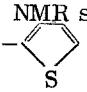
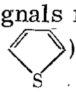
at 0° were filtered off, washed with MeOH, and vacuum-dried. Obtained 0.6 g (14%) of a substance with mp 102.2-103.8°. Found: C 73.12; H 7.78; S 10.80; B 3.77; N 4.86%. $C_{18}H_{22}BSN$. Calculated: C 73.22; H 7.51; S 10.85; B 3.66; N 4.74%. PMR spectrum ($CDCl_3$): signals from protons of adamantane system (0.55-2.71 ppm) and signals from aromatic protons of pyridine and thienyl protons (6.21-8.05 ppm). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): broad signals from carbon atoms with boron 26.4 ($B-CH_2$) and 45.2 ($B-CH-$); signals from other carbon atoms in 1-boraadamantane: three doublets at 32.16, 32.99, and 39.54 (CH); three triplets at 34.70, 40.33, and 41.90 (CH_2), and signals from carbon atoms of heterocyclic fragments, thiophene: 120.09 d, 121.88 d, 125.65 d, and 154.87 s ($-C$); pyridine: 124.84 d, 138.81 d, and 144.52 d. Mass spectrum: 295 (M^+), 216 ($M^+ - Py$) (maximum peak).

CONCLUSIONS

From 2-propargylthiophene and triallylborane, 2-(2-thienyl)-1-boraadmantane has been obtained.

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POLY(DIPHENYLPHOSPHINYLMETHYL) ARENES, ORGANOPHOSPHORUS EXTRACTANTS FOR TRANSPLUTONIUM ELEMENTS

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UDC 542.91:547.1'118

In previous papers the synthesis and extraction properties for tervalent transplutonium elements, europium and sexivalent uranium are described of new organophosphorus extractants, viz. the oxides of di-, tri-, and tetraphosphines based on the isomeric xylenes, mesitylene, and durene [1, 2].

The present study was conducted to develop a previously advanced thesis concerning the inclusion in the ligand molecule of fragments which restrict its conformational mobility as a method of imparting high selec-

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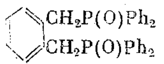
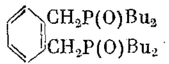
tivity to the reagent [3]. In the series of extractants studied previously the selectivity of extraction depends on the mutual position of the functional diphenylphosphinylmethyl groups in the benzene nucleus. For example, high selectivity towards uranium has been noted for the ortho-isomer of bis(diphenylphosphinylmethyl)benzene (I), in contrast to the other reagents containing two, three or two pairs of diphenylphosphinylmethyl groups in the meta-position relative to each other.

A theoretical conformational calculation of the molecules of these ligands, not combined in a complex, is made in [4]. For the ligand (I) a global minimum energy is found, corresponding to a distance of 0.28 nm between the oxygen atoms of the phosphoryl groups present in the ortho-position. This explains the preference for chelation by the ligand (I) of metal ions for whose coordination polyhedron the distance cited is characteristic (0.26-0.28 nm in the case of the uranyl ion). Since for ligands having a meta-position of the phosphoryl groups the energy varies little with a change in the distance between the oxygen atoms, they do not exhibit selectivity towards ions of different radius.

To confirm the effect found for the ortho-position of coordination centers in the complexing agent in this paper the synthesis and extraction properties of reagents (II)-(IV) containing phosphinylmethyl substituents in the ortho-position of the aromatic ring are described.



(I)



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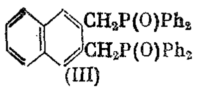

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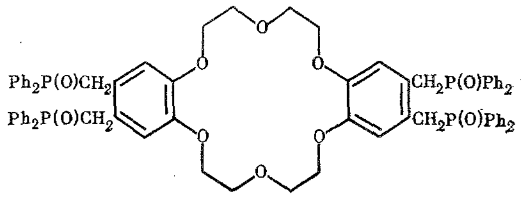
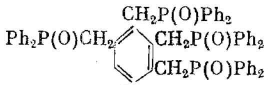
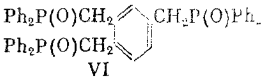


(IV)

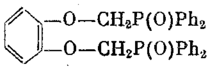


(V)

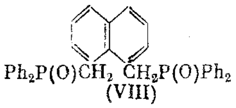


VI

For comparison, the diphosphine dioxide (VII) analogous to ligand (I), and the diphosphine dioxide (VIII), having a peri-naphthylenic bridge



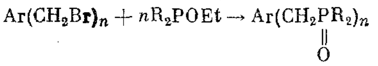
(VII)



(VIII)

were also synthesized from catechol.

The reagents (III)-(VI), (VIII) were synthesized by the Arbuzov reaction from the corresponding, well-known bromomethyl derivatives and the ethyl ester of diphenylphosphinic or dibutylphosphinic acid in the synthesis of (II)



$$\mathrm{Ar(CH_2Br)}_n + n\mathrm{R_2POEt} \rightarrow \mathrm{Ar(CH_2}\underset{\underset{\displaystyle O}{\|}}{\mathrm{P}}\mathrm{R_2)}_n$$

$$R = Ph,\ Bu,\ n = 2—4.$$

The reaction products, crystalline polyoxides of polyphosphines, are isolated in good yields. The dioxide (VII) was synthesized by the reaction of the disodium salt of catechol with diphenylchloromethylphosphine

$$\mathrm{C_6H_4(ONa)_2 + 2ClCH_2P(O)Ph_2 \rightarrow (VII)}$$

The reagents synthesized were tested as extractants for tervalent americium and europium and sexivalent uranium (^{241}Am, $^{152-154}$Eu, ^{233}U). Extraction from 1-15 M HNO_3 was carried out with an equal volume of a 0.025 M solution of the reagent in $CHCl_3$. After allowing to settle and separating the phases the radioactivity of aliquot portions of them was measured and the distribution coefficients (D) calculated. The results of the measurements are presented in Figs. 1 and 2.

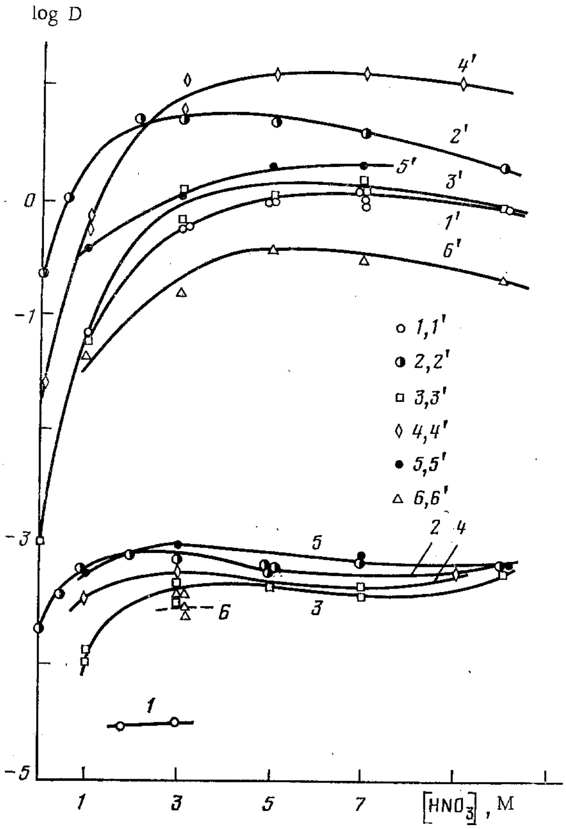


Fig. 1

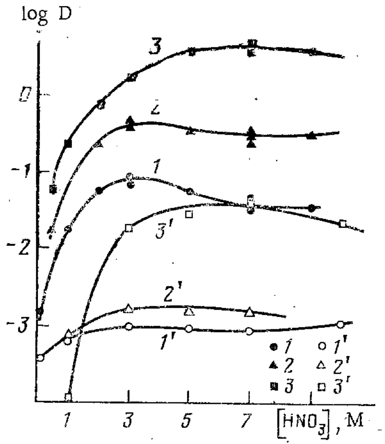


Fig. 2

Fig. 1. Extraction of americium (1-6) and uranium (1'-6') by 0.025 M solutions of the reagents: (I), (1, 1'); (II) (2, 2'); (III), (3, 3'); (IV), (4, 4'); (V), (5, 5'); and (VII), (6, 6') in chloroform from nitric acid solutions.

Fig. 2. Extraction of americium (1, 1'), europium (2, 2'), and uranium (3, 3') by a 0.025 M solution of reagent (VI) (1, 2, 3) and a 0.01 M solution of reagent (VIII) (1', 2', 3') in chloroform from nitric acid solutions.

A comparison of the extraction power and selectivity of reagents containing one or two pairs of phosphinylmethyl groups occupying the ortho-position in the bridging aromatic ring (benzene, naphthalene, dibenzo-18-crown-6) shows (see Fig. 1) that all the ligands of this type have a high extracting power and selectivity. The separation factors for the U/Am couple is everywhere fairly high and varies from $1.9 \cdot 10^4$ for (I) and (IV) to $8.3 \cdot 10^2$ for (VII), whereas the separation factors for Am and Eu are very low. It is interesting that for the compound (VII) (curves 6 and 6'), in which the phosphinylmethyl groups are separated from the aromatic ring by oxygen atoms, the lengthening of the side chains has little effect on the selectivity of the reagent but on the whole impairs the extraction properties.

The curves presented in Fig. 2 for the extraction of Am, Eu, and U by the tridentate reagent (VI), also containing two out of three phosphinylmethyl groups in the ortho-position, show that the reagent (VI) differs in selectivity from reagents (I)-(V) and is similar to the reagents we described previously in [1], where two P = O groups of the substituents occupying the meta-position participate in complex formation with Am [1, 4]: f U/Am = 24.0; f Eu/Am = 6.02 in 3 M HNO_3. In the case of reagent (VI) it would seem that phosphinylmethyl groups not occupying the ortho- and meta-position also participate in complex formation.

The compound (VIII), in which a rigid, transoidal arrangement of the phosphinyl groups with an increase in distance between the oxygen atoms (~ 3.7 Å) is observed compared with reagent (I), differs from all the reagents listed above by low extracting power, solubility ($\leq$ 0.01 M), and selectivity (see Fig. 2).

A comparison of the extracting power of reagents (I) and (II), which differ in the substituents at the phosphorus atoms (see Fig. 1, curves 1, 1' and 2, 2') would seem to show a regular increase in D_{Am} and D_U (~by factors of 15 and 10, respectively) when the phenyl substituents are replaced by less electronegative substituents, viz. butyl. However, this contradicts the "phenyl effect" which we established previously [5].

So far, we have considered the appearance of a phenyl effect in the extraction of Am in systems containing tetraphenylmethylenediphosphine dioxide, where Am is readily extracted. As shown by the calculations in [6], the reagent has a stable conformer, the structure of which is favorable for closing a ring containing Am without substantial loss in conformation energy. The stacking interaction of the phenyl rings provides an increased rigidity of this ligand compared with the alkyl-substituted analogs and, as a result, a higher extracting power. In the present case we are dealing with reagent (I), the structure of whose most stable conformer is unfavorable for complex formation with Am, due to the too low distance between the reaction centers ($R_{O\ldots O}$) [4]. The stacking interaction of phenyl rings provides an enhanced rigidity of the structure compared with the butyl-substituted analog (reagent (II)) but in the present case this plays a negative role. It is possible that a change to conformations having a larger $R_{O\ldots O}$ distance is achieved for the butyl analog having a less rigid structure and this is the reason for the increase in extraction compared with the phenyl-substituted reagent.

The results obtained confirmed the suggestion made previously [1] that selectivity in the group of reagents studied is determined by the mutual position in the bridging aromatic ring of a pair of substituents containing functional P=O groups; as was shown in [1], all the reagents having substituents in the meta-position exhibit the same selectivity as the reagents described in the present study, which have substituents in the ortho-position. Here the selectivity is virtually independent of the number of pairs of substituents and of the nature of the substituents at the phosphorus atoms.

EXPERIMENTAL

1,2-Bis(diphenylphosphinylmethyl)benzene (I), mp 284-285°C, synthesized by the method in [1] with a yield of 94%.

1,2-Bis(dibutylphosphinylmethyl)benzene (II). A mixture of 2 g o-xylylene dibromide [7] and 4.5 g of ethyl dibutylphosphinic acid [8] in 10 ml of xylene was heated to 140°C for ~ 30 min (in a current of N_2); after diluting the hot reaction mixture with hexane the precipitate was recrystallized from methylethyl ketone (MEK). Yield of (II), 2 g (62%), mp 181°C. Found: C 67.2; H 10.1; P 14.0. Calculated for $C_{24}H_{44}O_2P_2$: C 67.6; H 10.4; P 14.5%.

2,3-Bis(diphenylphosphinylmethyl)naphthalene (III). Prepared analogously to (II) by the reaction of 2 g of 2,3-dibromomethylnaphthalene [9] and 4 g of ethyldiphenylphosphinic acid (EDPA) in 10 ml of xylene; the precipitate deposited was washed with hot benzene and recrystallized from alcohol. Yield of (III) 3.3 g (93%), mp 286-287°C. Found: C 77.9; H 5.5; P 11.1%. Calculated for $C_{36}H_{30}O_2P_2$: C 77.7; H 5.4; P 11.1%.

Bis(4,5-diphenylphosphinylmethylbenzo)-18-crown-6 (IV). Prepared analogously to (II) from 1.47 g bis(4,5-dibromomethylbenzo)-18-crown-6 [10] and 3 g EDPA in 10 ml xylene. Yield of (IV), recrystallized from an alcohol–chloroform mixture, 1.3 g (54%), decomp. temp. > 325°C. Found: C 70.7; H 5.5; P 10.0%. Calculated for $C_{72}H_{68}O_{10}P_4$: C 71.0; H 5.6; P 10.2%.

1,2,3,4-Tetrakis(diphenylphosphinylmethyl)benzene (V). Prepared analogously to (II) from 2 g 1,2,3,4-tetrabromomethylbenzene [11] and 7.6 g EDPA in 15 ml xylene. Yield of (V), recrystallized from MEK, 2.3 g (55%), mp 263-265°C. Found: C 74.5; H 5.7; P 13.0%. Calculated for $C_{58}H_{50}O_4P_4$: C 74.5; H 5.4; P 13.2%.

1,2,4-Tris(diphenylphosphinylmethyl)benzene (VI). Prepared analogously to (II) by the reaction of 1.95 g 1,2,4-tribromomethylbenzene [12] and 4 g EDPA in 10 ml xylene; after diluting the hot reaction mixture with hexane the precipitate was recrystallized from MEK. Yield of (VI) 2.3 g (58%), mp 238-240°C. Found: C 75.7; P 13.0%. Calculated for $C_{45}H_{39}O_3P_3$: C 75.0; H 5.5; P 12.9%.

1,8-Bis(diphenylphosphinylmethyl)naphthalene (VIII). Obtained from 2 g 1,8-dibromomethylnaphthalene [13] and 6 g EDPA in 12 ml xylene, after recrystallization from chloroform, 3.4 g (96%) (VIII), mp 356-357°C. Found: C 77.6; H 5.3; P 11.2%. Calculated for $C_{36}H_{30}O_2P_2$: C 77.7; H 5.4; P 11.1%.

1,2-Bis(diphenylphosphinylmethoxy)benzene (VII). To a solution of 0.37 g Na in 6 ml of alcohol was added 0.88 g catechol in 5 ml DMPA and 4 g chloromethyldiphenylphosphine oxide in 15 ml DMPA (in a current of N_2). The mixture was heated in a sealed ampul for 6 h at 150°C. The precipitate was separated off and the filtrate evaporated to dryness in vacuum. The residue was dissolved in chloroform, washed with aqueous NaOH solution, then with water to pH 7, and dried with Na_2SO_4. The solvent was removed and the residue recrystallized from MEK. Obtained, 1.7 g (39%) (VII), mp 172-173°C. Found: C 71.1; H 5.7; P 11.5. Calculated for $C_{32}H_{28}O_4P_2$: C 71.4; H 5.2; P 11.5%.

CONCLUSIONS

1. New diphenylphosphinylmethyl substituted arenes, derivatives of benzene, naphthalene, and dibenzo-18-crown-6 have been synthesized.

2. The extraction properties of these ligands having limited conformational mobility have been studied relative to tervalent transplutonium elements, europium, and sexivalent uranium.

3. It has been shown that the extraction selectivity is dependent on the relative position of the coordination centers in the aromatic nucleus.

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PRODUCTION OF SOME DERIVATIVES OF 1,3,2-DIOXASTIBINANE AND THEIR VIBRATIONAL SPECTRA

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and I. Kh. Shakirov

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It is known that 2-alkyl- and 2-ethoxy-1,3,2-dioxastibolanes are high-melting coordination polymers insoluble in organic solvents [1]. The existence of intermolecular interactions with the formation of strong Sb_2O_2 bridging bonds in 2-methoxy-4,5-benzo-1,3,2-dioxastibolane [2] and Sb...O and Sb...Cl interactions in chlorodiethoxy- and dichloroethoxyantimony [3] in the crystalline state was established by x-ray crystallographic analysis. According to the data from cryoscopic and ebullioscopic measurements in benzene, 2-tert-butyl-1,3,2-dioxastibolanes exist in the monomeric form, are readily soluble, and melt at lower temperatures [4].

Earlier we described the synthesis of a series of 2-chloro and 2-methoxy derivatives of 1,3,2-dioxastibinane and their vibrational [5] and PMR [6] spectra. The compounds are characterized by high melting points,

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A. M. Butlerov Chemical Institute, V. I. Ul'yanov-Lenin Kazan' State University. A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1846-1851, August, 1984. Original article submitted June 27, 1983.

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