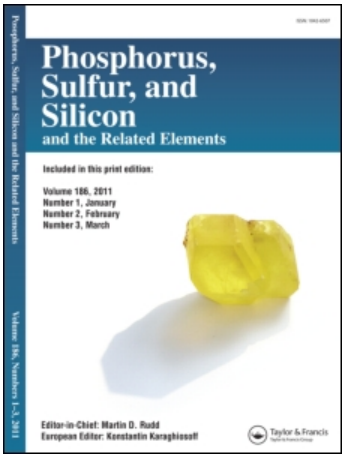

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL TRIESTER PHOSPHITES

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL TRIESTER PHOSPHITES

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A method for one-pot synthesis of either symmetrical or unsymmetrical triester phosphites [$(RO)_3P$ or $(RO)(R^1O)_2P$, $(RO)(R^1O)(R^2O)P$ and ROP$\langle O \rangle (CH_2)_n$; R, R^1, R^2 = alkyl or phenyl] at room temperature is proposed.

Hexaalkyltriamides of phosphorous acid and amidophosphite intermediates [$P(NR^*_2)_3$ and $ROP(NR^*_2)_2$, $(RO)_2PNR^*_2$, $(RO)(R^1O)PNR^*_2$; $R^* = CH_3$, C_2H_5], activated by imidazole and carbon disulfide, are used as new phosphorylating reagents.

Six phosphite and thiophosphate triester derivatives of phenol, cis-9-octadecene-1-ol, cholesterol, β-sitisterol, 1,3-butane diol and 1-nonanol have been synthesized in high final yields (85–94%).

Key words: Triester phosphites; amidophosphites; reagent; phosphorylation; thiophosphates; activation.

It is known that triester phosphites can by synthesized by alcoholysis (or phenolysis) of N,N-substituted hexaalkyltriamides of phosphorous acid, monoester and diester amidophosphites.[1,2] As a rule, the phosphorylation is carried out at 80–170°C for up to 20 h to give the corresponding triesters in yields ranging from 28 to 80%.[1–7] These rather severe conditions lead to various side-reactions (disproportionation, transesterification etc.)[2,8] and considerably limit the scope of these phosphorylating reagents. The one-pot synthesis of unsymmetrical triester phosphites by means of hexaalkyltriamides of phosphorous acid has not so far been described in the literature.

We now propose a method for the synthesis of triester phosphites, according to which:

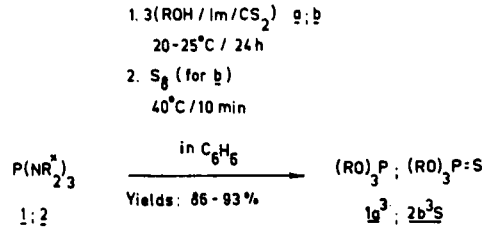
—hexaalkyltriamides of phosphorous acid, monoester and diester amidophosites may be used as phosphorylating reagents at room temperature after their activation by an equimolar mixture of imidazole and carbon disulfide;

—unsymmetrical phosphites can be obtained via monoester or diester intermediates in a one-pot procedure, using as starting reagents hexaalkyltriamides of phosphorous acid, activated by iodine.[9]

RESULTS AND DISCUSSION

The tris-(N,N-dimethyl)-amide, **1** and the tris-(N,N-diethyl)-amide, **2** of phosphorous acid were used as base reagents.

† Author to whom all correspondence should be addressed.



SCHEME 1 For **1**: $R^* = CH_3$; **2**: $R^* = C_2H_5$; Im: Imidazole; **a** and **1a**[3]: R = Phenyl; **b** and **2b**[3]**S**: R = cis-9-Octadecenyl.

Phenol, **a**, cis-9-octadecene-1-ol, **b**, cholesterol, **c**, β-sitosterol, **d**, 1,3-butane diol, **e** and 1-nonanol, **f** were selected as model substrates containing phenolic, primary and secondary hydroxyl functions.

Symmetrical phosphites may be obtained by a one-step procedure at molar ratio—hexaalkyltriamide of phosphorous acid/substrate/imidazole/carbon disulfide 1/3/3/3 (Scheme 1).

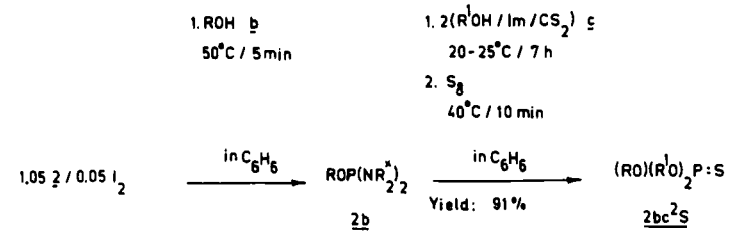
The preparation of unsymmetrical derivatives, $(RO)(R^1O)_2P$, permits the use of two alternative approaches.

In the first case, one equivalent of monester intermediate, **2b**,[9] may directly be applied to two equivalents of an equimolar mixture of the substrate, **c**, imidazole and carbon disulfide (Scheme 2). Using the same approach, bifunctional alcohols (such as **e**) in a molar ratio with imidazole and carbon disulfide of 1/2/2, can be treated stoichiometrically with monoester intermediates, **2c**; **2d**, to give cyclic phosphites (Scheme 3). Thus, compounds, **2ceS**; **2deS**, were synthesized at room temperature for 20 min, instead of 6 h heating at 120–130°C, usig the classical procedure.[10]

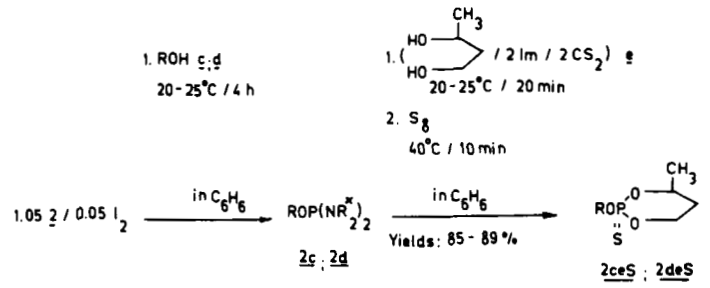
According to the second approach, an equimolar mixture of the substrate, **b**, imidazole and carbon disulfide can be treated with the symmetrical diester intermediate, **1c**[2], stoichiometrically (Scheme 4). On this way we resynthesized compound, **2bc**[2]**S** ≡ **1c**[2]**bS**.

The use of an unsymmetrical diester amidophosphite (such as **1bc**) offers the possibility for the preparation of triester derivatives with the highest degree of unsymmetry, $(RO)(R^1O)(R^2O)P$. Thus, compound, **1bcfS** was directly obtained by successive phosphorylation of **b**, **c** and **f** (Scheme 5).

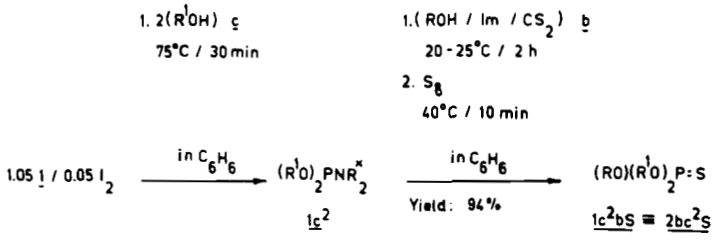
With only one exeption, **1a**,[3] the structures of the phosphites prepared were proven after chemical transformation to the corresponding thiophosphates.



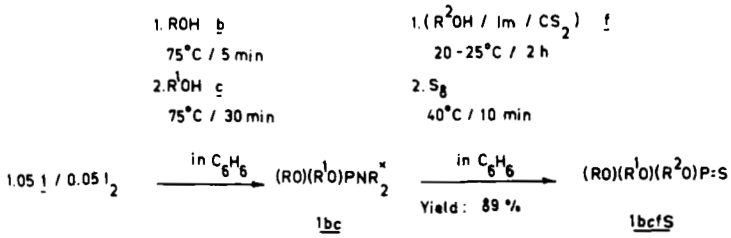
SCHEME 2 For **b**, **2b** and **2bc**[2]**S**: R = cis-9-Octadycenyl; **c** and **2bc**[2]**S**: R^1 = Cholesteryl; **2b**: $R^* = C_2H_5$.



SCHEME 3 For **c**, **2c** and **2ceS**: R = Cholesteryl; **d**, **2d** and **2deS**: R = β-Sitosteryl; **2c** and **2d**: $R^* = C_2H_5$.



SCHEME 4 For **c**, **1c²** and and **1c²bS**: R^1 = Cholesteryl; **b** and **1c²bS**: R = cis-9-Octadecenyl; **1c²**: $R^* = CH_3$.



SCHEME 5 For **b**, **1bc** and **1bcfS**: R = cis-9-Octadecenyl; **c**, **1bc** and **1bcfS**: R^1 = Cholesteryl; **f** and **1bcfS**: R^2 = nonanyl; **1bc**: $R^* = CH_3$.

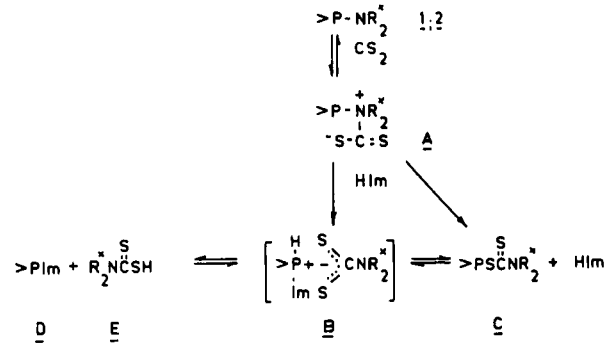
The reactions of carbon disulfide with amides of phosphorous acid have been systematically studied.[11-17] The combined activation of a P—N bond by both carbon disulfide and imidazole has not so far been discussed in the literature.

By preliminary model studies we have established that:

—after treatment of the phosphamide, **2**, with carbon disulfide and imidazole in a molar ratio of 1/3/3, the presence of the tris(N,N-diethyldithiocarbamoyl)-phosphite (type **C**; ^{31}P NMR: $\delta = -59.8$ ppm s) and the N,N-diethylammonium salt of N,N-diethyldithiocarbamic acid (a derivative of **E**: m.p. 77–78°C) may be detected in the reaction mixture (Scheme 6):

—the tris(N,N-diethyldithiocarbamoyl)-phosphite itself does not possess phosphorylating ability at room temperature (20–25°C) but it may be activated by adding imidazole;

—the phosphorylating ability of the tris-(N,N-dimethyl)-amide of phosphorous



SCHEME 6 HIm: Imidazole; $R^* = CH_3$ (or C_2H_5).

acid, **1**, is approximately five times higher than that of the tris-(N,N-diethyl)-amide of phosphorous acid, **2**, after identical activation by carbon disulfide and imidazole.

Thus, we assume that the high reactivity observed at the triester formation stage is due to the formation of an activated complex, **B** in equilibrium with the imidazole and the other components (types **C**, **D** and **E**) of the reaction system. In this context, the phosphorylation procedure has to be interpreted as a nucleophilic substitution on phosphorus in the activated imidazolides, **B**, formed in situ.

This hypothesis is under investigation and will be discussed in details elsewhere.

EXPERIMENTAL

The tris-(N,N-dimethyl)-amide, **1** and the tris-(N,N-diethyl)-amide, **2** of phosphorous acid were prepared as previously described.[9] Cis-9-octadecene-1-ol, **b** (Merck) was additionally purified by column chromatography. 1,3-Butane diol, **e** (Merck) was dried over molecular sieves 3 Å and freshly distilled. All other reagents were GR, or of purity in excess of 98% (Merck). Solvents were dried prior to use. The reactions were run in anhydrous conditions under an atmosphere of argon.

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 mobile phases used were: chloroform/*n*-hexane 20/80 (system A); *n*-hexane/diethyl ether 40/60, v/v (system B).

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

^{1}H NMR spectra were recorded on a Bruker WH-360 spectrometer at 360.13 MHz. ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane (TMS). ^{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 TMS. ^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer at 36.46 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 either by the Microanalytical Service Laboratory, University of Plovdiv, or by the Microanalytical Laboratory, Bulgarian Academy of Sciences.

Tris(phenyl)-phosphite, 1a;[3] Typical procedure. To a solution of phenol (**a**; 8.47 g; 90 mmol), imidazole (6.13 g; 90 mmol) and carbon disulfide (6.85 g; 90 mmol) in benzene (200 mL), tris-(N,N-dimethyl)-amide of phosphorous acid (**1**; 4.90 g; 30 mmol) was added, and the reaction mixture was stirred at room temperature (20–25°C) for 24 h. The precipitated N,N-dimethylammonium salt of N,N-dimethyldithiocarbamic acid was filtered and the solvent was removed under reduced pressure.

The residue was subjected to distillation in vacuum (5.33×10^2Pa) and the fraction at b.p. 201–204°C was collected.

Yield of **1a**[3]: 8.01 g (86%); n_D^{20}: 1.5822 (Reference 18: n_D^{20}: 1.5815). ^{31}P NMR-{^{1}H} (C_6D_6): δ = 127.6 ppm (s).

Tris(cis-9-octadecene-1-O-)-thiophosphate, 2b[3]S. To a solution of cis-9-octadecene-1-ol (**b**; 0.806 g; 3 mmol), imidazole (0.204 g; 3 mmol) and carbon disulfide (0.228 g; 3 mmol) in benzene (50 mL), tris-(N,N-diethyl)-amide of phosphorous acid (**2**; 0.247 g; 1 mmol) was added and the reaction mixture was left at room temperature for 24 h. Then sulphur (0.032 g; 1 mmol) was added and the transformation to the thiophosphate, **2b[3]S**, was carried out at 40°C for 10 min. The solvent was removed under reduced pressure and the compound was extracted from the residue with *n*-hexane (2 × 50 mL). The precipitate was filtered and the crude derivative was purified by TLC using system A as mobile phase, and then diethyl ether for eluting the product from the silica gel adsorbent.

Yield of **2b[3]S**: 0.81 g (93%); n_D^{20}: 1.4758; Rf: 0.60 (system A).

$C_{54}H_{105}O_3PS$ calc. C 74.92, H 12.25, P 3.58, S 3.71.
(865.7) found C 74.69, H 12.25, P 3.60, S 3.67.

^{1}H NMR (C_6D_6): δ = 0.95 (t, 9H, CH_3—, J = 6.0 Hz); 1.32 (m, 66H, —CH_2—); 1.60 (quint, 6H, CH_2—CH_2—O, J = 8.0 Hz); 2.13 (quint, 12H, CH_2—CH═, J = 6.0 Hz); 4.13 (q, 6H, CH_2—O, J = 8.0 Hz); 5.52 ppm (t, 6H, CH═, J = 6.0 Hz). ^{31}P NMR—{^{1}H} (C_6D_6): δ = 67.3 ppm (s).
IR (KBr): ν = 3010 (CH═); 1650 (C═C); 1010, 810 (PO—C, P—OC); 625 cm^{-1} (P═S).

Cis-9-octadecene-1-O-bis(cholesteryl-3-O-)-thiophosphate, **2bc[2]S.** A mixture of iodine (0.013 g; 0.05 mmol) and the tris-(N,N-diethyl)amide of phosphorous acid (**2**; 0.259 g; 1.05 mmol) in benzene (25 mL) was heated at 50°C for approximately 20 min until the precipitate dissolved. Cis-9-octadecene-1-ol (**b**; 0.268 g; 1 mmol) was added and after 5 min the reaction system was cooled to room temperature. A solution of cholesterol (**c**; 0.773 g; 2 mmol), imidazole (0.136 g; 2 mmol) and carbon disulfide (0.152 g; 2 mmol) in benzene (25 mL) was added and the mixture was left under these conditions for 7 h. The transformation to thiophosphate, **2bc[2]S**, was performed by adding sulphur (0.034 g; 1.05 mmol) and heating at 40°C for 10 min. The crude product was then isolated and purified as described for **2b[3]S** (variant I).

A mixture of iodine (0.013 g; 0.05 mmol) and the tris-(N,N-dimethyl)-amide of phosphorous acid (**1**; 0.171 g; 1.05 mmol) in benzene (25 mL) was heated at 75°C for approximately 15 min until the precipitate dissolved. Cholesterol (*c*; 0.773 g; 2 mmol) was added and the reaction system was kept under these conditions for 30 min. A solution of cis-9-octadece-ne-1-ol (**b**; 0.268 g; 1 mmol), imidazole (0.068 g; 1 mmol) and carbon disulfide (0.076 g; 1 mmol) in benzeene (25 mL) was added at room temperature, and the mixture was left for 2 h with stirring. The resulting precipitate was filtered off and the transformation to thiophosphate, **1c[2]bS**, was performed the same way as described for *variant I*. The crude product was isolated and purified as described for **2b[3]S** (variant II).

Yield of **2bc[2]S**: 1.00 g (91%); n_D^{50}: 1.5100; Rf: 0.62 (system A): variant I; Yield of **1c[2]bS**: 1.03 g (94%); n_D^{50}: 1.5106; Rf: 0.62 (system A): variant II.

$C_{72}H_{125}O_3PS$ calc. C 78.46, H 11.46, , P 2.81, S 2.91.
(1102.1) found C 78.56, H 11.44, P 2.85, S2.95.

^{13}C NMR—{^{1}H} (C_6D_6): δ = 14.9 (s, C-18); 23.5 (s, C-17); 26.5 (s, C-2); 28.2 (s, C-8, C-11); 30.0–30.6 (m, C-5–C-7, C-12–C-15); 31.0 (s, C-4); 31.1 (s, C-3); 32.8 (s, C-16); 68.6 (s, C-1); 130.7 (s, C-9, C-10): cis-9-octadecene-1-0-fragment; 12.6 (s, C-18); 19.5 (s, C-21); 19.8 (s, C-19); 21.8 (s, C-11); 23.3 (S, C-26); 23.5 (s, C-27); 24.8 (s, C-23); 25.1 (s, C-15); 28.9 (s, C-25); 29.1 (s, C-16); 30.7 (s, C-2); 32.6 (s, C-7); 32.8 (s, C-8); 36.9 (s, C-20); 37.2 (s, C-10, C-22); 37.7 (s, C-1); 40.4 (s, C-24); 40.7 (s, C-12); 41.0 (s, C-4); 43.1 (s, C-13); 50.7 (s, C-9); 57.0 (s, C-17); 57.5 (s, C-14); 79.4 (d, C-3, J = 3.0 Hz); 123.6 (d, C-6, J = 17.0 Hz); 140.4 ppm (d, C-5, J = 3.0 Hz): cholesteryl-3-0-fragment.
^{31}P NMR-{^{1}H} (C_6D_6): δ = 64.3 ppm (s).
IR (KBr): ν = 3010 (CH═); 1650 (C═C); 1010, 800 (PO—C, P—OC); 660 cm^{-1} (P═S).

2-(Cholesteryl-3-O-)-1,3-butylenethiophosphate, **2ceS.** 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 (25 mL) was heated at 75°C for approximately 10 min until the precipitate dissolved. After cooling to room temperature, cholesterol (**c**; 0.773 g; 2 mmol) was added and the mixture was kept under these conditions for 4 h. Then 1,3-butane diol (**e**; 0.180 g; 2 mmol), imidazole (0.272 g; 4 mmol) and carbon disulfide (0.305 g; 4 mmol) were added and the reaction system was stirred for 20 min. Sulphur (0.067 g; 2.1 mmol) was added at 40°C for 10 min to give the thiophosphate derivative, **2ceS**. The solvent was removed under reduced pressure and the compound was extracted from the residue with *n*-hexane (2 × 50 mL). After filtration, solvent was distilled off and the product was crystallized from acetone at −10°C.

Yield of **2ceS**: 0.95 g (89%); m. p. 129–131°C (from acetone), (Reference 10: m.p. 128–130°C); Rf: 0.63; 0.76 (system B).
^{13}C NMR—{^{1}H} (C_6D_6): δ = 12.5 (s, C-18); 19.5 (s, C-21); 19.9 (s, C-19); 21.9 (s, C-11); 23.2 (s, C-26); 23.4 (s, C-27); 24.8 (s, C-23); 25.0 (s, C-15); 28.8 (s, C-25); 29.0 (s, C-16); 31.7 (s, C-2); 32.7 (s, C-7, C-8); 36.6 (s, C-20); 37.2 (s, C-10, C-22); 38.0 (s, C-1); 40.4 (s, C-24); 40.7; (s, C-12), 42.2 (s, C-4); 43.1 (s, C-13); 51.0 (s, C-9); 57.2 (s, C-17); 57.5 (s, C-14); 74.2 (d, C-3, J = 19.5 Hz); 122.9 (s, C-6); 141.1 (s, C-5): cholesteryl-3-O-fragment; 23.6 (s, CH_3-4); 37.3 (s, C-5); 60.0 (s, C-6); 65.8 ppm (s, C-4): 1,3-butylene-fragment.
^{31}P NMR—{^{1}H} (C_6D_6): δ = 57.0; 62.2 ppm (each s, 2:1).
IR (KBr): ν = 1024/992, 810/775 (PO—C, P—OC); 652 cm^{-1} (P═S).

2-(β-Sitosteryl-3-O-)-1,3-butylenethiophosphate, **2deS**. Using β-sitosterol (**d**; 0.829 g; 2 mmol), the derivative was synthesized and purified identically as described for **2ceS**.
Yield of **2deS**: 0.96 g (85%); m.p. 120–121°C (from acetone), (Reference 10: m.p. 118–120°C); Rf: 0.65; 0.77 (system B).
^{13}C NMR-{^{1}H} (C_6D_6): δ = 12.5 (s, C-18); 12.7 (s, C-29); 19.5 (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); 29.0 (s, C-16); 30.3 (s, C-25); 31.7 (s, C-2); 32.7 (s, C-7, C-8); 35.0 (s, C-22) 37.0 (s, C-10, C-20); 38.0 (s, C-1); 40.7 (s, C-12); 42.2 (s, C-4); 43.1 (s, C-13); 46.9 (s, C-24); 51.0 (s, C-9); 57.0 (s, C-17); 57.5 (s, C-14); 74.2 (d, C-3, J = 19.9 Hz); 122.8 (s, C-6); 141.1 (s, C-5); β-sitosteryl-3-O-fragment; 23.6 (s, CH_3-4); 37.3 (s, C-5); 60.0 (s, C-6); 65.9 ppm (s, C-4): 1,3-butylene-fragment.
^{31}P NMR-{^{1}H} (C_6D_6): δ = 59.9; 62.2 ppm (each s, 2:1).
IR (KBr): ν = 1025/980, 805/775 (PO—C, P—OC); 650 cm^{-1} (P═S).

Cis-9-octadecene-1-O-(cholesteryl-3-O-)-(nonane-1-O-)-thiophosphate, **1bcfS**. 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 (25 mL) was heated at 75°C until the precipitate dissolved. Cis-9-octadecene-1-ol (**b**; 0.537 g; 2 mmol), and after 5 min, cholesterol (**c**; 0.773 g; 2 mmol), were added. The reaction system was treated under these conditions for 30 min, and then it was cooled to room temperature. A solution of nonane-1-ol (**f**; 0.289 g; 2 mmol), imidazole (0.136 g; 2 mmol) and carbon disulfide (0.152 g; 2 mmol) in benzene (25 mL) was added, and the mixture was stirred for 2 h. The transformation to thiophosphate, **1bcfS**, was performed by adding sulphur (0.067 g; 2.1 mmol) and heating at 40°C for 10 min. The formed precipitate was filtered off, the solvent was removed under reduced pressure, and the compound was extracted from the residue with *n*-hexane (2 × 50 mL). The precipitate was filtered off, part of the solvent was distilled off, and **1bcfS** 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 **1bcfS**: 1.53 g (89%); n_D^{20}: 1.5013; Rf:0.58 (system A).
$C_{54}H_{99}PS$ calc. C 75.44, H 11.63, P 3.61 S 3.73.
(859.6) found C 75.30, H 11.62, P 3.57, S 3.79.
^{13}C NMR-{^{1}H} (C_6D_6): δ = 14.6 (s, C-18); 23.6 (s, C-17); 26.5 (s, C-2); 28.2 (s, C-8, C-11); 30.0–30.7 (m, C-5–C-7, C-12–C-15); 31.0 (s, C-4); 31.1 (s, C-3); 32.8 (s, C-16); 68.6 (s, C-1); 130.6 (s, C-9, C-10):cis-9-octadecene-1-0-fragment; 12.6 (s, C-18); 19.5 (s, C-21); 19.8 (s, C-19); 21.8 (s, C-11); 23.6 (s, C-26); 23.6 (s, C-27); 24.8 (s, C-23); 25.1 (s, C-15); 28.9 (s, C-25); 29.1 (s, C-16); 30.7 (s, C-2); 32.6 (s, C-7, C-8); 36.9 (s, C-20); 37.2 (s, C-10, C-22); 37.9 (s, C-1); 40.4 (s, C-24); 40.8 (s, C-12); 41.0 (s, C-4); 43.1 (s, C-13); 50.7 (s, C-9); 57.0 (s, C-17); 57.4 (s, C-14); 79.4 (d, C-3, J = 17.5 Hz); 123.6 (d, C-6, J = 18.0 Hz); 140.3 (s, C-5); cholesteryl-3-O-fragment; 14.6 (s, C-9); 23.3 (s, C-8); 26.5 (s, C-3): 30.0–30.7 (m, C-4, C-5); 31.0 (s, C-6); 31.1 (s, C-7); 32.8 (s, C-2); 68.7 ppm (s, C-1): nonane-1-O-fragment.
^{31}P NMR-{^{1}H} (C_6D_6): δ = 65.7 ppm (a).
IR (KBr): ν = 3010 (CH═); 1650 (C═C); 1000, 810, (PO—C, P—OC); 650 cm^{-1} (P═S).

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