Heteroatom Chemistry
Volume 10, Number 4, 1999

Synthesis of (Poly)alkoxymethylphosphine Oxides by Classical and Phase Transfer Catalyzed Williamson Reactions

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Received 25 November 1998; revised 29 December 1998

ABSTRACT: *(Poly)alkoxymethylphosphine oxides were synthesized by the Williamson reaction starting from (poly)hydroxymethyl or (poly)chloromethylphosphine oxides. For the first time, the use of phase transfer catalysis for the synthesis of (O)PCOC bridges is demonstrated.* Heteroatom Chem 10: 307–311, 1999

INTRODUCTION

Phosphine oxides demonstrate an exceptional potential for the complexation of hard cations, like actinides [1], and a very good stability to radiolysis and hydrolysis. Therefore, they can be of interest for the selective recovering of actinides from nuclear wastes [2].

RESULTS

We are interested in the synthesis of new phosphine oxides with the PCOC pattern involving one phosphorus atom or more [3]. These compounds were scarcely studied and offer two different kinds of complexing oxygen atoms in the phosphine oxide group and in the ether function. Moreover, in order to benefit from chelating effects, our goal was the synthesis of PCOC compounds by the use of chloromethylphosphine oxide precursors. Although the Williamson reaction appears to be a good process in this case, some problems may occur, particularly due to the formation of the undesired phosphine oxide carbanion [4]. Furthermore, chloromethylphosphine oxides undergo the Williamson reaction with alkoxides, but the poor leaving character of chlorine requires the use of high boiling solvents like toluene or xylene [5]: under these conditions, some alkyl [6], aryl [7], and pyridinoethers [8] have been synthesized in moderate yields.

In such a classical Williamson reaction, we used the sodium salt of triethyleneglycol monomethyl ether **1**, formed with sodium hydride, to obtain the corresponding phosphine oxides **3–5** from tris-(chloromethyl)phosphine oxide **2** (Scheme 1).

Mono-, di-, and trisubstitution products have been obtained as main products by adjustment of the proportions of alkoxide **1** and phosphine oxide **2**. The trisubstituted compound **5** is the easiest to synthesize, using a slight excess of alkoxide. To the opposite, in the synthesis of **3**, the formation of disubstituted product **4** is minimized to less than 5% by the use of two equivalents of **2**. The disubstituted product **4** is the hardest to obtain and requires us to work in the strict stoichiometric conditions. Under the same conditions, the reaction of **2** with a slight excess of 2-benzyloxyethanol gives the trisubstituted product **6** in 72% yield.

By analogy, the alkoxides corresponding to hydroxymethylphosphine oxides allow us to synthesize the (O)PCOCP(O) bridge by reaction with chloromethylphosphine oxides: thus, di-, tri-, and tetra-

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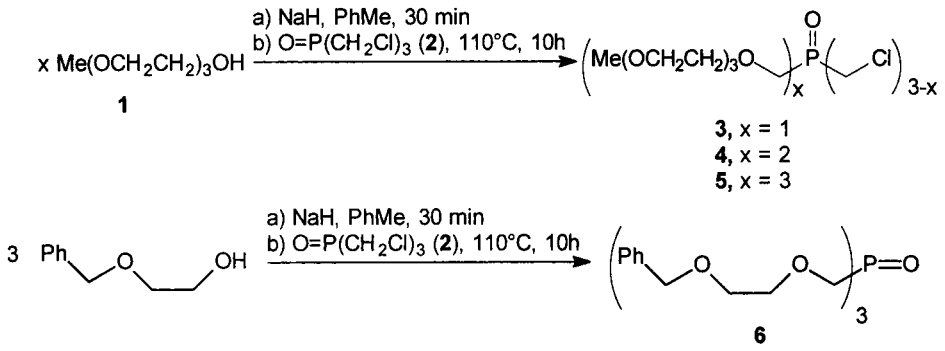
 CCC 1042-7163/99/040307-05



SCHEME 1

phosphorus compounds **7–9** were synthesized in moderate yields (Scheme 2).

With more reactive halogenated reagents, Williamson reactions under phase transfer catalysis conditions using tetrabutylammonium bromide (TBABr) as a catalyst are more advisable. Indeed, this procedure is significantly easier than the traditional Williamson ether synthesis and generally provides a better yield [9]. α,α'-Dibromo *o*-xylene **10** undergoes a double substitution by reaction with diphenylhydroxymethylphosphine oxide **11** to give the diphosphine dioxide **12** (Scheme 3).

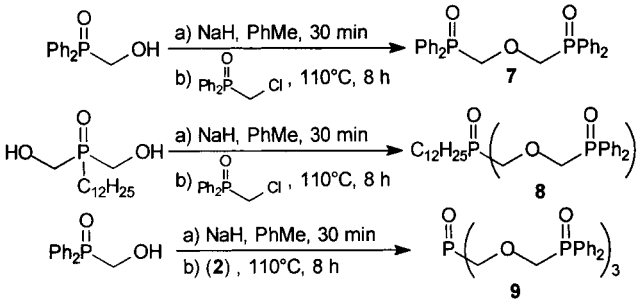
Monosubstitution product **13** was also obtained in 50% yield using a threefold excess of **10**. Subsequent reaction of **13** with bis(hydroxymethyl)dodecylphosphine oxide **14** affords the triphosphine trioxide **15** in 86% yield (Scheme 4).

With dichloromethane as a solvent and a reagent, phosphine oxide acetals are obtained: reaction of **11** in dichloromethane leads to 1,5-bis(diphenylphosphino)-2,4-dioxapentane dioxide **16** in quantitative yield. A kinetic study of this reaction by ^{31}P NMR spectroscopy does not enable us to observe the formation of the intermediary chloromethylether, which is probably too reactive and gives right away the acetal **16** [10].

In the same conditions, cyclic acetals are obtained by reaction with bis(hydroxymethyl)phosphine oxide: **17** is synthesized in 56% yield by the reaction of **14** with dichloromethane. This reaction provides us an alternate way to the synthesis of 1,3,5-dioxaphosphorinane-1-oxides [11] (Scheme 5).

CONCLUSION

In conclusion, the classical Williamson reaction is an efficient way to synthesize (poly)alkoxymethylphosphine oxides: under these conditions, both combinations of a polyalkoxide/monohalo compound and a polyhalo compound/monoalkoxide can be used. Phase transfer catalysis conditions allow the



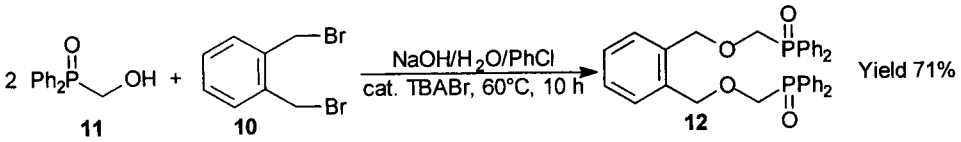
SCHEME 2

synthesis of polyphosphine polyethers in good yields from reactive halogenated reagents, and the use of dichloromethane extends this reaction to the synthesis of a linear or cyclic acetal.

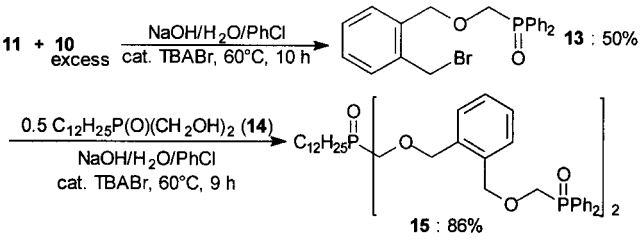
EXPERIMENTAL

Melting points were determined using a Wild Leitz 350 instrument and are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ (unless otherwise specified), locked on solvent deuterium and referenced to residual solvent protons. IR spectra were obtained with a Perkin-Elmer 377 instrument. Mass spectra were measured with a Jeol JMS DX-300 spectrometer. Merck silica gel 60 (0.063–0.20 mm) was used for column chromatography. Commercially available solvents and reagents were used without further purification.

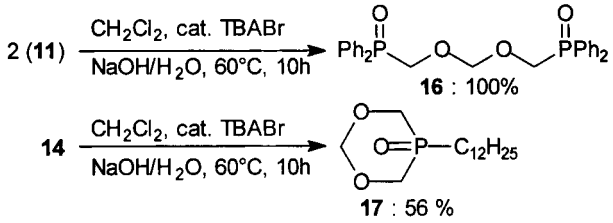
Bis(chloromethyl)-2,5,8,11-tetraoxadodecylphosphine Oxide (**3**). To a stirred solution of **2** (5.00 g, 25.6 mmol) and 0.49 g of NaH 65% (13.2 mmol) in 50 mL of dry toluene, 2.10 g (12.8 mmol) of **1** was added and refluxed for 3 hours. After addition of water, the pH was adjusted to 7 by 1 M HCl, extracted by dichloromethane, and dried on Na_2SO_4. The residue was chromatographed on silica gel (AcOEt/



SCHEME 3



SCHEME 4



SCHEME 5

MeOH 95/5 eluent). **3** (Rf = 0.2) was isolated in 46% yield (1.89 g) as a colorless liquid. ^{31}P NMR: δ = 40.00 (s). ^{1}H NMR: δ = 3.27 (s, 3 H, $^{8}CH_3$); 3.42–3.47 (m, 2 H, $^{7}CH_2$); 3.52–3.58 (m, 4 H, $^{3,6}CH_2$); 3.55 (s, 4 H, $^{4,5}CH_2$); 3.65–3.70 (m, 2 H $^{2}CH_2$); 3.69 (d, 2 H, $^{2}J_{HP}$ = 6.1 Hz, PC$\underline{H}_2$Cl); 4.08 (d, $^{2}J_{HP}$ = 5.6 Hz, $^{1}CH_2$). ^{13}C NMR: δ = 33.30 (d, $^{1}J_{PC}$ = 68.3 Hz, P$\underline{C}H_2$Cl); 58.92 (s, $^{8}CH_3$); 64.04 (d, $^{1}J_{PC}$ = 88.0 Hz, $^{1}CH_2$); 70.25, 70.46 (2 s, $^{3,6}CH_2$); 70.52 (s, $^{4,5}CH_2$); 71.85 (s, $^{7}CH_2$); 73.13 (d, $^{3}J_{PC}$ = 10.3 Hz, $^{2}CH_2$). IR (Film NaCl): 2930 (m), 2870 (m), 1198 (m), 1184 (m), 1103 (vs). MS (FAB$^+$, NBA): m/z = 323 (82) MH$^+$, 203 (20), 103 (27), 59 (100).

Bis(2,5,8,11-tetraoxadodecyl)-chloromethylphosphine Oxide (**4**). Same manipulation as for **3**: 2.00 g of **2** (10.2 mmol), 0.84 g of NaH 65% (22.7 mmol), and 3.36 g (20.1 mmol) of **1**. Chromatographic eluent: AcOEt/MeOH (95/5) and AcOEt/MeOH (85/15). **4** is obtained in 56% yield (2.54 g) as colorless oil. ^{31}P NMR: δ = 40.50 (s). ^{1}H NMR: δ = 3.30 (s, 6 H, $^{8}CH_3$); 3.46–3.49 (m, $^{7}CH_2$); 3.54–3.59 (m, $^{3,6}CH_2$); 3.56 (s, $^{4,5}CH_2$); 3.67–3.74 (m, $^{2,9}CH_2$); 4.01 (d, $^{2}J_{HP}$ = 4.95 Hz, $^{1}CH_2$). ^{13}C NMR: δ = 33.51 (d, $^{1}J_{PC}$ = 63.63 Hz, $^{9}CH_2$); 58.93 (s, $^{8}CH_3$); 64.64 (d, $^{1}J_{PC}$ = 82.57 Hz, $^{1}CH_2$); 70.29, 70.48 (2 s, $^{3,6}CH_2$); 70.54, 70.56 (s, $^{4,5}CH_2$); 71.87 (s, $^{7}CH_2$); 73.15 (d, $^{3}J_{PC}$ = 9.26 Hz, $^{2}CH_2$). IR (Film NaCl): 2920 (m), 2868 (vs), 1193 (m), 1105 (vs). MS (FAB$^+$, NBA): m/z = 451 (43) MH$^+$, 103 (20), 59 (100).

Tris(2,5,8,11-tetraoxadodecyl)phosphine Oxide (**5**). Same manipulation as for **3**: 3.62 g of **2** (18.5 mmol), 2.42 g of NaH 65% (65.5 mmol) in 60 mL of dry toluene and 10.68 g (65.0 mmol) of **1**. After the treatment of reaction mixture, excess of **1** was removed by vacuum distillation. **5** is obtained in 57% yield (5.97 g) as colorless oil. ^{31}P NMR: δ = 40.50 (s). ^{1}H NMR: δ = 3.33 (s, 9 H, $^{8}CH_3$); 3.48–3.53 (m, 6 H, $^{7}CH_2$); 3.58–3.62 (m, 12 H, $^{3,6}CH_2$); 3.60 (s, 12 H, $^{4,5}CH_2$); 3.70–3.75 (m, 6 H, $^{2}CH_2$); 3.98 (d, 6 H, $^{2}J_{HP}$ = 4.7 Hz, $^{1}CH_2$). ^{13}C NMR: δ = 58.41 (s, $^{8}CH_3$); 64.51 (d, $^{1}J_{PC}$ = 78.2 Hz, $^{1}CH_2$); 69.91, 70.04 (2 s, $^{3,6}CH_2$); 70.15, 70.18 (2 s, $^{4,5}CH_2$); 71.51 (s, $^{7}CH_2$); 72.71 (d, $^{3}J_{PC}$ = 8.6 Hz, $^{2}CH_2$). IR (film NaCl): 2870 (vs), 1246 (m), 1183 (m), 1106 (vs). MS (FAB$^+$, NBA): m/z = 579 (44) MH$^+$, 459 (5), 103 (22), 59 (100), 45 (19).

Tris(6-phenyl-2,5-dioxahexyl)phosphine Oxide (**6**). Same manipulation as for **3**: 6.02 g of **2** (30.8 mmol), 2.49 g of NaH 95% (98.5 mmol) in 80 mL of dry toluene, and 15.00 g (98.5 mmol) of 2-benzyloxyethanol. Chromatographic eluent: AcOEt and AcOEt/MeOH (95/5). **6** is obtained in 72% yield (12.07 g) as colorless oil. ^{31}P NMR: δ = 40.50 (s). ^{1}H NMR: δ = 3.57–3.79 (AA′BB′ spin system, 12 H, OC$\underline{H}_2$ C$\underline{H}_2$O); 4.04 (d, 6 H, $^{2}J_{HP}$ = 4.7 Hz, PC$\underline{H}_2$); 4.51 (s, 6 H, C$\underline{H}_2$Ph); 7.27–7.33 (m, 15 H, Ph). ^{13}C NMR: δ = 65.03 (d, $^{1}J_{PC}$ = 78.2 Hz, $^{1}CH_2$); 69.28 (s, $^{3}CH_2$); 73.21 (s, $\underline{C}H_2$Ph); 73.23 (d, $^{3}J_{PC}$ = 8.6 Hz, $^{4}CH_2$); 127.67 (s, *p*CH); 127.68 (s, *o*CH); 128.40 (s, *m*CH); 138.14 (s, *i*C). IR (film NaCl): 3020 (s), 2875 (vs), 1440 (vs), 1240 (m), 1185 (m), 1105 (vs).

Bis(diphenylphosphinomethyl)ether Dioxide (**7**). Same manipulation as for **3**: 1.14 g of (chloromethyl)diphenylphosphine oxide (4.5 mmol), 0.17 g of NaH 65% (4.5 mmol) in 50 mL of dry toluene, and 1.00 g (4.5 mmol) of **11** are refluxed during 8 hours. Chromatographic eluent: AcOEt/MeOH (95/5). **7** is obtained in 46% yield (0.93 g). ^{31}P NMR: δ = 26.88 (s). ^{1}H NMR: δ = 4.39 (d, 4 H, $^{2}J_{PH}$ = 5.7 Hz, CH_2); 7.31–7.38 and 7.52–7.60 (2 m, 20 H, Ph). ^{13}C NMR: δ

= 71.81 (dd, $^1J_{PC}$ = 85.0 Hz, $^3J_{PC}$ = 9.9 Hz, CH_2); 128.57 (d, $^3J_{PC}$ = 12.2 Hz, *m*CH); 130.48 (d, $^1J_{PC}$ = 98.7 Hz, *i*C); 131.36 (d, $^2J_{PC}$ = 9.7 Hz, *o*CH); 132.23 (d, $^4J_{PC}$ = 2.9 Hz, *p*CH). IR (KBr): 2883 (m), 1441 (s), 1434 (s), 1422 (m), 1199 (vs), 1174 (vs), 1123 (s), 1096 (vs), 980 (m), 883 (s), 824 (s), 770 (m), 753 (vs), 716 (s), 699 (vs), 511 (vs), 470 (s).

Bis(*3-diphenylphosphino-2-oxapropyl*)*dodecylphosphine Trioxide* (**8**). Same manipulation as for **3**: 1.67 g of (chloromethyl)diphenylphosphine oxide (6.7 mmol), 0.20 g of NaH 65% (5.4 mmol) in 50 mL of anh. toluene, and 0.75 g (2.7 mmol) of **14** are refluxed during 8 hours. Chromatographic eluent: AcOEt/MeOH (95/5). **8** is obtained in 56% yield (1.91 g) as yellow oil. ^{31}P NMR: δ = 27.78 (s, $\underline{P}Ph_2$); 44.24 (s, P). ^{1}H NMR: δ = 0.73 (t, 3 H, $^3J_{HH}$ = 6.2 Hz, CH_3); 1.03–1.20 and 1.24–1.30 (2 m, 22 H, CH_2); 3.71 (AB part of ABX spin system, 4 H, $PC\underline{H}_2O$); 4.13 and 4.19 (AB part of ABX spin system, $^2J_{HH}$ = −11.8 Hz, $^2J_{HP}$ = 5.6 Hz, $^2J_{HP}$ = 4.6 Hz, 4 H, $C\underline{H}_2PPh_2$); 7.26–7.42 and 7.57–7.67 (2 m, 20 H, Ph). ^{13}C NMR: δ = 14.00 (s, $^{12}CH_3$); 20.31 (d, $^2J_{PC}$ = 4.3 Hz, $^2CH_2$); 22.50 (s, $^{11}CH_2$); 23.98 (d, $^1J_{PC}$ = 64.0 Hz, $^1CH_2$); 28.84, 29.14, 29.20, 29.39, 29.44, 29.51 (6 s, $^{4,5,6,7,8,9}CH_2$); 30.77 (d, $^3J_{PC}$ = 13.6 Hz, $^3CH_2$); 31.71 (s, $^{10}CH_2$); 67.77 (dd, $^1J_{PC}$ = 77.4 Hz, $^3J_{PC}$ = 10.1 Hz, $P\underline{C}H_2O$); 71.29 (dd, $^1J_{PC}$ = 85.1 Hz, $^3J_{PC}$ = 8.9 Hz, $\underline{C}H_2PPh_2$); 128.55, 128.58 (2 d, $^3J_{PC}$ = 11.9 Hz, $^3J_{PC}$ = 11.9 Hz, *m*CH); 130.30 (d, $^1J_{PC}$ = 100.1 Hz, *i*C); 131.17, 131.28 (2 d, $^2J_{PC}$ = 9.4 Hz, $^2J_{PC}$ = 9.5 Hz, *o*CH); 132.24 (s, *p*CH). IR (KBr, $CHCl_3$): 2970 (s), 2910 (vs), 2845 (s), 1430 (s), 1192 (vs), 1170 (vs), 1115 (vs), 1090 (vs), 686 (vs), 657 (vs).

Tris(*3-diphenylphosphino-2-oxapropyl*)*phosphine Tetraoxide* (**9**). Same manipulation as for **3**: 0.75 g of **2** (3.8 mmol), 0.50 g of NaH 65% (13.3 mmol), and 3.12 g (13.4 mmol) of **11**. Chromatographic eluent: AcOEt/MeOH (90/10) and AcOEt/MeOH (50/50). **9** is obtained in 68% yield (2.04 g) as pale yellow oil. ^{31}P NMR: δ = 27.98 (s, $\underline{P}Ph_2$); 39.83 (s, P). ^{1}H NMR: δ = 3.75 (d, 6 H, $^2J_{PH}$ = −4.2 Hz, PCH_2O); 4.21 (d, 6 H, $^2J_{PH}$ = −5.3 Hz, PCH_2O); 7.43–7.54 and 7.67–7.78 (2 m, 30 H, Ph). ^{13}C NMR: δ = 66.70 (dd, $^1J_{PC}$ = 76.7 Hz, $^3J_{PC}$ = 10.5 Hz, $^1CH_2$); 71.48 (dd, $^1J_{PC}$ = 85.0 Hz, $^3J_{PC}$ = 8.2 Hz, $^3CH_2$); 128.78 (d, $^3J_{PC}$ = 11.9 Hz, *m*CH); 130.14 (d, $^1J_{PC}$ = 100.5 Hz, *i*C); 131.33 (d, $^2J_{PC}$ = 9.5 Hz, *o*CH); 132.49 (d, $^4J_{PC}$ = 2.8 Hz, *p*CH). IR (KBr): 3000 (s), 1438 (s), 1200 (vs broad), 1124 (s), 1096 (s).

1,2-Bis(*3′-diphenylphosphino-2′-oxapropyl*)*benzene Dioxide* (**12**). To a stirred solution of **10** (1.01 g, 3.8 mmol), **11** (1.70 g, 7.5 mmol), and tetrabutylammonium bromide (TBABr) (0.10 g, 0.36 mmol) in 50 mL of CH_2Cl_2, 10 mL of NaOH 20% was added and heated for 28 hours. Reaction mixture is extracted by CH_2Cl_2, neutralized, and dried on Na_2SO_4. The residue is chromatographed on silica gel (AcOEt/MeOH 95/5 eluent). **12** is isolated in 71% yield (1.54 g) as a white crystalline solid; mp 193°C. ^{31}P NMR: δ = 28.11 (s). ^{1}H NMR: δ = 4.10 (d, 4 H, $^2J_{PH}$ = 6.5 Hz, $^{3'}CH_2$); 4.63 (s, 4 H, $^{1'}CH_2$); 7.18 (m, 4 H, Ph); 7.43–7.57, 7.74–7.82 (2 m, 20 H, $P\underline{Ph}_2$). ^{13}C NMR: δ = 68.08 (d, $^1J_{PC}$ = 88.0 Hz, $^{3'}CH_2$); 73.01 (d, $^3J_{PC}$ = 11.7 Hz, $^{1'}CH_2$); 128.22 (s, *o′*CH); 128.55 (d, $^3J_{PC}$ = 11.8 Hz, *m*CH); 129.28 (s, *m*CH); 131.06 (d, $^1J_{PC}$ = 99.6 Hz, *i*C); 131.45 (d, $^2J_{PC}$ = 9.4 Hz, *o*CH); 132.18 (d, $^4J_{PC}$ = 2.8 Hz, *p*CH); 135.24 (s, *i′*C). MS (FAB$^+$, NBA): m/z = 567 (70) MH^+, 335 (18), 242 (100), 215 (32) $Ph_2P(O)CH_2^+$, 201 (9) Ph_2PO^+.

2-Bromomethyl-1-(*3′-diphenylphosphino-2′-oxapropyl*) *Benzene Oxide* (**13**). Same manipulation as for **12**: to **10** (9.47 g, 35.9 mmol), **11** (2.79 g, 12.0 mmol), and TBABr (0.35 g, 1.1 mmol) in 70 mL of PhCl, 10 mL of NaOH 20% was added and heated at 50°C for 10 hours. Chromatographic eluent: AcOEt. **13** is obtained in 50% yield (2.49 g) as yellow oil. ^{31}P NMR: δ = 28.43 (s). ^{1}H NMR: δ = 4.27 (d, 2 H, $^2J_{PH}$ = 6.5 Hz, $C\underline{H}_2P$); 4.32 (s, 2 H, $C\underline{H}_2Br$); 4.76 (s, 2 H, $C\underline{H}_2O$); 7.22–7.32 (m, 4 H, Ph); 7.44–7.57, 7.73–7.83 (2 m, 10 H, $P\underline{Ph}_2$). ^{13}C NMR: δ = 30.52 (s, $\underline{C}H_2Br$); 68.18 (d, $^1J_{PC}$ = 87.9 Hz, $\underline{C}H_2P$); 73.06 (d, $^3J_{PC}$ = 11.5 Hz, $\underline{C}H_2O$); 128.59 (d, $^3J_{PC}$ = 11.9 Hz, *m*CH); 128.80, 128.97 (2 s, *o*,*o′*CH); 130.23, 130.76 (2 s, *m*,*m′*CH); 130.98 (d, $^1J_{PC}$ = 99.4 Hz, *i*C); 131.48 (d, $^2J_{PC}$ = 9.4 Hz, *o*CH); 132.22 (d, $^4J_{PC}$ = 2.7 Hz, *p*CH); 135.15 (s, *i*C ∼ O); 136.60 (s, *i*C ∼ Br).

Bis[3-[2′-(*3″-diphenylphosphino-2″-oxapropyl*)*-phenyl]-2-oxapropyl]dodecylphosphine Trioxide* (**15**). Same manipulation as for **12**: to **13** (2.26 g, 5.3 mmol), **14** (0.68 g, 2.4 mmol), and TBABr (0.16 g, 0.5 mmol) in 50 mL of PhCl, 10 mL of NaOH 20% was added and heated at 50°C for 9 hours. Chromatographic eluent: AcOEt/MeOH (97/3) and AcOEt/MeOH (93/7). **15** is obtained in 86% yield (1.97 g) as colorless viscous oil. ^{31}P NMR: δ = 28.2 (s, P); 44.6 (s, PPh_2). ^{1}H NMR: δ = 0.86 (t, $^2J_{HH}$ = 6.4 Hz, $^{12}CH_3$); 1.29–1.50, 1.64–1.80 (m, 22 H, $^{1-11}CH_2$); 3.65, 3.70 (m, 4 H, $^2J_{HH}$ = 12.8 Hz, $^2J_{PH}$ = 5.4 Hz, $^2J_{PH}$ = 6.5 Hz, $PC\underline{H}_2O$); 4.18 (d, 4 H, $^2J_{PH}$ = 6.2 Hz, $C\underline{H}_2PPh_2$); 4.39, 4.43 (2 d, 4 H, $^2J_{HH}$ = 12.35 Hz, $OC\underline{H}_2Ar$); 4.63 (s, 4 H, $OC\underline{H}_2Ar$); 7.19–7.24, 7.41–7.51, 7.68–7.79 (3 m, 24 H, Ph). ^{13}C NMR: δ = 14.11 (s, $^{12}CH_3$); 20.67 (d, $^3J_{PC}$ = 4.4 Hz, $^3CH_2$); 22.67 (s, $^{11}CH_2$); 24.31 (d, $^1J_{PC}$ = 64.7 Hz, $^1CH_2$); 29.15, 29.32, 29.37, 29.59, 29.61 (5 s, $^{4-9}CH_2$); 31.10 (d, $^2J_{PC}$ = 13.4 Hz, $^2CH_2$); 31.89 (s, $^{10}CH_2$); 64.88 (d, $^1J_{PC}$ = 80.3 Hz, $P\underline{C}H_2O$); 68.01 (d,

$^1J_{PC}$ = 87.7 Hz, $\underline{C}H_2PPh_2$); 72.73 (d, $^3J_{PC}$ = 11.3 Hz, $O\underline{C}H_2Ar$); 73.04 (d, $^3J_{PC}$ = 11.3 Hz, $O\underline{C}H_2Ar$); 128.11, 128.38 (2 s, CH); 128.56 (d, $^3J_{PC}$ = 11.8 Hz, *m*CH); 128.92, 129.54 (2 s, CH); 131.05 (d, $^1J_{PC}$ = 99.4 Hz, *i*C); 131.42 (d, $^2J_{PC}$ = 9.4 Hz, *o*CH); 132.18 (d, $^4J_{PC}$ = 2.8 Hz, *p*CH); 134.83, 135.71 (2 s, C). MS (FAB$^+$, NBA): m/z = 947 (100) MH$^+$, 731 (30), 335 (68), 215 (92), 185 (75).

1,5-Bis(*diphenylphosphino*)*-2,4-dioxapentane Dioxide* (**16**). To a stirred solution of **11** (1.00 g, 4.3 mmol) and TBABr (0.12 g, 0.44 mmol) in 50 mL of CH_2Cl_2, 5 mL of NaOH 20% was added and heated for 70 hours. Reaction mixture was extracted by CH_2Cl_2, neutralized, and dried on Na_2SO_4. **16** was isolated in 100% yield (1.04 g) as a white crystalline solid; mp 175–176°C. ^{31}P NMR: δ = 27.67 (s). ^{1}H NMR: δ = 4.08 (d, 4 H, $^2J_{PH}$ = 6.0 Hz, $PC\underline{H}_2$); 4.68 (s, 2 H, $OC\underline{H}_2O$); 7.26–7.49, 7.65–7.76 (2 m, 20 H, Ph). ^{13}C NMR: δ = 65.26 (d, $^1J_{PC}$ = 88.2 Hz, $P\underline{C}H_2$); 97.66 (t, $^3J_{PC}$ = 10.5 Hz, $O\underline{C}H_2O$); 128.62 (d, $^3J_{PC}$ = 11.8 Hz, *m*CH); 130.68 (d, $^1J_{PC}$ = 100.4 Hz, *i*C); 131.34 (d, $^2J_{PC}$ = 9.4 Hz, *o*CH); 132.28 (d, $^4J_{PC}$ = 2.8 Hz, *p*CH). IR (KBr): 3045 (m), 3012 (m), 1425 (s), 1170 (vs), 1114 (s), 1097 (s), 1036 (s), 1017 (m), 953 (m), 861 (m), 746 (s), 737 (s), 714 (vs), 695 (vs), 540 (vs), 531 (vs), 514 (vs). MS (FAB$^+$, NBA): m/z = 477 (88) MH$^+$, 245 (92) $Ph_2P(O)CH_2OCH_2^+$, 215 (23) $Ph_2P(O)CH_2^+$, 91 (100).

Dodecyl-3,5-dioxa-1-phosphacyclohexane Oxide (**17**). To a stirred solution of **14** (1.50 g, 5.4 mmol) and TBABr (0.16 g, 0.57 mmol) in 50 mL of CH_2Cl_2, 25 mL of NaOH 15% was added and heated for 22 hours. Reaction mixture was extracted by CH_2Cl_2, neutralized, and dried on Na_2SO_4. The residue was chromatographed on silica gel (AcOEt/MeOH 95/5 eluent). **17** was isolated in 55% yield (0.85 g) as a white crystalline solid; mp 84°C. ^{31}P NMR: δ = 22.4 (s). ^{1}H NMR: δ = 0.85 (t, 3 H, $^3J_{HH}$ = 6.5 Hz, $^{12}CH_3$); 1.18–1.68 (m, $^{2-11}CH_2$); 1.98–2.04 (m, 2 H, $^1CH_2$); 4.09 (m, 2 H, $^2J_{HH}$ = −14.1 Hz, $^2J_{PH}$ = 3.2 Hz, $PC\underline{H}_2O$ ax); 4.37 (m, 2 H, $^2J_{HH}$ = −14.1 Hz, $^2J_{PH}$ = 8.1 Hz, $^4J_{HH}$ = 3.2 Hz, $^4J_{PH}$ = 1.0 Hz, $PC\underline{H}_2O$ eq); 4.68 (dd, 1 H, $^2J_{HH}$ = −6.9 Hz, $^4J_{HP}$ = 2.1 Hz, $OC\underline{H}_2O$ ax); 4.93 (ddt, 1 H, $^2J_{HH}$ = −6.9 Hz, $^4J_{HH}$ = 1.0 Hz, $^4J_{HP}$ = 2.0 Hz, $OC\underline{H}_2O$ eq). ^{13}C NMR: δ = 14.07 (s, $^{12}CH_3$); 20.65 (d, $^3J_{PC}$ = 4.3 Hz, $^3CH_2$); 22.64 (s, $^{11}CH_2$); 23.55 (d, $^1J_{PC}$ = 66.1 Hz, $^1CH_2$); 29.08, 29.31, 29.57 (s, $^{4-9}CH_2$); 30.90 (d, $^2J_{PC}$ = 13.8 Hz, $2CH_2$); 31.86 (s, $^{10}CH_2$); 67.75 (d, $^1J_{PC}$ = 68.5 Hz, $P\underline{C}H_2O$); 95.79 (d, $^3J_{PC}$ = 9.1 Hz, $O\underline{C}H_2O$). IR (KBr): 2996 (m), 2965 s, 2913 (vs), 2840 (vs), 1468 (m), 1461 (m), 1256 (m), 1212 (m), 1201 (m), 1177 (s), 1155 (vs), 1083 (vs), 1058 (m), 1032 (vs), 957 (s). MS (FAB$^+$, NBA): m/z = 291 (100) MH$^+$, 73 (26).

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