extractants with respect to a representative of the group of transplutonium elements (TPE) - trivalent americium, ²⁴¹Am.

From the extraction curves of Am obtained with 0.1 M solutions of reagents (I)-(VI) in DCE as functions of HNO₃ concentration (Fig. 1) it follows that the replacement of alkoxy substituents on the P atom by alkyl or aryl significantly raises the extraction capability of the reagent. Replacement of butyl radicals on P by phenyl increases the distribution coefficient D_{Am} still more (approximately 60 times).

Replacement of one of the phenyl radicals in (II) by ethyl (reagent (V)) causes decrease of D_{Am} by nearly two orders of magnitude (curves 2 and 5). Similar rise in the extraction capability of the reagent upon replacement of the alkyl substituents by more electronegative ones such as phenyl has been noted during studies of the reaction of bidentate ligands containing phosphoryl groups with NaI [8], with copper chlorides [9], and later during study of the extraction properties of these reagents [10]. In the present work this phenomenon was first observed for bidentate ligands in which only one of the two functional groups is phosphoryl. The nature of this phenomenon is not completely clear [11].

From Fig. 1 it can be seen that difference between the radicals on the N atom does not affect the extraction properties of the reagent, but does show up on its solubility. Thus, reagents (I) and (II), which have the same substituents on P but different ones (butyl and ethyl, respectively) on N, differ little in extraction properties with respect to Am(III) (curves 1 and 2), but differ substantially in solubility in organic solvents. Reagent (I) is highly soluble in $CHCl_3$, DCE, 1,2,4-trichlorobenzene, o-dichlorobenzene, CCl_4 , perchloroethylene, diethylbenzene, o-xylene, benzene, and methyl isobutyl ketone. Reagent (II), of all the solvents enumerated, dissolves only in $CHCl_3$ and DCE.

EXPERIMENTAL

IR spectra were obtained on UR-20 apparatus in tablets with KBr, and the ^{31}P NMR spectra on Bruker HX-90 apparatus (external standard 85% H_3PO_4), and the mass spectra on an AEI-MS-30 mass spectrometer.

Purification of the phosphine oxides from oxides of impurities was done by column chromatography on neutral Al_2O_3 (active II).

Dibutylamide of Chloroacetic Acid. To 11.3 g (0.1 mole) of the chloroanhydride of chloroacetic acid in 100 ml of ether were added with stirring 12.9 g (0.1 mole) of Bu_2NH in 50 ml of ether at -10 to 15° . Another 100 ml of ether were added after the reaction was finished. The precipitate was filtered off on the following day. The solvent was removed from the filtrate and the residue was distilled. The amount of 9.7 g (46.9%) of product was obtained, bp 140° (8 mm), n_D^{20} 1.4676. Found: C 58.5; H 9.7; Cl 17.7%. Calculated for $C_{10}H_{20}ClNO$: C 58.4; H 9.7; Cl 17.3%.

Oxide of Diphenyl[dibutylcarbamoylmethyl]phosphine (I). To 9.1 g (40 mmoles) of N,N-dibutylchloroacetamide at 190° in a current of argon were gradually added 10.2 g (40 mmoles) of O-ethylidiphenylphosphinite. Vigorous evolution of EtCl was observed. The mixture was stirred 1 h at $200^\circ C$. The heavy oil which formed crystallized upon standing. After distillation was obtained 6.8 g (70%) of (I), mp $81-82^\circ C$. After chromatography on Al_2O_3 , $R_f = 0.85$ (benzene:ether = 4:1).

Oxide of Diphenyl[diethylcarbamoylmethyl]phosphine (II). To 4.2 g (30 mmoles) of N,N-diethylchloroacetamide at $150^\circ C$ were added 6.4 g (30 mmoles) of O-ethylidiphenylphosphinite and held for 1 h at $150^\circ C$. The reaction mixture crystallized upon cooling. Obtained 7.2 g (87.6%) of (II), mp $168-170^\circ C$, R_f 0.78 (eluent benzene:alcohol = 4:1).

Oxides of Phosphines (III), (IV), (V). The oxides were prepared in manner analogous to that for (I) and (II). The substances were purified by double distillation and the purity controlled by TLC on Al_2O_3 . Qualitative reaction for the presence of a double bond gives a negative result: Color change was not observed upon prolonged holding of the compounds in CH_2Cl_2 with a small amount of Br_2 . The substances were isolated in unchanged form.

Dibutyl[diethylcarbamoylmethyl]phosphonate (VI). To 6.4 g (40 mmoles) N,N-diethylchloroacetamide at 120° were added 10.6 g (40 mmoles) of $(BuO)_3P$ and the mixture was heated 1 h at $160^\circ C$. After distillation, 8.2 g (62.6%) of (VI) was obtained, bp $170-172^\circ C$ (3 mm), n_D^{20} 1.4558. Found: P 10.0%. Calculated for $C_{14}H_{30}O_4NP$: P 10.1%.

Reaction of the Oxide of Diphenyl[dibutylcarbamoylmethyl]phosphine (I) with Benzaldehyde. The amount of 0.3 g (0.006 g-atom) of potassium, dispersed in 50 ml of absolute xylene by the Brule method, and 2.5 g (6 mmoles) of (I) in 50 ml of xylene were heated during vigorous stirring in an atmosphere of argon for 2 h at $115-125^\circ C$. To the K salt formed was added 1.1 g (10 mmoles) of benzaldehyde and the mixture was heated 1.5 h at $120^\circ C$. The precipitate was filtered off, dissolved in water, and the solution was acidified with HCl to complete precipitation. The material which fell out was filtered off. Obtained was 1.5 g of product, mp $189-190^\circ C$. Melting temperature of a mixed sample with diphenylphosphinic acid was $190-192^\circ C$ (compare [12]).

The xylene solution was evaporated and the residue distilled. Obtained was 1.4 g (82.3%) of dibutylamide of cinnamic acid, bp $145-147^\circ C$ (1 mm), n_D^{20} 1.5295. Found: C 78.2; H 9.6; N 5.4%. Calculated for $C_{17}H_{25}NO$: C 78.8; H 9.6; N 5.4%. IR spectrum (ν , cm^{-1}): 1610 (C=O), 1650 (C=C).

Reaction of the Oxide of Diphenyl[diethylcarbamoylmethyl]phosphine (II) with Benzaldehyde. In a manner analogous to the preceding, from 0.4 g (0.01 g-atom) of potassium, 3.2 g (10 mmoles) of (II), and 1.3 g (12 mmoles) of benzaldehyde was obtained 2.0 g of diphenylphosphinic acid, 0.3 g of the original (II), mp 166-167°, and 0.82 g (40%) of the diethylamide of cinnamic acid, bp 152° (2 mm), mp 60-62°C. Found: C 76.3; H 8.3; N 6.7%. Calculated for C₁₃H₁₇NO: C 76.8; H 8.4; N 6.9%. IR spectrum (ν , cm⁻¹): 1600 (C=O), 1650 (C=C).

Alkylation of the Oxide of Diphenyl[dibutylcarbamoylmethyl]phosphine (I). To 0.4 g (0.01 g-atom) of potassium, dispersed by the Brule method in 50 ml of xylene, was added 3.8 g (10 mmoles) of (I) in 50 ml of xylene and boiled with stirring in a current of argon to complete dissolution of the potassium (~ 7 h). The reaction mixture was concentrated (50 ml of xylene driven off), 2.2 g of EtBr was added and heated 12 h at 60°C. Along with a voluminous precipitate of the K salt of (I), a precipitate of KBr was isolated, which was filtered off, the solvent was concentrated, and the residue (2.6 g of viscous liquid) was distilled. The amounts of 0.5 g of the original (I) and 1.6 g (20.0%) of the diethylamide of α -diphenylphosphorylbutyric acid (VII), bp 225-227° (1 mm), n_D^{20} 1.5423, were obtained. Found: P 7.3; N 3.8%. Calculated for C₂₄H₃₄NO₂P: P 7.8; N 3.5%.

Complex of the Oxide of Diphenyl[dibutylcarbamoylmethyl]phosphine (I) with Uranyl Nitrate. To a solution of 0.4 g (1 mmole) of (I) in 10 ml of CHCl₃ was added a solution of 2.3 g (3 mmoles) of uranyl nitrate in 10 ml of water and shaken in a separatory funnel for 5 min. The organic layer was separated from the water, the crystals falling out from the CHCl₃ being filtered off, washed with water, and dried in vacuum. The amount of 0.6 g (73.2%) of the complex, mp 222-223°, was obtained. Found: P 4.1; N 5.4%. Calculated for C₂₂H₃₀N₃O₁₀PU: P 4.1; N 5.4%. The rest of the complexes were prepared in analogous manner (see Table 2).

Extraction of TPE by Reagents (I)-(VI). Extraction from 1-15 M HNO₃ was done by equal volumes of reagents in DCE over a period of 3 min (time sufficient for establishment of equilibrium). After standing and separation of the phases, the γ activities of their aliquot parts were measured and the distribution coefficients D were calculated.

CONCLUSIONS

1. Oxides of dialkyl(diaryl)[dialkylcarbamoylmethyl]phosphines have been synthesized and characterized.
2. The character of the substituents on the phosphorus atom substantially influences the extraction properties of the compounds obtained with respect to Am(III), the p-phenyl-substituted derivatives being most effective.

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