Notes

A New and Improved Preparation of Acylic σ-Dialkoxyphosphoranes

Isabel Mathieu-Pelta and Slayton A. Evans, Jr.*

The William Rand Kenan, Jr., Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

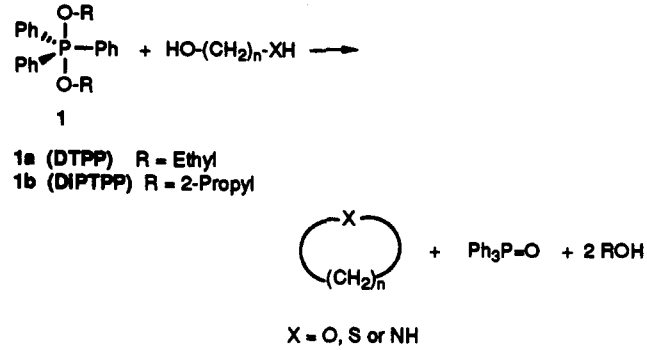
Received August 3, 1993 (Revised Manuscript Received December 7, 1993)

Introduction

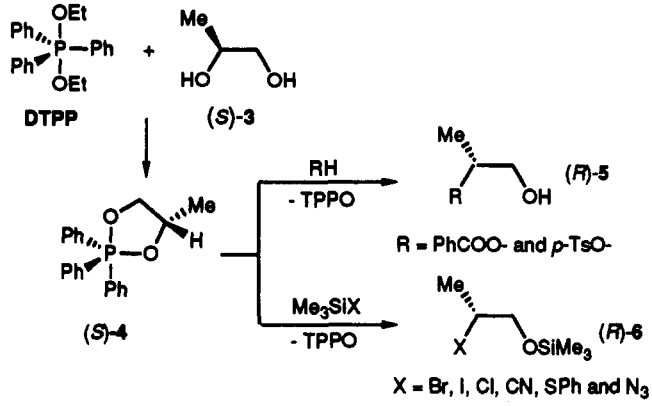
Acyclic σ-dialkoxytriphenylphosphoranes 1 are versatile cyclodehydrating reagents and exhibit a broad range of applications in organic synthesis.[1] These pentavalent dioxaphosphorus species promote the smooth cyclohydration of 1,2-diols to epoxides,[2] 4- and 1,5-diols to tetrahydrofurans and tetrahydropyrans, respectively,[3] 1,2-amino alcohols to the corresponding aziridines,[4] and α,ω-mercapto alcohols to the respective cyclic sulfides.[5] Cyclodehydration of "active hydrogen" species employing diethoxytriphenylphosphorane (DTPP; **1a**) especially proceed under neutral and very mild reaction conditions. The resulting heterocycles are produced in high yields in a single synthetic sequence (*i.e.*, no site-selective functionalizations of the precursor are required!). In addition, enantiopure 1,2-amino alcohols (from α-amino acids) and 1,2-diols (from enantiopure ethyl lactate) are cyclodehydrated with DTPP to the corresponding chiral aziridines[4] and epoxides,[2] respectively, with largely retention of configuration at the sterogenic centers.

More recently, we have demonstrated that (*S*)-4-methyl-2,2,2-triphenyl-1,3,2λ⁵-dioxaphospholane [(*S*)-4], prepared from the bis(transoxyphosphoranylation) of (*S*)-1,2-propanediol (3) with DTPP,[6] underwent a highly regioselective ring opening and a subsequent stereospecific substitution in the presence of organic acids[7,8] and with several trimethylsilyl reagents.[9] These transformations are unique in that the nucleophilic substitutions occur at the most sterically-hindered carbon to afford the thermodynamically less stable C-2–X derivatives (*i.e.*, **5** and **6**) with essentially complete inversion of stereochemistry at the C-2 stereogenic center (Scheme 2).

Scheme 1. Cyclodehydration of Active Hydrogen Compounds Using DTPP



Scheme 2. Regioselective and Stereospecific Substitution of 1,2-Propanediol Using DTPP



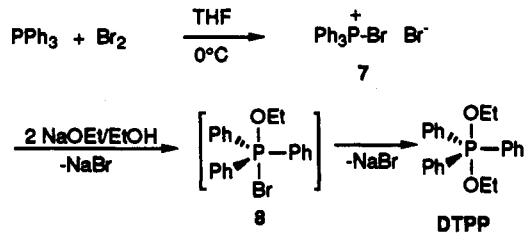
The synthetic utilities of acyclic σ-dialkoxyphosphoranes 1, and especially DTPP, have been described over the past few years.[2b,10] Despite the fact that DTPP can be obtained in excellent yield by either (a) the oxidative addition of diethyl peroxide to triphenylphosphine (TPP)[11] or (b) the oxidation of TPP with dialkylazodicarboxylates in the presence of excess alcohol (*e.g.*, the Mitsunobu procedure),[12] these two methods are characterized by nontrivial drawbacks. In the former case, the preparation and purification of diethyl peroxide are crucial, and the synthetic protocol demands extreme precautions because of the explosively hazardous nature of diethyl peroxide, especially when scale-ups to larger quantities of DTPP are required. In the latter case, the Mitsunobu methodology ultimately affords diethyl- and diisopropylhydrazine dicarboxylates (from the respective commerically-available diethyl and diisopropyl azodicarboxylate precursors), and these diamine byproducts are often difficult to completely remove from the desired dioxaphosphoranes.

Because of the excellent potential of DTPP in a broad range of cyclodehydration applications, it seemed pertinent

(1) Robinson, P. L.; Kelly, J. W.; Evans, S. A., Jr. *Phosphorus Sulfur*, **1986**, *26*, 15–24.
(2) (a) Chang, B. C.; Conrad, W. E.; Denney, D. B.; Denney, D. Z.; Edelman, R.; Powell, R. L.; White, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 4004. (b) Robinson, P. L.; Barry, C. N.; Kelly, J. W.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5210. (c) Bass, S. W.; Barry, C. N.; Robinson, P. L.; Evans, S. A., Jr. *ACS Symp. Ser.* **1981**, *171*, 165. (d) Robinson, P. L.; Barry, C. N.; Bass, S. W.; Jarvis, S. E.; Evans, S. A., Jr. *J. Org. Chem.* **1983**, *48*, 5396.
(3) (a) Kelly, J. W.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7681. (b) Murray, W. T.; Kelly, J. W.; Evans, S. A., Jr. *J. Org. Chem.* **1987**, *52*, 525.
(4) Kelly, J. W.; Eskew, N. L.; Evans, S. A., Jr. *J. Org. Chem.* **1986**, *51*, 95.
(5) Robinson, P. L.; Kelly, J. W.; Evans, S. A., Jr. *Phosphorus Sulfur* **1987**, *31*, 59.
(6) Murray, W. T.; Evans, S. A., Jr. *J. Org. Chem.* **1989**, *54*, 2440.
(7) (a) Pautard, A. M.; Evans, S. A., Jr. *J. Org. Chem.* **1988**, *53*, 2300. (b) Pautard-Cooper, A.; Evans, S. A., Jr. *J. Org. Chem.* **1989**, *54*, 2485.
(8) Kelly, J. W.; Robinson, P. L.; Murray, W. T.; Anderson-Eskew, N.; Pautard-Cooper, A.; Mathieu-Pelta, I.; Evans, S. A., Jr. *Phosphorus Chemistry*; ACS Symposium Series 486; American Chemical Society: Washington, DC, **1992**; pp 186–201.
(9) Mathieu-Pelta, I., Evans, S. A., Jr. *J. Org. Chem.* **1992**, *57*, 3409.
(10) Kelly, J. W. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1986.
(11) (a) Denney, D. B.; Denney, D. Z.; Chang, B. C.; Marsi, K. L. *J. Am. Chem. Soc.* **1969**, *91*, 5243. (b) Chang, B. C.; Conrad, W. E.; Denney, D. B.; Denney, D. Z.; Edelman, R.; Powell, R. L.; White, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 4004.
(12) Mitsunobu, O. *Synthesis* **1981**, *1*.

0022-3263/94/1959-2234$04.50/0

Scheme 3. Preparation of DTPP



and quite appropriate to develop an economically-efficient, clean, and safe method for the production of homogeneous DTPP in large quantities. In addition, a simultaneous goal was to develop a versatile synthetic protocol so that other acyclic σ-dialkoxytriphenylphosphoranes 1 would be synthetically accessible as well. We have now achieved these objectives and report herein an excellent procedure for preparing DTPP.

Results and Discussion

Preparation of DTPP. Bromine (Br_2) was added to TPP to form a yellow suspension of bromotriphenylphosphonium bromide[13] (7) which was directly reacted with sodium ethoxide (2.0 equiv) to afford DTPP in 70–80% yield, presumably through transient intermediate phosphorane 8 (Scheme 3). Because of the low solubility of NaOEt in ethereal solvents, THF or diethyl ether combined with ethanol was used as a "cosolvent." In order to determine the importance of the corresponding alcohol as a cosolvent, a series of experiments were performed where the ratios of NaOEt/EtOH were varied from 0.001 to >100. Potassium carbonate (K_2CO_3) was added in order to scavenge HBr which resulted from the direct reaction of ethanol with bromonium salt 7. The optimum yield of DTPP was obtained with an equimolar quantity of NaOEt and EtOH, and the progress of the reaction was monitored by ^{31}P NMR analysis: DTPP (δ −54.9 ppm), TPP (δ −5.9 ppm), and triphenylphosphine oxide (TPPO; δ 27.2 ppm).

Diethoxyphosphorane **1a** was isolated and purified employing a solvent exchange procedure which removed sodium bromide (NaBr) and TPPO. After removal of insoluble NaBr in the initial filtration, the supernatant solvent was removed under reduced pressure, and the resulting solid residue was suspended in anhydrous hexanes solvent to precipitate TPPO. Removal of insoluble TPPO afforded a clear solution of DTPP (50–60%) in hexanes solvent from which the molarity was easily determined. When DTPP was prepared on a large scale (*ca.* 100 g, 0.38 mol TPP), centrifugations was more convenient for the removal of the insoluble materials. The larger scale reactions were performed in diethyl ether in the absence of K_2CO_3.

Removal of the solvent under reduced pressure gave a light-green oil which contained DTPP (93%) and TPPO (7%) as determined by ^{31}P NMR (C_6D_6). Repetition of the purification step several times gave DTPP (>96% purity) as a colorless, crystalline material which was soluble in anhydrous hexanes.

Determination of the Molarity of the DTPP Solution. The molarity of the solution of DTPP in hexanes was determined by ^{31}P NMR using a "standard solution" of trimethyl phosphite, $P(OMe)_3$, of known concentration.

(13) Okada, I.; Ichimura, K.; Sudo, R. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1185.

Table 1. Acyclic σ-Dialkoxytriphenylphosphoranes 1

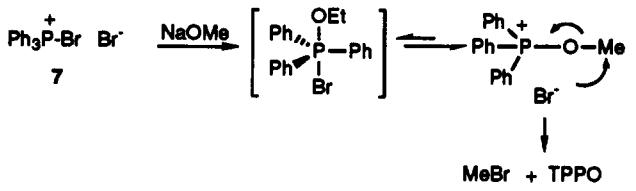
dialkoxyhosphoranes	^{31}P NMR δ (ppm)	sodium alkoxide method[a] (%)	Mitsunobu reaction[a] (%)
1a, R = Et (DTPP)	−54.9	85	94
1b, R = *i*-Pr (DiPTPP)	−50.1	88	15
1c, R = Me	−52.3	0	74
1d, R = *n*-amyl	−55.8	70	84
1e, R = cyclohexyl	−49.5	>50	40
1f, R = *t*-butyl		0	0

[a] The percent composition of the σ-dialkoxytriphenylphosphoranes were determined from the relative ^{31}P NMR absorption intensities of the phosphoranes and TPPO.

The ^{31}P NMR integrations corresponding to DTPP (δ −54.9 ppm) and $P(OMe)_3$ (δ 141.2 ppm) were determined, and the molarity, M, of the solution of DTPP was directly calculated (see the Experimental Section). The precision of the determination of the molarity, M, employing this method was corroborated by ^1H NMR spectroscopy. The reaction of DTPP (1 equiv) with 1,2-propanediol (**3**; 1 equiv) affords 4-methyl-2,2,2-triphenyl-1,3,2λ⁵-dioxaphospholane (**4**) in quantitative yield.[6] The disappearance of the triplet at δ 0.85 ppm (CH_3) and the quintet at δ 2.75 ppm (CH_2) was confirmation that all of the DTPP was consumed. Formation of phosphorane **4** was monitored by the appearance of a doublet at δ 1.20 ppm (CH_3) which was attributed to the ring methyl group.

Generalization of the Procedure. It was also important to ascertain if this procedure could be applicable for the general preparation of various acyclic σ-dialkoxytriphenylphosphoranes 1 where the alkyl group, R, is primary, secondary, or even tertiary. Sodium alkoxide suspensions were prepared as described in the preparation of DTPP employing methanol, 2-propanol, *n*-amyl alcohol, cyclohexanol, and 2-methyl-2-propanol. In each case, the alcohol used to prepare the sodium alkoxide was also added to the suspension in an equimolar ratio of alkoxide/alcohol as the corresponding co-solvent. The yield of the different σ-dialkoxytriphenylphosphoranes 1 obtained using this new procedure compared to those obtained using the Mitsunobu reaction are listed in Table 1. The yields were determined by ^{31}P NMR analysis of the crude reaction mixture and based on the quantity of TPP. Diisopropoxytriphenylphosphorane (DiPTPP, **1b**) was formed in 88% yield using isopropyl alkoxide/isopropyl alcohol, and **1b** was obtained as a crystalline, colorless solid in >92% purity by the precipitation of TPPO from hexanes solvent. Bis(*n*-amyloxy)triphenylphosphorane (**1d**) was also realized in 70% yield, while bis(cyclohexyloxy)triphenylphosphorane (**1e**) was obtained in a modest 50% yield. When sodium methoxide was used, there was no evidence of the formation of phosphorane **1c**, presumably because of a competitive and facile Arbusov displacement of the methyl group by bromide ion in the intermediate species described in Scheme 4. The Mitsunobu reaction is an efficient methodology (74–94%) for preparation of σ-dialkoxytriphenylphosphoranes 1 where the alkyl group, R, is methyl or primary; however, an increase in the steric bulk of the alkyl group causes a dramatic decrease in the yield of 1 [e.g., 40% for **1e** (R = cyclohexyl) and 14% for **1b** (R = 2-propyl)]. Di-*tert*-butoxyphosphorane **1f** could not be formed using either the new methodology or the Mitsunobu reaction, presumably due to the presence of severe repulsive steric interactions between the methyl

Scheme 4. Phosphorane Decomposition via an Arbusov Displacement



groups and the equatorial phenyl groups in the trigonal bipyramidal conformation of **1f**.[14]

Conclusions

A wide range of acyclic σ-dialkoxytriphenylphosphoranes **1** can be prepared safely, conveniently, and in good yields (50–88%) before isolation to homogeneity by reacting bromotriphenylphosphonium bromide **7** with the sodium alkoxide. DTPP (**1a**) and DiPTPP (**1b**) are probably the most synthetically useful dialkoxytriphenylphosphoranes, and they are obtained in excellent purity (92–96%).

There are several noteworthy advantages of this current procedure over existing methods: (a) The requisite dialkoxytriphenylphosphorane (*i.e.*, DTPP) can be prepared in a relative short time (*ca.* 1 day). This is in contrast to the requirement of *ca.* 1 week for the preparation of small quantities of DTPP using the old methodology, where the preparation and purification of diethyl peroxide were the time- and quantity-limiting sequences. (b) Employing the current protocol, the precursors (*i.e.*, sodium, ethanol, bromine, diethyl ether, and TPP for the preparation of DTPP) are commercially available and relatively inexpensive. (c) The dialkoxyphosphoranes are conveniently purified by solvent exchanges under reduced pressure coupled with the removal of insoluble materials through a series of centrifugations in different solvents (*i.e.*, diethyl ether and hexanes). (d) A wide range of σ-dialkoxyphosphoranes are available in good yields (50–88%) even with secondary alcohols. (e) The shelf-life of DTPP in hydrocarbon or ethereal solvents is substantial (>1 year) without measurable loss of activity. However, all of these dioxaphosphoranes are "hydrolytically-sensitive" and should be stored, and ultimately used in a "moisture-free" environment (*i.e.*, anhydrous solvents and dry nitrogen or argon atmospheres).

Experimental Section

All ^1H, ^{13}C, and ^{31}P NMR data were obtained on a 200-MHz NMR spectrometer (^1H at 200 MHz, ^{13}C at 50 MHz, and ^{31}P at 81 MHz) using tetramethylsilane and 85% H_3PO_4 as internal and external standards (δ = 0.00 ppm), respectively. The 2D NMR data were obtained on a 400-MHz spectrometer. All solvents were dried according to published methods,[15] and all the experiments were performed under an inert atmosphere of argon.

Diethoxytriphenylphosphorane (DTPP; 1a). Anhydrous ethanol (95%, 23.4 mL, 0.38 mol) was added to sodium (9.25 g, 0.40 mol), which was finely cut and suspended in anhydrous THF (60 mL) at such a rate that a moderate reflux was maintained. After the mixture was stirred overnight at *ca.* 25 °C, an additional 20 mL of dry ethanol was added, and the resulting suspension was stirred for 1 h at *ca.* 25 °C. In a two-necked flask equipped with a condenser, an argon inlet, and a septum, bromine (32 g, 0.20 mol) was slowly added (syringe) at 0 °C (ice bath) to a solution of TPP (52.4 g, 0.200 mol) in anhydrous diethyl ether (250 mL), under an argon atmosphere, to afford a light yellow suspension of bromotriphenylphosphonium bromide (**7**) [^{31}P NMR (THF); δ 49.7 ppm]. The reaction mixture was cooled to −78 °C (dry ice–acetone), and the THF suspension of NaOEt/EtOH was added at once under a high flow of argon gas. The reaction mixture was vigorously stirred (*ca.* 30 min) while the temperature was controlled (dry-ice acetone bath) in order to avoid reflux, after which the orange suspension turned light-brown, and became more *soluble*. Sodium bromide was decanted, and the reaction mixture was centrifuged in a 500-mL dry plastic bottle until a clear solution was obtained (2500 rpm/15 min). The relative composition of DTPP (70–80%) in THF was determined by ^{31}P NMR (C_6D_6).

Purification of DTPP. The solvent of the supernatant was removed under reduced pressure using a distillation apparatus in which the receiving flask was cooled to −78 °C. Anhydrous hexanes (250 mL) were added to the resulting residue, forcing the precipitation of TPPO. The suspension was transferred to a 500-mL, dry plastic bottle and centrifuged to afford a clear solution of DTPP in hexanes. Repetition of this purification step gave a 50–60% of DTPP as a colorless, crystalline substance whose molarity (*vide infra*) was determined in anhydrous hexanes. Analytical GLC analysis of DTPP in hexanes indicated the presence of trace amounts of TPPO. **DTPP:** ^{31}P NMR (C_6D_6) δ −54.9 ppm; ^1H NMR (C_6D_6) δ 0.85 (t, 6H, $^3J_{HCCH}$ = 6.95 Hz), 2.75 (quint, 4H, $^3J_{HCCH}$ = 6.8 Hz, $^3J_{PH}$ = 6.8 Hz), 7.2, and 8.3 ppm (m, 15H); ^{13}C NMR (C_6D_6) δ 16.4 (d, $^3J_{PC}$ = 5.7 Hz), 57.4 (d, $^2J_{PC}$ = 7.2 Hz), 127.3–133.8, and 139 ppm (d, $^1J_{PC}$ = 174.5 Hz, *ipso*-carbon); MS (*m/z*) 353 (M + 1), 307 (M − C_2H_5O), 277, 201, 183, 152 and 77.

Determination of the Molarity of a DTPP Solution. The molarity of the solution was determined using ^{31}P NMR and referenced to a standard solution of trimethyl phosphite [$P(OMe)_3$]. A 0.127 M solution of $P(OMe)_3$ in benzene solvent [prepared in a sealed 4-mm NMR tube in the presence of chromium acetylacetate (0.023 M)] was introduced into 2 mL of the DTPP solution in a 10-mm NMR tube. The separate addition of 70 mg of anhydrous chromium acetylacetate (0.1 M solution) to the solution of DTPP was necessary to obtain accurate NMR integrations that reflect the relative intensities and ultimately the concentrations of the respective species. The ^{31}P NMR integrations corresponding to DTPP (δ −54.9 ppm) and to $P(OMe)_3$ (δ 141.2 ppm) were recorded, and the molarity, M, of the solution of DTPP was directly calculated using the following equation:

$$\frac{[P(OMe)_3]}{[DTPP]} = \left(\frac{\text{integration for } P(OMe)_3}{\text{integration for DTPP}}\right)\left(\frac{6.47}{0.7}\right) = \frac{0.127\ M}{M}$$

The numerical values, 6.47 and 0.7, correspond to an area correction factor and a sensitivity correction, respectively.[16] The precision of the determination of the molarity, M, by this method was corroborated by ^1H NMR spectroscopy by reacting DTPP with 1 equiv of 1,2-propanediol (**3**) to afford 4-methyl-2,2,2-triphenyl-1,3,2λ⁵-dioxaphospholane (**4**).

4-Methyl-2,2,2-triphenyl-1,3,2λ⁵-dioxaphospholane (4). The hexanes solvent of 4.72 mL of 0.635 M DTPP (3.0 mmol) was removed *in vacuo*, and the solid residue was dissolved in anhydrous dichloromethane solvent under anhydrous conditions. 1,2-Propanediol (**3**) (228 mg, 3.0 mmol) was added to this solution, and the reaction mixture was stirred at *ca.* 25 °C for 15 min. The solvent and residual ethanol were removed *in vacuo* to afford a quantitative yield of dioxaphospholane **4**: ^1H NMR ($CDCl_3$) δ 1.2 (d, $^3J_{HCCH}$ = 7.0 Hz), 3.2 (m, 1H, $^3J_{PH}$ = 8.6 Hz, $^2J_{HCH}$ = 8.6 Hz, $^3J_{HCCH}$ = 7.15 Hz), 3.7 (m, 1H, $^3J_{PH}$ = 17.8 Hz, $^2J_{HCH}$ = 8.6 Hz, $^3J_{HCCH}$ = 5.9 Hz), and 4.05 ppm (m, 1H, $^3J_{PH}$ = 8.6 Hz, $^3J_{HCCH}$ = 7.0 Hz, $^3J_{HCCH}$ = 5.9 Hz, $^3J_{HCCH}$ = 7.15 Hz); ^{13}C NMR ($CDCl_3$) δ 19.1 (d, $^3J_{PC}$ = 7.0 Hz), 65.4, 68.1 (d, $^2J_{PC}$ = 1.51 Hz), 126–133,

(14) von Itzstein., M.; Jenkins, I. D. *Aust. J. Chem.* **1983**, *36*, 557.
(15) Gordon, J. A.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, New York, 1972.

(16) (a) The area correction factor (6.47) corresponds to the ratio of the volume of the sample in the 10-mm NMR tube and the volume of the insert in the 4-mm NMR tube. (b) The sensitivity factor (0.7) was determined experimentally using as sample solutions of triphenylphosphine, bis(triphenylphosphoranylidene) ammonium chloride (PPNCl), and chromium acetyl acetate in known concentrations.

and 146 ppm (*ipso*-carbon C_6H_5, $^1J_{PC}$ = 117.5 Hz); ^{31}P NMR ($CDCl_3$) δ −37.2 ppm. The ^1H NMR coupling constants were assigned using 2D NMR techniques.

Diisopropoxytriphenylphosphorane (DiPTPP). In a flask equipped with a condenser was added (under argon) dry 2-propanol (15.3 mL, 0.200 mol) to a suspension of sodium metal (4.6 g, 0.20 mol) in anhydrous THF (30 mL). After the mixture was refluxed overnight, an additional 13 mL of 2-propanol was added to the suspension of *i*-PrONa in THF which was subsequently stirred for an additional 0.5 h. The total volume of the suspension was recorded, and the molarity was determined based on the quantity of sodium metal. In a two-necked flask, triphenylphosphine (524 mg, 2.00 mmol) was reacted with 1 equiv of Br_2 (0.32 g, 2.00 mmol) in anhydrous diethyl ether (15 mL) under an argon atmosphere to afford a light-yellow suspension of bromotriphenylphosphonium bromide (7). Phosphonium ion 7 was allowed to react at *ca.* 25 °C with 4.00 mmol of *i*-PrONa (1.15 mL of the 3.45 M solution in THF/*i*-PrOH solvents prepared as previously described) to afford a brown suspension. After completion of the reaction, the reaction mixture was centrifuged until a clear solution was obtained. The ^{31}P NMR analysis of the supernatant indicated the presence of DiPTPP (80%; δ −50.1 ppm) and TPPO (20%; δ 26.4 ppm). The purification procedure for DiPTPP was the same as the one described above for DTPP.

DiPTPP: ^{31}P NMR (C_6D_6) δ −50.1 ppm; ^1H NMR (C_6D_6) δ 0.55 (d, 6H, $^3J_{HCCH}$ = 5.8 Hz, 3.4 (sept, 1H, $^3J_{HCCH}$ = 5.66 Hz), 7.2 and 8.2 ppm (m, 15H); ^{13}C NMR (C_6D_6) δ 24.3 (d, $^3J_{PC}$ = 2.2 Hz), 63.9 (d, $^2J_{PC}$ = 9.3 Hz), 126.9–132.3, and 140 ppm (d, J = 176 Hz).

Bis(*n*-amyloxy)triphenylphosphorane (**1d**) and bis(cyclohexyloxy)triphenylphosphorane (**1e**) were prepared following the same procedure as the one described for DiPTPP, but were not purified. **Bis(*n*-amyloxy)triphenylphosphorane (1d)**: ^{31}P NMR (C_6D_6) δ −55.8 ppm. **Bis(cyclohexyloxy)triphenylphosphorane (1e)**: ^{31}P NMR (C_6D_6) δ −49.5 ppm. **Dimethoxytriphenylphosphorane (1c)**: ^{31}P NMR (C_6D_6) δ −52.3 ppm.

Acyclic σ-Dialkoxytriphenylphosphoranes Using the Mitsunobu Procedure. These reactions were conducted in 10-mL NMR tubes under argon atmosphere. Triphenylphosphine (524 mg, 2.00 mmol) was dissolved in anhydrous THF (4 mL) and allowed to react with 1 equiv of diisopropylazodicarboxylate (404 mg, 2.00 mmol) at 0 °C. Two equiv of dry alcohol (4.0 mmol) were added to the resulting suspension, and the reaction mixture was shaken until a homogeneous solution was obtained. The yield of the reaction was determined by ^{31}P NMR analysis, based on the quantity of triphenylphosphine.

Acknowledgment is made to the National Science Foundation and Rhône-Poulenc, Agrochimie, for support of this research as well as for a fellowship from Rhône-Poulenc to I.M.P. We are also grateful to ATOCHEM of North America, Elf Aquitaine, for a generous supply of triphenylphosphine.

Supplementary Material Available: ^1H, ^{13}C, and ^{31}P NMR for the isolated dialkoxyphosporanes, DTPP and DiPTPP, and ^{31}P NMR data for dioxaphosphoranes **1c-d** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.