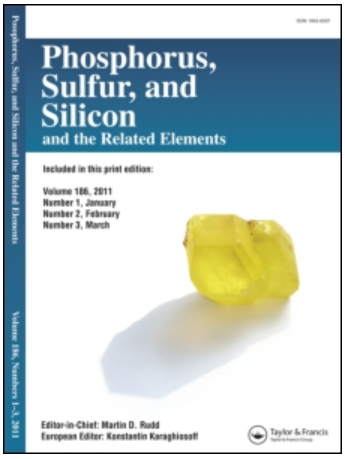

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METAL(I) AND METAL(II) DERIVATIVES OF DIETHYL (2-OXO-1-PHENYL) ETHYLPHOSPHONATE: SYNTHESIS, STRUCTURE AND REACTIVITY

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METAL(I) AND METAL(II) DERIVATIVES OF DIETHYL (2-OXO-1-PHENYL) ETHYLPHOSPHONATE: SYNTHESIS, STRUCTURE AND REACTIVITY

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The synthesis and structures of sodium, potassium, calcium and magnesium derivatives of 2-diethoxyphosphonyl-2-phenylethen-1-ol **1** (**2, 3, 4** and **5** respectively) are described. The alkaline salts **2** and **3** are proven to be pure (E)-enolates, while the alkaline earth metal complexes **4** and **5** are diastereomeric mixtures of (Z) and (E) enolate forms. The reactivity of the metal derivatives is studied in reactions of acylation, alkylation and carbonylolefination. Only O-acetylated (**6**) and O-benzylated (**7**) products are obtained as a mixture of diastereomers, where the derivatives of (E)-enol forms predominate. The reaction of carbonylolefination of **4** and benzaldehyde does not occur with the choosen conditions.

Keywords: Diethyl (2-Oxo-1-Phenyl)ethylphosphonate; Na- and K-salts; Ca- and Mg-complexes; (Z)- and (E)-acetyl derivatives; (Z)- and (E)-benzyl derivatives; NMR (^{1}H, ^{13}C, ^{31}P)

INTRODUCTION

Earlier we studied the reactivity of β-phosphorylated aldehydes in reaction of metal complexformation with some nontransition[1,2] and transition[3–5] metals. It was shown, that while the chelate structure is characteristic for the lithium derivatives of β-phosphorylated ketones, esters and amides[6], the corresponding derivatives of β-phosphorylated aldehydes exist as

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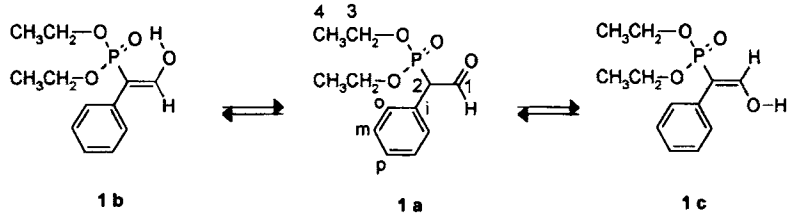
(Z)-enolates[1,2], mixtures of (Z) and (E)-enolates[1,2] or almost pure (E)-enolate[7] forms.

Previous studies on the synthesis and structure of calcium and magnesium complexes of β-phosphorylated ketones and esters[8–11] have proven their chelate trimeric structure[11].

Investigations about the coordination chemistry of the phosphorylated aldehydes with alkaline and alkaline earth metals are not wide-spread. In view of the considerable differences in the structure of metal complexes of phosphorylated ketones and aldehydes, in the present work we studied synthesis, structure and reactivity of sodium, potassium, calcium and magnesium derivatives of 2-diethoxyphosphonyl-2-phenylethen-1-ol **1** (compounds **2, 3, 4** and **5** respectively).

RESULTS AND DISCUSSION

The sodium derivative **2** was obtained by the reaction of sodium in THF at room- or at low temperature with the phosphonate **1,** the latter being available in its tautomeric forms **1a-c** (Scheme 1, Table I)[2]. The NMR-spectra of **1a-c** demonstrate, that the relative ratio of the three compounds depends strongly on the type of the solvent, the concentration, the temperature and the content of water. Depending on these parameters, we always found different amounts of impurities in the spectra. Nevertheless, for the reaction with salts all three forms seem to be available to participate.

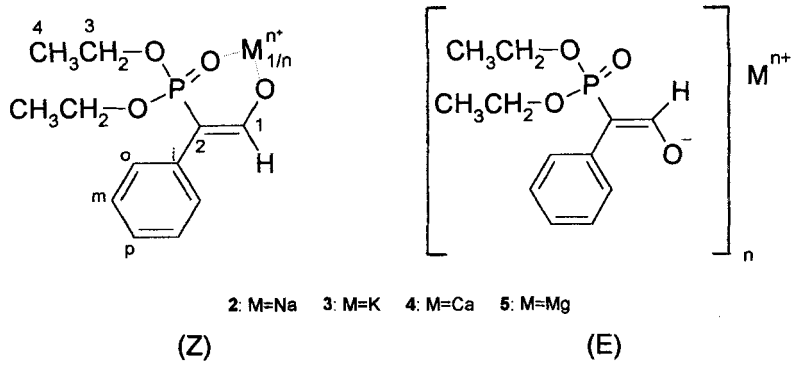


SCHEME 1 Aldo-enol tautomerism of Diethyl (2-Oxo-1-phenyl)ethylphosphonate **1**

The isolated crystalline product **2** is soluble in DMSO and THF, slightly soluble in $CHCl_3$ and insoluble in CCl_4 and diethylether. The absence of the band for a carbonyl group in the IR spectrum and the appearance of a strong band at 1555 cm^{-1} (C=C) prove the enolate structure of the sodium

derivative **2.** The ^{1}H-NMR spectrum in DMSO of the crude reaction mixture as well as of the purified (by washing with diethylether) product **2** indicates the presence of only (E)-enolate (E)-**2** (see Table I). The doublet at $\delta = 8.65$ ppm, $J_{HP} = 3.4$ Hz is well correlated with cis-oriented phosphorus and hydrogen atoms in the (E)-tautomer (Fig. 1). ^{31}P- and ^{13}C-NMR spectra (Table I and Experimental) affirm the availability of only one isomer and the comparatively large value of $^{3}J_{C1P}$ (23.0 Hz) is characteristic for (E)-enolate structures.[2,12]

For reasons of comparison, it is mentioned here that this (E)-**2** isomer was synthesized under the same reaction conditions as for the preparation of 1-Li[2] (2 hrs at –70°C and overnight at –20°C, see Experimental).



2: M=Na **3**: M=K **4**: M=Ca **5**: M=Mg

(Z) (E)

FIGURE 1 (Z)- and (E)-structures of the Metal(I) and Metal(II) Derivatives **2**, **3**, **4** and **5**

In contrast, for the sodium derivative of diethoxyphosphonoacetone Cotton and Schunn[13] considered a (Z)-enolate structure in crystalline form and in benzene solution, while in $CHCl_3$ Petrov et. al.[9] found both (Z) and (E) enolate forms.

The potassium derivative **3** is obtained in a NMR tube in DMSO-d_6 using an equimolar quantity of t-BuOK and phosphonate **1**. For the investigation of the reactivity of **3** we succeeded to isolate it in almost pure state (see Experimental) but it is extremely hygroscopic and too unstable to be analyzed. The NMR (^{1}H and ^{13}C) data prove that analogously to the sodium derivative **2**, the potassium salt **3** is a pure (E)-enolate form (E)-**3** (see Table I and Experimental). This conclusion is based on the small value of $^{3}J_{HP}$ (3.50 Hz) for the proton at C1 and the large value of $^{2}J_{CP}$ (23.01 Hz) for C1.

TABLE I NMR data of phosphonates **1** – **7** in DMSO [$CDCl_3$]

Compound	*δH(ppm)/J(Hz)*				*^{31}P (ppm)*
	H1	*H3*	*H4*		
1 (1a, 1b, 1c)	9.75 t(**1a**) J= 2.01	3.86–3.99 m **1a, 1b, 1c**	1.08–1.25, m **1a, 1b, 1c**	4.85 dd HH=2.1, HP=27.4 H2 in **1a;** 10.88s, OH in **1c;** 11.35 d, HH=12.1, OH in **1b;** 7.16-8.14 m, Ph in **1a, b,c,** and H1 in **1b, 1c**	23.71 (E)-enol 22.94 (ald) 24.57 (Z)-enol
(E)-**2**	8.65 d J=3.4	3.71–3.83 m	1.09 t J=7.1	6.68 t J=7.6 H-p 6.98 t J=7.6, H-m 7.87 d J=7.6, H-o	37.46
(E)-**3**	8.67 d J=3.50	3.89 q J=7.2	1.19 t J=7.2	6.70 t J=7.13,H-p 6.99 t J=7.49, H-m 7.89 d J=7.97, H-o	24.30
(Z)-**4**	8.34 d J=39.4 (8.46, d; 8.70, d) (J=40.62; 37.97)	3.70–4.00 m	1.10 m J=8.52	7.14–7.20 broad, Ph	28.81 [26.40 and 24.09]
(E)-**4**	8.52 d J=4.4	3.70–4.00 m	1.10 m J=8.52	6.67 t, H-p 7.03 t, H-m 7.85 d, H-o	35.91
(Z)-**5**	8.26 d J=40.62 (8.14 d; 8.10 d) (J=40.28 ; 39.97)	3.76–4.08 m	1.10 t J=6.50	6.90–7.40 m, Ph	29.08 [27.67 and 26.43]
(E)-**5**	8.44 bs	3.76–4.08 m	1.10 t J=6.50	6.76 t J=7.92, H-p 6.89 t J=7.90, H-m 7.82 d J=8.20, H-o	35.68
(Z)-**6**	7.59 d J=33.9	3.91–4.07 m	1.18 t J=7.04	2.26 s, H-6 7.29–7.42 m, Ph	14.19
(E)-**6**	7.97 d J=11.89	3.91–4.07 m.	1.18 t J=7.04	2.13 s, H-6 7.29–7.42, Ph	19.12
(Z)-**7**		3.80–3.99,m	1.10 t	5.16 s, H-5 7.12–7.43 m, Ph and H-1	17.39
(E)-**7**		3.80–3.99, m	1.14 t	5.15 s, H-5 7.12–7.43 m, Ph and H-1	21.97 J=9.8

Recently we described the lithium derivative of the phosphonate **1** (**1**-Li), which in $CHCl_3$ exists only as (Z)-enolate-chelate[2]. This result was confirmed later for **1**-Li in DMSO, when the spectra were recorded immediately after dissolving of the sample as well as after staying in this solvent for 15 min. (δ_H 8.5 ppm H1, J_{HP} = 39 Hz).

Because all the derivatives **1**-Li, **2** and **3** are well soluble in THF, we compared the stereochemistry of the three compounds in this solvent. It was stated[14] in studies about the acetylation of compounds similar to **1**, that the (E)-acetylated product is preferred because of a reduced mobility of the hydroxyl proton in the (Z)-chelated starting material. This does not correspond to our observation that the keto-enol-equilibrium **1a-c** starts with an excess of the (E)-isomer and ends up with a predominance of the (Z)-isomer after 90 minutes in THF and $CHCl_3$. The difference in the steric structure of the studied alkaline derivatives is probably due to the specificity of the metal ion. The larger atomic radius of sodium and potassium ions as well as the weaker bond with the enol oxygen atom do not promote formation of (Z)-chelate by inner coordination with the PO group. In our previous paper[2] we have concluded that unlike β-dicarbonyl compounds intermolecular H-bonding in (E)-tautomers of phosphonates seems to have a similar stabilizing effect as the intramolecular H-bonding in the (Z)-tautomer. Our present results, testifying predominance of the steric effects, confirm this idea.

The calcium derivative **4** is obtained from the phosphonate **1** using CaH_2 in anhydrous methanol. The isolated product is a white crystalline substance, soluble in DMSO, poorly soluble in $CHCl_3$ and ether. The absence of a band for the carbonyl group in the IR spectrum as well as the presence of a strong band at 1550 cm^{-1} indicate that only enolate form(s) is (are) available. In nujol two bands for phosphoryl groups (ν 1160 and 1180 cm^{-1}) as well as for C=C bonds (ν 1550 and inflex at 1560 cm^{-1}) are present. In $CHCl_3$ solution only one band for the P=O group (ν 1170 cm^{-1}) and the C=C bond (ν 1535 cm^{-1}) are detected which we attribute to the isomer (Z)-**4**. The elemental analysis of C, H and Ca corresponds to the ratio ligand:metal 2:1, that is the simplest structure is L_2Ca [L= $(C_2H_5O)_2P(O)C(Ph)=CH\text{-}O^-$]. The NMR data ($^1H$ and ^{31}P) in DMSO of the obtained reaction mixture testify the presence of both enolate forms ((E) and (Z), Fig. 1).

In the ^1H-NMR spectrum (in DMSO) the doublet at δ_H = 8.34 ppm (Cl-H) with J_{HP} = 39.4 Hz we attribute to the (Z)-enolate (Z)-**4** (trans ori-

ented phosphorus and hydrogen atoms), while the doublet at 8.52 ppm with J_{HP} = 4.4 Hz is consistent with cis-oriented phosphorus and hydrogen atoms in (E)-**4**. The ratio of the two sets of signals, determined in the raw product washed with methanol is (Z)/(E)~ 1.5:1. A variable temperature study shows, that the signals which are attributed to the (Z)-compound are invariant against increasing temperature which strenghtens the idea of an intramolecular stabilisation, while the signals for the (E)-compound show some broadening with increasing temperature due to an increased mobility of this species compared to the (Z)-compound. Nevertheless, no coalescence is observed up to 353°K.

The ^{31}P-NMR spectrum shows two signals at δ_P= 28.81 and 35.91 ppm. In relation to the ^{1}H-NMR the upfield signal is attributed to the isomer (Z)-**4** and the latter to (E)-**4**.

The ^{13}C-NMR spectrum of **4** (see Experimental) also contains two sets of signals. The smaller value of $^2J_{C1P}$ (8.6 Hz) in (Z)-**4** and the larger value of $^2J_{C1P}$ (17.1 Hz) in (E)-**4** are in agreement with the literature data for (Z)- and (E)-metal complexes of diethyl(oxoethyl)phosphonates[2,12]. The analysis of the ^{13}C-NMR spectral data shows that $^1J_{C2P(E)} > {}^1J_{C2P(Z)}$, the same dependence is observed in the case of alkaline metal complexes of ketophosphonates[12].

The compensation of the electron demand at the oxygen due to complexation leads to a considerable downfield shift of the ^{13}C-signal of C1 in (Z)-**4** and (E)-**4** relative to the starting ligand **1** ($\Delta\delta_{Cl}$ being 22 and 16 ppm respectively). The signal for C2 and the phosphorus signal react alternatively as is to be expected.

In $CDCl_3$ the NMR (^{1}H and ^{31}P) data show the presence of two (Z)-forms: (Z)-$\mathbf{4}_1$ (δ_H 8.46 ppm, δ_P 26.40 ppm, J_{HP} 40.62 Hz) and (Z)-$\mathbf{4}_2$ (δ_H 8.70 ppm, δ_P 24.09 ppm, J_{HP} 37.93 Hz) in the ratio $\mathbf{4}_1/\mathbf{4}_2$= 7:1. This can be different oligomeric forms or one of them is a chelated isomer while the other is an intermolecularly bonded (Z)-isomer. Sometimes, obviously depending on the quality of the solvent, a third compound with somewhat broadened lines is observed which vanishes with time to yield some unidentified impurities. As a general rule, spectra in $CDCl_3$ are difficult to be reproduced and depend strongly on the purity of the compound as well as the solvent.

The magnesium complex **5** is prepared in anhydrous methanol by the reaction of **1**-Na (obtained from **1** and sodium hydroxide) and a solution of magnesium acetate tetrahydrate. The product (white crystals) is soluble in

DMSO, $CHCl_3$ and ether. The elemental analysis indicates a structure with a ligand/metal ratio 2:1 and the coordination of one molecule of water. The IR spectrum (nujol) is similar to that of the calcium derivative **4** (see Experimental). According to the NMR data (^1H, ^{31}P and ^{13}C, see Table I and Experimental) in DMSO the solution obviously contains several enolates in a slow equilibrium. Only the most prominent signals are given in Table I and the experimental part, because we can not assign the signals undoubtfully. In the ^1H-NMR a signal for H1 (δ_{H1} 8.26 ppm, d, J_{HP} 40.62 Hz) is presented as broad doublet and assumed to belong to (Z)-**5**. This signal is accompanied by several others, broadened and less intense dubletts, but obviously with a large coupling constant. A signal for (E)-**5** may be assumed at δ_{H1}= 8.44 ppm (broad). Additionally, the aromatic as well as the aliphatic resonances are broadened and unstructured compared to the other compounds we have investigated. This observation is confirmed by the ^{31}P-NMR spectrum, which contains several more or less sharp signals in an area from 26 to 32 ppm with the most intense one at 29.08 ppm, and a very broad signal at 35.68 ppm. The sharper signals all show large couplings (38.2 – 43.9 Hz) in a proton coupled spectrum and are in agreement with trans oriented phosphorus and hydrogen atoms in (Z)-isomers. The ^{13}C-NMR is in agreement with these results and only some prominent resonances can be given. The situation is much better in a ^1H-NMR spectrum at increased temperature (357°K): the aromatic and aliphatic signals get structured and two signals remain at 8.26 ppm (J_{PH} 40.5 Hz) and 8.50 ppm in a ratio of 15:1. The downfield signal is still broadened and a coupling constant can only be estimated to be ~ 6 Hz. Coming back to room temperature, the former situation is reestablished. Thus, we assume that this are not decomposition processes but a slow equilibrium between several (Z)-configured oligomers. Compared to the Ca-compound, the availablity of the metal atom to form oligomers or coordinations with the solvent is increased, mainly due to steric reasons introduced by the increase of the atomic radius.

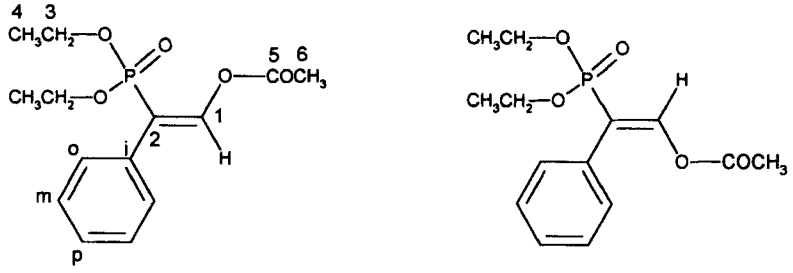
In $CDCl_3$ the situation is quite similar, although two isomers (Z)-**5** in the ratio 3:1 (major isomer: δ_H 8.14 ppm H1, J_{PH} 40.28 Hz, δ_P 27.67 ppm; minor isomer: δ_H 8.10 ppm H1, J_{PH} 39.97 Hz, δ_P 26.43 ppm) dominate the spectrum and ride on top of a broadened underground. The broadening is observed also for the aromatic and aliphatic resonances as well as in the ^{31}P-NMR. Because of the properties of the solvent, spectra at increased temperature give no further information.

We consider that, with increasing radius of the metal atom the more or less defined and stabilized situation of a chelated (Z)-form is weakened and obviously intermolecularly bonded oligomers play a more and more important role in the stabilization of the complexes, where additional rotational isomers about the C-(O-Metal)-bond can be assumed.

The reactivity of the obtained metal complexes is studied in reactions of acylation, alkylation and carbonylolefination.

According to the literature data[14] the acylation of α-phosphorylated propionaldehyde and butyraldehyde leads to O-acylated derivatives of the (E)-enol form. The acylation of enol tautomers is characteristic also for the metal derivatives of dialkyl-2-oxopropylphosphonates[8,15], but independently on the nature of the metal ion and the acylhaloid, derivatives of the (Z)-enol form are obtained[8,15].

We carried out an acylation with acetylchloride of the sodium salt **2**, calcium salt **4**, previously described lithium salt **1**-Li as well as an acylation of the free ligand **1** (see Table II). In all cases the isolated 1-acetyloxy-2-diethoxyphosphonyl-2-phenylethen **6** is exclusively a derivative of the enol form of **1** ($\nu_{C=C}$ 1640 cm^{-1}) (Fig. 2).



(Z)-**6** (E)-**6**

FIGURE 2 (Z)- and (E)-Structures of the acetyloxy-phosphonate **6**

The NMR spectra show that the products are either acetylated (E)-enol or mixtures of acetylated (E)- and (Z)-isomers (see Table II). The (Z)/(E) ratio is determined on the basis of the integral intensity of the signals for CH protons as well as for CH_3-CO protons in ^{1}H-NMR. The value of J_{HP} (11.89 Hz) in the major component of **6** is characteristic for cis-oriented

hydrogen and phosphorus atoms in (E)-enol form, while the larger value of J_{HP} (33.90 Hz) in the minor component is correlated with (Z)-form. The large value of J_{CIP} (28.5 Hz) in the major component also corresponds to derivatives of (E)-enols[2,12]. In $CHCl_3$ solution the ratio of the isomers (Z)-**6**/(E)-**6** (obtained from **1**-Li) changes from 1:4 to 1:20 after 10 days. The considerable quantity of the starting ligand **1b** and acetic acid (^{1}H- and ^{13}C-NMR) leads to the idea of a lower stability of the (Z)-acylated product in comparison with the (E)-acylated one.

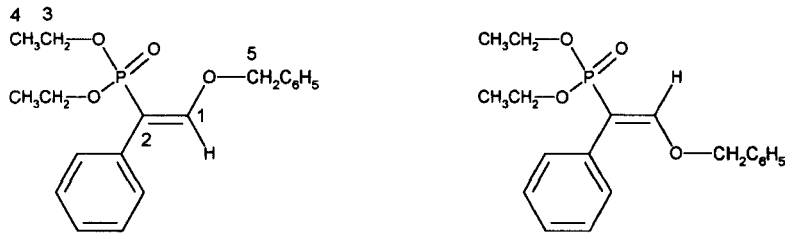
TABLE II Yields (%) and (Z)/(E) ratio of acetyl (**6**) and benzyl (**7**) derivatives, obtained from **1** as well as from the salts **1**-Li, **2**, **3** and **4** determined by NMR in DMSO

Derivative	*From 1*		*From 1-Li*		*From 2*		*From 3*		*From 4*	
	Yield (Z)/(E)		*Yield (Z)/(E)*		*Yield (Z)/(E)*		*Yield (Z)/(E)*		*Yield (Z)/(E)*	
Acetyl **6**	57	0:1	75	0:1	72	1:6			47	1:60
Benzyl **7**							77	1:1.2	48	1:1

Our results show, that independently of the configuration of the starting metal complexes [**1**-Li is pure (Z)-enolate, **2** is pure (E)-form and **4** is ~ 1.5 : 1 (Z)/(E) mixture] the (E)-acylated product is preferred. Even the reaction with the free ligand **1** yields a derivative of the (E)-enol **1c**, although in solution ($CHCl_3$, THF) it is a mixture of three forms (Scheme 1). According to ^{1}H-NMR in $CDCl_3$ the ratio (Z)-**1**/(E)-**1** after 30 min changes from 9:1 to 24:1. A possible explanation includes both electronic and steric factors: repulsion of the rich in electrons PO and oxyacetyl groups in (Z)-isomers and stereo favorable structure of the (E)-isomer.

The alkylation of β-phosphorylated carbonyl compounds, analogously to β-dicarbonyl compounds, usually leads to C-alkylated products. Thus the alkylation of alkaline derivatives of dialkoxyphosphonylaceton[9,16,17] as well as of diphenylphosphinylaceton[18] proceeds with the formation of the carbon carbon bond. In the present work we study the reactivity of the potassium and calcium complexes (**3** and **4** respectively) towards benzylchloride. The reactions are carried out for 4 hrs at reflux in THF (for **3**) or at 80°C in DMF (for **4**).

The isolated benzylated product **7** is a derivative of the enol form, that is O-alkylation occurs (Fig. 3).



(Z)-7 (E)-7

FIGURE 3 (Z)- and (E)-Structures of the benzyloxy-phosphonate **7**

In the IR spectrum of **7** the band for the C=C bond (ν 1625 cm^{-1}) is shifted to higher frequencies in comparison to the starting metal enolates **3** and **4** ($\Delta\nu$~ 70 cm^{-1}). This value is very near to that of the C=C bond in the starting **1c** (ν 1635 cm^{-1}) and indicates some similarity in their structure in contrast to the metal derivatives. In the ^{1}H-NMR spectrum (DMSO) two very close lying signals are observed for two different CH_2 groups (δ_H 5.15 and 5.16 ppm). Thus, the ratio is determined from the ^{31}P-NMR spectrum. In the ^{13}C-NMR spectrum two signals for C5 (at 75.23 and 75.34 ppm) as well as two signals for Cl, C2 and C3 are present, $^{2}J_{C1P}$ for one of the isomers being 26.1 Hz ($^{2}J_{C1P}$ for the other isomer probably is very small because the signal at 159.9 ppm appears uncoupled).

The signals for the CH-protons in both diastereomers of **7** in the ^{1}H-NMR spectrum are hidden in the multiplet of the Ph groups, which prevents their identification on the basis of the corresponding $^{3}J_{HP}$ values. The attribution of (Z)- and (E)-isomers as well as the determination of the relative ratios is performed on the basis of the ^{31}P-NMR (proton coupled spectrum). The bigger value of $^{3}J_{PH}$ (34.2 Hz) is characteristic for (Z)-**7** (trans oriented hydrogen atom and phosphoryl group) and the smaller $^{3}J_{PH}$ (9.8 Hz) for (E)-**7**. Additionally, the larger value of $^{2}J_{C1P}$ (26.1 Hz) is also consistent with an (E)-configuration[2,12] and confirms the above attribution. The ratio (Z)-**7**/(E)-**7** was determined to be 1 :1.2.

In the case of alkylation of **3** and **4** we did not succeed to isolate analytically pure **7**: a certain quantity of DMF as well as a small impurity of diethoxybenzyl phosphonate (product of termal decomposition of **4**) are detected in the analyzed product.

The observed rather unusual O-alkylation of the β-phosphorylated carbonyl compounds could be explained with the higher stability of the enolate forms of the studied phosphonate, due to electronic and steric factors. Although in THF and $CHCl_3$ the free ligand **1** exists in three forms (see Scheme 1) the equilibrium is shifted to the enolate structures of the alkaline and alkaline earth derivatives. The steric hindrance of α-substituted aldehyde **1a** prevents also a transition state with participation of the corresponding carbenium ion.

An attempt for the carbonylolefination of the calcium derivative **4** was carried out with benzaldehyde in DMF for 3 hrs at 80°C. The isolated quantitatively unreacted aldehyde (as 2,4-dinitrophenylhydrazon) as well as the absence of any proofs in tlc and glc for α-phenylzimtaldehyde or other alkenes indicates that this reaction does not proceed.

In this case obviously the absence, or unsufficient quantity of the indispensable carbenium ion $(EtO)_2P(O)\underline{C}(Ph)CHO$, makes the carbonylolefination and autocarbonylolefination impossible.

EXPERIMENTAL

The ligand **1** was prepared according to the literature.[19]

The ^1H-,^{31}P- and ^{13}C-NMR spectra were recorded on a Varian Gemini 200 BB or on a Bruker WM-250 spectrometer in either 5 or 10 mm tubes at room temperature. ^1H-NMR spectra were referenced to internal TMS, ^{13}C-NMR spectra to the solvent signals (DMSO-d_6= 39.5 ppm, $CDCl_3$ = 77.0 ppm) and ^{31}P-NMR spectra to external 85% aq H_3PO_4. The ^{13}C multiplicities were determined via APT spectra[20]. The multiplicities mentioned in the text are given relative to the phosphorus coupling.

The IR spectra were registered on SPECORD-71 IR. The solvents THF, diethyl ether and hexane were dried by destillation from sodium benzophenone. The synthesis of **2**,**3**,**4**,**5**,**6** and **7** were carried out under argon.

(E)-2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato-sodium *2*

a. To a suspension of sodium (0.150 g, 6.5 mmol) in 5 ml of THF a solution of the ligand **1** (1.40 g, 5.5 mmol) in 6 ml of THF was added dropwise for 30 min. at 20–25°C under argon. The reaction mixture was

stirred for 1 hr at room temperature, filtered and the solvent was removed in vacuum. The residual oil was stirred with 15 ml of ether for 15 min., the precipitate was filtered off, washed with 10 ml of ether and dried 2 hrs in vacuum to give (E)-2-diethoxyphosphonyl-2-phenyl-ethen-1-olato-sodium **2** (1.10 g, 72%), m.p. 192–195°C. The product is soluble in DMSO, THF, slightly soluble in $CHCl_3$ and is not soluble in CCl_4 and ether.

$C_{12}H_{16}O_4PNa$ (278.15) Calc.%: C,51.81;H,5.79;Na, 8.26. Found%:C, 51.73; H, 5.85; Na, 8.20.

υ_{max}(nujol)/cm^{-1} 1030 and 1065 (P-O-C), 1150, 1170 and 1190, (P=O), 1555 (C=C) (^{1}H-NMR see Table I)

(E-**2**) : $^{13}C\{^1H\}$-NMR (DMSO-d_6): δ_C 16.40 [2 C, d, J(CP) 6.8 Hz, C-4]; 58.91 [2 C, d, J(CP) 4.9 Hz, C-3]; 85.28 [1 C, d, J(CP) 193.2 Hz, C-2]; 121.08 [1 C, s, C-p]; 125.92 [2 C, d, J(CP) 8.6 Hz, C-o]; 126.60 [2 C, s, C-m]; 140.00 [1 C, d, J(CP) 12.1 Hz, C-i]; 175.47 [1 C, d, J(CP) 23.0 Hz, C-1].

b. From an equimolar quantity of **1** and sodium (2.75 g atom) in THF for 2 hrs at –70°C and overnight at –20°C 33% unreacted sodium was separated. After treatement as described in a) (E)-**2** was isolated (yield 53%).

(E)-2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato-potassium *3*

a. The potassium derivative **3** was obtained in a NMR tube using DMSO-d_6 as solvent. An equimolar quantity of the phosphonate **1** and t-BuOK were mixed in the tube and the spectra were recorded (^{1}H-NMR see Table I) after 10 min.

(E)-**3**: $^{13}C\{^1H\}$-NMR: δ_C 16.68 [2 C, d, J(CP) 6.69 Hz, C-4], 58.93 [2 C, d, J(CP) 4.03 Hz, C-3]; 84.20 [1 C, d, J(CP) 193.7 Hz, C-2], 120.13 [1 C, s, C-p]; 125.84 [2 C, d, J(CP) 8.7 Hz, C-o]; 126.67 [2 C, s, C-m]; 140.74 [1 C, d, J(CP) 12.22 Hz, C-i]; 177.06 [1 C, d, J(CP) 23.01, C-1].

b. To a solution of t-BuOK (0.230 g, 2 mmol) in 3 ml of anhydrous THF a solution of the phosphonate **1** (0.520 g, 2 mmol) was added in inert atmosphere. The reaction mixture was stirred for 1 hr at room temperature, the solvent was evaporated in vacuum and the remaining oil was washed with hexane/ether 20:2 for 30 min. The yellow crystalline precipitate was filtered off and dried in vacuum to give 0.470 g = 80%

(E)-2-diethoxyphosphonyl-2-phenyl-ethen-1-olato-potassium **3.** The product is very hygroscopic and unstable in the air.

ν_{max} ($CHCl_3$)/cm^{-1} 1025 and 1060 (P-O-C), 1160 (P=O), 1550 (C=C).

Bis-(2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato)-calcium *4*

To a solution of the ligand **1** (0.560 g, 2.2 mmol) in 3 ml of anhydrous methanol calcium hydride (0.042 g, 1 mmol) was added under argon at room temperature. Several minutes later gas evolved, the suspension of hydride disappeared and after that a new precipitate was formed. Methanol (6 ml) was added, the mixture was stirred for 45 min., filtered, the precipitate was washed with methanol (5 ml and dried in vacuum to give (Z)+(E) bis-(2–diethoxyphosphonyl-2-phenylethen-1-olato) calcium **4** (0.370 g, 67%), m.p. 191–193°C. The product is soluble in DMSO, slightly soluble in $CHCl_3$ and ether.

$C_{24}H_{32}O_8P_2Ca$ (550.43) Calc.%: C, 52.37; H, 5.85; Ca, 7.28. Found % : C, 52.28; H, 6.06; Ca, 7.05. ν_{max} (nujol)/cm^{-1} 1020 and 1060 (P-O-C), 1160 and 1180 (P=O), 1555 and 1560 (infl.) (C=C).

(^{1}H-NMR see Table I)

$^{13}C\{^1H\}$-NMR (DMSO-d_6)(Z)-**4**: δ_C 16.36 [2 C, d, J(CP) 6.9 Hz, C-4], 60.13 [2 C, d, J(CP) 3.7 Hz, C-3], 87.33 [1 C, d, J(CP) 187.7 Hz, C-2], 121.90 [1 C, s, C-p], 126.65 [2 C, d, J(CP) 5.8 Hz, C-o], 126.89 [2 C, s, C-m], 140.13 [1 C, d, J(CP) 11.5 Hz, C-i], 178.35 [1 C, d, J(CP) 8.6 Hz, C-1] (E)-**4**: δ_C 16.21 [2 C, d, J(CP) 5.8 Hz, C-4], 59.39 [2 C, d, J(CP) 4.1 Hz, C-3], 88.79 [1 C, d, J(CP) 194.8 Hz, C-2], 123.04 [1 C, s, C-p], 126.95 [2 C, d, J(CP) 7.5 Hz, C-o], 127.8 [2 C, s,. C-m], 138.50 [1 C, d, J(CP) 11.1 Hz, C-i], 172.32 [1 C, d, J(CP) 17.1 Hz, C-1].

Bis-(2-Diethoxyphosphonyl-2-phenylethen-1-olato)-magnesium *5*

To a solution of the ligand **1** (0.560 g, 2.2 mmol) in 3 ml of anhydrous methanol in an argon atmosphere powdered sodium hydroxide (0.80 g, 2.0 mmol) was added, followed by a solution of magnesium acetate tetrahydrate (0.210 g, 1.0 mmol) in 2 ml of methanol. The mixture was stirred for 24 hrs at room temperature, the solvent was evaporated in vacuum, 15 ml of H_2O was added and stirred for 15 min. The precipitate was filtered off, washed with water (10 ml), hexane/ether 10:2 (12 ml) and ether (2 ml) and dried in vacuum to give (Z)+(E) bis(diethoxyphosphonyl-2-phe-

nylethen-1-olato) magnesium **5** (0.450 g, 81%), with m.p. 269–271°C. The product is soluble in DMSO, $CHCl_3$, ether.

$C_{24}H_{32}O_8P_2H_2O$ (552.66). Calc. % : C, 52.15; H, 6.19; Mg, 4.39. Found % : C, 51.93; H, 6.03; Mg, 4.26. ν_{max} (nujol)/cm^{-1} 1020 and 1050 (P-O-C), 1165 (infl.) and 1185 (P=O), 1555 (C=C)

(^{1}H-NMR see Table I)

$^{13}C\{^1H\}$-NMR (DMSO-d_6) (Z)-**5**: δ_C 16.11 [2 C, d, J(CP) 6.18 Hz, C-4], 60.70 [2 C, s, C-3], 88.85 [1 C, d, J(CP) 181. Hz, C-2], 123 – 128.1 [m, Ph], 139.0 [1 C, s, C-i], 176.3 [1 C, s, C-1].

$^{13}C\{^1H\}$-NMR ($CDCl_3$) (Z)-**5** (major): δ_C 15.99 [2 C , d, J(CP) 6.81 Hz, C-4], 61.38 [2 C, s, C-3], 92.70 [1 C, d, J(CP) 180.12 Hz, C-2], 124.3 – 129.8 [m, Ph], 137.72 [1 C, d, J(CP) 9.93 Hz, C-i], 174.12 [1 C, d, J(CP) 6.19, C-1]; (Z)-**5** (minor): δ_C 15.43 [2 C, s, C-4], 60.95 [2 C, s, C-3], 91.11 [1 C, d, J(CP) 180.50 Hz, C-2], 138.18 [1 C, s, C-i], 175.53 [1 C, m, C-1]

1-Acetyloxy-2-diethoxyphosphonyl-2-phenylethen *6*

a. To a solution of sodium derivative **2** (1.5 g, 5.39 mmol) in 22 ml of anhydrous THF in an argon atmosphere a solution of freshly distilled acetyl chloride (0.66 g, 8.5 mmol) in 6 ml of THF was added. The stream of argon was stopped and the reaction mixture was stirred for 3 hrs at room temperature. The solvent and the excess of acetyl chloride were evaporated in vacuum, 20 ml of anhydrous ether was added to the remained oil and the mixture was stirred for 30 min. The precipitation was filtered off, washed with ether (2×3 ml) the solvents were evaporated in vacuum to give 1.13 g (72%) oily 1-acetoxy-2-diethoxyphosphonyl-2-phenylethen **6** [(Z)/(E) ratio = 1:11, ^{1}H-NMR in DMSO]. The product is soluble in most organic solvents.
$C_{14}H_{19}O_5P$ (298.207) Calc.%: C, 56.38; H, 6.41; P, 10.38. Found%: C, 55.84; H, 6.57; P, 9.93. ν_{max}(film)/cm^{-1}: 1020 and 1060 (P-O-C), 1150 (infl.) and 1190 (P=O), 1640 (C=C), 1785 (C=O).
(^{1}H-NMR see Table I)
$^{13}C\{^1H\}$-NMR (DMSO-d_6) (E)-**6**: δ_C 16.10 [2 C, d, J(CP) 5.95 Hz, C-4], 20.53 [1 C, s, C-6], 61.91 [2 C, d, J(CP) 5.4 Hz, C-3], 113.12 [1 C, d, J(CP) 183.63 Hz, C-2], 127.91 [1 C, s, C-p], 128.34 [2 C, s, C-m], 129.16 [2 C, d, J(CP) 5.59 Hz, C-o], 131.44 [1 C, d, J(CP) 5.37 Hz, C-i], 144.63 [1 C, d, J(CP) 28.42 Hz, C-1], 167.27 [1 C, s, C-5].

b. The same procedure was used for (Z)-2-diethoxyphosphonyl-2-phenylethen-1-olato lithium[2] (**1b**-Li) (0.86 g, 3.3 mmol) in 10 ml of THF and acetyl chloride (0.38 g, 4.9 mmol) in 5 ml of 0.74 g (75%) of **6** was obtained.
c. From calcium derivative **4** (0.80 g, 1.45 mmol; (Z)/(E) ratio=1.5:1 in DMSO) and acetylchloride (0.22 g, 2.9 mmol) at the same conditions the yield of **6** was 47%, (Z)/(E)=1:60 (determined by ^{1}H-NMR in DMSO). The product contained impurities of diethoxybenzyl phosphonate as well as of the starting ligand **1** (tlc, NMR)
d. To a solution of the ligand **1** (1.53 g, 6.0 mmol) in 12 ml of anhydrous benzene and 2.0 g of triethylamine, acetylchloride (0.48 g, 6.15 mmol) was added dropwise by cooling. The mixture was stirred for 3 hrs at ambient temperature and 30 min at 60°C. The precipitate of sodium chloride was filtered off and washed with benzene. After evaporation of the solvent and vacuum distillation of the residue, 1.0 g (57%) of 1-acetyloxy-2-diethoxyphosphonyl-2-phenylethen (E)-**6** was isolated with b.p. 145–149°C/0.6 mm.

1-Benzyloxy-2-diethoxyphosphonyl-2-phenylethen *7*

Benzylchloride (0.55 g, 4.4 mmol) in 4 ml of THF was added to a solution of **3** (1.29 g, 4.4 mmol) in 8 ml of THF. The reaction mixture was refluxed for 4 hrs (tlc control), the precipitation of potassium chloride was filtered off and washed with THF. After evaporation of the solvent a pale yellow oil of 1-benzyloxy-2-diethoxyphosphonyl-2-phenylethen **7** was isolated as a mixture of isomers in ratio (Z)/(E) =1 : 1.2 (yield by NMR 77%).

$\nu_{max}(CHCl_3)/cm^{-1}$: 1025 and 1060 (P-O-C), 1165 (P=O), 1625 (C=C)
(^{1}H-NMR see Table I)

$^{13}C\{^1H\}$-NMR (DMSO-d_6): (Z)-**7**: δ_C 16.05 [2 C, d, J(CP) 3 Hz, C-4], 61.04 [2 C, d, J(CP) 5.5 Hz, C-3], 75.34 [1 C, s, C-5], 106.0 [1 C, d, J(CP) 180.0 Hz, C-2], 126.86 [1 C, s, C-p], 127.81 [2 C, s, C-m], 128.33 [2 C, d, J(CP) 5.8 Hz, C-o], 128.84 – 129.23 [6 C in $C_6H_5CH_2$], 136.13 [1 C, d, J(CP) 8.3 Hz, C-i], 159.93 [1 C, s, C-1].

(E)-**7**: δ_C 16.14 [2 C, d, J(CP) 2.5 Hz, C-4], 61.21 [2 C, d, J(CP) 5.1 Hz, C-3], 75.23 [1 C, s, C-5], 105.3 [1 C, d, J(CP) 190.0 Hz, C-2], 126.56 [1 C, s, C-p], 128.09 [2 C, s, C-m], 128.64 [2 C, d, J(CP) 7.6 Hz, C-o], 128.84 – 129.23 [6 C in $C_6H_5CH_2$], 136.65 [1 C, d, J(CP) 7.5 Hz, C-i], 158.78 [1 C, d, J(CP) 26.2 Hz, C-1].

Analogously from the calcium derivative **4** (0.84 g, 1.5 mmol) in 4 ml of DMF and benzylchloride (0.38 g, 3 mmol) in 2 ml of DMF after heating for 4 hrs at 80°C the benzyloxy-derivative **7** was isolated (0.78 g, 75%). The obtained product **7** is a diastereomeric mixture (NMR, tlc), ((E)-**7**:(Z)-**7** = 1:1)

Attempt for the reaction of carbonylolefination of the calcium derivative **4**

To a solution of **4** (0.280 g, 0.5 mmol) in 4 ml of anhydrous DMF freshly destilled benzaldehyde (0.106 g, 1 mmol) was added under argon and the reaction mixture was heated for 3 hours at 80°C. After cooling, water (4 ml) was added and the mixture was extracted with ether (2x15 ml) and CH_2Cl_2 (2×15 ml). Half of the organic layer was concentrated in vacuum, the residue was dissolved in ethanol and this solution was used for quantitative determination of benzaldehyde. The yield of 2,4-dinitrophenylhydrazon of benzaldehyde[21] was quantitative: 0.143 g, with m.p. 234–236°C.

Diethyl (2-oxo-1-phenyl)phosphonate *1*

$^{13}C\{^1H\}$-NMR ($CDCl_3$) **1c:** δ_C 16.18 [2 C, d, J(CP) 6. 1 Hz, C-4], 60.86 [2 C, d, J(CP) 4.9 HZ, C-3], 102.25 [1 C, d, J(CP) 192.1 Hz, C-2], 126.30 [1 C, s, C-p], 127.92 [2 C, s, C-m], 129.27 [2 C, d, J(CP) 6.17 Hz, C-o], 133.33 [1 C, d, J(CP) 6.9 Hz, C-i], 156.26 [1 C, d, J(CP) 25.1 Hz, C-1].

$^{13}C\{^1H\}$-NMR ($CDCl_3$) **1b :** δ_C 16.19 [2 C, d, J(CP) 6.36 Hz, C-4], 62.34 [2 C, d, J(CP) 5.0 Hz, C-3], 99.85 [1 C, d, J(CP) 174.64 Hz, C-2], 125.74–132.84 [m, Ph], 134.39 [1 C, d, J(CP) 7.09 Hz, C-i], 162.65 [1 C, d, J(CP) 5.22 Hz, C-1].

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