One-Pot Synthesis of Phosphonic Acid Diesters

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Phosphonic acid diesters are useful intermediates in chemistry,[1] and finding new synthetic routes to these compounds constitutes a valuable target. Known preparations include transesterification of easily available members of the family,[2] acidolyses or hydrolyses of phosphorochloridites or mixed anhydrides,[3−5] addition of phosphonic acid to oxiranes,[6] or alcoholysis of bis(*N*,*N*-dimethylamino) phosphonate.[7] Among these, the hydrolysis of phosphorochloridites, probably the more convenient synthetic access, requires the preliminary preparation of the latter, with possible yield limitations.

This paper describes the direct reaction of phosphonic acid with various hydroxy compounds in the presence of dicyclohexylcarbodiimide (DCCI), which avoids the drawbacks of the above-mentioned methods. Mixing the reagents in tetrahydrofuran (THF) initiates a fast process that, when monitored by ^{31}P NMR spectroscopy, shows the immediate replacement of the phosphonic acid signal by a peak at 112.3 ppm corresponding to phosphorous anhydride.[8] A doublet assigned to the phosphonate ester progressively grows as the reaction of P_4O_6 with the hydroxyl compound proceeds (Scheme 1). After 1 h in most cases, the remaining peaks are those of the expected diester and minor amounts of monophosphonate as a side product. Compounds **1**−**10** are prepared in good yields by this method (Table 1). In the ^{31}P NMR spectra, the PH signals used to identify compounds **1, 2, 4**−**6**, and **10**, consist of two pseudotriplets (for **2**, **10**) or two pseudoquintuplets (for **1** and **4**−**6**).

These products are sensitive toward moisture, which explains the presence in the crude mixture of minor amounts (10−20%) of monophosphonates. However, their low solubility allows a clean and easy separation. The structures of all these compounds were established by elemental analyses, NMR, and mass spectrometry. As an example of the efficiency of the method, the labile isopropylidene masking groups in compound **2** did not suffer any cleavage. The unexpected complexity of the ^{13}C NMR spectrum possibly reflects the existence of conformers stabilized by hydrogen bonding (Chart 1).

Bis(trimethylsilyl) phosphonate was previously prepared from phosphonic acid and bis(trimethylsilyl)-amine.[9] With the present method, the *bis*(triphenylsilyl) ester **3** was obtained in 75% yield by reaction 1 from the cheap commercial triphenylsilanol.

In addition to the above examples of monofunctional alcohols, difunctional compounds were reacted under the specified conditions. 1,3-Propanediol gave the 6-membered ring ester **6**. Triethyleneglycol and 1,10-decanediol provide, respectively, macrocyclic esters **4** and **5** (Chart 2), as shown by their analytical and spectral data. The molecular weight (325) of **4**, determined by cryoscopy, indicates the presence of the mono and dinuclear compounds in relative amounts of 1:2, with minor quantities of tri- and tetranuclear macro rings detected in the mass spectrum.

Scheme 1

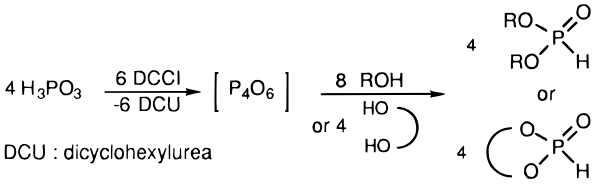
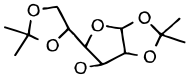
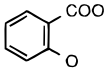
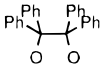
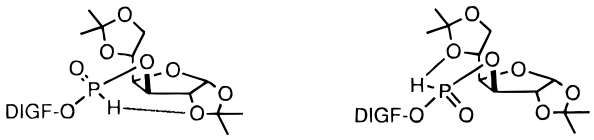


Table 1. Phosphonates Prepared via Reaction 1

Compd	Mono- or dihydroxy group	Yield[a]	^{31}P NMR		
			δ ^{31}P[b] (solvent)[c]	$^{1}J_{P-H}$	$^{3}J_{P-H}$ [d]
1	n-$C_{16}H_{33}O$	70 (65)[e]	6.4 (A)	680	2q 8.4
2		57	7.1 (B)	723	2t 10
3	Ph_3SiO	75	-16 (B)	710	
			-15.4 (C)	718	
4	$O(CH_2CH_2O)_3$	60	9.1 (B)	704	2q 9.7
5	$O(CH_2)_{10}O$	60	6.6 (B)	684	2q
			7.3 (C)		13.5
6	$O(CH_2)_3O$	65 (39)[f]	1.70 (B)	678	2q 13.5
7		50	-3.7 (C)	766	
		80[g]	-1.8 (D)	779	
		(58)[h]	-0.8 (E)	785	
8		70	13.9 (A)	714	
		(57)[f]	16.7 (D)	717	
9		65	15.6 (A)	727	
			16.8 (D)	736	
10		60	23.4, (C)	734	2t
			21.6 (A)	727	13.2
					2t
					13.9

[a] Literature yields (in parentheses) are based on trichlorophosphane. [b] In ppm. [c] Solvents: (A) C_6D_6; (B) THF; (C) CH_2Cl_2; (D) CH_3CN; (E) DMF. [d] In Hz; q : quintuplet, t : triplet. [e] Reference 7. [f] Reference 4. [g] From reaction 4. [h] Reference 3.

Chart 1



DIGF : Diisopropylidene glucofuranose

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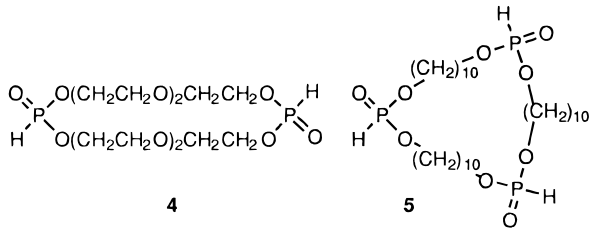
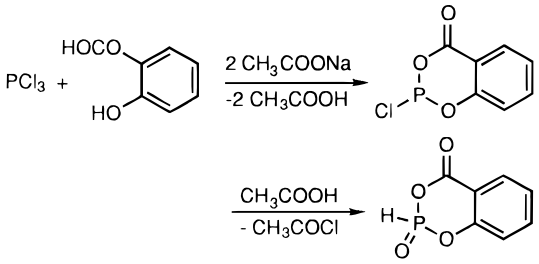
S0022-3263(95)01308-9 CCC: $12.00

Chart 2



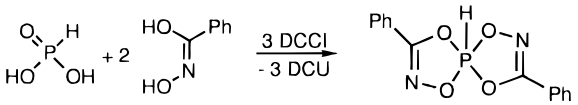
4 **5**

Scheme 2



7

Scheme 3



11

In the case of **5**, the cryoscopic measurement (average molecular weight 727) shows a predominance (2:1) of the trinuclear compound over the tetranuclear one. These compounds could not be separated. Analogous large ring compounds were previously prepared from aryldichlorophosphane oxide and triethylene glycol.[10]

Phosphonate **7**, previously described as a phosphite,[3] could be obtained quantitatively from salicylic acid; however, it was contaminated by *ca.* 5% dicyclohexylurea. An analytical purity product resulted from the ultrasound-induced precipitation of the contaminant from the ethyl acetate solution or by an alternate reaction between trichlorophosphane and salicylic acid in the presence of dry sodium acetate (2 equiv), as depicted in Scheme 2.

References to organophosphorus compounds derived from the hindered benzopinacol are not frequent.[11] Reaction 1 applies to this compound, although it proceeds slowly to give phosphonate **9**. Heating to 70−80 °C or sonication significantly increases the reaction rate. On the other hand, similar reactions starting from catechol and α-hydroxyisobutyric and benzhydroxamic acids lead to the corresponding known spirophosphoranes.[12−14] When applied to benzhydroxamic acid, the present method constitutes an alternate access to these spiranic molecules, as illustrated by the preparation of compound **11** (Scheme 3).[14]

In summary, reaction 1 has the advantage to start from cheap commercial compounds and to avoid intermediate steps, as in previous methods. Dicyclohexylurea, the sole byproduct is easily removed by precipitation, which can be made easier by ultrasonic irradiation. The mild conditions are compatible with the presence of sensitive protecting groups, and the versatility of the reaction makes it useful for synthetic purposes.

Experimental Section

Commercially available reagents were used as received. Phosphonic acid was dried in a microwave oven for 20 min. THF, acetonitrile, and ethyl acetate were dried on 3 Å molecular sieves. THF was kept on sodium wire. Melting points are not corrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with TMS as internal (^{1}H and ^{13}C) and 85% H_3PO_4 as external (^{31}P) standards. Cryoscopic measurements were carried out in DMSO (analytical grade dried on 3 Å molecular sieves; mp 18.49 °C; K [measured with phenylphosphonic acid] = 4.21 K·kg·mol^{-1} (lit.[15,16] 4.07−4.39 K·kg·mol^{-1}). Low-resolution mass spectra were recorded with chemical ionization (CH_4). High-resolution spectra were recorded with electron impact in a V.G. Autostec Q. apparatus (8000 < resolution < 10 000, 70 eV), in the Centre d'Etudes de Structure, d'Analyse de Molecules Organiques, Talence, France). Elemental analyses were carried out by the "Service de microanalyses, Ecole Nationale Supérieure de Chimie de Toulouse". Sonications were effected in a 47 kHz Kerry ultrasonic bath at room temperature.

Preparation of Phosphonates 1, 2, 4−6, 8, and 10. General Procedure a. Phosphonic acid (0.42 g, 5 mmol) in 5 mL of THF was rapidly added to a solution of the hydroxyl compound (5 mmol of diol or 10 mmol of alcohol) and DCCI (2.06 g, 10 mmol) in 15 mL of the same solvent. An exothermic reaction took place, and the mixture was kept at room temperature with liquid nitrogen. After the ^{31}P NMR spectrum had shown the absence of a low field signal, the crude mixture was sonicated for 30−60 min at room temperature. Dicyclohexylurea was filtered off, and then the solvent was evaporated to give the phosphonates in an analytical purity as indicated below in each individual case.

Procedure b for Compounds 3 and 11. DCCI (2.06 g, 10 mmol) in 10 mL of THF was added to phosphonic acid (0.42 g, 5 mmol) and hydroxyl compound (10 mmol of triphenylsilanol and 5 mmol of salicylic or benzhydroxamic acids) in THF (10 mL). An exothermic reaction took place. The reaction was completed under sonication, and then isolation and purification were effected as described below.

Bis(hexadecyl) Phosphonate (1).[7] The reaction was run in THF:CH_2Cl_2 (1:1). After precipitation, the urea was filtered off at 50 °C and washed with CH_2Cl_2 (10 mL). The solvent was evaporated and the solid dissolved in hot pentane (10 mL). The residual urea was filtered off, and then compound **1** precipitated. Yield: 70%. Mp: 51−53 °C (lit. not given).

Bis(1,2:5,6-diisopropylidene-D-glucose) Phosphonate (2). The reaction mixture was allowed to stand at −5 °C for 24 h, and then the urea was removed. Addition of pentane precipitated the residual urea and small amounts of **2**. After decantation and evaporation of the supernatant at 0.01 Torr, **2** was obtained as a hygroscopic powder, in 57% yield. Small amounts of the monophosphonate (5−10%) were eliminated by addition of an equivalent quantity of triethylamine to the crude dissolved in diethyl ether and filtration of the salt. NMR spectra confirmed the absence of dicyclohexylurea. ^{1}H NMR (C_6D_6, 80.1 MHz): 6.91 (d, 1 H, $^{1}J_{PH}$ = 726 Hz), 5.82 (d, 2 H, $^{3}J_{PH}$ = 3 Hz), 4.93−3.87 (m, 12 H), 1.38, 1.31, 1.22 (24 H) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): 112.56, 112.45, 111.68, 109.81, 109.7, 109.4, 105.8 (d, $^{3}J_{PC}$ = 9.4 Hz), 85.88, 84.38, 81.12, 81.03 (d, $^{3}J_{PC}$ = 6.1 Hz), 79.3 (d, $^{2}J_{PC}$ = 4.7 Hz), 78.81 (d, $^{2}J_{PC}$ = 6.7 Hz), 75.28, 73.58, 73.00, 72.65, 67.89, 67.84, 67.62, 27.14, 27.04, 26.91, 26.75, 26.33, 26.18, 25.48, 25.23 ppm. MS (DCI) *m/z*: 567 (M + 1, 100), 509, 261. HRMS: calcd for $C_{24}H_{39}O_{13}P$ 567.2206, found 567.2183.

Bis(triphenylsilyl) Phosphonate (3). With the above purification procedure, a microcrystalline powder was obtained

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in 75% yield. Mp: 150−151 °C. ^{1}H NMR (C_6D_6, 80.1 MHz): 7.1 (d, 1H, PH, $^1J_{PH}$ = 710 Hz), 7.83−7.58, 7.2−7.0 (m, 30 H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 135.44, 132.05, 130.67, 128.20 ppm. MS *m/z*: 627 (M + 29, 10), 599 (M + 1, 20), 521 (100). HRMS: calcd for $C_{36}H_{31}O_3PSi_2$ 597.1471, found 597.1473.

Triethyleneglycol Phosphonate 4: Reaction Run in THF:CH_2Cl_2 (1:1). After separation of urea and solvent evaporation, the resulting oil was dissolved in acetonitrile (5 mL) and kept at 0 °C for 24 h. Residual urea was removed and the solvent evaporated to give an oil (60%). ^{1}H NMR ($CDCl_3$, 80.1 MHz): 6.9 (d, 1 H, $^1J_{PH}$ = 713 Hz), 4.28−4.02 (m, 4 H), 3.7, 3.63, 3.60 (8 H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 70.50, 70.17 (d, $^3J_{PC}$ = 5.2 Hz), 64.47 (d, $^2J_{PC}$ = 5.7 Hz) ppm. MS (DCI) *m/z*: 785 (4M + 1, <1), 589 (3M + 1, 5), 393 (2M + 1, 75), 197 (M + 1, 100). MW (cryoscopic) 325. Anal. Calcd for $(C_6H_{13}O_5P)_n$: C, 36.73; H, 6.68. Found: C, 36.54; H, 7.06.

1,10-Decanediol Phosphonate 5. After urea removal and THF evaporation, the thick oil was dissolved in ethyl acetate (5 mL). The residues of urea were filtered off, and the solvent was removed to give an oil (60%) that solidified at 0 °C. ^{1}H NMR ($CDCl_3$, 80.1 MHz): 6.75 (d, 1 H, $^1J_{PH}$ = 694 Hz), 4.06−3.95 (m, 4 H), 1.84−1.25 (m, 16 H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 65.81 (d, $^2J_{PC}$ = 5.5 Hz), 30.4 (d, $^3J_{PC}$ = 6.2 Hz), 29.38, 29.07, 25.48 ppm. MS (DCI) *m/z*: 881 (4M + 1, 3), 661 (3M + 1, 25), 441 (2M + 1, 100), 221 (M + 1, 30). MW (cryscopic) 727. Anal. Calcd for $(C_{10}H_{21}O_3P)_n$: C, 54.54; H, 9.61. Found: C, 54.25; H, 9.79.

2-Oxo-1,3,2-dioxaphosphorinane (6):[4] purified as for compound **2** to give needles (65%). Mp: 28−30 °C. ^{1}H NMR ($CDCl_3$, 80.1 MHz): 6.8 (d, 1 H, $^1J_{PH}$ = 678 Hz), 4.56−4.21 (m, 2 H), 2.32−1.83 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 67.27 (d, $^2J_{PC}$ = 6.2 Hz), 25.93 (d, $^3J_{PC}$ = 8.1 Hz) ppm. MS (DCI) *m/z*: 123 (M + 1, 100).

2,4-Dioxo-5,6-benzo-1,3,2-dioxaphosphorinane (7).[3] (1) Salicylic acid (1.38 g, 10 mmol), trichlorophosphane (1.4 g, 10 mmol), and anhydrous sodium acetate (1.64 g, 20 mmol) were stirred in 25 mL of diethyl ether for 4 h. After this period, the ^{31}P NMR peak of PCl_3 was replaced by those of 2-chloro-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (148 ppm, 65%),[17] 2-acetoxy-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (114.5 ppm, 25%),[18] and phosphonate **7** [−3.8 ppm (proton decoupled), 10%]. Precipitated NaCl was separated by centrifugation, and the supernatant was kept under an inert atmosphere at room temperature. Compound **7** crystallized as needles that were separated, washed with Et_2O, and dried under vacuum. Yield: 80%. Mp: 120 °C dec. ^{1}H NMR ($CDCl_3$, 80.1 MHz): 7.62 (d, 1H, $^1J_{PH}$ = 763 Hz), 8.9−7.16 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 162.07, 153.92 (d, $^2J_{PC}$ = 7 Hz), 151.15 (d, $^2J_{PC}$ = 5.6 Hz), 138.51, 136.29, 131.96, 130.74, 126.21, 119.32, 117.55, 119.56 (d, $^4J_{PC}$ = 9.6 Hz), 113.52 (d, $^3J_{PC}$ = 4.8 Hz). MS (DCI) *m/z*: 185 (M + 1, 30), 139 (100).

(2) From phosphonic acid, procedure b was followed. After completion, urea was filtered off. The ^{31}P NMR spectrum exhibited the doublet of product **7**. Solvent evaporation gave a white sticky powder, washed with Et_2O (10 mL). The product separated as a microcrystalline powder that was taken up in ethyl acetate and sonicated for 30 min to force the residual urea to crystallize. After its removal, diethyl ether was added, and compound **7** was crystallized by cooling to −20 °C. Yield: 50%.

2-Oxo-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (8).[4] The reaction was run in THF without cooling. Urea was separated after sonication for 1 h. Solvent evaporation gave a powder that was washed with diisopropyl ether (10 mL) and then dissolved in ethyl acetate. Residual urea was removed, and **8** was isolated as microcrystals after solvent evaporation. Yield: 70%. Mp: 98−102 °C. ^{1}H NMR ($CDCl_3$, 80.1 MHz): 7.2 (d, 1H, $^1J_{PH}$ = 706 Hz), 1.44 and 1.34 (ds, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 88.96, 24.68 (d, $^3J_{PC}$ = 3.6 Hz), 23.97 (d, $^3J_{PC}$ = 5.4 Hz) ppm. MS (DCI) *m/z*: 165 (M + 1, 100).

2-Oxo-4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane (9). The reaction was run in THF without cooling. After precipitation of urea, the mixture was stirred at 70−80 °C for 6 h, urea was removed, and the solvent was evaporated. The powder was dissolved in ethyl acetate (10 mL) and sonicated for 30 min to crystallize the urea. The solvent was evaporated from the filtrate, and the resulting powder was dispersed in diethyl ether (10 mL) and kept at 0 °C for 24 h. Compound **9** was filtered and dried under vacuum. Yield: 65%. Mp: 176−178 °C. ^{1}H NMR ($CDCl_3$, 80.1 MHz): 7.32 (d, 1 H, $^1J_{PH}$ = 727 Hz), 7.46−7.00 (m, 20 H) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): 141.3 (d, $^3J_{PC}$ = 5 Hz), 140.37 (d, $^3J_{PC}$ = 4.5 Hz), 129.49, 129.14, 128.39, 128.18, 128.02, 127.6, 127.43, 126.95, 83.63 ppm. MS (DCI) *m/z*: 413 (M + 1, 100), 183 (100). Anal. Calcd for $C_{26}H_{21}O_3P$: C, 75.73; H, 5.13. Found: C, 75.98; H, 5.45.

Bis(1,2:5,6-diisopropylidene-D-mannitol) Phosphonate (10). After urea separation and concentration of the filtrate, pentane (5 mL) was added. Compound **10** precipitated at −20 °C as microcrystals. Yield: 60%. Mp: 72−74 °C. ^{1}H NMR (C_6D_6, 200 MHz): 7.24 (d, 1H, $^1J_{PH}$ = 727.4 Hz), 4.17, 3.61 (m, 8H), 1.27 (s, 3H), 1.25 (s, 3H), 1.09 (s, 3H), 1.01 (s, 3H) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): 110.5, 110.4, 81.5, 79.2, 75.4, 74.5, 66.74, 64.77, 26.74, 26.19, 24.86, 24.33 ppm. MS *m/z*: 309 (M + 1, 100). Anal. Calcd for $C_{12}H_{21}O_7P$: C, 46.75; H, 6.86. Found: C, 46.41; H, 7.02.

2,7-Diphenyl-3,8-diaza-1,4,6,9-tetraoxa-5-hydrido-5λ^5-phosphaspiro[4.4]2,3,7,8-nonene (11).[14] Benzhydroxamic acid (0.7 g, 5 mmol) in a 1:1 mixture of THF:CH_2Cl_2 was added to the phosphonic acid (0.42 g, 5 mmol) DCCI (2.06 g, 10 mmol) mixture. After 30 min at rt, the urea was filtered off. The solvents were evaporated to give a sticky powder that was washed with benzene (15 mL). An oil was separated, and evaporation of the supernatant gave **11** in 62% yield. Mp: 136−138 °C (lit.[14] mp 140 °C). ^{1}H NMR ($CDCl_3$, 80.1 MHz): 8.78 (d, 1H, $^1J_{PH}$ = 889 Hz), 7.96−7.8, 7.44−7.24 (m, 10 H) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): 165.0 (d, $^2J_{PC}$ = 8.9 Hz), 132.42, 128.85, 126.73, 124.32 (d, $^3J_{PC}$ = 3.7 Hz) ppm.

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(18) 2-Acetoxy-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane was prepared from trichlorophosphane (5 mmol), salicylic acid (5 mmol), and sodium acetate (15 mmol) in diethyl ether. Crystals are obtained after filtration of NaCl and solvent evaporation. Mp: 73−76 °C (lit.[3] mp 72−74 °C). ^{31}P NMR ($CDCl_3$, 32.44 MHz): 114.5. ^{1}H NMR ($CDCl_3$, 80.1 MHz): 8.11−7.04 (m, 4 H), 2.12 (d, 3 H, $^4J_{PH}$ = 1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 169.7 (d, $^2J_{PC}$ = 6.3 Hz), 153.0 (d, $^2J_{PC}$ = 6.7 Hz), 137.05, 131.08 (d, $^3J_{PC}$ = 2.8 Hz), 124.83, 119.6, 116.8 (d, $^3J_{PC}$ = 11.7 Hz), 21.8 (d, $^3J_{PC}$ = 2.2 Hz) ppm.