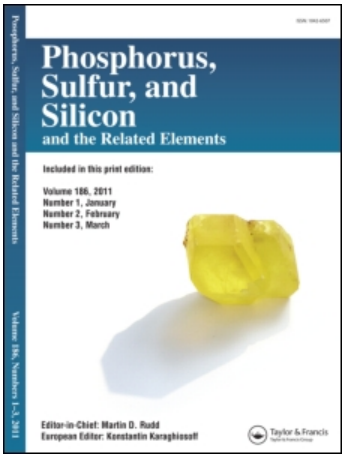

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Unexpected Reactivity of Ethyl 2-(Diethylphosphono)Propionate Toward 2,2-Disubstituted-1,3-cyclopentanediones

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To cite this Article Aav, R. , Kanger, T. , Pehk, T. and Lopp, M.(2005) 'Unexpected Reactivity of Ethyl 2-(Diethylphosphono)Propionate Toward 2,2-Disubstituted-1,3-cyclopentanediones', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 7, 1739 — 1748
To link to this Article: DOI: 10.1080/10426500590885309
URL: http://dx.doi.org/10.1080/10426500590885309

Phosphorus, Sulfur, and Silicon, 180:1739–1748, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590885309

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Unexpected Reactivity of Ethyl 2-(Diethylphosphono)Propionate Toward 2,2-Disubstituted-1,3-cyclopentanediones

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A Horner-Wadsworth-Emmons reagent-ethyl 2-(diethylphosphono)propionate in the reaction with 2,2-disubstituted-1,3-cyclopentanediones, results in 4-oxohexanoic acid ethyl ester derivative up to 90% isolated yield. ^{31}P-^{13}C- and ^{1}H-NMR study of the intermediates of the reaction involving the ethyl 2-(diethylphosphono)propionate was accomplished.

Keywords 2,2-Disubstituted-cyclopentanedione; ^{31}P-^{13}C- and ^{1}H-NMR-study; γ-ketoester; phosphoryl-stabilized carbanion; retro-aldol cleavage

INTRODUCTION

1,3-Cyclopentanedione derivatives have become significant compounds in the chemical synthesis as the building blocks of natural compounds.[1–4] Among the methods for the construction of the carbon skeleton of those compounds, carbonyl olefinations (including intramolecular asymmetric olefination[1]) with phosphoryl-stabilized

Received August 24, 2004; accepted August 26, 2004.

We would like to thank the Estonian Science Foundation for supporting the present work through Grant Numbers 5628, 5133, 4976 and also A.-M. Müürisepp for the mass spectra and T. Kailas for the infrared spectra of the coumpounds reported herein.

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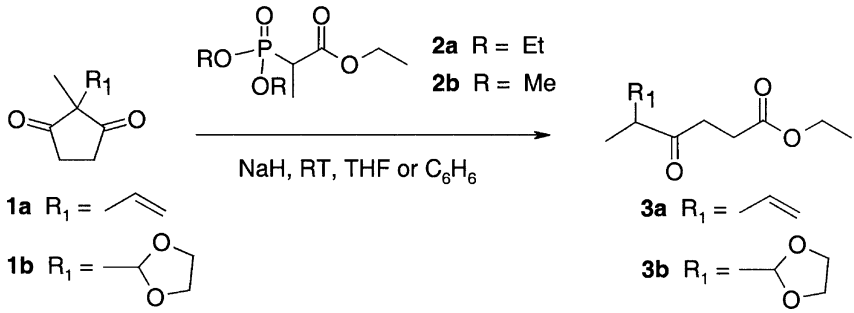
carbanions has achieved outstanding prominence.[5,6] On the other hand, ethyl 2-(diethylphosphono)propionate is a common Horner-Wadsworth-Emmons (HWE) reagent, which has been used successfully in reaction with a great number of different ketones.[7–12] In this article we describe an unexpected direction of the reaction of 2,2-disubstituted 1,3-cyclopentanediones **1a** and **1b** with ethyl 2-(diethylphosphono)propionates **2a** and **2b**, leading to ring cleavage and formation of ethyl ester **3** (Scheme 1).



SCHEME 1 Reaction of 2,2-disubstituted 1,3-cyclopentanediones with ethyl 2-(diakylphosphono)propionates.

RESULTS AND DISCUSSION

Retro-Aldol Reaction of 2,2-Disubstituted 1,3-Cyclopentanediones Initiated by Phosphonate Anion

When constructing the D-ring of a cytotoxic 9,11-secosterol,[13,14] we intended to use ethyl 2-(diethylphosphono)propionate for olefination of 2,2-disubstituted 1,3-cyclopentanediones, which should lead to a desymmetrization of the skeleton. Surprisingly enough, diketones **1a** and **1b** with the HWE reagent **2a** (ethyl 2-(diethylphosphono)propionate anion did not result in C-olefination of the carbonyl group and no HWE product was detected. Instead, ethyl γ-ketoesters (**3a** and **3b**, correspondingly), which form from the cleavage of the cyclopentane ring, were isolated[15] (Scheme 1). When performing the reaction in THF, these γ-ketoesters were obtained in 68% and 62% yield, correspondingly (Table I, entries 1 and 3). In benzene the reaction proceeded faster and γ-ketoester **3a** was isolated even in 90% yield (Table I, entry 2).

The retro-aldol ring cleavage of 2,2-disubstituted 1,3-cyclopentanediones is known. There are examples describing retro-aldol ring cleavage caused by an attack of different nucleophiles to the carbonyl group in 2,2-disubstituted 1,3-cyclopentanediones.[16–19] In the reaction

TABLE I Isolated Yields of Esters 3 in the Reaction of Phosphonates 2a and 2b with 1,3-Diketones 1a and 1b

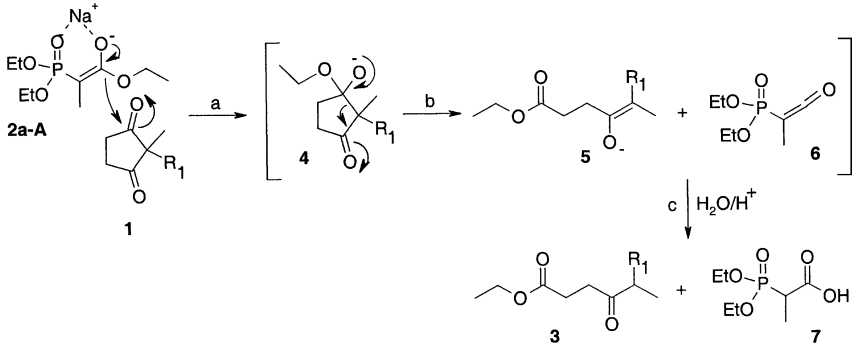
Entry	Phosphonate	Diketone	Solvent/reaction time (h)	Isolated yield of product
1	**2a**	**1a**	THF/3	68% **3a**
2	**2a**	**1a**	C_6H_6/1	90% **3a**
3	**2a**	**1b**	THF/3	62% **3b**
4	**2b**	**1a**	THF/6	16% **3a** (49% of **1a** recovered)

of 2,2-disubstituted 1,3-cyclohexanediones with methyl dimethylphosphonate anion, a nucleophilic attack to the carbonyl group was accomplished by the phosphonate carbanion and the ring was subsequently cleaved.[20] Under the same reaction conditions with 1,3-cyclopentanediones, the reactions stopped after nucleophilic attack of phosphonate carbanion and for cleavage of cyclopentane ring, an additional base-promoted step was required.[21] Our data (Table I) suggest that a new reaction occurs in which the retro-aldol cleavage is initiated by a nucleophilic attack of ethoxy group instead of the expected phosphonate carbanion.

The molecule of ethyl 2-(diethylphosphono)propionate **2a** contains two different kinds of ethoxy groups: two at phopshorus and one at carboxylic acid ethyl ester. These both groups could be potential nucleophilic sites. In order to elucidate which of those groups is involved in the reaction, the dimethyl phosphonate **2b** was used instead of diethyl phosphonate **2a** in the reaction with **1a** (Table I, entry 4). The reaction with phosphonate **2b** was slower than with **2a**, but the main product of the reaction was the same—ethyl ester **3a**. So, it is evident that the nucleophilic ethoxy group does not originate from the phophorus ethoxy groups, but from the carboxylic ester moiety. The latter conclusion was supported also by isolating 2-(diethylphosphono)propionic acid **7** among the reaction products in the case of using diethyl phosphonate **2a**. The result may be rationalized as follows: (a) ethoxy group of phosphonate anion **2a-A** attacks ketone;1 (b) retro-aldol cleavage of cyclopentane ring occurs, ketene **6** is generated from the phosphonate **2a** and (c) quenching the reaction with water (addition of proton to **5** and hydrolysis of ketene **6**) generates ketoester **3** and phosphonate carboxylic acid **7** (Scheme 2).

NMR Study of the Phosphonate Anion

A number of publications dedicated to the structure of phosphonate-stabilized carbanions based on the IR, NMR and X-ray analysis have



SCHEME 2 The proposed mechanism of reaction between 2-(diethylphosphono)propionate and 2,2-disubstituted-1,3-cyclopentadiones.

appeared from different research groups.[22–29] According to these studies, the metallated phosphonate anions give different associates depending on the solvent, additives, and temperature. Additionally, the equilibrium between conformational isomers depends on the reaction medium. According to our knowledge, there is only one preliminary communication published on the NMR analysis of α-substituted phosphonate methyl ester anion, but the structures of the equilibrated compounds were not fully characterized.[30] No data about the NMR analysis of ethyl 2-(diethylphosphono)propionate anion have been published. Knowing the structural variability of metallated phosphonates in different conditions, we made an attempt to explore the anion formation and its structure in the solution by NMR. From the structural features of the anion, we expected to find out the reason why instead of the ylidic carbon, the ethoxy group acted as a nucleophile in the reaction of 1,3-diketones **1a** and **1b** with ethyl 2-(diethylphosphono)propionate **2a**.

First, we followed the formation of the 2-(diethylphosphono)-propionate anion using ^{31}P-NMR spectra (Table II). We established that the excess of NaH is needed to deprotonate fully phosphonate **2a**. At equimolar hydride amount,[31] the formation of phosphonate-sodium bidentate chelate (**2a-chelate**, Figure 1) was observed. A similar intermediate was described earlier in the case of α-unsubstituted phosphonate esters, when less than 1 eq of base was used.[26,27]

According to these data, we may propose that phosphonate **2a**, **2a-chelate** and anion **2a-A** are in equilibrium, giving rise to quite broad ^{31}P- ^{13}C- and ^{1}H-NMR peaks, which indicate the exchange processes between isomers. At the same time, the ^{31}P- and ^{13}C-NMR peaks of phosphonate **2a** measured in the protonated condition (without

TABLE II The ^{31}P-NMR Shifts of Ethyl 2-(Diethylphosphono)-propionate 2a, Na-Chelate of Neutral Phosphonate 2a-Chelate and Its Anion 2a-A

			2a-A	
	2a	**2a**-chelate	In equilibrium conditions, in presence of **2a**	In totally deprotonated condition
δ^{31}P (ppm)	24.1	32.2	42.5	41.36, 42.34, 43.00, 43.29 (broad)

base present) were sharp and existed in one conformation (no change observed). Surprisingly enough, in totally deprotonated conditions (an excess - 5 eq of NaH was used), the ^{31}P-NMR of anion **2a-A** gave three sharp signals of approximately equal intensity on the top of a basic broad line, which probably shows the presence of different fixed conformers. There are reports about similar phosphonates in the literature, in which *Z*- and *E*-isomers coexist (Figure 1), having a difference in 0.5–2 ppm of the respective ^{31}P-NMR shifts.[27,32,33] The additional lines in the spectrum may be rationalized by an assumption that phosphonate anions could give metal chelates not only through oxygen-atoms, but also involving carbon-atom and exist as dimers.[22,24,26]

In ^{13}C- and ^{1}H-NMR spectra of anion **2a-A** (Table III) at room temperature we followed the appearance of broad resonance signals, probably due to conformational exchange processes between isomers. In the ^{13}C-NMR spectrum of phosphonate **2a**, the P-C(3) carbon (see atom

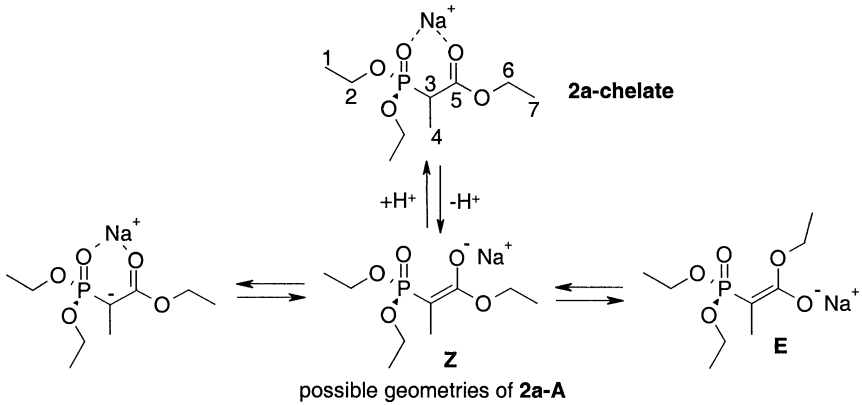


FIGURE 1 Proposed structures of Na-chelate of phosphonate **2a-chelate** and its anion **2a-A**.

TABLE III The ^{13}C- and ^{1}H-NMR Shifts and Coupling Constants of Ethyl 2-(Diethylphosphono)-propionate 2a and Its Anion 2a-A

	2a		**2a-A** (in totally deprotonated conditions)	
Atom[a]	δ^{13}C (ppm), J (Hz)	δ^{1}H (ppm), J (Hz)	δ^{13}C (ppm), J (Hz)	δ^{1}H (ppm), J (Hz)
1	16.37 16.41	1.09 (t $J_{HH} = 7.1$) 1.12 (t $J_{HH} = 7.1$)	16.38 (br) 16.43 (br)	1.08–1.28 (br)
2	62.22 (d^2 $J_{PC} = 6.9$) 62.28 (d^2 $J_{PC} = 6.7$)	3.95–4.09 (m)	60.46 (br)	3.75–4.08 (br)
6	61.03		57.62 (br)	4.12–4.28 (br)
3	39.77 (d^1 $J_{PC} = 132.2$)	2.99 (dq^2 $J_{PH} = 23.5$; $J_{HH} = 3 \times 7.2$)	45.77 (d^1 $J_{PC} = 217.9$ br) 46.13 (d^1 $J_{PC} = 212.8$ br) 46.57 (d^1 $J_{PC} = 211.9$ br)	—
4	11.94 (d^2 $J_{PC} = 6.2$)	1.42 (dd^3 $J_{PH} = 17.8$; $J_{HH} = 7.2$)	12.39 (br)	2.00 (br d^3 $J_{PH} = 13.4$) 2.05 (br d^3 $J_{PH} = 12.1$) (1:2)
5	169.66 (d^2 $J_{PC} = 4.7$)	—	173.3 (d^2 $J_{PC} = 26.3$ br)	—
7	14.06	1.03 (t $J_{HH} = 7.1$)	15.45 (br)	1.3–1.4 (br)

[a]See atom numeration in Figure 1.

numeration in Figure 1) had a doublet at δ 39.77 ppm with $^{1}J_{PC} = 132.2$ Hz. In the spectrum of anion **2a-A**, the presence of three sets of doublets (P-C(3), δ 45–46 ppm) were detected, all having $^{1}J_{PC} \sim 215$ Hz, indicating the formation of three ylidic carbon atoms in approximately planar geometry. In the ^{1}H-NMR spectrum of **2a-A**, methyl protons (on C-4) were seen in two sets of doublets in 1:2 ratios, the latter is probably the sum of signals of two isomers (1:1 + 1). This result is in good agreement with the ^{31}P-NMR spectra, suggesting coexistence of different slowly exchanging isomers of **2a-A**.

We also tried to follow the reaction of 1,3-diketone **1a** with ethyl 2-(diethylphosphono)propionate **2a** by the NMR analysis. In the case of approximately 1 equivalent of base, ^{31}P-NMR spectra showed the presence of Na-chelate of phosphonate **2a**-chelate (δ 32.2 ppm) and phosphonate anion **2a-A** (δ 42.5 ppm) (Table II). Addition of 0.5 equivalent of diketone **1a** did not affect much the ^{31}P-NMR spectrum, which indicates that the reaction does not proceed in the closest P-neighborhood. On the other hand, in ^{1}H-NMR spectra a fast (within 20 min) conversion of diketone **1a** into ester **3a**, through enolate **5** (characteristic singlet of olefin bonded CH_3 at δ 1.95 ppm) was clearly observed. It was difficult to establish the definite number (and structures) of phosphorous intermediate(s) because of signal broadening. It is noteworthy that in totally deprotonated conditions (when 5 equivalents of NaH were used), the

reaction was considerably slower: after 12 h only 50% of ester **3a**[34] was formed (in the presence of **2a-chelate** the reaction was complete in 20 min). Kayser et al.[35] observed analogous reactivity dependence in their studies of structure and reactivity of phosphonium ylides stabilized by a carbonyl function in Wittig reaction.[35]

As a result of the present study, a new nucleophilic character of ethyl 2-(diethylphosphono)propionate **2a** was established. The latter reaction could be used for synthesis of ethyl 5,5-disubstituted 4-ketoesters from 2,2-disubstituted 1,3-diketones. The presence of conjugated acid of phosphonate anion (**2a**) accelerates the reaction rate. The NMR-study showed that different anionic species of ethyl 2-(diethylphosphono)propionate **2a** anion coexist in the reaction medium. This definitely means that the nucleophility of ylidic carbon is lowered because of the charge delocalization and therefore, sterically hindered diketone approaches more easily another nucleophilic center—the ethoxy moiety, thus, driving the reaction toward the ester formation.

EXPERIMENTAL

All reactions, sensitive to the moisture or oxygen, were carried out under the argon atmosphere and in the oven-dried glassware. Commercial reagents were used as received. All solvents were distilled. C_6D_6 was distilled over Na and THF over Na/benzophenone ketyl prior to use. Full assignment of ^{13}C- and ^{1}H-NMR chemical shifts is based on the 1D and 2D FT NMR spectra on a Bruker AMX 500 instrument. Solvent peaks in ^{13}C- and ^{1}H-NMR and external 85% H_3PO_4 peak in ^{31}P-NMR were used as chemical shift references. The mass spectra were recorded on a Hitachi M80B spectrometer using electron ionization (EI) at 70 eV or chemical ionization (CI) with isobutane. IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR infrared spectrophotometer.

2-(1,3-Dioxolan-2-ylmethyl)-2-methylcyclopentane-1,3-dione (1b)

Ozonolysis of 2-allyl-2-methyl-1,3-cyclopentanedione at $-78^{\circ}C$, followed by reaction with dimethylsulphide yielded expected aldehyde.[36]

To a solution of 520 mg (3.38 mmol, 1 eq) of crude aldehyde in 11 mL of toluene was added 1.88 mL (33.8 mmol, 10 eq) of ethylene glycol and 58 mg (0.34 mmol, 0.01 eq) of *p*-TsOH. Reaction mixture was refluxed in Dean-Stark apparatus for 2.5 h. The sodium bicarbonate saturated solution was added, product extracted with CH_2Cl_2, organic

layers washed with brine and dried on $MgSO_4$. Product was purified by column chromatography on silica gel, yielding has 457 mg (68%) of diketone **1b** as colorless oil.

^{1}H-NMR (500.1 MHz, $CDCl_3$) δ 4.87 (1H, t, $J = 5.3$ Hz, H-2′), 3.72–3.82 (4H, m, H4′,5′), 2.76 (4H, s, H4,5), 2.18 (2H, d, $J = 5.3$ Hz, 2-CH_2), 1.09 (3H, s, 2-Me).
^{13}C-NMR (125.7 MHz, $CDCl_3$) δ 216.34 (C-1,3), 100.74 (C-2′), 64.70 (C-4′,5′), 52.67 (C-2), 39.42 (C-2-CH_2), 34.65 (C-4,5), 21.60 (C-2Me).
MS-CI: 199 $[M+1]^+$, 181, 137, 87, 73, 45.

Typical Procedure for Esterification

To a suspension of 5 mmol NaH (60% dispersion in mineral oil, washed with petroleum ether) in 6 mL of dry solvent the solution of 5 mmol of phosphonate **2** in 4 mL solvent was slowly added at room temperature and under inert gas atmosphere. After completion of hydrogen evolution, the ylide was stirred additionally for 30 min. Subsequently 1 mmol of 1,3-diketone **1** was added and the mixture stirred additionally for 3 h at RT, reaction mixture was quenched with brine and extracted with EtOAc, dried on $MgSO_4$ and purified by column chromatography on silica gel.

Ethyl 5-Methyl-4-oxoocta-7-enoate (3a)

As in typical procedure described from diketone **1a** 14 mg (0,09 mmol) and ethyl 2-(diethylphosphono)propionate **2a** 111 mg (0.47 mmol) in 2 mL benzene 17 mg (90%) of ester **3a** was isolated as slightly yellow oil.

^{1}H-NMR (500.1 MHz, $CDCl_3$): δ 5.70 (1H, tdd, J = 2 × 7.0, 10.1 and 17.3 Hz, H-7), 5.01 and 5.02 (2H, m, H-8), 4.11 (2H, q, $J = 7.2$ Hz, CH_2O), 2.77 and 2.72 (2H, m, H-3), 2.62 (1H, m, H-5), 2.55 and 2.56 (2H, m H-2), 2.40 and 2.10 (2H, m, H-6), 1.23 (3H, t. $J = 7.2$ Hz, CH_3), 1.09 (3H, d, $J = 7.0$ Hz, H-5Me).
^{13}C-NMR (125.7 MHz, $CDCl_3$): δ 211.80 (C-4), 172.74 (C-1), 135.50 (C-7), 116.79 (C-8), 60.49 (CH_2O), 45.78 (C-5), 36.94 (C-6), 35.69 (C-3), 27.79 (C-2), 15.91 (C-5Me), 14.08 (Me).
MS-EI: 198$[M^+]$, 183, 152, 129, 101, 85, 69.
IR: (neat) υ: 3079; 2979; 2935; 1738; 1715; 1642; 1459; 1414; 1357; 1351; 1302; 1206; 1175; 1097; 1035; 1002; 917 cm^{-1}.

Ethyl 6-[1,3]-Dioxolan-2-yl-5-methyl-4-oxohexanoate (3b)

As in typical procedure described, from diketone **1b** 107 mg (0.54 mmol) and ethyl 2-(diethylphosphono)propionate **2a** 601 mg (2.5 mmol) in 6.5 mL THF, the 82 mg (62%) of oily ester 3b was isolated.

^{1}H-NMR (500.1 MHz, $CDCl_3$): δ 4.86 (1H, t, $J = 2 \times 4.5$ Hz, H-2′), 4.12 (2H, q, $J = 7.2$ Hz, CH_2O), 3.91–3.95 and 3.80–3.83 (4H, m, H4′, H5′), 2.85 and 2.74 (2H, m, H-3), 2.80 (1H, m, H-5), 2.53 and 2.58 (2H, m H-2), 2.17 and 1.67 (2H, m, H-6), 1.24 (3H, t. $J = 7.2$ Hz, CH_3, 1.14 (3H, d, $J = 7.0$ Hz, H-5Me).
^{13}C-NMR (125.7 MHz, $CDCl_3$): δ 211.80 (C-4), 172.85 (C-1), 102.64 (C-2′), 64.92 and 64.71 (C-4′, C-5′), 60.50 (CH_2O), 41.22 (C-5), 36.60 (C-6), 35.58 (C-3), 27.91 (C-2), 17.35 (C-5Me), 14.13 (Me).
MS-CI: 245[M+1]$^+$, 227, 199, 183, 158, 100.

2-(Diethylphosphono)propionic Acid (7) [CAS nr 30094-28-1]

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 9.1 (bs, 1H, COOH), 4.18 (m, 4H, $2 \times CH_2O$), 3.06 (dq, 1H, $J_{CH} = 7.3$, $J_{PH} = 23.9$ Hz, H-2), 1.42 (dd, 3H, $J_{CH} = 7.3$, $J_{PH} = 18.1$ Hz, H-3), 1.33 (2t, 6H, $J_{CH} = 7.3$ Hz, $2 \times CH_3$).
^{13}C NMR (125.7 MHz, $CDCl_3$): δ 171.71 ($J_{PC} = 3.8$ Hz, C-1), 63.35 and 63.04 ($J_{PC} = 6.7$ Hz, $2 \times OCH_2$), 39.16 ($J_{PC} = 132.8$ Hz, C-2), 16.26 and 16.25 ($J_{PC} = 5.9$ Hz, 2xCH_3), 11.56 ($J_{PC} = 6.4$ Hz, C-3).
MS-EI: 210[M$^+$], 192, 165, 138, 109, 99.

(1-Ethoxycarbonyl-ethyl)triphenylphosphonium bromide [CAS nr 30018-16-7]

Prepared as described by W. G. Dauben et al.[37]

MS-EI: 362, 317, 289, 277, 262, 183.
IR (KBr) v: 1736; 1438; 1300; 1238; 1190; 1110; 1015; 996; 748; 725; 692; 535; 516 cm^{-1}.

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