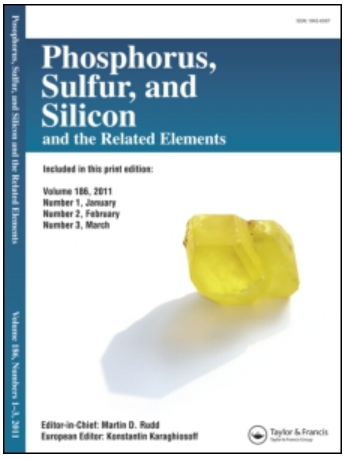

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL AMIDOPHOSPHITES

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL AMIDOPHOSPHITES

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A method is proposed for one-pot synthesis of either symmetrical or unsymmetrical diester amidophosphites, developed on the basis of tris-(N,N-dimethyl)-amide/or tris-(N,N-diethyl)-amide/of phosphorous acid, activated by iodine, as a new phosphorylating reagent.

Nine thiophosphate, phosphite and phosphite monoester and diester derivatives of 1-O-stearoyl-ethane-2-ol, cholesterol, β-sitosterol and R,S-α-tocopherol have been synthesized under mild conditions (20–75°C) and in high final yields (83–98%).

At present, various methods and reagents are useful in the phosphorylation of compounds containing a free hydroxyl group.[1–3] In this respect, the acyclic triamides of phosphorous acid are of special interest.[4,5] Being polyfunctional, however, these reagents cannot be subjected to stoichiometrical alcoholysis (or phenolysis) if monoester derivatives are desired. Consequently, three equivalents of the triamide are usually employed.[5–7] This excludes the possibility of obtaining unsymmetric diesters directly. Combined with the rather severe conditions needed (in some cases thermal treatment up to 140–160°C[4,6]), the scope of the phosphorylating reagents mentioned is considerably limited.

We now propose a method for one-pot synthesis of either symmetrical or unsymmetrical diester amidophosphites under mild conditions, by means of a new phosphorylating reagent developed on the basis of tris-(N,N-dialkyl)-amides of phosphorous acid activated by the addition of iodine at the optimum molar ratio 1.05:0.05.

RESULTS AND DISCUSSION

The tris-(N,N-dimethyl)-amide of phosphorous acid, **1** and the tris-(N,N-diethyl)-amide of phosphorous acid, **2**, both activated by iodine were used.

1-O-Stearoylethane-2-ol, **a**, cholesterol, **b**, β-sitosterol, **c** and R,S-α-tocopherol, **d** were selected as model lipid substrates containing primary, secondary or sterically hindered phenolic hydroxyl functions.

The reaction takes place either at room temperature or on moderate heating (70–75°C) in stoichiometric ratio with the substrates chosen, to give the respective monoester derivatives **2aS**, **2bS**, **2dS** in practically quantitative yield (Scheme 1):

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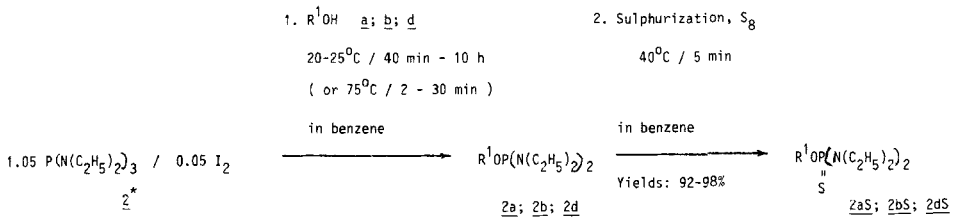
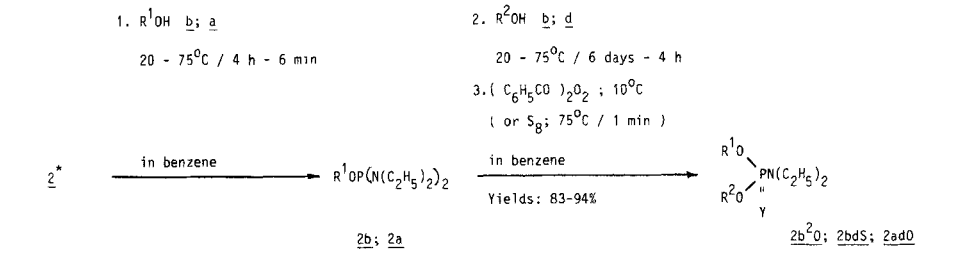


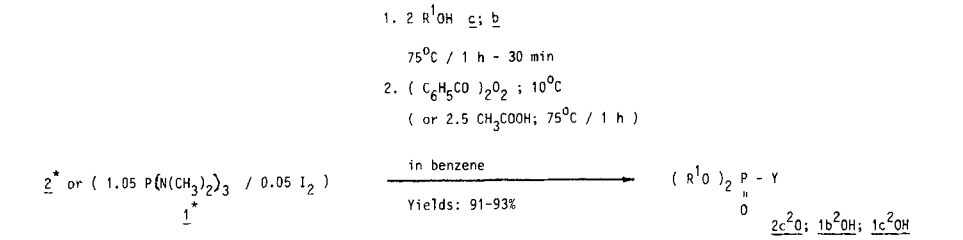
SCHEME 1 For **a**, **2a** and **2aS**: R^1 = 1-O-Stearoylethyl; **b**, **2b** and **2bS**: R^1 = Cholesteryl; **d**, **2d** and **2dS**: R^1 = R,S-α-Tocopheryl.

The next step, regarding the synthesis of symmetrical, **2b²O** or unsymmetrical, **2bdS**, **2adO** diesters, may be performed also in high yield by directly reacting the previously prepared monoester intermediate, **2b**, **2a** with the equivalent quantity of another substrate (Scheme 2):



SCHEME 2 For **2b²O**: R^1 = Cholesteryl; R^2 = Cholesteryl; Y = O: **2b2S**: R^1 = Cholesteryl; R^2 = R,S-α-Tocopheryl; Y = S; **2adO**: R^1 = 1-O-Stearoylethyl; R^2 = R,S-α-Tocopheryl; Y = O.

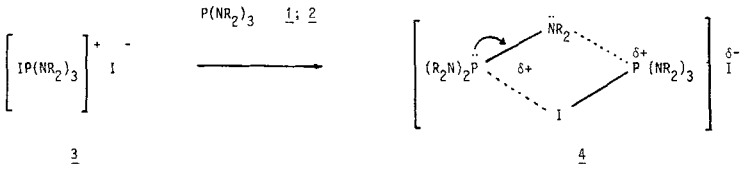
Symmetrical diester compounds may be obtained also, **2c²O**, by a one-step synthesis at molar ratio: reagent/substrate 1/2 (Scheme 3):



SCHEME 3 For **c** and **2c²O**: R^1 = β-Sitosteryl; Y = $N(C_2H_5)_2$; **1b²OH**: R^1 = Cholesteryl; Y = H; **1c²OH**: R^1 = β-Sitosteryl; Y = H.

On the basis of the synthesized P^{III} mono- or diester derivatives a wide range of additional transformations[2,5,8] could be performed. Thus, in all cases,the structures of the amidophosphites (Schemes 1–3) prepared were proven after convenient chemical transformations to thiophosphates, **2aS**, **2bS**, **2dS**, **2bdS**, phosphates, **2b²O**, **2adO**, **2c²O**, and phosphites, **1b²OH**, **1c²OH**.

It could be suggested that the demonstrated high selectivity of the reagent is due to the action of an initial quasi-phosphonium compound,[9] **3**, which forms an activated complex, **4**, with the triamide of phosphorous acid, **1**, **2** by electrophilic orientation on nitrogen (Scheme 4). As a result, one of the amido groups in the



SCHEME 4 For **1**: R = CH_3; **2**: R = C_2H_5.

triamide, **1**, **2** is converted to a good leaving group and could then be easily substituted by nucleophilic attack on phosphorous. We have established by preliminary model studies that the quasi-phosphonium derivatives themselves do not possess a phosphorylation ability under the experimental conditions given.

Basic compounds such as pyridine, triethylamine, diethylamine etc. considerably decrease the rate of phosphorylation.

EXPERIMENTAL

The tris-(N,N-dimethyl)-amide of phosphorous acid, **1**, and the tris-(N,N-diethyl)-amide of phosphorous acid, **2**, were prepared according to ref.[10,11] 1-O-Stearoylethane-2-ol, **a**, was prepared according to Reference 12. Dibenzoylperoxide (Merck) was used as a 10% benzene solution and dried over molecular sieve 3 Å. All other reagents were GR, or of purity in excess of 98% (Merck). Solvents were dried prior to use. Reaction conditions were kept strictly anhydrous.

Preparative thin-layer chromatography (TLC) was performed on 20 × 20 cm plates and stationary phase of silica gel G (Merck) with a layer thickness of 2 mm; after 1 h activation at 120°C. The following mobile phases were used: chloroform (system A); n-hexane/diethyl ether 95/5 (system B); n-hexane/chloroform 80/20, v/v (system C).

The melting points were determined on a Kofler melting point apparatus and are uncorrected.

^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at 100.62 MHz. ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane (TMS). ^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer at 32.44 MHz. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. IR spectra were recorded on a Perkin-Elmer 337 spectrometer. Peak positions are reported in cm^{-1}.

Elemental analyses were performed by the Microanalytical Service Laboratory, University of Plovdiv.

1-O-Stearoylethane-2-O-bis(N,N-diethylamido)-thiophosphate, 2aS; Typical procedure. A mixture of iodine (0.025 g; 0.1 mmol) and the tris-(N,N-diethyl)-amide of phosphorous acid (**2**; 0.519 g; 2.1 mmol) in benzene (50 mL) was heated at 75°C in a stream of argon for about 15 min until the precipitate dissolved, **2**.* The solution was cooled to room temperature (20–25°C), 1-O-stearoylethane-2-ol (**a**; 0.657 g; 2 mmol) was added, and the reaction system was kept under these conditions for 40 min (The same procedure was also carried out at 75°C for about 1 min.). Then sulphur (0.067 g; 2.1 mmol) was added and the mixture was heated at 40°C for 5 min to give the thiophosphate derivative, **2aS**. Part of the solvent was removed under vacuum and the compound was isolated by TLC using system A as mobile phase, and then diethyl ether for eluting the product from the silica gel adsorbent.

Yield of **2aS**: 1.03 g (96%); n_D^{50}: 1.4615; Rf: 0.62 (system A). $C_{28}H_{59}N_2O_3PS$ calc. C 62.86 H 11.14 N 5.24 P 5.79 S 6.00 (535.0) found C 62.57 H 11.12 N 5.20 P 5.83 S 6.04 ^{13}C NMR – $\{^1H\}(C_6D_6)$: δ = 14.2 (s, C-18); 23.3 (s, C-17); 25.7 (s, C-3); 30.0–30.6 (m, C-4–C-15); 32.7 (s, C-16); 34.6 (s, C-2); 63.6 (d, OCH_2CH_2OP, J = 10.0 Hz); 64.5 (s, OCH_2CH_2OP); 173.2 (s, C-1): 1-O-stearoylethane-2-O-fragment; 14.9 (s, CH_3CH_2N); 40.7 ppm (s, CH_2N). ^{31}P NMR – $\{^1H\}(C_6D_6)$: δ = 77.7 ppm (s). IR (KBr): ν = 1750 (C=O); 1020, 790 (PO-C, P-OC); 720 (P-N); 695 cm^{-1} (P=S).

Cholesteryl-3-O-bis(N,N-diethylamido)-thiophosphate, **2bS**. Using cholesterol (**b**; 0.773 g; 2 mmol), the derivative was synthesized at room temperature (4 h) or at 75°C (6 min), and then purified (system B) the same way as described for **2aS**.

Yield of **2bS**: 1.09 g (92%); m.p. 73.0–74.5°C (from diethyl ether); Rf: 0.52 (system B).

$C_{35}H_{65}N_2OPS$ calc. C 70.87 H 11.07 N 4.72 P 5.23 S 5.41 (593.1) found C 70.55 H 11.13 N 4.77 P 5.25 S 5.46 ^{13}C NMR – $\{^1H\}(C_6D_6)$: δ = 12.5 (s, C-18); 19.6 (s, C-21); 19.9 (s, C-19); 21.9 (s, C-11); 23.2 (s, C-26); 23.5 (s, C-27); 24.8 (s, C-23); 25.1 (s, C-15); 28.8 (s, C-25); 29.1 (s, C-16); 30.8 (d, C-2, J = 4.4 Hz); 32.7 (s, C-7, C-8); 36.7 (s, C-20); 37.2 (s, C-22); 37.3 (s, C-10); 37.8 (s, C-1); 40.4 (s, C-24); 40.8 (s, C-12); 41.2 (d, C-4, J = 5.2 Hz); 43.1 (s, C-13); 50.8 (s, C-9); 57.1 (s, C-17); 57.5 (s, C-14); 76.6 (d, C-3, J = 3.7 Hz); 123.3 (s, C-6); 140.9 (s, C-5): cholesteryl-3-O-fragment; 14.7 (d, CH_3CH_2N, J = 3.7 Hz); 41.0 ppm (d, CH_2N, J = 3.7 Hz). ^{31}P NMR – $\{^1H\}(C_6D_6)$: δ = 77.2 ppm (s). IR (KBr): ν = 1010, 790 (PO-C, P-OC); 730 (P-N); 695 cm^{-1} (P═S).

R,S-α-Tocopheryl-6-O-bis(N,N-diethylamido)-thiophosphate, **2dS**. Using R,S-α-tocopherol (**d**; 0.861 g; 2 mmol), the derivative was synthesized within 10 h at room temperature (or for 40 min at 75°C) and then purified (system A) as described for **2aS**.

Yield of **2dS**: 1.24 g (98%); n_D^{20}: 1.5137; Rf: 0.90 (system A). $C_{37}H_{69}N_2O_2PS$ calc. C 69.74 H 10.94 N 4.40 P 4.87 S 5.03 (637.2) found C 69.53 H 10.90 N 4.35 P 4.88 S 5.00 ^{13}C NMR – $\{^1H\}(C_6D_6)$: δ = 12.8 (s, CH_3-5); 15.3 (s, CH_3-7); 15.8 (s, CH_3-8); 23.3 (s, CH_3-2); 32.2 (s, C-3); 41.0 (s, C-4); 75.4 (s, C-2); 118.3 (s, C-5, C-10); 123.6 (s, C-7, C-8); 144.1 (d, C-9, J = 8.9 Hz); 149.3 (s, C-6): nucleus; 20.4 (s, CH_3-4, CH_3-8); 21.7 (s, C-13); 21.9 (s, CH_3-12); 24.4 (d, C-2, J = 11.1 Hz); 25.4 (s, C-10); 25.7 (s, C-6); 28.8 (s, C-12); 33.6 (s, C-4); 33.7 (s, C-8); 38.4 (s, C-3, C-5, C-7, C-9); 40.3 (s, C-1, C-11): chain, R,S-α-tocopheryl-6-O-fragment; 14.5 (d, CH_3CH_2N, J = 4.2 Hz); 41.6 ppm (d, CH_2N, J = 4.2 Hz). ^{31}P NMR – $\{^1H\}(C_6D_6)$: δ = 72.6 ppm (s). IR (KBr): ν = 1250, 840 (PO-C, P-OC_{aryl}); 725 (P-N); 690 cm^{-1} (P═S).

Bis(cholesteryl-3-O-)-(N,N-diethylamido)-phosphate, **2b²O**; *Typical procedure.* To a solution of the reagent, **2***, prepared as described for **2aS**, cholesterol (**b**; 0.773 g; 2 mmol) was added and the reaction system was kept in a stream of argon at room temperature for 4 h. The same quantity of cholesterol (**b**; 0.773 g; 2 mmol) was then added, and the mixture was left under the same conditions for 6 days. Dibenzoylperoxide (0.509 g; 2.1 mmol) was added dropwise at 10°C to give the phosphate derivative, **2b²O**. Part of the solvent was removed under vacuum and the compound was crystallized from benzene/acetone.

Yield of **2b²O**: 1.48 g (83%); m.p. 147–149°C (from benzene/acetone), Rf: 0.43 (system A). $C_{58}H_{100}NO_3P$ calc. C 78.19 H 11.35 N 1.57 P 3.49 (889.6) found C 78.22 H 11.30 N 1.57 P 3.43 ^{13}C NMR – $\{^1H\}(C_6D_6)$: The spectrum is very similar to that of **2bS**. ^{31}P NMR – $\{^1H\}(C_6D_6)$: δ = −2.0 ppm (s). IR (KBr): ν = 1250 (P═O); 1015, 795 (PO-C, P-OC); 730 cm^{-1} (P-N).

Cholesteryl-3-O-(R,S-α-tocopheryl-6-O-)-(N,N-diethylamido)-thiophosphate, **2bdS**. Using **2***, cholesterol (**b**; 0.773 g; 2 mmol) (first step: 75°C; 6 min) and R,S-α-tocopherol (**d**; 0.861 g; 2 mmol) (second step: 75°C; 4 h).

The transformation to thiophosphate, **2bdS**, was done with sulphur (0.067 g; 2.1 mmol) at the temperature indicated. The compound was isolated by TLC using system C as mobile phase, and then diethyl ether for eluting the product from the silica gel adsorbent.

Yield of **2bdS**: 1.79 g (94%); n_D^{50}: 1.5149; Rf: 0.44 (system C). $C_{60}H_{104}NO_3PS$ calc. C 75.79 H 11.05 N 1.47 P 3.26 S 3.38 (950.8) found C 75.85 H 11.00 N 1.44 P 3.30 S 3.41 ^{13}C NMR – $\{^1H\}(C_6D_6)$: δ = 12.7 (s, C-18); 19.9 (s, C-21); 30.6 (s, C-2); 37.9 (d, C-1, J = 17.2 Hz): cholesteryl-3-O-fragment; R,S-α-tocopheryl-6-O-fragment: 23.4 (d, CH_3-2, J = 16.0 Hz); 32.2 (s, C-3): nucleus; 20.5 (d, CH_3-4, J = 10.0 Hz); 20.6 (d, CH_3-8, J = 10.0 Hz): chain; 15.0 (s, CH_3CH_2N); 40.8 ppm (d, CH_2N, J = 7.5 Hz). ^{31}P NMR – $\{^1H\}(C_6D_6)$: δ = 70.3 ppm (s). IR (KBr): ν = 1245, 840 (PO-C, P-OC_{aryl}); 1010, 790 (PO-C, P-OC); 720 (P-N); 685 cm^{-1} (P = S).

1-O-Stearoylethane-2-O-(R,S-α-tocopheryl-6-O-)-(N,N-diethylamido)-phosphate, **2adO**. Using **2***, 1-O-stearoylethane -2-ol (**a**; 0.657 g; 2 mmol) (first step: 20–25°C; 40 min) and R,S-α-tocopherol (**d**; 0.861 g; 2 mmol) (second step: 65°C; 5 h).

The transformation to phosphate, **2adO**, was done with dibenzoylperoxide (0.509 g; 2.1 mmol) at 10°C. The compound was isolated by TLC (system A) as described for **2bdS**.

Yield of **2adO**: 1.61 g (92%); n_D^{50}: 1.4672; Rf: 0.24 (system A). $C_{53}H_{98}NO_6P$ calc. C 72.62 N 11.29 N 1.60 P 3.54 (876.5) found C 72.72 H 11.20 N 1.61 P 3.50 ^{13}C NMR – $\{^1H\}$ (C_6D_6): δ = 14.2 (s, C-18); 63.6 (d, OCH_2CH_2OP, J = 10.0 Hz); 64.5 (s, OCH_2CH_2OP); 173.2 (s, C-1): 1-O-stearolyethane-2-O-fragment; R, S-α-tocopheryl-6-O-fragment: 12.7 (s, CH_3-5); 23.4 (d, CH_3-2, J = 16.0 Hz): nucleus; 20.3 (s, CH_3-4, CH_3-8); 24.3 (d, C-2, J = 16.0 Hz): chain; 14.9 (s, CH_3CH_2N); 40.7 ppm (s, CH_2N). ^{31}P NMR – $\{^1H\}(C_6D_6)$: δ = −0.2 ppm(s). IR (KBr): ν = 1740 (C═O); 1250, 840 (PO-C, P-OC_{aryl}); 1030, 790 (PO-C, P-OC); 725 cm^{-1} (P-N).

Bis(β-sitosteryl-3-O-)-(N,N-diethylamido)-phosphate, **2c²O**. A mixture of the reagent, **2***, and

β-sitosterol (**c**; 1.659 g; 4 mmol) in benzene (50 mL) was heated in a stream of argon at 75°C for 1 h. The procedures for the transformation to phosphate and the isolation of compound, **2c²O**, are identical with those described for **2b²O**.

Yield of **2c²O**: 1.76 g (93%); m.p. 140–145°C (from benzene/acetone); Rf: 0.45 (system A). $C_{62}H_{108}NO_3P$ calc. C 78.66 H 11.52 N 1.48 P 3.27 (946.7) found C 78.72 H 11.55 N 1.50 P 3.24 ^{13}C NMR – $\{^1H\}(C_6D_6)$: $\delta = 12.5$ (s, C-18); 12.7 (s, C-29); 19.4 (s, C-26); 19.6 (s, C-27); 19.8 (s, C-21); 19.9 (s, C-19); 21.9 (s, C-11); 24.1 (s, C-28); 25.1 (s, C-15); 27.4 (s, C-23); 29.1 (s, C-16); 30.3 (s, C-25); 31.0 (s, C-2); 32.7 (s, C-7, C-8); 35.0 (s, C-22); 37.1 (s, C-10, C-20); 37.9 (s, C-1); 40.7 (s, C-12); 41.5 (s, C-4); 43.1 (s, C-13); 46.9 (s, C-24); 50.9 (s, C-9); 57.0 (s, C-17); 57.5 (s, C-14); 77.1 (s, C-3); 123.2 (s, C-6); 140.9 (s, C-5): bis(β-sitosteryl-3-O-)-fragment; 14.8 (s, CH_3CH_2N); 40.7 ppm (s, CH_2N). ^{31}P NMR – $\{^1H\}(C_6D_6)$: $\delta = -2.1$ ppm(s). IR (KBr): $\nu = 1250$ (P=O); 1010, 795 (PO-C, P-OC); 730 cm^{-1} (P-N).

Bis(cholesteryl-3-O-)-phosphite, **1b²OH.** A mixture of iodine (0.025 g; 0.1 mmol) and the tris-(N,N-dimethyl)-amide of phosphorous acid (**1**; 0.343 g; 2.1 mmol) in benzene (50 mL) was heated at 75°C in a stream of argon for about 20 min until the precipitate dissolved, **1***. Cholesterol (*b*; 1.547 g; 4 mmol) was added and the system was kept under the same conditions for 30 min. The transformation to phosphite, **1b²OH**, was accomplished with acetic acid (0.150 g; 2.5 mmol) for 1 h at the temperature indicated, whereupon part of the solvent was removed under vacuum and the compound was crystallized from benzene/acetone.

Yield of **1b²OH**: 1.51 g (92%); m.p. 176–177°C (from benzene/acetone); Rf: 0.51 (system A). $C_{54}H_{91}O_3P$ calc. C 79.14 H 11.22 P 3.78 (819.5) found C 79.06 H 11.25 P 3.70 ^{13}C NMR – $\{^1H\}(C_6D_6)$: $\delta = 12.5$ (s, C-18); 19.5 (s, C-21); 31.0 (d, C-2, $J = 21.7$ Hz); 41.4 (d, C-4, $J = 17.2$ Hz); 140.1 ppm (s, C-5). ^{31}P NMR (C_6D_6): $\delta = 2.6$ ppm (d, $J_{P\text{-}H} = 671.6$ Hz). IR (kBr): $\nu = 2390$ (PH); 1260 (PO); 1010, 798 cm^{-1} (PO-C, P-OC).

Bis(β-sitosteryl-3-O-)-phosphite, **1c²OH**. Using β-sitosterol (**c**; 1.659 g; 4 mmol), the derivative, **1c²OH**, was synthesized and isolated as described for **1b²OH**.

Yield of **1c²OH**: 1.59 g (91%); m.p. 165–168°C (from benzene/acetone); Rf: 0.53 (system A). $C_{58}H_{99}O_3P$ calc. C 79.56 H 11.42 P 3.54 (875.6) found C 79.48 H 11.45 P 3.50 ^{13}C NMR-$\{^1H\}(C_6D_6)$: $\delta = 12.5$ (s, C-18); 12.7 (s, C-29); 19.7 (s, C-19, C-21); 31.0 (d, C-2, $J = 17.2$ Hz); 41.4 (d, C-4, $J = 17.2$ Hz); 140.3 ppm (s, C-5). ^{31}P NMR (C_6D_6): $\delta = 2.7$ ppm (d, $J_{P\text{-}H} = 671.6$ Hz). IR (KBr): $\nu = 2390$ (PH); 1260 (PO); 1015, 795 cm^{-1} (PO-C, P-OC).

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