Expanding the Field of Phosphorus-Containing Fatty Acid Derivatives: Synthesis of 1,2-Oxaphospholene Derivatives and Alkenyl Phosphonates from α-Keto Allenes

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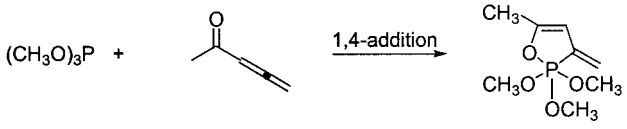
The first successful preparation of phosphorus-containing heterocyclic fatty acid derivatives is described. Reaction of the C_{18} α-keto allene **1** and the C_{18} α-keto chloroallene **2** with trimethyl phosphite gave the 1,2-oxaphospholene derivatives **4** and **6**, respectively. Hydrolysis of **4** and **6** furnished the corresponding alkenyl phosphonate **5** and alkenyl chlorophosphonate **7**, respectively. α-Chloro-α′-keto allene **3** gave the oxaphospholene derivative **8**. The various intermediates and products were identified by a combination of spectroscopic and spectrometric techniques.

Introduction

One of the main resolutions promulgated at the United Nations Conference on Environmental and Developments held in Rio de Janeiro in 1992 was to encourage environmentally sound and sustainable use of renewable natural resources.[1,2] Oils and fats of vegetable and animal origin make up the greatest proportion of the current consumption of renewable feed stocks in the chemical industry. Fats and oils therefore offer to chemistry a large number of possibilities for application, which can seldom be met by petrochemicals.[2]

Remarkably, only very few fatty compounds containing phosphorus-carbon bonds have been reported in the chemical literature. Swern et al.[3] reported on radical additions of dialkyl phosphites to unsaturated fatty compounds such as methyl oleate and obtained a regioisomeric mixture of the 9- and 10-dialkylphosphonooctadecanoates, which have been applied as plasticizers for PVC. We are interested in expanding the field of phosphorus-containing fatty acid derivatives and have focussed on the regioselective synthesis of heterocyclic phosphorus-containing derivatives.

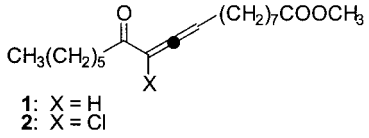
Buono et al. reacted simple α-keto allenes with trialkyl phosphites and obtained regioselectively the corresponding oxyphosphoranes containing a 1,2-oxaphospholene ring and an additional exocyclic double bond.[4,5] We thought to apply this reaction to various fatty compounds containing the α-keto allene functionality to obtain regioselectively the respective oxaphospholenes (Scheme 1). We obtained interesting and unexpected results showing once more that there are important differences of reactivity between a simple substrate and a long chain substrate containing additional functionality.



Scheme 1. Reaction of trimethyl phosphite with an α-keto allene to give the oxaphospholene

Results and Discussion

From our previous investigations we had three α-keto allenes (Figure 1) available to examine the reaction with tri-



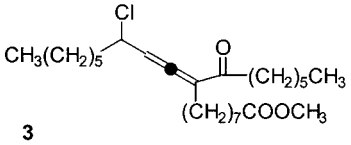


Figure 1. α-Keto allenes **1**, **2** and **3** as starting materials for the synthesis of phosphorus-containing fatty acid derivatives

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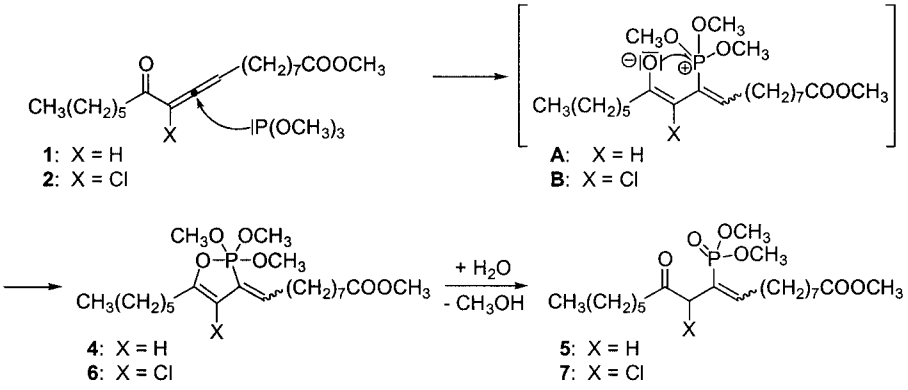


Scheme 2. Proposed mechanism of the formation of the alkenyl phosphonates **5** and **7** from the reaction of α-keto allene **1** and α-keto chloroallene **2**, respectively, with trimethyl phosphite

methyl phosphite. Methyl 12-oxo-9,10-octadecadienoate (**1**) was prepared starting from methyl ricinoleate.[6] Methyl santalbate [methyl (*E*)-octadec-11-en-9-ynoate from Sandalwood seed oil, *Santalum album*] was converted in a multistep reaction into methyl 11-chloro-12-oxo-9,10-octadecadienoate (**2**).[7] The α-chloro-α′-keto allene **3** was obtained by Friedel−Crafts acylation of methyl santalbate.[8]

According to the work of Buono et al.[5] we reacted compound **1** with one equivalent of previously distilled trimethyl phosphite in dichloromethane by stirring at room temperature for 43 h (Scheme 2). The solvent was then removed in vacuo to give an oil, which we were able to identify as the expected oxaphospholene **4**. The crude oxaphospholene **4** was formed as an inseparable 1:1 *Z*/*E*-isomeric mixture with regard to the exocyclic double bond, as confirmed by H,H-COSY, HMQC, and HMBC measurements. Unfortunately, an assignment of the *Z*- and *E*-isomers was not successful due to missing ^{1}H NMR NOE contacts. Therefore, the signals of the respective other isomer are marked with an asterisk in the following discussion. Also, the ^{31}P NMR spectrum shows a significant signal for the pentacoordinate phosphorus in **4** at δ = −42.55 ppm (the phosphorus nuclei of the *E*/*Z*-isomers happen to give isochronic shifts) which corresponds well to the values of other oxaphospholenes observed by Buono et al.[5]

During the course of the subsequent column chromatography with petroleum ether/ethyl acetate/methanol (7:3:1), however, hydrolytic ring opening occurred due to water bound to the silica gel. Thus, we isolated the open-chain alkenyl phosphonate **5** as a colourless oil in 64% yield in the end (Scheme 2). This could be confirmed by assignment of the respective NMR signals by H,H-COSY, HMQC, and HMBC measurements.

As expected the resulting alkenyl phosphonate **5** was also obtained as a 1:1 *Z*/*E*-isomeric mixture that was not separable either. According to the work of Srebnik characteristic chemical shifts for alkenyl phosphonates are usually observed at about δ = 20 ppm in the ^{31}P NMR spectrum.[9] This corresponds well to the value of δ = 24.40 ppm observed for **5**. Also, the ^{13}C NMR signals at δ = 205.96 and 205.97 ppm coming from the carbonyl groups at C-12/C-12* as well as the signals at δ = 40.56 and 40.65 ppm, which could unambiguously be assigned to C-11/C-11*, clearly prove the opening of the oxaphosphalene ring, giving rise to the alkenyl phosphonate structure.

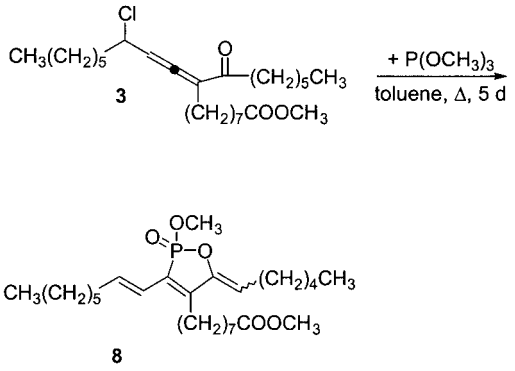
A similar behaviour was found for α-keto chloroallene **2**, although we had to change the solvent to toluene, raise the reaction temperature to 110 °C, and extend the reaction time to five days in order to get complete conversion of **2** and to obtain the respective chloro-substituted alkenyl phosphonate **7**, after evaporation of the solvent and column chromatography on silica gel with petroleum ether/diethyl ether/methanol (7:3:1), as a yellow oil in 53% yield — again as an inseparable 1:1 *Z*/*E*-isomeric mixture. In the ^{31}P NMR spectrum we observed a single, incidentally isochronic signal at δ = 21.38 ppm which again corresponds to the expected value for alkenyl phosphonates of about δ = 20 ppm.[9] Also, the chemical shifts of the ^{13}C NMR signals for C-11/C-11* and C-12/C-12* again support the formation of the open-chain compound. Interestingly, the chloro substituent seems to have a fixing influence on the conformation of one of the two isomers concerning the free rotation of the phosphorus substituent. This is reflected in the NMR signals of the two methoxy groups bound to the phosphorus atom. In the ^{13}C NMR spectrum we observed three signals at δ = 52.50, 52.54 and 52.57 ppm. One signal for the isomer where free rotation is still allowed, which therefore has equivalent methoxy groups, and two signals for the fixed isomer in which one can distinguish between the two methoxy groups. This observation is confirmed by the ^{1}H NMR spectroscopic data, where two singlets at δ = 3.73 and 3.77 ppm (intensity of three protons each) for the fixed isomer and one singlet at δ = 3.75 ppm (intensity of six protons) for the non-fixed isomer were found.

However, as we are dealing with a mixture we were not able to identify the crude chloro oxaphospholene **6** by NMR spectroscopy in the way that we did for the crude oxaphospholene **4**.

The observed readily occurring hydrolysis of the oxaphospholenes **4** and **6** to give the alkenyl phosphonate has not been reported up to now and opens up a new access to this important group of compounds.[9]

As with **2** the reaction of α-chloro α′-keto allene **3** with one equivalent of trimethyl phosphite in dichloromethane

gave no conversion, even under reflux. However, this was finally achieved by boiling in toluene for three days. Surprisingly, after evaporation of the solvent and column chromatography on silica with petroleum ether/ethyl acetate (10:3) as eluent oxaphospholene **8** was isolated as a colourless oil in 44% yield (Scheme 3).



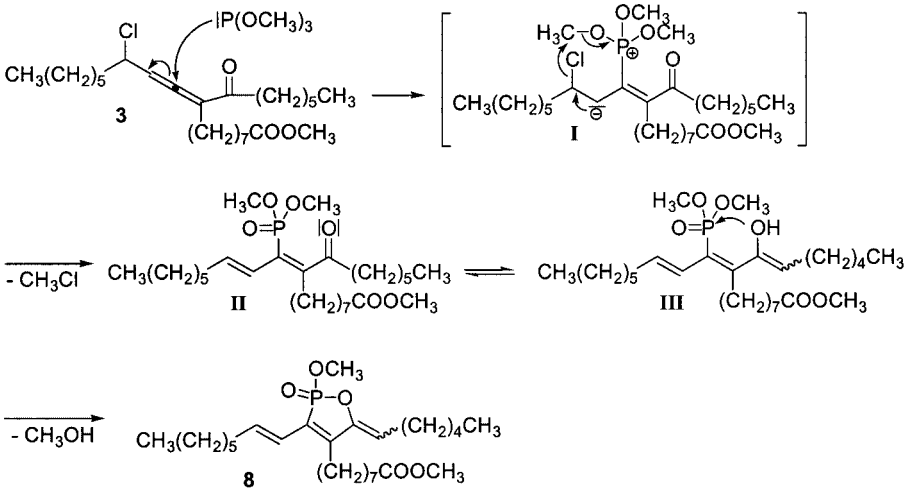
Scheme 3. Synthesis of oxaphospholene **8** from chloroketo allene **3** and trimethyl phosphite

Compound **8** proved to be sensitive towards decomposition, but nevertheless the analysis of the NMR spectroscopic data (including H,H-COSY, HMQC and HMBC measurements) clearly confirmed the proposed structure. Unfortunately, oxaphospholene **8** was again formed as an inseparable 1:1 *Z*/*E*-isomeric mixture with regard to the exocyclic double bond between C-19 and C-20, and again, all our efforts to definitely assign signals either to the *Z*- or the *E*-isomer failed due to missing analysable ^{1}H NMR NOE contacts. However, the other exocyclic double bond between C-9 and C-10 was found to be *trans*-configured in both isomers, as indicated by vicinal coupling constants of $^3J_{H,H}$ = 15.8 Hz each. Furthermore, the signal at δ = 35.92 ppm — once again the signals for both isomers happen to be isochronic in the ^{31}P NMR spectrum recorded in $CDCl_3$ — is in very good agreement with the data of Brel, who observed ^{31}P chemical shifts for these kind of oxaphospholene derivatives in the range δ = 31−35 ppm.[10] Unfortunately, the ^{1}H and ^{13}C NMR spectra recorded from the [D]chloroform solution proved to be only poorly resolved and the compound was found to decompose rather rapidly. However, upon changing the solvent to [D_6]benzene we were able to obtain much better resolved ^{1}H and ^{13}C NMR spectra and we also observed a much higher stability of **8** in this solvent.

With regard to the results reported by Buono[4] the formation of compound **8** was not expected. A plausible mechanism for the formation of the isolated oxaphospholene **8** is outlined in Scheme 4.

The reaction starts with a nucleophilic attack of the phosphite at the central allenic carbon atom to form intermediate **I** with a carbanionic centre near to the reactive chloro substituent, which seems to be more favourable than the intermediate most probably formed during the reactions discussed above (intermediate **A** in Scheme 2) that lack the chloro substituent in this position. Intermediate **I** is transformed into intermediate **II** in an elimination-dealkylation sequence eliminating a molecule of methyl chloride and thus resulting in the formation of a C,C and a P,O double bond. A similar reaction was reported by Zemlicka et al. when reacting an α-chloroallene with triethyl phosphite.[11] An alternative to the first two reaction steps proposed by Zemlicka could be an S_N2' reaction type. Finally, the intramolecular condensation of the respective enol **III** with elimination of one molecule of methanol forms **8** containing the oxaphospholene ring and an exocyclic double bond, different to oxaphospholene **4**.

In conclusion, the reaction of α-keto allenes with trimethyl phosphite could successfully be applied to suitable fatty acid compounds thus giving rise to the new and different phosphorus-containing heterocyclic derivatives **4** and **8**. Although the oxaphospholenes proved to be quite sensitive and could not be isolated or characterised in all cases this method clearly offers a promising approach to phosphorus-



Scheme 4. Proposed mechanism of the formation of oxaphospholene **8** from α-chloro α′-keto allene **3** and trimethyl phosphite

containing heterocyclic fatty acid derivatives. Furthermore, a new synthesis of alkenyl phosphonates by hydrolysis of the oxaphospholenes was reported.

Experimental Section

General: All chemicals and solvents were purchased from standard chemical suppliers. Dichloromethane was refluxed under an inert atmosphere over calcium hydride and distilled. Toluene was refluxed and distilled under an inert atmosphere over sodium. Methanol was refluxed over magnesium for two hours and then distilled. Petroleum ether (60:80) and ethyl acetate were distilled prior to use. Trimethyl phosphite was treated with sodium, filtered and distilled under an inert atmosphere. For all liquid chromatographic separations Silica gel 60 (40−63 μm) from Merck was used.

Analytical Equipment: NMR: Bruker DRX 500, ^{1}H NMR (500.1 MHz), ^{13}C NMR (125.8 MHz). TMS as internal standard. ^{31}P NMR (202.5 MHz), 85% H_3PO_4 as external standard. $CDCl_3$ and [D_6]benzene were used as solvents. All spectra were recorded at 300 K. The assignment of the NMR signals was done on the basis of ^{1}H, ^{13}C, H,H-COSY, HMQC and HMBC measurements. An assignment of the *Z*- and *E*-isomers failed in all cases due to missing ^{1}H NMR NOE contacts. In the following the signals of the respective other isomer are marked with an asterisk. MS: Finnigan MAT 95. Elemental Analysis: Mikroanalytisches Labor Beller, 37004 Göttingen.

Reaction of Methyl 12-Oxo-9,10-octadecadienoate (1) with Trimethyl Phosphite

Crude Product: Methyl 9-(5-Hexyl-2,2,2-trimethoxy-2λ^5-[1,2]-oxaphosphol-3-ylidene)nonanoate (4): A solution of methyl 12-oxo-9,10-octadecadienoate (**1**; 0.50 g, 1.46 mmol) in 20 mL of dry dichloromethane was cooled to 0 °C under argon atmosphere. Freshly distilled trimethyl phosphite (1.89 mL, 1.46 mmol) was then added. After 43 h of stirring at room temperature (monitored by TLC) the solvent was removed in vacuo yielding 0.68 g of the crude product **4** as a yellow oil. ^{1}H NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 0.88 (t, *J* = 7.0 Hz, 6 H, H-18/H-18*), 1.15−1.25 (m, 36 H, H-3/H-3*, H-4/H-4*, H-5/H-5*, H-6/H-6*, H-7/H-7*, H-13/H-13*, H-15/H-15*, H-16/H-16*, H-17/H-17*), 2.20 (m, 8 H, H-8/H-8*, H-14/H-14*), 2.30 (t, *J* = 7.0 Hz, 4 H, H-2/H-2*), 3.54, 3.57 [2 × s, 2 × 9 H, $P(OMe)_3$/$P(OMe)_3$*], 3.66 (s, 6 H, CO_2Me/CO_2Me*), 5.40, 5.48 (2 × s, 2 × 1 H, H-11/H-11*), 6.24, 6.28 (2 × t, *J* = 7.2 Hz, 2 × 1 H, H-9/H-9*) ppm. ^{13}C NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 13.89, 13.94 (C-18/C-18*), 22.37, 22.46, 24.82, 26.32, 28.71, 28.95, 28.98, 29.01, 29.17, 30.79, 30.95, 31.48, 31.57, 33.96 (C-2/C-2*, C-3/C-3*, C-4/C-4*, C-5/C-5*, C-6/C-6*, C-7/C-7*, C-8/C-8*, C-13/C-13*, C-14/C-14*, C-15/C-15*, C-16/C-16*, C-17/C-17*), 51.25 (CO_2Me/CO_2Me*), 54.57, 54.65 [$P(OMe)_3$/$P(OMe)_3$*], 97.03, 97.28 (C-11/C-11*), 129.26, 130.87 (C-10/C-10*), 140.16, 140.21 (C-9/C-9*), 158.59, 158.66 (C-12/C-12*), 174.12 (C-1/C-1*) ppm. ^{31}P NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = −42.55 ppm. MS/CI (isobutane): *m*/*z* (%) = 448.9 (52), 433.0 (30) $[MH]^+$, 419.1 (100), 401.2 (63), 341.2 (25).

After Column Chromatography: Methyl 10-(Dimethoxyphosphoryl)-12-oxo-9-octadecenoate (5): The crude product **4** was purified by column chromatography with petroleum ether/diethyl ether/methanol (7:3:1). Product **5** (R_f = 0.22) was obtained as a colourless oil (0.39 g, 0.93 mmol, 64%) as a mixture of two isomers. ^{1}H NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 0.84 (t, *J* = 6.8 Hz, 6 H, H-18/H-18*), 1.24−1.26 (m, 24 H, H-4/H-4*, H-5/H-5*, H-6/H-6*, H-15/H-15*, H-16/H-16*, H-17/H-17*), 1.40 (m, 4 H, H-7/H-7*), 1.53 (m, 4 H, H-14/H-14*), 1.56 (m, 4 H, H-3/H-3*), 2.05 (m, 4 H, H-8/H-8*), 2.25 (t, *J* = 7.4 Hz, 4 H, H-2/H-2*), 2.42 (m, 4 H, H-13/H-13*), 3.25, 3.29 (2 × s, 2 × 2 H, H-11/H-11*), 3.62, 3.62 (2 × s, 2 × 6 H, $PO(OMe)_2$/$PO(OMe)_2$*), 3.64 (s, 6 H, CO_2Me/CO_2Me*), 6.71, 6.76 (2 × t, 2 × *J* = 7.2 Hz, 2 × 1 H, H-9/H-9*) ppm. ^{13}C NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 13.88 (C-18/C-18*), 22.36 (C-17/C-17*), 23.62 (C-14/C-14*), 24.75 (C-3/C-3*), 28.09, 28.70, 28.86, 28.87, 29.00, 29.14, 29.29 (C-4/C-4*, C-5/C-5*, C-6/C-6*, C-7/C-7*, C-8/C-8*, C-15/C-15*), 31.45 (C-16/C-16*), 33.91 (C-2/C-2*), 40.56, 40.65 (C-11/C-11*), 42.49 (C-13/C-13*), 51.30 (CO_2Me/CO_2Me*), 52.21, 52.24 [$PO(OMe)_2$/$PO(OMe)_2$*], 120.23, 121.69 (C-10/C-10*), 151.72, 151.80 (C-9/C-9*), 174.08 (C-1/C-1*), 205.96, 205.97 (C-12/C-12*) ppm. ^{31}P NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 24.40 ppm. MS/CI (isobutane): *m*/*z* (%) = 419.8 (100) $[MH]^+$. MS/EI (70 eV): *m*/*z* (%) = 418.8 (100) $[M]^+$, 386.9 (77) $[M - CH_3OH]^+$, 305.9 (100) $[M - C_6H_{13}CO]^+$, 272.9 (74), 232.9 (88), 164.0 (100). $C_{21}H_{39}O_6P$ (418.5): calcd. C 60.27, H 9.39, P 7.40; found C 60.05, H 9.58, P 7.55.

Reaction of Methyl 11-Chloro-12-oxo-9,10-octadecadienoate (2) with Trimethyl Phosphite

Methyl 11-Chloro-10-(dimethoxyphosphoryl)-12-oxo-9-octadecenoate (7): Freshly distilled trimethyl phosphite (1.74 mL, 1.45 mmol) was added at room temperature to a solution of methyl 11-chloro-12-oxo-9,10-octadecadienoate (**2**; 0.50 g, 1.45 mmol) in 20 mL of dry toluene under an argon atmosphere. After 5 days stirring at 70 °C (monitored by TLC) the solvent was removed in vacuo and the remaining orange oil (0.81 g) was purified by column chromatography with petroleum ether/diethyl ether/methanol (7:3:1). Product **5** (R_f = 0.22) was obtained as a yellow oil (0.35 g, 0.77 mmol, 53%) as a mixture of two isomers. ^{1}H NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 0.88 (t, *J* = 6.8 Hz, 6 H, H-18/H-18*), 1.20−1.50 (m, 28 H, H-4/H-4*, H-5/H-5*, H-6/H-6*, H-7/H-7*, H-15/H-15*, H-16/H-16*, H-17/H-17*), 1.61 (m, 8 H, H-3/H-3*, H-14/H-14*), 2.17 (m, 4 H, H-8/H-8*), 2.30 (t, *J* = 6.8 Hz, 4 H, H-2/H-2*), 2.63 (m, 4 H, H-13/H-13*), 3.66 (s, 6 H, CO_2Me/CO_2Me*), 3.73, 3.77 [2 × s, 2 × 3 H, $PO(OMe)_2$], 3.75 [s, 6 H, $PO(OMe)_2$*], 5.11, 5.15 (2 × s, 2 × 2 H, H-11/H-11*), 6.86, 6.90 (2 × t, 2 × *J* = 7.1 Hz, 2 × 1 H, H-9/H-9*) ppm. ^{13}C NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 13.83 (C-18/C-18*), 22.29, 23.68, 24.70, 27.87, 28.55, 28.77, 28.94, 29.73, 29.86, 31.37, 33.85 (C-2/C-2*, C-3/C-3*, C-4/C-4*, C-5/C-5*, C-6/C-6*, C-7/C-7*, C-8/C-8*, C-14/C-14*, C-15/C-15*, C-16/C-16*, C-17/C-17*), 39.22 (C-13/C-13*), 51.25 (CO_2Me/CO_2Me*), 52.50, 52.54, 52.57 [$PO(OMe)_2$/$PO(OMe)_2$*], 59.01, 59.11 (C-11/C-11*), 124.20, 125.68 (C-10/C-10*), 156.03, 156.11 (C-9/C-9*), 173.98 (C-1/C-1*), 201.51, 201.55 (C-12/C-12*) ppm. ^{31}P NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 21.38 ppm. MS/CI (isobutane): *m*/*z* (%) = 453.9 (100) $[MH]^+$. MS/EI (70 eV): *m*/*z* (%) = 418.8 (100) $[M]^+$, 386.9 (77) $[M - CH_3OH]^+$, 305.9 (100) $[M - C_6H_{13}CO]^+$, 272.9 (74), 232.9 (88), 164.0 (100). HR MS/EI (70 eV). $C_{21}H_{38}ClO_6P$ $[M]^+$: calcd. 452.2093; found 452.2095. $C_{21}H_{38}ClO_6P$ (453.0): calcd. C 55.68, H 8.46, P 6.84; found C 56.59, H 8.51, P 6.25.

Reaction of Methyl 12-Chloro-9-heptanoyl-9,10-octadecadienoate (3) with Trimethyl Phosphite

Methyl 8-(3-Hexylidene-2-methoxy-5-oct-1-enyl-2-oxo-2,3-dihydro-2λ^5-[1,2]-oxaphosphol-4-yl)octanoate (8): Freshly distilled trimethyl phosphite (1.42 mL, 1.10 mmol) was added at room temperature to a solution of methyl 12-chloro-9-heptanoyl-9,10-octadecadienoate (**3**; 0.50 g, 1.10 mmol) in 20 mL of dry toluene under an argon atmosphere. After 3 days of heating at reflux (monitored by TLC) the solvent was removed in vacuo and the remaining yellow oil

(0.65 g) was purified by column chromatography with petroleum ether/ethyl acetate (10:3). Product **8** (R_f = 0.24) was obtained as a colourless oil (0.24 g, 0.49 mmol, 44%) as a mixture of two isomers. ^{1}H NMR (C_6D_6, 1:1 *Z*/*E* mixture): δ = 0.86, 0.87 (2 × t, 2 × *J* = 7.0 Hz, 2 × 6 H, H-18/H-18*, H-26/H-26*), 1.04−1.14 (m, 12 H, H-4/H-4*, H-15/H-15*, H-24/H-24*), 1.15−1.25 (m, 24 H, H-5/H-5*, H-6/H-6*, H-16/H-16*, H-17/H-17*, H-23/H-23*, H-25/H-25*), 1.27−1.37 (m, 12 H, H-7/H-7*, H-14/H-14*, H-22/H-22*), 1.49 (m, 4 H, H-3/H-3*), 2.02−2.12 (m, 12 H, H-2/H-2*, H-8/H-8, H-13/H-13*), 2.29 (m, 4 H, H-21/H-21*), 3.35 (s, 6 H, CO_2Me/CO_2Me*), 3.48, 3.50 [2 × s, 2 × 3 H, PO(OMe)/PO(OMe)*], 4.94, 4.95 (2 × t, 2 × *J* = 7.0 Hz, 2 × 1 H, H-20/H-20*), 6.20, 6.26 (2 × d, 2 × *J* = 15.8 Hz, 2 × 1 H, H-11/H-11*), 6.69, 6.69 (2 × dt, *J* = 15.8, 7.0 Hz, 2 × 1 H, H-12/H-12*) ppm. ^{13}C NMR (C_6D_6, 1:1 *Z*/*E* mixture): δ = 22.89, 22.77 (C-18/C-18*,C-26/C-26*), 25.10, 25.35, 25.48, 29.16, 29.19, 29.22, 29.30, 29.50, 29.59, 31.78, 31.93, (C-2/C-2*, C-3/C-3*, C-4/C-4*, C-5/C-5*, C-6/C-6*, C-7/C-7*, C-8/C-8*, C-14/C-14*, C-15/C-15*, C-16/C-16*, C-17/C-17*, C-22/C-22*, C-23/C-23*, C-24/C-24*), 25.97 (C-21/C-21*), 34.04, 33.96 (C-13/C-13*), 50.91 (CO_2*Me*/CO_2*Me**), 53.09, 53.15 [PO(OMe)/PO(OMe)*], 109.81, 109.89 (C-20/C-20*), 120.47, 120.57 (C-11/C-11*), 123.32, 124.58 (C-10/C-10*), 139.81, 139.86 (C-12/C-12*), 144.85, 144.98 (C-9/C-9*), 148.07, 148.19 (C-19/C-19*), 173.23 (C-1,C-1*) ppm. ^{31}P NMR ($CDCl_3$, 1:1 *Z*/*E* mixture): δ = 35.92 ppm. MS/CI (isobutane): *m*/*z* (%) = 482.4 (100) $[M]^+$. MS/EI (70 eV): *m*/*z* (%) = 482.1 (99) $[M]^+$, 450.1 (100) $[M - CH_3OH]^+$, 422.0 (54) $[M - CH_3OH - CO]^+$, 393.0 (49), 382.0 (74). HR MS/EI (70 eV). $C_{27}H_{47}O_5P$ $[M]^+$: calcd. 482.3161; found 482.3160.

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