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Synthesis of Diphosphine Dioxides for Extraction of Actinides Using Supported Liquid Membranes Technology

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ABSTRACT

A recurrent method for synthesis of diphosphine dioxides to be used for extraction of actinides from acidic aqueous solution is described. Selective phosphonium salt formation and cleavage permits the stepwise introduction of different bridges between the phosphorus atoms as well as various chains on them. The influence of the structural parameters on liquid-liquid extraction properties of plutonium, neptunium, and americium is studied. Plutonium and neptunium can be efficiently removed from radioactive contaminated liquid wastes, using the supported liquid membranes technology with the more lipophilic organophosphorus extractants.

INTRODUCTION

Nuclear fuel reprocessing operations produce liquid wastes having medium level activity. These are treated by evaporation in order to concentrate their radioactivity into the smallest possible volume [1–3]. The greater part of these concentrates has to be disposed of in geological formations after embedding with regard to their activity associated with long-life radionuclides (actinides, strontium, cesium, . . .). Therefore, it would be desirable to remove these very long-life radionuclides from the contaminated liquid wastes before embedding. This would allow, on the one hand, the volume and the radiotoxicity of the wastes to be reduced, and, on the other hand, part of these decontaminated wastes to be directed to surface repositories. One chemical separation process could be coupled transport through supported liquid membranes (SLM) using specific carriers [4,5]. Organophosphorus compounds have an exceptional ability for the extraction of hard cations, particularly actinides, but monodentate organophosphorus compounds, even the most powerful ones, such as alkyl phosphine oxides, only extract actinides (IV), (VI) and, to a less extent (V), from low-acidity media. As bidentate extractants, such as carbamoylmethylphosphine oxides [6], diphosphine dioxides [7] and diphosphoramides [8], are able to remove actinides (III), our strategy to improve actinide extracting power, is to synthesize and use as extractants cyclic diphosphine dioxides.

We have noticed an increase of interest in the literature for phosphorylated macrocycles, particularly those containing a P–O–C [9], P–N–C [10], or P–S–C [11] linkage. Yet, there has been no specific interest in balancing their acidic hydrolysis sensitivity, since the heteroelements linked to the tetracoordinated phosphorus do not participate in complexation. The far more stable compounds having a P–C

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linkage have even created a widespread interest in metal extraction: phosphines are able to coordinate soft transition metals [12], and easy interconversion between oxidation states allows binding of hard metals by phosphine oxides [13]. Macrocycles of this type have been described, but specific methods of synthesis are used [14]. It would be of interest to develop a versatile synthetic method in order to design tailor-made ligands with predetermined numbers and types of donor atoms and ring sizes, wellfitted to extraction of specific metal cations.

RESULTS AND DISCUSSION

Application of the Recurrent Synthetic Method

The use of the recurrent method reported earlier [15] allows us to use a stepwise approach to linear or cyclic organophosphorus extractants that are more and more efficient, controlling the size, type of bridges between the phosphorus atoms, number, type, and position of heteroatoms, and number and type of side chains (Scheme 1).

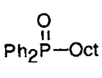
As we obtain a range of diphosphine dioxides **3**, **6**, **9**, the influence of the structural parameters (bridges between the two phosphoryls, side chains, and macrocyclic effect) on extractant properties can be studied. The recurrent method allows us to synthesize homologs of Lariat crown-ethers affording additional coordination sites in the side chains that can participate in the complexation of cations [16]. We have substituted one (**6b'2**) or two (**6b2**) phenyl groups by $-(CH_2)_2-OEt$ thanks to the nonspecificity of cleavage of the P–C bond in bis(β-functional)phosphonium salt **5b2** (Scheme 2). The departure of the alkyl chain instead of the phenyl group and the substitution of the methoxy by an ethoxy group (certainly due to the formation of an intermediate vinylphosphonium salt) have also been pointed out and quantified by ^{31}P NMR spectroscopy in the case of β-functional phosphonium salts **10** (Table 1, Scheme 3).

After chromatographic separation of the two compounds **6b2** and **6b'2**, we can then appreciate the importance of one or two additional coordination sites.

Since the distance between the two phosphorus atoms overcomes any steric influence directing the alkaline hydrolysis toward one or other of the diastereoisomers, approximately equal proportions of pure cis- and trans-stereoisomers **9bc** and **9bt** are obtained after separation by silica column chromatography. The structure of each isomer has been determined by X-ray single-crystal analysis [17], the difference in NMR and IR spectra being very small. Moreover, though diastereoisomers **9cc** and **9ct** have not been separated, ^{31}P NMR spectroscopy confirms that no diastereoselection phenomena can be seen. Nor is any steric influence noticed during the cyclization of the diphosphine **7b1**, and an equal proportion of cis- and trans-macrocyclic phosphonium salts **8b1c** and **8b1t** is obtained after cyclization. Alkaline hydrolysis, followed by chromatographic separation, leads to pure diastereoisomers **9b1c** and **9b1t**. Their structures have not been unambiguously determined, but we can assume by extrapolation of the results described before that the trans isomer is eluted first and therefore that **9b1c** and **9b1t** are, respectively, the cis- and trans-diastereoisomers (Scheme 4).

Extraction Results

The diphosphine dioxides obtained by the recurrent method (Table 2) have been first tested in liquid–liquid extraction. Since coefficients of distribution in extraction of neptunium [mainly (V)] were generally too low to be validly compared, discussion is thus based on the results obtained in the case of plutonium (IV) (Table 3). The results obtained are to be compared with those of monodentate ligands **15** and **16**, and to CMPO **17**, which has been considered until now to be the most powerful extractant of actinides [6].



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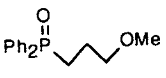

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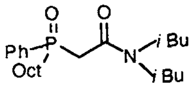

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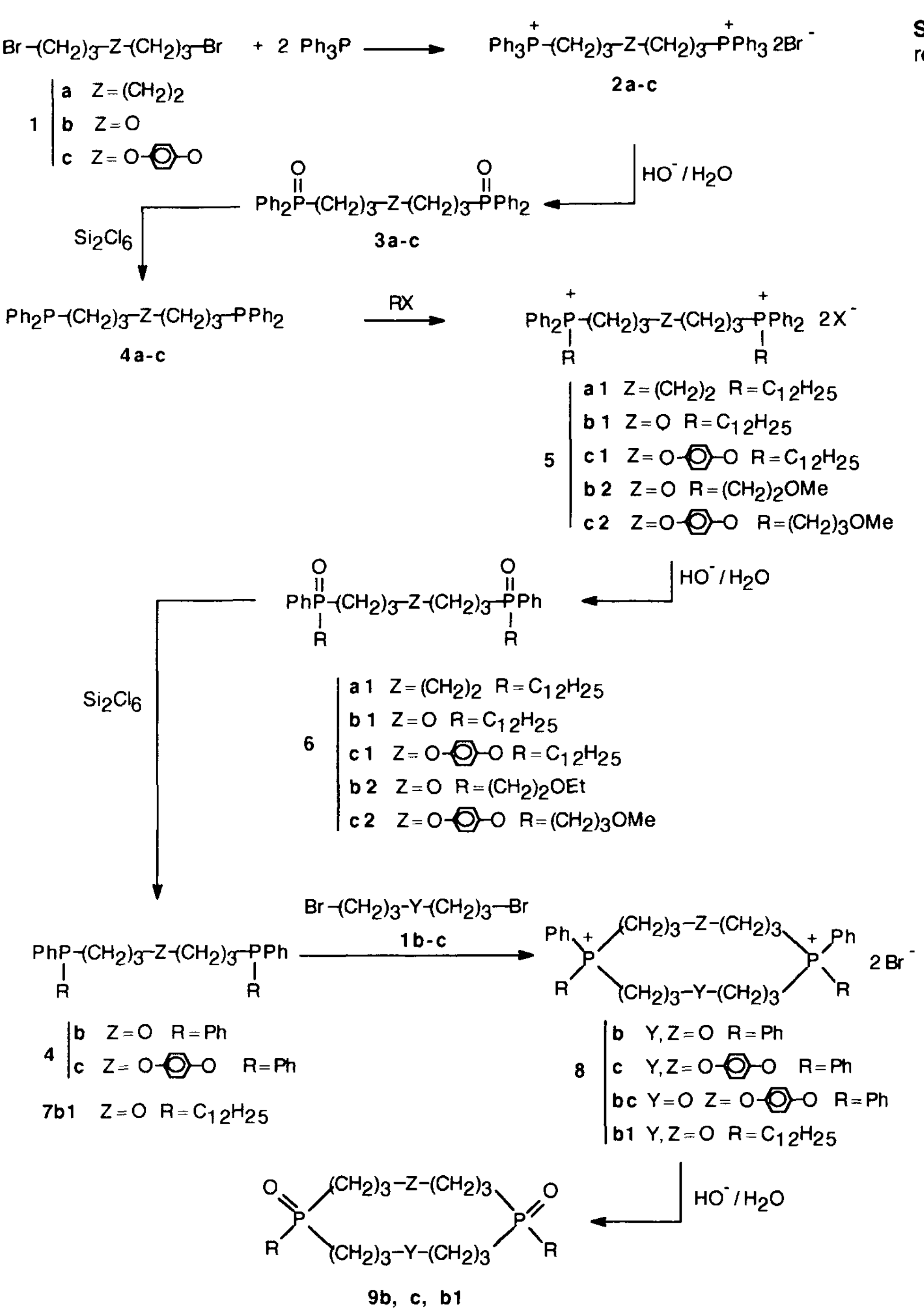
A comparison of the compounds **6b1** and **9b1c** shows that the distribution coefficients D_{Pu} are increased by a factor of 2 when the extractant is cyclic (Table 3). Moreover, as explained by Myasoedov et al. [7], the extractant ability is generally higher for the compound in the cis position than for that in the trans position.

The compounds **3a**/**6a1**, **3b**/**6b1**, **3c**/**6c1**, **9bt**/**9b1t**, and **9bc**/**9b1c** differ from the others only by the substituent: The replacement of the phenyl group by a less electronegative alkyl group increased the plutonium distribution coefficients. Another advantage of the long chain is that it results in a better solubilization of the extractant in nitrophenylhexylether (NPHE), the solvent commonly used in extraction studies (for instance, **6a1** is soluble in NPHE at a 10^{-2} M concentration, contrary to **3a**, which is insoluble at this concentration).

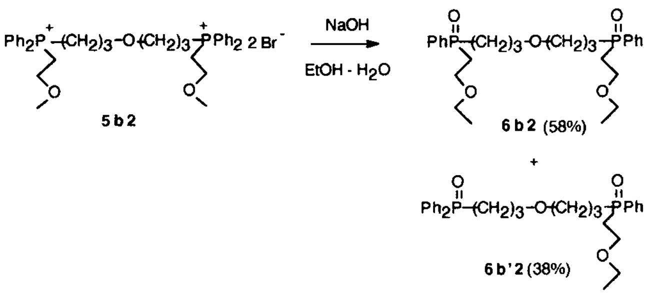
If we compare the acyclic compounds **3a**, **6b1**, **3c**, **6c1**, **6b2**, **6b'2**, and **6c2**, some tendencies can be observed: The replacement of a phenyl group by an ether substituent increased the extraction of plutonium, but the substitution of an alkyl by an ether substituent did not always increase the extraction ability of plutonium. Obviously, compounds with two ether substituents are more effective for the uptake of plutonium than those with only one ether substituent.

Examination of plutonium distribution coefficients shows that the substitution of a methylene group by an oxygen atom or a hydroquinone group



SCHEME 1 Application of the recurrent synthetic method.

in the bridge linking the two phosphoryl groups improved the extraction of plutonium. The hydroquinone group leads to a more effective compound for the uptake of plutonium than the oxygen atom. Compounds containing simultaneously alkyl groups linked to phosphoryl groups and hydroquinone groups in the bridge are very effective plutonium extractants because of the combination of the two effects. For instance, **6c1** is a very effective compound for the extraction of plutonium as its distribution coefficient ($D = 35$) is higher than the coefficient obtained with CMPO. It must be noticed that only **9b1c**, a macrocyclic compound, is more efficient than the linear compound **6c1**. The distribution co-



SCHEME 2 Alkaline hydrolysis of a bis(β-functional)phosphonium salt.

efficients for stripping of plutonium and neptunium, which are smaller than 0.07 and 0.05, respectively, should allow transport by use of the technology of supported liquid membranes.

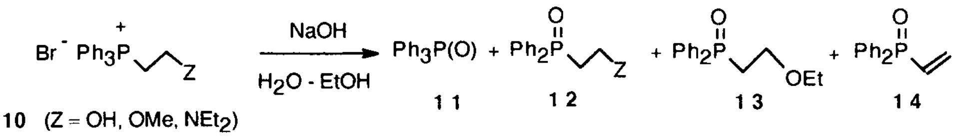
Transport Experiments

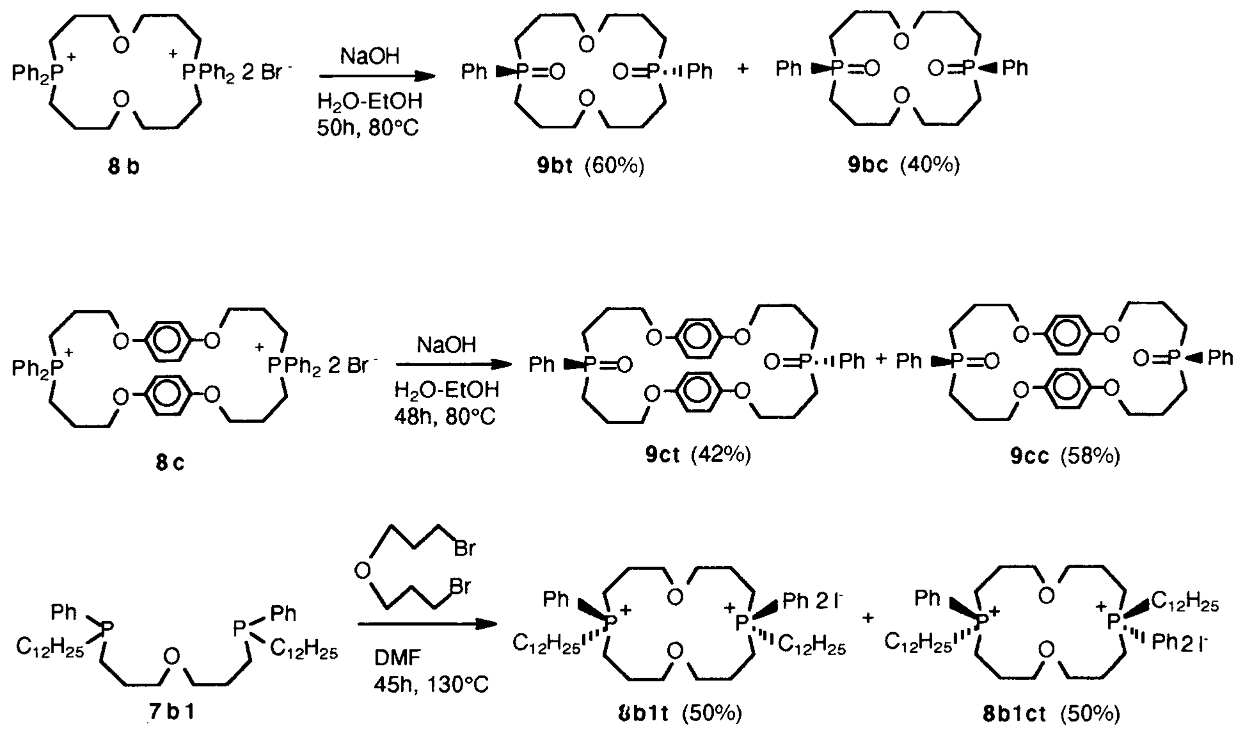
Supported Liquid Membranes. The selective solvents used for extraction are often very expensive and thus limit the use of the techniques mentioned previously; work was therefore carried out in this study on the use of selective solvents with liquid membranes technology.

Supported liquid membranes (SLM) are made up of two-aqueous phases separated by an organic phase. The aqueous phase, called the feed phase, contains the radioelements to be extracted by means of the organic phase. These are then carried to the other aqueous phase, called the stripping phase. The organic phase, constituted by an extractant dissolved in a diluent, impregnates a microporous support placed between the aqueous phases. The driving force of the process is attributable to the difference of the nitrate concentrations in the feed phase [$NaNO_3$ (4 M), HNO_3 (1 M)] and in the stripping phase (no nitrate). The transport mechanism that takes place is called co-transport, as the cation and the extractant transit through the membrane in the same direction.

The use of neutral carriers, such as a phosphine oxide, leads to the coupled co-transport of cations and nitrate anions through the SLM [18]. When concentrates of fission product solutions are used as the feed solution, and demineralized water as the stripping solution, the concentration gradient of the nitrate anions will force the transport of actinide cations against their own concentration gradient, thus

SCHEME 3 Alkaline hydrolysis of β-functional phosphonium salts **10**.





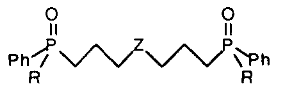
SCHEME 4 Study of the diastereoisomeric proportions.

leading to their concentration in the stripping solution. Nevertheless, the basicity as well as the polarity of the organic diluent that we have chosen to use in order to improve actinide extraction—by a better solvation of the complex paired anion in the membrane (nitrates are hydrated anions not easily extracted in major conventional organic solvents)—lead to substantial transport of nitric acid from the feed to the stripping solution. This reduces cation permeation through the SLM by decreasing the nitrate concentration gradient.

TABLE 1 Ratio (%) of Products from the Alkaline Hydrolysis of β-Functional Phosphonium Salts **10**

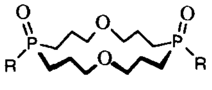
Z	11	12	13	14
OH	7	0	90	3
NEt_2	7	73	20	0
OMe	14	0	82	1

TABLE 2 Diphosphine Dioxides Tested in Liquid—Liquid Extraction



Z	R Ph	 $nC_{12}H_{25}$	 $(CH_2)_nOR'$
CH_2CH_2	**3a**	**6a1**	---
O	**3b**	**6b1**	**6b2** *
	**3c**	**6c1**	**6c2** **

* n = 2, R' = Et
** n = 3, R' = Me



R	cis	trans
Ph	**9bc**	**9bt**
$nC_{12}H_{25}$	**9b1c**	**9b1t**

TABLE 3 Results Obtained in Liquid–Liquid Extraction[a]

	Pu Extraction		Am Extraction	Np Extraction	
Compound	D. Pu	% Ext.	D. Am	D. Np	% Ext.
3a	0.06	5.7	<0.001	0.6	37.5
3b	0.11	9.9	<0.001	0.45	31
3c	17	94.9	0.0006	1	50
6a1	12	92.3	0.04	0.5	33.3
6b1	20	95.2	0.05	0.9	47.4
6c1	35	97.2	0.004	1.2	54.5
6b2	35	97.2	0.02	1.2	54.5
6b'2	14.2	93.3	0.01	1	50
6c2	30	96.8	0.004	4.1	80.4
9bt	0.1	9.1	<0.001	0.45	31
9bc	0.5	33.3	<0.001	0.35	25.9
9b1t	28	96.6	0.006	1.1	52.4
9b1c	41	97.6	0.01	1.8	64.3
15	0.16	13.8	<0.001	0.19	16
16	5	83.3	0.003	0.35	25.9
17	22	95.6	1.2	0.85	45.9

[a]Feed solution: $NaNO_3$ (4 M) + HNO_3 (1 M); solvents used: nitrophenyloctylether or nitrophenylhexylether; and strip solution: oxalic acid (0.5 M) or trisodium citrate (0.25 M).

Permeability Determination. The transport of ^{237}Np, ^{239}Pu, ^{241}Am from synthetic aqueous solutions of $NaNO_3$ (4 M) and HNO_3 (1 M), was followed by regular measurement of the decrease of radioactivity in the feed solution by α spectrometry analysis. This allowed graphical determination of the constant permeabilities P ($cm \cdot h^{-1}$) of actinide permeation through the SLM for 6–7 hours, by plotting the logarithm of the ratio C/C^0 vs. time, as described in the model of mass transfer proposed by Danesi [5]

$$\ln \frac{C}{C^0} = -\frac{\varepsilon \cdot S}{V} \cdot P \cdot t$$

where C is concentration of the cation in the feed solution at time t ($mol \cdot l^{-1}$); C^0 is initial concentration of the cation in the feed solution ($mol \cdot l^{-1}$); ε is volumic porosity of the SLM (%); S is membrane surface area (cm^2); V is volume of feed and stripping solutions (cm^3); and t is time (h).

Transport experiments were carried out under the same conditions as those previously described with the most promising compounds; their permeability dropped following the decreasing order (Table 4): P_{Pu} **17** > **9b1c** > **6c1** > **6a1** > **9b1t** > **6c1** > **6c2** > **6b2**; P_{Np} **6c1** > **9b1c**, **9b1t** > **17** > **6b1** > **6a1** > **6b2**, **6c2**.

CMPO **17**, although exhibiting smaller distribution coefficients than **9b1c**, is a slightly better carrier for plutonium. The relatively low permeability determined with some extractants (**6b2**, **6c2**) can be explained by the parasitic competition of H_3O^+, or by insufficient stripping of cations, in spite of the presence of an actinide complexing agent in the stripping solution, such as oxalic acid or sodium citrate.

In the case of neptunium, the hydroquinonic bridged compound **6c1** and, to a lesser extent, mac-

TABLE 4 Results Obtained in Transport Experiments

	Permeability ($cm \cdot h^{-1}$)		Maximum Extracted	
Compound	Np	Pu	Np (%)	Pu (%)
6a1	0.23	2.37	38	85
6b1	0.62	2.47	41	98
6c1	1.43	1.95	60	87
6b2	0.1	0.37	45	80
6c2	0.1	0.94	60	90
9b1t	0.84	2.17	73	90
9b1c	0.84	3	47	86
17	0.74	3.44	68	100

rocyclic compounds **9b1c** and **9b1t**, are better carriers than CMPO.

These transport experiments confirmed the interest of implementing bidentate cyclic compounds such as **9b1c** or bidentate linear compounds such as **6c1** to achieve the α decontamination on supported liquid membranes.

EXPERIMENTAL

Synthesis of Extractants

Alkylations of phosphines and reduction of diphosphine dioxides were performed in a dry, oxygen-free nitrogen atmosphere, using standard Schlenk techniques. Benzene was dried by refluxing over, and distilling from, sodium benzophenone ketyl under N_2, the distillate being stored over sodium. DMF was dried by azeotropic distillation of water with benzene (10% v/v) at atmospheric pressure, followed by a distillation of DMF at 20 mm Hg under nitrogen, the distillate being stored on type 4 Å molecular sieves. The commercially available starting compounds were distilled under N_2. Since there is some danger of detonation on distillation [19], commercially available Si_2Cl_6 96% was used without further purification.

Melting points were determined using a METTLER FP5 or a Wild LEITZ 350 apparatus. Infrared spectra were recorded on a PERKIN-ELMER 377 spectrophotometer; IR samples were prepared as KBr pellets unless noted otherwise. Spectral bands are reported in cm^{-1}. The band intensity is noted as follows: vw = very weak; w = weak; m = medium; s = strong; vs = very strong. ^1H-NMR spectra were taken on either a BRUKER Ac 250 or a BRUKER Ac 200 instrument. The chemical shifts (δ) are reported in parts per million (ppm). Solvent provided the internal deuterium lock signal. The spin multiplicity is noted as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Proton decoupled ^{13}C and ^{31}P-NMR spectra were collected on a BRUKER Ac 200 instrument. Microanalyses were carried out by the Service Central de Microanalyse, CNRS, Montpellier. Mass spectral data were collected on a JEOL JMS-DX 300 spectrometer.

Notes: (a) To obtain the phosphonium salts as iodides or tetraphenylborates required anion exchange, carried out by repeated washing of a solution of phosphonium salts in CH_2Cl_2 or $CHCl_3$, with aqueous solutions of NaI or stirred in acetone with $NaBPh_4$. This operation will not be cited again below.

(b) Compounds with a hydroquinonic bridge **c** contain a few percent (less than 3%) of impurity (detected by ^1H, ^{13}C NMR and confirmed by mass spectroscopy), because of the presence in **1c** of the higher homolog ($Z = p\text{-}C_6H_4O_2\text{–}(CH_2)_3\text{–}p\text{-}C_6H_4O_2\text{–}$).

*Preparation of Linear Bisphosphonium Salts **2** or **5***

General Procedure for the Synthesis of Salts **2**. A mixture of appropriate dihalogenated reagent, triphenylphosphine (2.5 equivalents) in anhydrous dimethylformamide, is refluxed during 16 hours under nitrogen. After cooling, and concentration of DMF, the residue obtained is dissolved in $CHCl_3$. The precipitation of the salt in ether (volume ratio $CHCl_3/Et_2O$:1/10) is followed by crystallization in $CHCl_3$/AcOEt.

General Procedure for Synthesis of Salts **5**. A mixture of linear diphosphine and halogenated reagent (2.5 equivalents) in anhydrous dimethylformamide is warmed between 70 and 150°C (depending on the alkylating agent used) during more than 20 hours under nitrogen. After cooling, evaporation of the solvent, and exchange of anion with NaI or $NaBPh_4$, the crude oil is precipitated in a tenfold volume of ether or hexane and the solid obtained is crystallized from $CHCl_3$/AcOEt.

The yields, NMR, IR, and mass characteristics of the disalts obtained are gathered in Table 5. Specific details are given for each compound.

1,8-Octamethylene Bis-triphenylphosphonium Dibromide **2a**. Yield = 78%. mp = 262°C ($CHCl_3$/AcOEt). IR: 1010vw, 1030vw, 1070vw, 1115vs, 1165vw, 1180w, 1190w, 1235w, 1250m.

4-Oxa-1,7-heptamethylene Bis-triphenylphosphonium Dibromide **2b**. Yield = 87%. mp = 260°C ($CHCl_3$/AcOEt). Anal. calcd. for ($C_{42}H_{42}Br_2OP_2$ + 1/2 H_2O): C, 63.57; H, 5.46; O, 3.02. Found: C, 63.62; H, 5.46; O, 2.77. IR: 1010vw, 1030w, 1050w, 1075w, 1110vs, 1160w, 1190m, 1210vw, 1225w.

1,4-Bis(3-triphenylphosphoniopropoxy)benzene Dibromide **2c**. Yield = 90%. mp = 268°C ($CHCl_3$/AcOEt) (litt. 250°C) [15]. IR: 1035s, 1070w, 1110vs, 1160w, 1182m, 1230vs. ^{13}C NMR ($CDCl_3$, c = 0.7 M): δ = 19.69 (d, $^1J_{PC}$ = 52.7 Hz, CH_2–P); 22.83 (s, C–CH_2–C); 66.97 (d, $^3J_{PC}$ = 16.5 Hz, CH_2–O); 115.61 (s, phenolic C); 118.01 (d, $^1J_{PC}$ = 83.3 Hz, ipso); 130.51 (d, $^3J_{PC}$ = 12.6 Hz, meta); 133.60 (d, $^2J_{PC}$ = 10.0 Hz, ortho); 135.12 (d, $^4J_{PC}$ = 2.8 Hz, para); 152.38 (s, phenolic C–O).

1,8-Octamethylene Bis-dodecyldiphenylphosphonium Diiodide **5a1**. Reaction conditions: 140°C during 80 hours. Yield = 70%. mp = 112°C. IR: 1025vw, 1065vw, 1085w, 1115s, 1157m, 1175vw, 1220vw, 1235vw.

4-Oxa-1,7-heptamethylene Bis-dodecyldiphenylphosphonium Bistetraphenylborate **5b1**. Reaction conditions: 150°C during 20 hours. $\text{Yield}_{\text{crude}}$ = 96%. mp = 270°C. Anal. calcd. for $C_{102}H_{102}B_2O_2P_2$: C,

TABLE 5 Yields and Spectroscopic Characteristics of Linear Bisphosphonium Salts **2** or **5**

Compound	*Yield (%)*	*$\delta^{31}P$*[a]	*δ^1H NMR*[a,b] *(J_{in}, Hz)*				*Mass*[c] *$(M - X)^+$*
			C–CH_2–P	*C–CH_2–O*	*C–CH_2–C*	*CH_3*	
2a	78	24.7	3.50–3.65 (m, 4H)	—	1.22 (m, 4H)[d] 1.57 (m, 8H)[d]	—	715
2b	87	25.5	3.67 (4H) (t, $^3J_{HH}$ = 5)	3.75–4.00 (m, 4H)	1.70–2.00 (m, 4H)	—	703
2c	90	24.4	3.45–3.65 (m, 4H)	4.05–4.15 (m, 4H)	2.00–2.20 (m, 4H)	—	795
5a1	70	28.4	3.09 (m, 8H)[e]	—	0.95–1.25 (m, 36H) 1.40 (m, 16H)[d]	0.74 (t, 6H, $^3J_{HH}$ = 7)	947
5b1	96	26.6	2.90–3.13 (m, 8H)	3.39 (4H) (t, $^3J_{HH}$ = 6)	1.11 (m, 32H)[d] 1.36 (m, 8H)[d] 1.53–1.73 (m, 4H)	0.76 (6H) (t, $^3J_{HH}$ = 6)	
5c1	82	28.6	31.6 (m, 4H)[e] 3.41 (m, 4H)[e]	4.02 (m, 4H)[d]	1.15 (m, 32H)[d] 1.47 (m, 8H)[d] 1.98 (m, 4H)[e]	0.82 (6H) (t, $^3J_{HH}$ = 6)	450[f]
5b2	99	30.1	3.30–3.65 (m, 8H)	3.30–3.65 (m, 8H)	1.14 (4H) (t, $^3J_{HH}$ = 7)	3.01 (s, 6H)	
5c2	99	29.0	3.25–3.80 (m, 8H)	3.25–3.80 (m, 4H) 4.00–4.20 (m, 4H)	1.75–2.10 (m, 8H)	3.23 (s, 6H)	835

[a] The solvent used is $CDCl_3$ except for **2c**, **5b1** (CD_3OD).

[b] The aromatic protons give a multiplet from 7.40 to 8.00 except for **5b1** (9.10–9.50) with supplementary singlet at 6.80, 6.66 for **2c**, **5c1** and a multiplet 6.60–6.80 for **5c2**.

[c] Fast Atomic Bombardment in nitrobenzyl alcohol.

[d] $\Delta\nu/2$ = 11–15 Hz.

[e] $\Delta\nu/2$ = 27 Hz.

[f] $(M - 2Br)^{2+}/2$.

85.82; H, 7.20; O, 1.12. Found: C, 85.02; H, 7.30; O, 0.98. IR: 1035w, 1065w, 1140w, 1150w, 1180vw, 1220w.

1,4-Bis(3-dodecyldiphenylphosphoniopropoxy)-benzene Dibromide **5c1**. Reaction conditions: 140°C during 48 hours. Yield = 82%. mp = 56–57°C (Leitz). IR ($CHCl_3$): 1025m, 1052m, 1110s, 1170w, 1225s.

4-Oxa-1,7-heptamethylene Bis-(2′-methoxyethyl)-diphenylphosphonium Diiodide **5b2**. Reaction conditions: 100°C during 70 hours. Yield = 99%. IR: 1015vw, 1070vw, 1118s, 1165vw, 1230s.

1,4-Bis[3-(3′-methoxypropyl)diphenylphosphoniopropoxy]benzene Diiodide **5c2**. Reaction conditions: 70°C during 72 hours. Yield = 99%. IR: 1028w, 1060w, 1090w, 1113s, 1170w, 1230m. ^{13}C NMR ($CDCl_3$, c = 0.7 M): δ = 18.30 (d, C–CH_2–C, $^2J_{PC}$ = 2.7 Hz); 19.35 (s, C–CH_2–C); 22.16 (d, $^1J_{PC}$ = 21.1 Hz, CH_2–P); 22.47 (d, $^1J_{PC}$ = 20.5 Hz, CH_2–P); 58.60 (s, O–CH_3); 66.76 (d, $^3J_{PC}$ = 16.3 Hz, CH_2–O); 70.66 (d, $^3J_{PC}$ = 15.1 Hz, CH_2–O); 115.46 (s, phenolic C); 117.61 (d, $^1J_{PC}$ = 83.3 Hz, ipso); 130.34 (d, $^3J_{PC}$ = 10.2 Hz, meta); 132.88 (d $^2J_{PC}$ = 9.6 Hz, ortho); 134.82 (d, $^4J_{PC}$ = 2.9 Hz, para); 152.33 (s, phenolic C–O).

Preparation of Cyclic Bisphosphonium Salts 8

General Procedure for the Synthesis of Salts **8**. The cyclization is achieved under high dilution conditions obtained with a multistep dilution process based on solvent recycling [15]. The yields, NMR, IR, and mass characteristics of the disalts obtained are gathered in Table 6. Specific details are given for each compound.

5, 5,13,13-Tetraphenyl-1,9-dioxa-5,13-diphosphoniacyclohexadecane Dibromide **8b**. Yield = 41%. mp = 306–308°C ($CHCl_3$/AcOEt-Leitz). IR: 1000m, 1025m, 1055w, 1068m, 1080w, 1110vs, 1170m, 1188m, 1220w, 1230w, 1245m.

6,6,16,16-Tetraphenyl-1,11-di-p-phenylene-2,10, 12,20-tetraoxa-6,16-diphosphoniacycloeicosaphane Diodide **8c**. Yield = 16%. mp > 350°C ($CHCl_3$–MeOH/AcOEt-Leitz). IR: 1000s, 1032s, 1050w, 1070w, 1090w, 1112s, 1165w, 1175w, 1212w, 1230w.

6, 6, 14, 14-Tetraphenyl-1-p-phenylene-2,10,18-trioxa-6,14-diphosphoniacyclooctadecaphane Diodide **8bc**. Yield = 35% [15b].

5, 13-Didodecyl-5, 13-diphenyl-1, 9-dioxa-5, 13-di-

TABLE 6 Yields and Spectroscopic Characteristics of Macrocyclic Bisphosphonium salts **8**

Compound	Yield (%)	$\delta^{31}P^a$	^1H NMR (J_{in}, Hz)^{a,b}				Mass^c $(M - X)^+$
			C–CH$_2$–P	C–CH$_2$–O	C–CH$_2$–C	CH$_3$	
8b	41	28.5	3.10–3.34 (m, 8H)	3.38 (8H) (t, $^3J_{HH}$ = 5)	1.60–1.80 (m, 8H)	—	649
8c	16	27.8	3.05–3.80 (m, 8H)	3.85–4.30 (m, 8H)	1.80–2.30 (8H)	—	881
8b1	57	32.32^d 32.46^d	2.65–3.85 (m, 12H)	2.65–3.85 (m, 8H)	1.4–2.15 (m, 48H)	0.86 (t, $^3J_{HH}$ = 7, 6H)	881

[a] The solvent used is $CDCl_3$ except for **8c** (DMSO-d_6).

[b] The aromatic protons give a multiplet from 7.50 to 8.05 with supplementary singlet at 6.72 for **8c**.

[c] Fast Atomic Bombardment in nitrobenzyl alcohol.

[d] Two diastereoisomers whose signals have the same intensity.

phosphoniacyclohexadecane Diiodide **8b1**. Mixture of cis- and trans-isomers. Yield = 57%. mp = 172–174°C ($CHCl_3$/AcOEt/hexane-Leitz). IR: 1000vw, 1030w, 1050w, 1100s, 1117s, 1160w, 1185vw, 1220w. Anal. calcd. for $C_{48}H_{84}I_2O_2P_2$: C, 57.13; H, 8.39; O, 3.17. Found: C, 57.43; H, 8.19; O, 3.90. ^{13}C NMR ($CDCl_3$, c = 0.09 M) characteristic signals: δ = 13.90 (s, CH_3); 69.15 (d, $^3J_{PC}$ = 10.0 Hz, CH_2O); 117.33 (d, $^1J_{PC}$ = 79.1 Hz, ipso); 117.40 (d, $^1J_{PC}$ = 80.0 Hz, ipso); 130.09 (d, $^3J_{PC}$ = 11.8 Hz, meta); 132.26 (d, $^2J_{PC}$ = 9.3 Hz, ortho); 132.35 (d, $^2J_{PC}$ = 8.9 Hz, ortho); 134.11 (s, para).

Alkaline Hydrolysis of Bisphosphonium Salts

General Procedure for the Synthesis of Diphosphine Dioxides **3** *and* **9**. The hydrolysis of the bisphosphonium salts is achieved using 10 equivalents of sodium hydroxide (5 N) in water with an organic solvent (homogeneous: ethanol; heterogeneous: toluene or benzene). After concentration (if ethanol is used), extraction of the aqueous phase with dichloromethane, the organic phases are combined, washed to neutrality, dried with Na_2SO_4, then concentrated. The residue is crystallized or chromatographed. The yields, NMR, IR, and mass characteristics of the linear and cyclic diphosphine dioxides obtained are gathered, respectively, in Tables 7 and 8. Specific details are given for each compound.

1,8-Octamethylene bis-diphenylphosphine Dioxide **3a**. Reaction conditions: 20 hours in refluxing benzene/H_2O. Yield = 89%. mp = 168°C (benzene/heptane). IR: 1007w, 1027w, 1067m, 1077w, 1099s, 1105s, 1117vs, 1157s, 1177vs, 1225m. Anal. calcd. for $C_{32}H_{36}O_2P_2$: C, 74.69; H, 7.05; O, 6.22. Found: C, 74.46; H, 7.17; O, 6.52.

4-Oxa-1,7-heptamethylene bis-diphenylphosphine Dioxide **3b**. Reaction conditions: 24 hours in refluxing benzene/H_2O. Yield = 97%. mp = 151°C (benzene/hexane). IR: 1025w, 1028m, 1040m, 1055w, 1070m, 1075w, 1105vs, 1120vs, 1160m, 1185vs, 1200vs, 1210m, 1220m. Anal. calcd. for $C_{30}H_{32}O_3P_2$: C, 71.70; H, 6.42; O, 9.55. Found: C, 71.95; H, 6.63; O, 9.89.

1,4-Bis(3-diphenylphosphinopropoxy dioxide) Benzene **3c**. Reaction conditions: 48 hours in refluxing EtOH/H_2O. Yield = 82%. mp = 183°C (benzene/hexane). IR: 1015m, 1025s, 1065m, 1105m, 1118s, 1185vs, 1220vs, 1230vs. Anal. calcd. for $C_{36}H_{36}O_4P_2$: C, 72.72; H, 6.10; O, 10.76. Found: C, 72.49; H, 6.30; O, 10.92.

1,8-Octamethylene bis-dodecylphenylphosphine Dioxide **6a1**. Reaction conditions: 120 hours in refluxing benzene/H_2O. Yield = 100%. mp = 57°C. IR: 1027vw, 1070w, 1112s, 1164vs. Anal. calcd. for $C_{44}H_{76}O_2P_2$: C, 75.60; H, 10.96; O, 4.58. Found: C, 75.58; H, 11.57; O, 5.19.

4-Oxa-1,7-heptamethylene Bis-dodecylphenylphosphine Dioxide **6b1**. Reaction conditions: 120 hours in refluxing benzene/H_2O. Yield = 63%. mp = 70°C (benzene/hexane). IR: 1012vw, 1025w, 1070m, 1113vs, 1165vs, 1185m, 1205m, 1220m. Anal. calcd. for $C_{44}H_{72}O_2P_2$: C, 73.43; H, 10.56; O, 6.99. Found: C, 73.10; H, 9.57; O, 6.97.

1,4-Bis(3-dodecylphenylphosphinopropoxy dioxide) Benzene **6c1**. Reaction conditions: 86 hours in refluxing benzene/H_2O. Yield = 47%. mp = 67–68°C (benzene/hexane-Leitz). IR: 1020w, 1070w, 1114m, 1161s, 1169s, 1241s. Anal. calcd. for $C_{48}H_{76}O_2P_2$: C, 74.00; H, 9.83; O, 8.21. Found: C, 72.84; H, 10.17; O, 8.28. ^{13}C NMR ($CDCl_3$, c = 0.2M) characteristic signals: δ = 13.98 (s, CH_3); 68.13 (d, $^3J_{PC}$ = 13.9 Hz, CH_2O); 115.21 (s, phenolic C); 128.51 (d, $^3J_{PC}$ = 11.1 Hz, meta); 130.27 (d, $^2J_{PC}$ = 8.8 Hz, ortho); 131.41 (d, $^4J_{PC}$ = 2.7 Hz, para); 132.19 (d, $^1J_{PC}$ = 92.2 Hz, ipso); 152.76 (s, phenolic C–O).

4-Oxa-1,7-heptamethylene Bis-(2′-ethoxyethyl)-phenylphosphine Dioxide **6b2**. Reaction conditions: 96 hours in refluxing EtOH/H_2O. Yield = 58%. mp = 73–74°C (Leitz). Rf = 0.23 (SiO_2–AcOEt/MeOH 70/30–UV). IR: 1000vw, 1012m, 1035w, 1050w,

TABLE 7 Yield and Spectroscopic Characteristics of Linear Diphosphine Dioxides **3** or **6**

Compound	Yield (%)	δ^{31}P[a]	^{1}H NMR (J_{in}, Hz)[a,b]				
			C–CH_2–P	C–CH_2–O	C–CH_2–C	CH_3	Mass[c]
3a	89	33.0	2.10–2.25 (m, 4H)	—	1.10–1.20 (m, 4H) 1.25–1.30 (m, 4H) 1.45–1.65 (m, 4H)	—	$(M + H)^+ = 515$
3b	97	33.2	2.10–2.40 (m, 4H)	3.36 (4H) (t, $^3J_{HH}$ = 6)	1.70–2.00 (m, 4H)	—	$M^{+\cdot} = 502$
3c	82	33.2	2.30–2.60 (m, 4H)	3.94 (4H) (t, $^3J_{HH}$ = 6)	2.00–2.20 (m, 4H)	—	$M^{+\cdot} = 594$
6a1	100	41.2	1.70–2.00 (m, 8H)	—	1.10–1.70 (m, 52H)	0.86 (6H) (t, $^3J_{HH}$ = 6.8)	$(M + H)^+ = 699$
6b1	63	41.1	1.45–2.10 (m, 8H)	3.20–3.40 (m, 4H)	1.21 (m, 36H)[e] 1.45–2.10 (m, 8H)	0.87 (6H) (t, $^3J_{HH}$ = 6)	$(M + H)^+ = 687$
6c1	47	41.0	1.10–2.25 (m, 8H)	3.89 (4H) (t, $^3J_{HH}$ = 4.6)	1.10–2.25 (m, 44H)	0.87 (6H) (t, $^3J_{HH}$ = 6)	$M^{+\cdot} = 778$
6b2	58	39.6	1.60–2.40 (m, 8H)	3.25–3.80 (m, 12H)	1.60–2.40 (m, 4H)	1.11 (3H) (t, $^3J_{HH}$ = 7) 1.12 (3H) (t, $^3J_{HH}$ = 7)	$M^{+\cdot} = 494$
6b′2	38	33.3[d] 39.5[d]	1.55–2.40 (m, 6H)	3.25–3.80 (m, 8H)	1.55–2.40 (m, 4H)	1.07 (3H) (t, $^3J_{HH}$ = 7)	$M^{+\cdot} = 498$
6c2	99	41.2	1.60–2.30 (m, 8H)	3.00–3.50 (m, 4H) 3.70–4.00 (m, 4H)	1.60–2.30 (m, 8H)	3.00–3.50 (m, 6H)	$M^{+\cdot} = 586$

[a] The solvent used is $CDCl_3$.
[b] The aromatic protons give a multiplet from 7.20 to 8.00 with supplementary singlet at 6.74 for **3c** and 6.60–6.80 (m) for **6c2**.
[c] Electronic impact except for **3a** (FAB in GT), **6a1** and **6b1** (FAB in NOBA).
[d] Both signals have the same intensity.
[e] $\Delta\nu/2 = 10$ Hz.

TABLE 8 Yields and Spectrostopic Characteristics of Macrocyclic Diphosphine dioxides **9**

Compounds	Yield (%)	δ^{31}P[a]	^{1}H NMR (J_{in}, Hz)[a,b]				Mass[c] $M^{+\cdot}$
			C–CH_2–P	C–CH_2–O	C–CH_2–C	CH_3	
9bt	43	41.7	1.65–2.40 (m, 8H)	3.35–3.65 (m, 8H)	1.65–2.40 (m, 8H)	—	448
9bc	29	41.1	1.65–2.35 (m, 8H)	3.45–3.65 (m, 8H)	1.65–2.35 (m, 8H)	—	448
9c	31	45.8[d] 45.7[d]	1.50–2.40 (m, 8H)	3.80–4.00 (m, 8H)	0.85–1.00 (m, 8H)	—	632
9b1t	43	50.0	1.50–1.90 (m, 12H)	3.35–3.55 (m, 8H)	1.20–1.90 (m, 48H)	0.87 (6H) (t, $^3J_{HH}$ = 6.5)	632
9b1c	56	49.6	1.50–1.90 (m, 12H)	3.45–3.55 (m, 8H)	1.20–1.90 (m, 48H)	0.85 (6H) (t, $^3J_{HH}$ = 6.5)	632

[a] The solvent used is $CDCl_3$ except for **9c** (CD_3OD).
[b] The aromatic protons give a multiplet from 7.20 to 8.00 with supplementary singlet at 6.76 for **9c**.
[c] Electronic impact.
[d] Two diastereoisomers.

1070m, 1113vs, 1127vs, 1165vs, 1220m. Anal. calcd. for $C_{26}H_{40}O_5P_2$: C, 63.15; H, 8.15; O, 16.18. Found: C, 63.22; H, 8.29; O, 16.06. ^{13}C NMR ($CDCl_3$, c = 0.25M): δ = 14.85 (s, CH_3); 21.62 (d, $^2J_{PC}$ = 3.9 Hz, C–CH_2–C); 27.04 [d, $^1J_{PC}$ = 69.8 Hz, CH_2–P(O)]; 31.06 [d, $^1J_{PC}$ = 67.4 Hz, CH_2–P(O)]; 63.52 (d, $^2J_{PC}$ = 1.9 Hz, CH_2–O); 66.05 (s, Me–CH_2–O); 70.29 (d, $^3J_{PC}$ = 14.8 Hz, CH_2–O); 128.42 (d, $^3J_{PC}$ = 11.3 Hz, meta); 130.12 (d, $^2J_{PC}$ = 9.0 Hz, ortho); 131.44 (d, $^4J_{PC}$ = 2.7 Hz, para); 132.15 (d, $^1J_{PC}$ = 83.8 Hz, ipso).

4-Oxa-1,7-heptamethylene (2′-ethoxyethyl)phenylphosphine Diphenylphosphine Dioxide **6b′2**. Reaction conditions: 96 hours in refluxing EtOH/H_2O. Yield = 38%. Rf = 0.37 (SiO_2–AcOEt/MeOH 70/30–UV). IR: 1000w, 1025w, 1075m, 1106vs, 1112vs, 1183s. ^{13}C NMR ($CDCl_3$, c = 0.25M): δ = 14.86 (s, CH_3); 21.65 (d, $^2J_{PC}$ = 3.9 Hz, C–CH_2–C); 21.77 (d, $^2J_{PC}$ = 3.6 Hz, C–CH_2–C); 26.20 [d, $^1J_{PC}$ = 73.0 Hz, CH_2–P(O)]; 27.02 [d, $^1J_{PC}$ = 69.7 Hz, CH_2–P(O)]; 31.06 [d, $^1J_{PC}$ = 67.4 Hz, CH_2–P(O)]; 63.51 (d, $^2J_{PC}$ = 2.1 Hz, CH_2–O); 66.08 (s, Me–CH_2–O); 70.20 (d, $^3J_{PC}$ = 14.6 Hz, CH_2–O); 70.29 (d, $^3J_{PC}$ = 14.8 Hz, CH_2–O); 128.47 (d, $^3J_{PC}$ = 10.6 Hz, meta); 128.48 (d, $^3J_{PC}$ = 11.6 Hz, 2 meta); 130.13 (d, $^2J_{PC}$ = 9.1 Hz, ortho); 130.56 (d, $^2J_{PC}$ = 9.3 Hz, 2 ortho); 131.49 (d, $^4J_{PC}$ = 3.0 Hz, para); 131.55 (d, $^4J_{PC}$ = 2.9 Hz, 2 para); 132.08 (d, $^1J_{PC}$ = 93.7 Hz, ipso); 132.74 (d, $^1J_{PC}$ = 98.5 Hz, 2 ipso).

1,4-Bis[3-(3′-methoxypropyl)phenylphosphinopropoxy Dioxide]benzene **6c2**. Reaction conditions: 72 hours in refluxing benzene/H_2O. Yield = 99%. IR: 1027vw, 1049w, 1062w, 1107vs, 1157w, 1187vw, 1212m. ^{13}C NMR ($CDCl_3$, c = 0.25M): δ = 21.68 (d, $^2J_{PC}$ = 3.8 Hz; C–CH_2–C); 26.58 [d, $^1J_{PC}$ = 69.3 Hz, CH_2–P(O)]; 26.70 [d, $^1J_{PC}$ = 69.8 Hz, CH_2–P(O)]; 58.35 (s, O–CH_3); 68.14 (d, $^3J_{PC}$ = 13.9 Hz, CH_2–O); 72.30 (d, $^3J_{PC}$ = 14.2 Hz, CH_2–O); 115.26 (s, phenolic CH); 128.60 (d, $^3J_{PC}$ = 11.2 Hz, meta); 130.35 (d, $^2J_{PC}$ = 8.9 Hz, ortho); 131.55 (d, $^4J_{PC}$ = 2.8 Hz, para); 131.93 (d, $^1J_{PC}$ = 93.0 Hz, ipso); 152.80 (s, phenolic C–O).

Trans-5,13-diphenyl-1,9-dioxa-5,13-diphosphacyclohexadecane Dioxide **9bt**. Reaction conditions: 50 hours in refluxing EtOH/H_2O. Yield = 43%. Rf = 0.4 (SiO_2–AcOEt/MeOH 70/30–UV). mp = 170.5–171°C (benzene/hexane-Leitz). IR: 1029m, 1047m, 1055m, 1073s, 1100vs, 1155vs, 1165vs, 1175vs, 1232s. Anal. calcd. for $C_{24}H_{34}O_4P_2$: C, 64.28; H, 7.64; O, 14.27. Found: C, 64.03; H, 7.58; O, 13.97. ^{13}C NMR ($CDCl_3$, c = 0.35M): δ = 22.15 (d, $^2J_{PC}$ = 3.7 Hz, C–CH_2–C); 26.20 [d, $^1J_{PC}$ = 69 Hz, CH_2–P(O)]; 69.94 (d, $^3J_{PC}$ = 12.0 Hz, CH_2–O); 128.49 (d, $^3J_{PC}$ = 11.1 Hz, meta); 130.11 (d, $^2J_{PC}$ = 8.8 Hz, ortho); 131.43 (d, $^4J_{PC}$ = 2.7 Hz, para); 132.67 (d, $^1J_{PC}$ = 92.7 Hz, ipso). The determination of the trans stereoisomerism has been achieved by X-ray diffraction analysis [17].

Cis-5,13-diphenyl-1,9-dioxa-5,13-diphosphacyclohexadecane Dioxide **9bc**. Reaction conditions: 50 hours in refluxing EtOH/H_2O. Yield = 29%. Rf = 0.27 (SiO_2–AcOEt/MeOH 70/30–UV). mp = 175–176°C (benzene/hexane-Leitz). IR: 1000m, 1015w, 1025m, 1040m, 1057s, 1065s, 1075m, 1100vs, 1140s, 1148vs, 1161vs, 1175vs, 1213m. Anal. calcd. for $C_{24}H_{34}O_4P_2$: C, 64.28; H, 7.64; O, 14.27. Found: C, 64.14; H, 7.85; O, 14.15. ^{13}C NMR ($CDCl_3$, c = 0.35M): δ = 22.15 (d, $^2J_{PC}$ = 3.8 Hz, C–CH_2–C); 27.43 [d, $^1J_{PC}$ = 69.1 Hz, CH_2–P(O)]; 69.88 (d, $^3J_{PC}$ = 11.3 Hz, CH_2–O); 128.49 (d, $^3J_{PC}$ = 11.1 Hz, meta); 130.05 (d, $^2J_{PC}$ = 8.8 Hz, ortho); 131.41 (d, $^4J_{PC}$ = 2.7 Hz, para); 132.96 (d, $^1J_{PC}$ = 92.6 Hz, ipso). The determination of the cis stereoisomerism has been achieved by X-ray diffraction analysis [17].

6,16-Diphenyl-1,11-di-p-phenylene-2,10,12,20-dioxa-6,16-diphosphacycloeicosaphane 6,16-Dioxide **9c**. Mixture of cis and trans diastereoisomers. Reaction conditions: 48 hours in refluxing EtOH/H_2O. Yield = 31%. Rf = 0.1 and 0.25 (SiO_2–AcOEt/MeOH 90/10–UV). mp = 231–233°C (benzene/hexane-Leitz). IR: 1040m, 1165m, 1215m. ^{13}C NMR (CD_3OD, c = 0.03M): δ = 22.57 (s, C–CH_2–C); 26.47 [d, $^1J_{PC}$ = 69.5 Hz, CH_2–P(O)]; 68.68 (d, $^3J_{PC}$ = 12.8 Hz, CH_2–O); 116.94 (s, phenolic CH); 131.06 (d, $^3J_{PC}$ = 11.4 Hz, meta); 130.31 (d, $^2J_{PC}$ = 9.2 Hz, ortho); 132.50 (d, $^1J_{PC}$ = 93 Hz, ipso); 133.29 (s, para); 153.93 (s, phenolic C–O).

5,13-Bis-dodecyl-1,9-dioxa-5,13-diphosphacyclohexadecane 5,13-Dioxide (a isomer) **9b1c**. Reaction conditions: 72 hours in refluxing EtOH/H_2O. Yield = 43%. Rf = 0.36 (SiO_2–AcOEt/MeOH 80/20–I_2). mp = 115–116°C (benzene/hexane-Leitz). IR: 1010w, 1030w, 1055vw, 1080w, 1105vs, 1145s, 1170s, 1198w, 1210m, 1225m, 1235m. Anal. calcd. for $C_{34}H_{74}O_4P_2$: C, 68.32; H, 11.78; O, 10.11. Found: C, 68.68; H, 11.51; O, 10.03. ^{13}C NMR ($CDCl_3$; c = 0.09M) characteristic signals: δ = 14.00 (s, CH_3); 70.29 (d, $^3J_{PC}$ = 12.6 Hz, CH_2–O).

5,13-Bis-dodecyl-1,9-dioxa-5,13-diphosphacyclohexadecane 5,13-Dioxide (β isomer) **9b1t**. Operating conditions: 72 hours in refluxing EtOH/H_2O. Yield = 56%. Rf = 0.1 (SiO_2–AcOEt/MeOH 80/20–I_2). mp = 128.5–129°C (benzene/hexane-Leitz). IR: 1017w, 1032w, 1060w, 1095s, 1117s, 1150vs, 1182m, 1210m, 1220m. Anal. calcd. for $C_{34}H_{74}O_4P_2$: C, 68.32; H, 11.78; O, 10.11. Found: C, 68.68; H, 11.71; O, 10.41. ^{13}C NMR ($CDCl_3$, c = 0.09M) characteristic signals: δ = 13.88 (s, CH_3); 70.29 (d, $^3J_{PC}$ = 12.2 Hz, CH_2–O).

Reduction of Diphosphine Dioxides

General Procedure for the Synthesis of Diphosphines 4 *and* 7. An excess of Si_2Cl_6 (2.5 equivalents) is added to a refluxing solution of diphosphine dioxide in benzene under nitrogen and reaction is continued for 1/2 hour. The reaction mixture is then cooled to 0°C, then hydrolyzed by adding a 37% aqueous sodium hydroxide solution (15 equivalents). After decantation of the filtrate, followed by extraction with $CHCl_3$, the organic phases are combined, washed with water to neutrality, and dried over Na_2SO_4. The removal of the solvent leads to the crude diphosphines. The yields, NMR, IR, and mass characteristics of the diphosphines obtained are gathered in Table 9. Specific details are given for each compound.

1,8-Octamethylene Bis-diphenylphosphine **4a**. Yield = 81%. mp = 107.5–108°C (Leitz). Homogeneous in TLC: Rf = 0.7 (SiO_2–$CHCl_3$–dyeing reagent: $NiBr_2$/EtOH). IR: 1000w, 1025m, 1065m, 1070m, 1095m, 1152vw, 1160vw, 1170vw, 1182vw, 1195vw, 1260w. Anal. calcd. for ($C_{32}H_{36}P_2$ + 1/2 H_2O): C, 78.19; H, 7.53. Found: C, 78.11; H, 7.78.

4-Oxa-1,7-heptamethylene Bis-diphenylphosphine **4b**. Yield = 89%. mp = 82°C. Single spot in TLC: Rf = 0.7 (SiO_2–$CHCl_3$–dyeing reagent: $NiBr_2$/EtOH). IR: 1000m, 1012w, 1030m, 1045m, 1070m, 1110vs, 1160w, 1165w, 1175vw, 1190vw, 1200w. Anal. calcd. for $C_{30}H_{32}OP_2$: C, 76.58; H, 6.86. Found: C, 76.03; H, 6.42.

1,4-Bis(3-diphenylphosphinopropoxy)benzene **4c**. Yield = 80%. mp = 97°C [litt. 99°C(MeOH)] [15]. Single spot in TLC: Rf = 0.7 (SiO_2–$CHCl_3$–dyeing reagent: $NiBr_2$/EtOH). IR: 1001w, 1025s, 1046s, 1068w, 1100w, 1110w, 1232vs. Anal. calcd. for $C_{36}H_{36}O_2P_2$: C, 76.85; H, 6.45. Found: C, 76.31; H, 5.88.

4-Oxa-1,7-heptamethylene Bis-dodecylphenylphosphine **7b1**. Yield = 68%. Precipitate in cold ethanol. Single spot in TLC: Rf = 0.75 (SiO_2–CH_2Cl_2–dyeing reagent: $NiBr_2$/EtOH). IR (film): 1000vw, 1030vw, 1070vw, 1112s, 1155vw, 1195vw.

Determination of Distribution Coefficients

The distribution coefficients *D* of actinides, defined as the equilibrium ratio of the actinide species between the organic and the aqueous phases, were determined at room temperature (25°C) by mixing the same volume of each phase at 100 rpm in a polypropylene test tube, and then measuring the radioactivity in each phase by α spectrometry.

The determination of *D* in the extraction experiments was performed by mixing 5 mL of the organic phase, i.e., a (0.01 M) solution of the studied extractant in Nitrophenylhexylether or Nitrophenyloctylether, and 5 mL aqueous feed solution [$NaNO_3$ (4 M), HNO_3 (1 M), and containing traces of actinide Pu (IV), Np [mainly (V)], or Am (III)]. Then, to determine *D* in the stripping experiments, 4 mL of the last organic phase was mixed with 4 mL of aqueous stripping solution containing an actinide complexing agent [oxalic acid (0.5 M) or sodium citrate (0.25 M)]. Duplicate runs of each experiment were routinely performed.

Supported Liquid Membranes. A thin flat sheet SLM device described by Stolwijk [20] was used. The volume of both aqueous solutions was 50 cm^3. The membrane was a ®Celgard 2500 (of 25 μm thickness and 45% volume porosity) polypropylene microporous support soaked with a 10^{-2} M solution of the tested compounds in Nitrophenylhexylether (NPHE). The surface area of the membrane was about 15–16 cm^2, depending on the device; the mass of the organic phase in the membrane is about 25 μg. This mass is determined by measuring the activity of the membrane after soaking it in an organic phase containing nuclides.

Permeability Determination

The transport of ^{237}Np, ^{239}Pu, ^{241}Am from synthetic aqueous solutions of $NaNO_3$ (4 M) and HNO_3 (1 M), was followed by regular measurement of the decrease of radioactivity in the feed solution and of the

TABLE 9 Yields and Spectroscopic Characteristics of Diphosphines **4** to **7**

				^1H NMR (J_{in}, Hz)[a,b]			
Compound	Yield (%)	$\delta^{31}P$[a]	C–CH_2–P	C–CH_2–O	C–CH_2–C	CH_3	Mass[c] M^+
4a	81	−15.6	2.06 (4H) (t, $^3J_{HH}$ = 7)	—	1.10–1.43 (m, 12H)	—	482
4b	89	−15.7	2.10–2.30 (m, 4H)	3.50 (4H) (t, $^3J_{HH}$ = 6)	1.70–1.90 (m, 4H)	—	470
4c	80	−15.9	1.70–2.40 (m, 4H)	3.98 (4H) (t, $^3J_{HH}$ = 6)	1.70–2.40 (m, 4H)	—	562
7b1	68	−23.9	1.50–1.70 (m, 8H)	3.36 (4H) (t, $^3J_{HH}$ = 6)	1.10–1.70 (m, 44H)	0.89 (6H) (t, $^3J_{HH}$ = 6)	

[a] The solvent used is $CDCl_3$.
[b] The aromatic protons give a multiplet from 7.20 to 7.60 with a supplementary multiplet 6.76–6.81 for **3c**.
[c] Electronic impact.

increase in the strip solution [sodium citrate (0.25 M)] by *α* spectrometry analysis. This allowed graphical determination of the constant permeabilities *P* (cm·h^{-1}) of actinide permeation through the SLM for 6–7 hours, by plotting the logarithm of the ratio C/C^0 vs. time.

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