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New Route to 1-Formylalkylphosphonates Using Diethyl Trichloromethylphosphonate as Precursor

Yannick Zanella, Sylvie Berté-Verrando, Rachel Dizière and Philippe Savignac

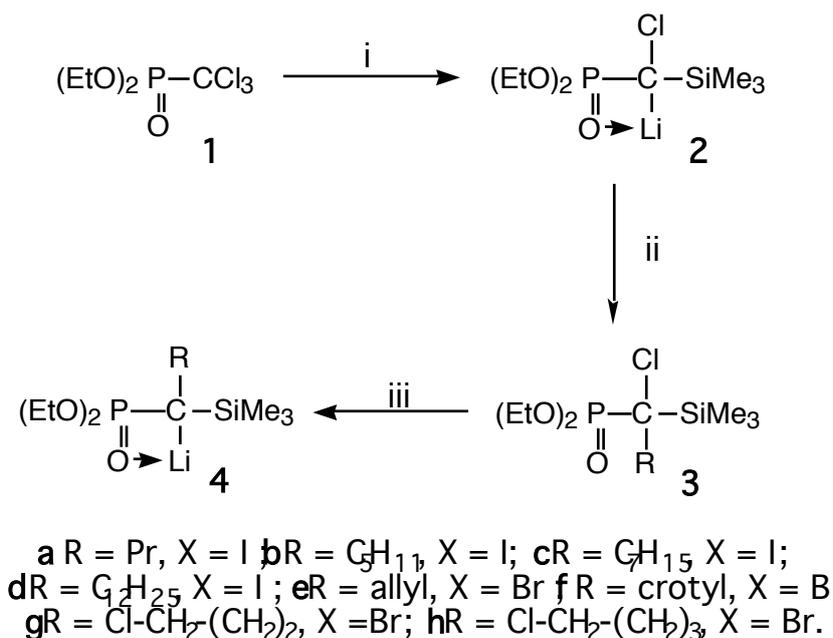
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Diethyl trichloromethylphosphonate **1** and chlorotrimethylsilane were converted in a three-step sequence by BuLi into α -phosphorylated α -silylated α -substituted carbanions **4**. On reaction with ethyl formate in the presence of chlorotrimethylsilane they give transient silylated acetals **8** which are readily hydrolysed in acid medium into 1-formylalkylphosphonates **7** which are isolated in good yields.

Diethyl trichloromethylphosphonate **1**, which is readily available on laboratory scale¹ and also commercially, has already been pointed out as a useful starting material². In a preceding paper we described a synthesis of medium size (4 - 6 membered) cycloalkylphosphonates³ based on the successive exchange of the three chlorine atoms of the phosphonate **1**. This process, which is summarized in Scheme 1, involves a three-step sequence. In the first step, addition of a mixture of diethyl trichloromethylphosphonate **1** and chlorotrimethylsilane (1.1 equiv.) to an excess of butyllithium (2.1 equiv.) in tetrahydrofuran (THF) at low temperature takes place through a double chlorine-lithium exchange to give the stable α -phosphorylated α -silylated α -chlorinated carbanion **2** ($\delta^{31}\text{P}$ (THF) +46.9). With these experimental conditions the condensation of two trimethylsilyl groups was never observed and alkylation of the carbanion **2** was achieved by reaction with alkyl halides⁴ (RX with X= Br, I). The so formed phosphonate **3** ($\delta^{31}\text{P}$ (THF) +24.7) is then submitted to the third chlorine-lithium exchange at low temperature to give a new α -phosphorylated α -silylated α -substituted stable

carbanion **4**. One component only was observed by ^{31}P NMR analysis ($\delta^{31}\text{P}$ (THF) +54) and the signal was assigned to carbanion **4**. By the use of this sequence a large variety of intermediates **4** (**a-h**) have been cleanly and quantitatively prepared ($\text{R} = \text{C}_3\text{H}_7, \text{C}_5\text{H}_{11}, \text{C}_7\text{H}_{15}, \text{C}_{12}\text{H}_{25}, \text{CH}_2=\text{CH}-\text{CH}_2, \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2, \text{Cl}-\text{CH}_2-(\text{CH}_2)_2, \text{Cl}-\text{CH}_2-(\text{CH}_2)_3$) (Scheme 1).

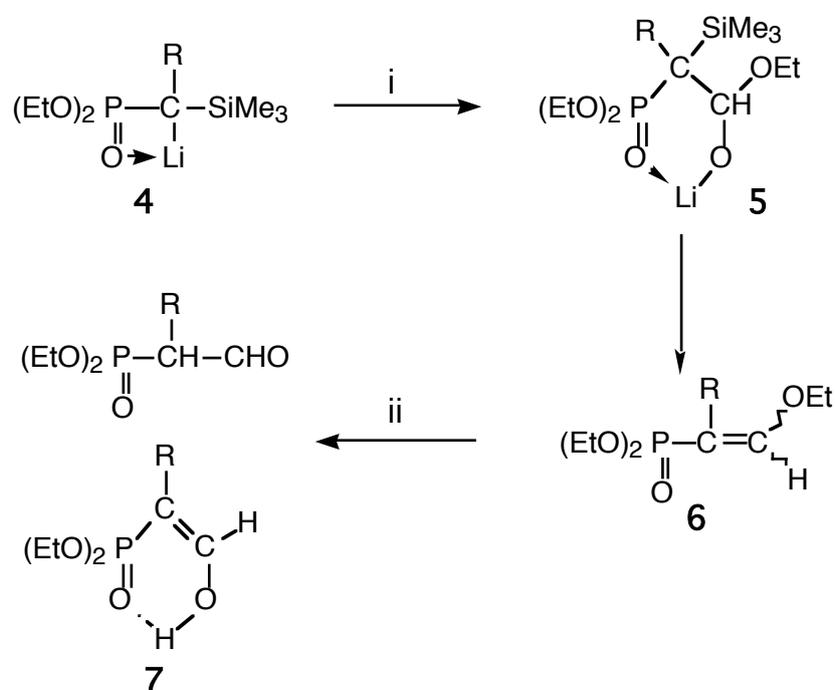


Scheme 1 : *Reagents and conditions* : i, BuLi (2.1 mol equiv.), ClSiMe₃ (1.1 mol equiv.), THF, -80°C ; ii, RX, THF, -30°C ; iii, BuLi (1.1 mol equiv.), THF, -80°C.

Results and Discussion

We envisaged that the phosphorylated carbanions **4** could provide new intermediates in the synthesis of 1-formylalkylphosphonates **7**. Thus, on treatment of carbanions **4** with ethyl formate, Peterson type reaction to afford two (E) and (Z) phosphorylated enol ethers was expected to occur⁴ *via* the elimination of lithiated silanol, hydrolysis of the so formed enol ethers being achieved by treatment in acidic medium. Previous approaches to 1-formylalkyl phosphonates are based on the condensation of α -lithioalkylphosphonates with dimethylformamide but limited by both the availability of the nucleophile and the reactivity of the electrophile⁵. In this paper we describe the results of experiments that were realized (i) to

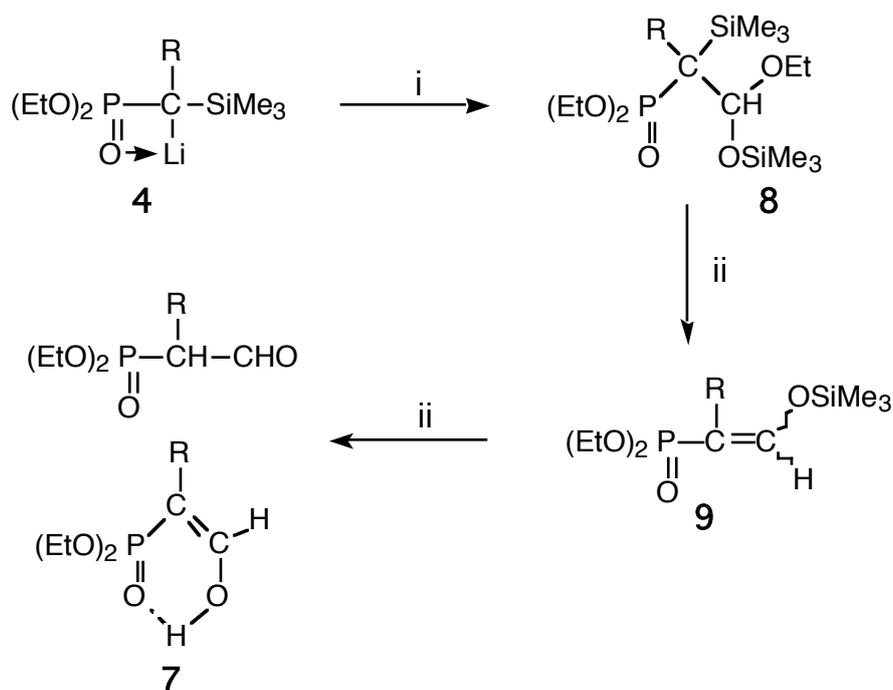
identify the factors that control the formation of **7** and (ii) to demonstrate the feasibility of this new approach. Two routes have been examined and each of these will be described in turn. In the first route (Scheme 2), carbanion **4a** (R= C₃H₇) taken as template, was treated with ethyl formate (1.1 equiv.) in THF at low temperature to give in quantitative yield the lithiated hemiacetal **5a** which spontaneously decomposes in an isomeric mixture of the two expected phosphorylated enol ethers **6a** resulting from an exclusive Peterson type reaction and easily identified by ³¹P NMR analysis ($\delta^{31}\text{P}$ (THF) +20 (E), (75%) and +25 (Z), (25%)). However, these were not isolated but, rather intercepted by directly pouring the cold crude product mixture into a cold biphasic mixture of hydrochloric acid (5M) and dichloromethane (CH₂Cl₂). Upon stirring of two phosphorylated enol ethers **6a** at 0°C over one hour the hydrolysis was complete and the corresponding 1-formyl 1-propylmethyl phosphonate **7a** was isolated in reasonable yield (55%) as a mixture of aldehyde ($\delta^{31}\text{P}$ (THF) +23) and enol ($\delta^{31}\text{P}$ (THF) + 27,7) after purification by double extraction acid and base. When similar treatment was repeated but with the hydrolysis step being carried out with a more concentrated hydrochloric acid solution (12M), **7a** was equally isolated in 55% yield.



Scheme 2 : Reagents and conditions : i, HCOOEt (1.1 mol equiv.), THF, -80°C; ii, HCl (5M) - CH₂Cl₂, -80°C to 0°C.

However, when the cold mixture of the two enol ethers **6a** was heated to room temperature and treated at that temperature with hydrochloric acid (5M) the two enol ethers **6a** did not behave in the same way as previously; hydrolysis was never complete and no evolution was observed after a while, thus it was not possible to isolate or purify the phosphorylated aldehyde **7a**. Attention was next turned to the use of carbanions **4b** and **4e**, as starting materials for the synthesis of 1-formylalkylphosphonates **7b** and **7e**. Carbanions **4b** and **4e** reacted with ethylformate to give the phosphorylated enol ethers **6b** and **6e** and finally, on acid hydrolysis **6b** and **6e** behave in the same way as **6a** to afford 1-formylalkylphosphonates **7b** and **7e** in low overall yields (30 and 50%, respectively).

This first route being dependent on a balance of factors (steric, temperature, concentration, etc) which could not be easily overcome, a simple and efficient protocol for construction of 1-formylalkylphosphonates **7** has been developed using the formation of an intermediate mixed acetal **8**. In the second route (Scheme 3) we assumed that the hydrolysis of a phosphorylated mixed acetal **8**, more sensitive to acid hydrolysis than the phosphorylated enol ethers **6**, could provide a new and better approach to 1-formylalkylphosphonates **7**.



Scheme 3 : Reagents and conditions : i, HCOOEt (1.1 mol equiv.), ClSiMe₃ (1.5 mol equiv.), THF, -90°C ; ii, HCl (2M) - CH₂Cl₂, 20°C, 60 min.

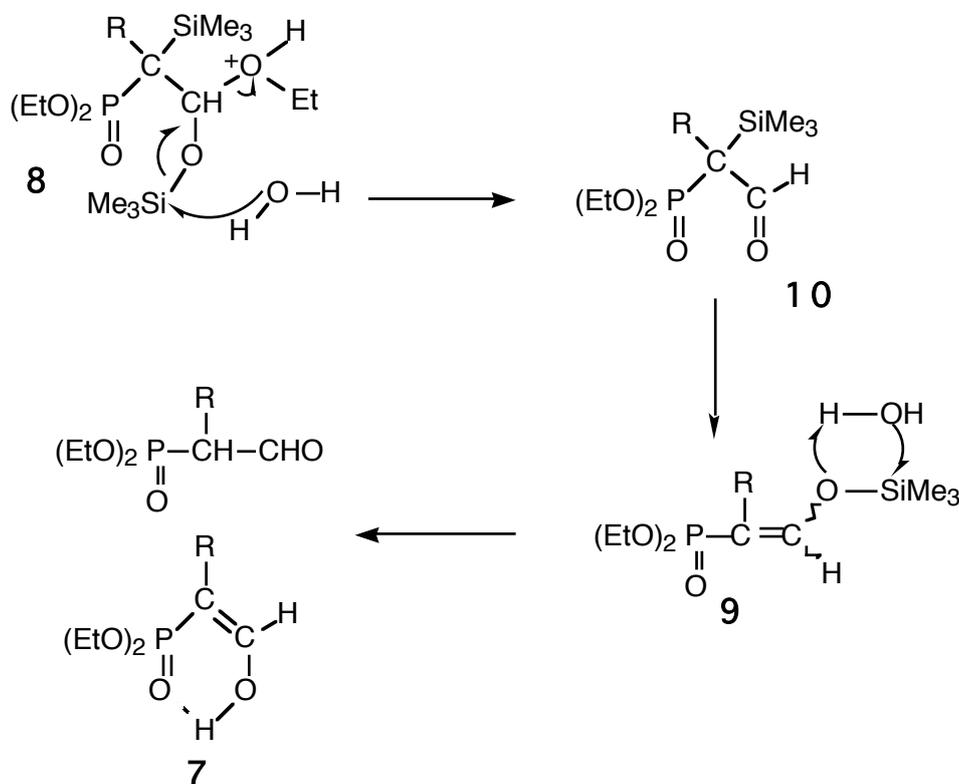
Thus, to investigate this approach, carbanion **4a** (R=C₃H₇) was allowed to react at low temperature (-90°C) with ethyl formate (1.1 equiv.) in the presence of an excess of chlorotrimethylsilane (1.5 equiv.). On reaction the desired mixed acetal **8a** was obtained as the major product ($\delta^{31}\text{P}$ (THF)+32.5) (94%) with a small quantity of enol ethers **6a** (6%). The reaction mixture was then allowed to return to room temperature and poured into a biphasic mixture of hydrochloric acid (2M) and CH₂Cl₂. After 60 min at room temperature (as judged by ³¹P NMR analysis) **8a** was completely hydrolysed to give a rather better overall yield of aldehyde **7a** (73%) as a mixture of aldehyde ($\delta^{31}\text{P}$ (THF-CH₂Cl₂), +22) and enol ($\delta^{31}\text{P}$ (THF-CH₂Cl₂) +27) after purification by double extraction acid and base.

The preference for the silylated enol ethers **9** in Scheme 3 was related to the ease of nucleophilic displacement at the OSiMe₃ ether group rather than the OEt ether group in the mixed acetal **8**. The proposal, which is illustrated in Scheme 4, for the hydrolysis of phosphorylated mixed acetal **8** into the 1-formylalkylphosphonate **7**, would involve initial nucleophilic attack of the silyl group to generate the intermediate α -silylated α -substituted formyl phosphonate **10**. Given the α -position of the silyl group to formyl group in **10**, [1,3]-rearrangement of **10** to deliver the transient silylated enol ether **9** becomes feasible, this one being more sensitive to acid hydrolysis than the corresponding OEt enol ether **6**.

This type of rearrangement has not been rigorously proven but it was suggested by both the oxophilic character of silicium and the enol form and it was considered to be the most reasonable explanation for the easy and complete hydrolysis of the mixed acetal **8**.

The preference for chlorotrimethylsilane as protecting group was confirmed after repeated reactions between carbanion **4a** and other chlorosilanes. On reaction with chlorotriethylsilane three components were observed by ³¹P NMR analysis; one of which was the mixed acetal ($\delta^{31}\text{P}$ (THF) +32.4) in reasonable yield (41%) and two other signals were assigned to the enol ethers ($\delta^{31}\text{P}$ (THF) +24.9 and +19.8). With chlorotriisopropylsilane the corresponding mixed acetal was not detectable and the two enol ethers were the only products observed. The influence of the formylating agent has also been examined and, using dimethylformamide in

association with chlorotrimethylsilane, formation of the corresponding mixed acetal was not detectable in the crude reaction mixture.



Scheme 4

Encouraged by these preliminary findings the synthesis of compounds **7** was explored in order to confirm the validity of the model reaction. Carbanions **4 (b-h)** were prepared as described in Scheme 1 and in an analogous way put in reaction with ethyl formate and chlorotrimethylsilane in excess (1.5 equiv.) at low temperature (-90°C) in THF. The influence of the alkyl moiety has been examined using saturated or unsaturated long chain. All were converted in quantitative yield into the desired mixed acetal **8** and on treatment in biphasic acid system underwent rearrangement and complete hydrolysis to give 1-formylalkylphosphonates **7 (b-h)** isolated in good yields (45-73%) after purification by double extraction acid and base. Thus a series of 1-formylalkylphosphonates **7 (a-h)** were synthesized and characterised. Structures of products were confirmed by NMR (^1H , ^{31}P , and ^{13}C) and mass spectrometry.

In conclusion, this 'one-pot' procedure describes a new methodology for the synthesis of 1-formylalkylphosphonates based on the condensation of α -phosphorylated α -silylated α -substituted carbanion with ethyl formate in the presence of chlorotrimethylsilane. It is interesting to note that the reported successive exchange of the three chlorine atoms of diethyl trichloromethylphosphonate **1** was very selective. In fact, no side-products were detected, showing that the possible polysilylation and the lithium-chlorine exchange pathways were uncompetitive reactions under these experimental conditions. Further work in this area is being focused on exploiting and extending the synthetic utility of diethyl trichloromethylphosphonate.

Experimental

^{31}P NMR, ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 instrument with 85% H_3PO_4 as external standard (positive chemical shifts are downfield of this reference) for ^{31}P NMR and CDCl_3 as internal standard for ^1H NMR and ^{13}C NMR; coupling constants are given in Hz. High-resolution mass spectra (HRMS) were recorded on VG ZAB-HSQ or Bruker CMS 47% ICR FT mass spectrometers. All reactions were carried out under an inert atmosphere and scrupulously anhydrous conditions. A Buchi GKR-50 apparatus with three flasks was used for distillation. The flask containing the crude product was in the upper part of the oven, and the collecting flask just outside.

General Procedure for the Synthesis of 1-Formylalkylphosphonates 7 a-h

Typical procedure for the synthesis of α -Phosphorylated α -silylated α -substituted carbanions 4 a-h - .To a stirred mixture of a 1.6 M hexane solution of BuLi (53 cm³, 84 mmol) and dry THF (100 cm³) cooled to -80°C were added dropwise trichloromethylphosphonate (10.2 g, 40 mmol) and ClSiMe₃ (4.8 g, 44 mmol) in THF (20cm³).Stirring was continued at -80°C for about 15 min until formation of carbanion **2** was complete, as indicate by ^{31}P NMR spectroscopy. The alkyl halide (RX) (44 mmol) in THF (10 cm³) was added dropwise at -

30°C then the stirred mixture was allowed to warm to room temperature until formation of phosphonate **3** was complete as proved by ^{31}P NMR spectroscopy. The mixture was cooled to -80°C and a solution of BuLi in hexane (28 cm³, 44 mmol) was added at this temperature. After few minutes carbanion **4** was obtained quantitatively.

via Enol ether route 7a

Ethyl formate (3.3 g, 44 mmol) in THF (20 cm³) was added dropwise at -80°C. The mixture was stirred for 15 min at this temperature then poured into an ice-cold mixture of hydrochloric acid (40 cm³ of 5M solution) and dichloromethane (40 cm³) and stirred at this temperature for 60 min. The aqueous layer was extracted with dichloromethane (3x30 cm³), then washed with a solution of sodium hydroxide (3x35 cm³ of 2M solution). The aqueous layers were separated and treated with hydrochloric acid (12 M) until acidic pH then extracted with dichloromethane (3x30 cm³). The organic layers were separated, washed with water (15 cm³), dried (MgSO₄) and evaporated under reduced pressure to afford crude product which was purified by distillation under reduced pressure using bulb-to-bulb apparatus.

via Mixed acetal route 7a-h

A mixture of ethyl formate (3.3 g, 44 mmol) and chlorotrimethylsilane (6.5 g, 60 mmol) in THF (20 cm³) were added dropwise at -90°C. The mixture was stirred for 15 min at this temperature then allowed to warm to room temperature and poured into an ice-cold mixture of hydrochloric acid (55 cm³ of 2M solution) and dichloromethane (40 cm³) and stirred at this temperature for 60 min. The aqueous layer was extracted with dichloromethane (3x30 cm³), then washed with a solution of sodium hydroxide (3x35 cm³ of 2M solution). The aqueous layers were separated and treated with hydrochloric acid (12 M) until acidic pH then extracted with dichloromethane (3x30 cm³). The organic layers were separated, washed with water (15 cm³), dried (MgSO₄) and evaporated under reduced pressure to afford crude product which was purified by distillation under reduced pressure using bulb-to-bulb apparatus. The large temperature range is due to the distillation of a mixture of the keto-enol tautomers.

O,O-Diethyl 1-propyl 2-oxoethylphosphonate 7a

(73%), b.p.(20 mmHg) 175-190°C; $\delta_P(\text{CDCl}_3)+23.17$ and $+27.76$; $\delta_H(\text{CDCl}_3)$ 0.94 (t, $^3J_{\text{H-H}}$ 7, $\text{CH}_3\text{-(CH}_2)_2$), 1.35 (t, $^3J_{\text{H-H}}$ 7, $\text{CH}_3\text{-CH}_2\text{-O}$), 1.9 (m, $\text{CH}_3\text{-(CH}_2)_2$), 3 (dm, $^2J_{\text{H-P}}$ 26, P-CH-CHO), 4.16 (m, $\text{CH}_3\text{-CH}_2\text{-O}$), 9.65 (d, $^3J_{\text{H-H}}$ 3, CHO); $\delta_C(\text{CDCl}_3)$ 13.9 (s, $\text{CH}_3\text{-(CH}_2)_2$, aldehyde), 14.2 (s, $\text{CH}_3\text{-(CH}_2)_2$, enol), 16.4 (d, $^3J_{\text{C-P}}$ 6.3, $\text{CH}_3\text{-CH}_2\text{-O}$, enol), 16.5 (d, $^3J_{\text{C-P}}$ 6, $\text{CH}_3\text{-CH}_2\text{-O}$, aldehyde), 21.7 (d, $J_{\text{C-P}}$ 13.7, CH_2 , aldehyde), 22.1 (s, CH_2 , enol), 25.8 (d, $J_{\text{C-P}}$ 4.6, CH_2 , aldehyde), 26.1 (d, $J_{\text{C-P}}$ 6.5, CH_2 , enol), 53.0 (d, $J_{\text{C-P}}$ 126.6, CH-CHO), 61.5 (d, $^2J_{\text{C-P}}$ 5.6, $\text{CH}_2\text{-O}$, enol), 63.1 (d, $^2J_{\text{C-P}}$ 7.5, $\text{CH}_2\text{-O}$, aldehyde), 99.5 (d, $J_{\text{C-P}}$ 196.3, C=CHOH), 157.2 (d, $^2J_{\text{C-P}}$ 29.0, =CHOH), 196.3 (d, $^2J_{\text{C-P}}$ 4.5, -CHO). (HRMS) (Found: M^+ , 222,1020. Calc for $\text{C}_9\text{H}_{19}\text{O}_4\text{P}$: M, 222.1020.

O,O-Diethyl 1-pentyl 2-oxoethylphosphonate 7b

(73%), b.p. (20 mmHg) 185-200°C; $\delta_P(\text{CDCl}_3) +22.47$ and $+27.40$. $\delta_H(\text{CDCl}_3)$ 0.83 (t, $^3J_{\text{H-H}}$ 6.5, $(\text{CH}_2)_4\text{-CH}_3$), 1.25 (dt, $^3J_{\text{H-H}}$ 7, $\text{CH}_3\text{-CH}_2\text{-O}$), 1.9 (m, $\text{CH}_3\text{-(CH}_2)_3\text{-CH}_2$), 2.9 (dm, $^2J_{\text{H-P}}$ 25, P-CH-CHO), 4.10 (m, $\text{CH}_3\text{-CH}_2\text{-O}$), 9.65 (d, $^3J_{\text{H-H}}$ 3, CHO); $\delta_C(\text{CDCl}_3)$ 14.4 (s, $\text{CH}_3\text{-(CH}_2)_4$), 16.6 (s, $^3J_{\text{C-P}}$ 6.8, $\text{CH}_3\text{-CH}_2\text{-O}$), 22.7 (s, CH_2 , aldehyde), 22.9 (s, CH_2 , enol), 24.2 (d, $^3J_{\text{C-P}}$ 6.3, CH_2 , enol), 28.4 (d, $^2J_{\text{C-P}}$ 13.3, CH_2 , aldehyde), 28.7 (s, CH_2 , enol), 31.9 (s, CH_2 , enol), 32.2 (s, CH_2 , aldehyde), 53.5 (d, $J_{\text{C-P}}$ 126.6, CH-CHO), 61.7 (d, $^2J_{\text{C-P}}$ 4.6, $\text{CH}_2\text{-O}$, enol), 63.3 (d, $^2J_{\text{C-P}}$ 6.9, $\text{CH}_2\text{-O}$, aldehyde), 99.8 (d, $J_{\text{C-P}}$ 195.6, C=CHOH), 157.4 (d, $^2J_{\text{C-P}}$ 29.2, =CHOH), 196.8 (s, -CHO). (HRMS) (Found: M^+ , 250,1333. Calc. for $\text{C}_{11}\text{H}_{23}\text{O}_4\text{P}$: M, 250,1333.

O,O-Diethyl 1-heptyl 2-oxoethylphosphonate 7c

(72%), b.p. (20 mmHg) 205-215°C; $\delta_P(\text{CDCl}_3)+22.47$ and $+27.40$; $\delta_H(\text{CDCl}_3)$ 0.81 (t, $^3J_{\text{H-H}}$ 6.4, $(\text{CH}_2)_4\text{-CH}_3$), 1.28 (dt, $^3J_{\text{H-H}}$ 7, $\text{CH}_3\text{-CH}_2\text{-O}$), 1.9 (m, $\text{CH}_3\text{-(CH}_2)_5\text{-CH}_2$), 2.9 (dm, $^2J_{\text{H-P}}$ 25, P-CH-CHO), 4.10 (m, $\text{CH}_3\text{-CH}_2\text{-O}$), 9.58 (d, $^3J_{\text{H-H}}$ 3, CHO); $\delta_C(\text{CDCl}_3)$ 14.2 (s, $\text{CH}_3\text{-(CH}_2)_6$), 16.3 (d, $^3J_{\text{C-P}}$ 6.6, $\text{CH}_3\text{-CH}_2\text{-O}$, enol), 16.4 (d, $^3J_{\text{C-P}}$ 5.7, $\text{CH}_3\text{-CH}_2\text{-O}$, aldehyde), 22.7 (s, CH_2 , aldehyde), 22.8 (s, CH_2 , enol), 23.6 (d, $J_{\text{C-P}}$ 4.4, CH_2 , aldehyde), 23.9 (d, $J_{\text{C-P}}$ 6.2, CH_2 , enol), 28.4 (d, $J_{\text{C-P}}$ 13.4, CH_2 aldehyde), 28.8 (s, CH_2 enol), 29.0 (s, CH_2 aldehyde), 29.3 (s, CH_2 enol), 29.4 (s, CH_2 aldehyde), 29.7 (s, CH_2 enol), 31.8 (s, CH_2 aldehyde), 32.0 (s, CH_2 enol), 53.1 (d, $J_{\text{C-P}}$ 126.5, CH-CHO), 61.3 (d, $^2J_{\text{C-P}}$ 4.7, $\text{CH}_2\text{-O}$, enol), 62.9 (d, $^2J_{\text{C-P}}$ 6.7, $\text{CH}_2\text{-O}$, aldehyde), 99.5 (d, $J_{\text{C-P}}$ 196.1, C=CHOH), 157.0 (d, $^2J_{\text{C-P}}$

29.2, =CHOH), 196.1 (s, -CHO). (HRMS) (Found: M⁺, 278, 1646. Calc. for C₁₃H₂₇O₄P M, 278.1646.

O,O Diethyl 1-dodecyl 2-oxoethylphosphonate 7d

(69%), b.p. (20 mmHg) 210-225°C; δ_H (CDCl₃) +22.76 and +28.45; δ_H (CDCl₃) 0.88 (t, ³J_{H-H} 6.4, (CH₂)₁₁-CH₃), 1.26 (m, CH₃-CH₂-O and CH₃-(CH₂)₁₀-CH₂), 1.9 (m, CH₂-(CH₂)₅-CH₃), 2.1 (m, P-CH-CH₂), 4.0 (m, CH₃-CH₂-O), 7.37 (d, ³J_{H-H} 10.7, P-C=CHOH), 9.60 (d, ³J_{H-H} 3, CHO) δ_C (CDCl₃) 14.1 (s, CH₃-(CH₂)₁₁), 16.2 (d, ³J_{C-P} 5.9, CH₃-CH₂-O, aldehyde), 16.4 (d, ³J_{C-P} 5.3, CH₃-CH₂-O, enol), 22.7 (s, CH₂), 23.5 (d, J_{C-P} 4.5, CH₂, enol), 23.8 (d, J_{C-P} 6.2, CH₂, aldehyde), 28.3 (d, J_{C-P} 13.6, CH₂, enol), 28.9 (d, J_{C-P} 22.1, CH₂, aldehyde), 29.3 (s, CH₂), 29.4 (s, CH₂), 29.6 (s, CH₂), 29.7 (s, CH₂), 32.0 (s, CH₂), 53.9 (d, J_{C-P} 126.3, CH-CHO), 60.9 (d, ²J_{C-P} 5.0, CH₂-O, aldehyde), 62.5 (d, ²J_{C-P} 6.8, CH₂-O, enol), 100.0 (d, J_{C-P} 195.2, C=CHOH), 156.5 (d, ²J_{C-P} 29.1 =CHOH), 196.1(d, ²J_{C-P} 4.5, -CHO). (HRMS) (Found: M⁺, 348.2429. Calc. for C₁₈H₃₇O₄P : M, 348.2429.

O,O-Diethyl 1-(2-propenyl) 2-oxoethylphosphonate 7e

(58%), b.p. (20 mmHg) 160-180°C; δ_P (CDCl₃) +22.04 and +27 13; δ_H (CDCl₃) 1.29 (t, ³J_{H-H} 7, CH₃-CH₂-O), 2.71 (m, CH₂-CH=CH₂), 3.01 (dm, ²J_{H-P} 26, P-CH-CHO), 4.11 (m, CH₃-CH₂-O), 5.0 (m, CH₂-CH=CH₂), 5.73 (m, CH₂-CH=CH₂), 9.60 (d, ³J_{H-H} 2.5 CHO); δ_C (CDCl₃) 16.4 (d, ³J_{C-P} 6.7, CH₃-CH₂-O enol), 16.6 (d, ²J_{C-P} 8.2, CH₃-CH₂-O aldehyde), 28.0 (d, ²J_{C-P} 3.8, CH₂-CH= aldehyde), 28.3 (d, ²J_{C-P} 6.9, CH₂-CH= enol), 52.6 (d, J_{C-P} 125.5, CH-CHO), 61.7 (d, ²J_{C-P} 4.5, CH₂-O enol), 63.4 (d, ²J_{C-P} 6.9, CH₂-O aldehyde), 97.4 (d, J_{C-P} 199.2, C=CHOH), 115.0 (s, CH=CH₂ enol), 117.7 (s, CH=CH₂ aldehyde), 134.5 (d, ³J_{C-P} 14.1, CH=CH₂ aldehyde), 136.0 (s, CH=CH₂ enol), 157.8 (d, ²J_{C-P} 28.9, =CHOH), 195.9 (m, CHO). (HRMS) (Found: M⁺, 220.0864. Calc. for C₉H₁₇O₄P ; M, 220.0864.

O,O Diethyl 1-(2-butenyl) 2-oxoethylphosphonate 7f

(55%), b.p. (20 mmHg) 205-210°C; δ_P (CDCl₃) +22.12 and +27.32; δ_H (CDCl₃) 1.32 (t, ³J_{H-H} 7, CH₃-CH₂-O), 1.61 (d, ³J_{H-H} 6, CH₃-CH=CH-CH₂), 2.59 (m, CH₃-CH=CH-CH₂), 3.0 (dm, ²J_{P-H} 26, P-CH-CHO), 4.19 (m, CH₃-CH₂-O), 5.38 (m, CH₃-CH=CH-

CH₂), 5.49 (m, CH₃-CH=CH-CH₂), 9.60 (d, ³J_{H-H} 3, CHO); δ_C (CDCl₃) 16.5 (d, ³J_{C-P} 7.2, CH₃-CH₂-O enol), 16.7 (d, ³J_{C-P} 9.3, CH₃-CH₂-O aldehyde), 18.1 (s, CH₃-CH=CH), 27.2 (d, ²J_{C-P} 6.1, CH₂-CH=CH), 53.8 (d, J_{C-P} 126.6, CH-CHO), 61.8 (d, ²J_{C-P} 4.1, CH₂-O enol), 63.3 (d, ²J_{C-P} 6.7, CH₂-O aldehyde), 98.2 (d, J_{C-P} 197.4, C=CHOH), 125.6 (s, CH=CH₂ enol), 127.1 (d, ³J_{C-P} 13.9, CH₂-CH= aldehyde), 128.7 (s, CH₂-CH= enol), 134.5 (d, ³J_{C-P} 14.1, CH=CH₂ aldehyde), 136.0 (s, CH=CH₂ enol), 157.6 (d, ²J_{C-P} 30.2, =CHOH), 196.4 (m, CHO). (HRMS) (Found M⁺, 234, 1029. Calc. for. C₁₀H₁₉O₄P ; M, 234., 1029.

O,O Diethyl 1-(3-Chloropropyl) 2-oxoethylphosphonate 7g

(45%), b.p. (20 mmHg) 190-205°C; δ_P (CDCl₃) +22.58 and +27.55; δ_H (CDCl₃) 1.2 (t, ³J_{H-H} 7, CH₃-CH₂-O), 1.85 (m, CH₂-CH₂-CH₂Cl), 2.1 (m, P-C-CH₂), 3.73 (t, ³J_{H-H} 2.4, CH₂-CH₂-CH₂Cl), 4.03 (m, CH₃-CH₂-O), 7.15 (d, ³J_{H-H} 10.8, P-C=CHOH). (HRMS) (Found M⁺ 256, 0632. Calc. for C₉H₁₈ClO₄P : M, 256.0631..

O,O-Diethyl 1-(4-chlorobutyl) 2-oxoethylphosphonate 7h

(50%), b.p. (20 mmHg) 225-240°C; δ_P (CDCl₃) +22.22 and +27.73; δ_H (CDCl₃) 1.3 (t, ³J_{H-H} 7, CH₃-CH₂-O), 1.45-2.20 (m, (CH₂)₃), 2.95 (m, P-CH-CHO), 3.49 (t, ³J_{H-H} 2.3, CH₂-(CH₂)₂-CH₂Cl), 4.13 (m, ³J_{H-H} and ³J_{H-P} 7, CH₃-CH₂-O), 7.33 (d, ³J_{H-H} 10.5, P-C=CHOH), 9.63 (d, ³J_{H-P} 2.66, P-CH-CHO); δ_C (CDCl₃) 16.3 (d, ³J_{C-P} 6.5, CH₃-CH₂-O enol), 16.4 (d, ³J_{C-P} 5.4, CH₃-CH₂-O aldehyde), 22.7 (s, CH₂ enol), 22.8 (s, CH₂ aldehyde), 25.7 (s, CH₂ aldehyde), 25.8 (s, CH₂ enol), 32.2 (s, CH₂ aldehyde and enol), 44.4 (s, CH₂-Cl aldehyde), 44.9 (s, CH₂-Cl enol), 52.9 (d, J_{C-P} 126.6, CH₂-CHO); 61.5 (d, ²J_{C-P} 4.9, CH₃-CH₂-O enol), 63.0 (d, ²J_{C-P} 6.8, CH₃-CH₂-O aldehyde), 98.9 (d, J_{C-P} 197.3, C=CHOH), 157.1 (d, ²J_{C-P} 28.7, C=CHOH), 195.8 (d, ²J_{C-P} 3.6, CHO). (HRMS) (Found M⁺ 270, 0787. Calc. for C₁₀H₂₀ClO₄P, M, 270.0787..

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