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1-Acetoxyvinyl Phosphonates: Facile Synthesis via Catalytic Acylation of Dialkyl Phosphites

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ABSTRACT

A new and facile method of synthesis of 1-acetoxyvinyl phosphonates (**2**) *has been found. Dialkyl phosphites react readily with acetic anhydride in acetonitrile solution in the presence of catalysts to produce* **2** *and acylphosphonates* (**1**) *as a minor product. The most efficient catalysts are metal compounds of variable valency: iron(II), iron(III), and cobalt(II) chlorides. The same compounds catalyze transformation of* **1** *into* **2** *in an acetonitrile solution of acetic anhydride.*

INTRODUCTION

1-Acetoxyvinyl phosphonates (**2**) are useful reagents for synthesis of phosphorus-containing polymers. They are also convenient precursors for the synthesis of acylphosphonates. A standard procedure for the preparation of acylphosphonates is the Arbusov reaction between acyl halides and trialkyl phosphites [1]. The only known method for the synthesis of 1-acetoxyvinyl phosphonates is the reaction of dialkyl phosphites with ketene [2].

It is well known that a direct acylation of dialkyl phosphites with acetic anhydride does not lead to **1** in satisfactory yields [3], although acylphosphonites and acylphosphinites can easily be synthesized from acetic anhydride and alkyl phosphonites or dialkyl phosphinites, respectively, in analytically pure form [3, 4]. The low yields of the products of the dialkyl phosphites acylation are due to both low activity of acetic anhydride as an acylation agent and secondary reaction of the formed acylphosphonate with the dialkyl phosphite [5].

In this communication a new, very simple method of catalytic acylation of some dialkyl phosphites with acetic anhydride in the presence of cobalt(II), iron(III), or cerium(III) chlorides is reported.

RESULTS AND DISCUSSION

We have found that the acylation of the P–H bond in dialkyl phosphites is catalyzed by some metal compounds with variable valency and can be carried out under mild conditions (80°C, 2–4 h) in acetonitrile solution. The activities of various catalysts in the reaction of dimethyl phosphite are shown in Table 1.

TABLE 1 Acylation of Dimethyl Phosphite to Mixtures of **1** and **2** (argon atmosphere,80°C, 3 eq of acetic anhydride, 5 mol % catalyst, acetonitrile solution)

Catalyst	*Reaction Time*	*% Conversion*^{a}
none	one week	<10
$NiCl_2$	18 hours	20
$CoCl_2(6H_2O)$	10 hours	75
$CoCl_2$	10 hours	80
$FeCl_2$	4 hours	90
$FeCl_3(6H_2O)$	3 hours	100
$CeCl_3$	10 hours	70
$SmCl_3$	18 hours	25

^{a} Conversion according to gas-chromatographic determination.

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TABLE 2 The Results of the Catalytic Acylation of Various Dialkyl Phosphites $(RO)_2P(O)H$ (argon atmosphere, 80°C, 3 eq of acetic anhydride, acetonitrile solution)

R	*Catalyst (5 mol %)*	*Time, h*	*Yield,*[a] % **1**	**2**
Me	$CoCl_2$	4	10	75
	$FeCl_2$	2	10	85
	$FeCl_3(6H_2O)$	2	5	60
Et	$CoCl_2$	4	10	80
	$FeCl_2$	2	10	85
	$FeCl_3(6H_2O)$	1.5	5	60
Pr	$CoCl_2$	4	15	80
	$FeCl_2$	2	10	90
	$FeCl_3(6H_2O)$	2	10	60
i-Pr	$CoCl_2$	4	10	85
	$FeCl_2$	2	10	90
	$FeCl_3(6H_2O)$	2	10	80
Bu	$CoCl_2$	3	15	75
	$FeCl_2$	2	10	85
	$FeCl_3(6H_2O)$	1.5	5	70

[a] According to the gas-chromatographic determination.

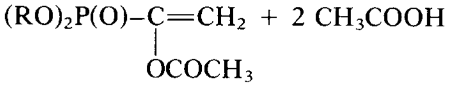
The best results have been obtained with iron(II), iron(III), or cobalt(II) chlorides. However, the main products under these conditions are 1-acetoxyvinyl phosphonates (**2**):

$$(RO)_2P(O)H + (CH_3CO)_2O \longrightarrow$$

$$(RO)_2P(O)\text{-}C(O)CH_3 + CH_3COOH \quad (1)$$

1

$$(RO)_2P(O)H + 2\,(CH_3CO)_2O \longrightarrow$$



$$(RO)_2P(O)\text{-}\underset{\displaystyle OCOCH_3}{\underset{|}{C}}{=}CH_2 + 2\,CH_3COOH$$

(2)

2

R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**)

2

The results of catalytic acylation reactions of various dialkyl phosphites are listed in Table 2.

Acylphosphonates (**1**) and 1-acetoxyvinyl phosphonates (**2**) were isolated by vacuum distillation (see Table 3).

Their physical constants correspond to the literature data [2]. The IR, ^{31}P, ^{1}H, and ^{13}C NMR spectra of these compounds are consistent with the structures of products **1** and **2** (see Experimental section). The IR spectra of **1** contain the absorp-

TABLE 3 Properties of Products **1** and **2** Obtained by Catalytic Acetylation[a] of Dialkyl Phosphites

	R	*BP, °C/p, Torr* Found	*[2]*	*Formula*	*Found/required, %* C	*H*	*P*
1a	Me	100/18	93/16	$C_4H_9PO_4$	31.60 31.59	6.00 5.96	20.40 20.37
2a	Me	136/18	129/11	$C_6H_{11}PO_5$	37.51 37.12	6.01 5.71	16.21 15.96
1b	Et	106/20	103/13	$C_6H_{13}PO_4$	40.50 40.01	7.37 7.27	17.00 17.19
2b	Et	137/18	135/13	$C_8H_{15}PO_5$	43.11 43.25	6.82 6.81	14.00 13.94
1c	Pr	130/16	—	$C_8H_{17}PO_4$	46.45 46.15	8.30 8.23	14.21 14.88
2c	Pr	65/0.1	—	$C_{10}H_{19}PO_5$	48.12 48.00	8.00 7.65	12.30 12.38
1d	*i*-Pr	110/16	—	$C_8H_{17}PO_4$	46.30 46.15	8.40 8.23	14.60 14.88
2d	*i*-Pr	138/16	—	$C_{10}H_{19}PO_5$	48.21 48.00	7.80 7.65	12.60 12.38
1e	Bu	132/16	128/13	$C_{10}H_{21}PO_4$	51.08 50.84	9.00 8.96	13.11 13.11
2e	Bu	72/0.1	161/10	$C_{12}H_{23}PO_5$	52.00 51.79	8.50 8.33	11.30 11.13

[a] See Experimental.

tion bands of stretching of the P=O bond ($1265–1260\ cm^{-1}$) and the C=O bond ($1700–1695\ cm^{-1}$). The products **2** exhibit the absorption bands of the P=O group ($1277–1260\ cm^{-1}$), the C=C group ($1640–1630\ cm^{-1}$), and the COO group ($1780–1770\ cm^{-1}$).

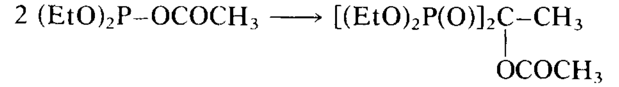
Acylphosphonates **1** can be seen as the result of the direct reaction of the dialkyl phosphite and the acid anhydride [3b, 6] or from the isomerization of an intermediate acylphosphite **3** [7]:

$$(RO)_2P(O)H + (R'CO)_2O \longrightarrow (RO)_2P(O)\text{–}COR' + R'COOH$$

$$(RO)_2P(O)H + (R'CO)_2O \longrightarrow \underset{\mathbf{3}}{(RO)_2P\text{–}O\text{–}COR'} + R'COOH$$

$$(RO)_2P\text{–}O\text{–}COR' \xrightarrow{H^+} (RO)_2P(O)\text{–}COR'$$

To check whether the last version can be realized in the presence of catalysts, we have treated acetyl diethyl phosphite **3b** with acetic anhydride in boiling acetonitrile solution contained cobalt(II) chloride. No appearance of **1b** could be observed after 6 h. Addition of acetic acid to the reaction mixture induced the transformation of no more than 10% of **3b** into a complex mixture of products. The content of **1b** according to the GLC analysis was not more than 5%. Our observations are consistent with the finding [2b], that **3b** isomerizes to 1-acetoxy-1,1-bis-(diethoxyphosphoryl)ethane in 50% yield after heating at 170°C during 6 h:



$$2\ (EtO)_2P\text{–}OCOCH_3 \longrightarrow [(EtO)_2P(O)]_2\underset{\displaystyle OCOCH_3}{\underset{|}{C}}\text{–}CH_3$$

Therefore, we assume that the compounds **3** are not intermediates of the catalytic reactions (1) and (2).

We cannot present complete mechanistic evidence for the suggestion that compounds **1** are intermediates of reaction (2). We have found that acetylphosphonates **1** undergo acylation with acetic anhydride in acetonitrile solution in the presence of cobalt(II) or iron(II) chloride to produce 1-acetoxyvinyl phosphonates **2**:

$$\mathbf{1} + (CH_3CO)_2O \longrightarrow \mathbf{2} + CH_3COOH \qquad (3)$$

These results are consistent with the known catalytic properties of cobalt(II) chloride in the acylation reactions of alcohols [8] and thiols [9].

According to the data of Table 4 the acylation reaction (3) requires more drastic conditions and leads to worse results than reaction (2). Nevertheless, we cannot completely exclude the catalytic acylation of dialkyl phosphites to be the result of reactions (1), which are accelerated in some way by the metalochlorides and reaction (3). It is possible, however, that it involves neither the intermediate **1** nor **3**.

To find out the role of metalocomplexes in catalytic reactions (1) and (2), we have checked the catalytic activity of various metal compounds (see Table 1). There is no apparent catalytic activity exhibited by either the metal compounds of constant valency ($AlCl_3$) or the metal compounds with very low (Sm(III)/Sm(II), $E < 0$ V) or very high (Ni(III)/Ni(II), $E > 2$ V) redox potentials.

In accord with other results of [10] one may suggest the following scheme (Scheme 1) of catalytic acylation. It involves a one electron transfer step to acetic anhydride from the dialkyl phosphite molecule, which disrupts easily [11]. The transfer is mediated by the metal ions M^{2+}/M^{3+} (M = Co, Fe). The whole catalytic cycle is assumed to take place in the metal coordination sphere. "This scheme is consistent with the possibility that the catalytic cycle is initiated by the oxidized form of the catalyst (for example Fe(III)). In this case the sequence of reactions of electron transfer from $(RO)_2P(O)H$ via Fe^{n+} to $(CH_3CO)_2O$ should be reversed."

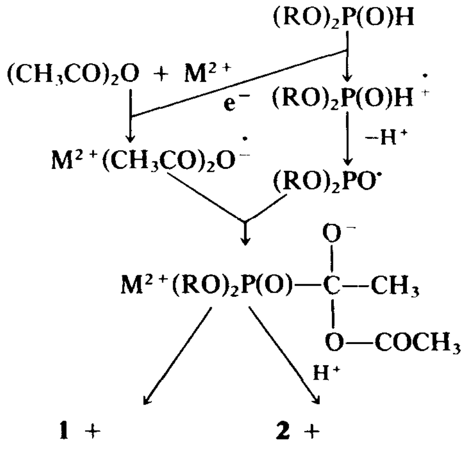
TABLE 4 Results of Catalytic Acetylation[a] of Acylphosphonates **1**

	R	*Reaction time, h*	*Yield of* **2**,[b] *%*
1a	Me	24	45
1b	Et	24	60
1c	Pr	24	35
1d	*i*-Pr	24	25

[a] See Experimental.
[b] According to gas-chromatographic determination.

EXPERIMENTAL

Dimethyl phosphite, diethyl phosphite, dipropyl phosphite, bis(iso-propyl) phosphite, dibutyl phosphite, and diethyl acetylphosphite were obtained according to usual methods [12]. Acetic anhydride was purified by distillation from anhydrous sodium



SCHEME 1

acetate. Inorganic salts used as catalysts were commercial reagents. Acetonitrile was distilled from calcium hydride before use.

Gas chromatographic analyses were carried out on a CHROM 5 gas chromatograph using a 3.0 m long column (3% OV-17 on CHROMATON N-Super 0.16–0.20 mm), with helium as a carrier gas and flame-ionization detection. ^{1}H, ^{31}P, and ^{13}C NMR spectra were determined on a Bruker WM-250 instrument. IR spectra were obtained on a Specord M-80 spectrometer.

General Procedure of Acylation of Dialkyl Phosphites

In a 100 mL round bottom flask connected with a vacuum-argon line and condenser were placed 30 mL of acetonitrile freshly distilled in an argon stream, 5 mol % of catalyst, and 30 mL (0.3 mol) of acetic anhydride. The mixture was stirred until dissolution of the catalyst was complete and then 0.1 mol of dialkyl phosphite was added. The solution was deaerated and the apparatus was filled with argon. Then the flask was placed in an oil bath (100°C). When the dialkyl phosphite had disappeared (gas-chromatographic control), the mixture was cooled, acetonitrile acetic acid, and excess of acetic anhydride were removed by distillation, and the residue was fractionally distilled in vacuo.

The following compounds were thus prepared.

Dimethyl Acetylphosphonate (**1a**)

^{1}H NMR ($CDCl_3$), δ 3.83 (6H, d OCH_3, $^{3}J_{PH}$ 11 Hz), 1.95 (3H, d $COCH_3$, $^{3}J_{PH}$ 5 Hz); ^{31}P NMR δ 23.4; IR, 1265 cm^{-1} (P=O), 1700 cm^{-1} (C=O).

Dimethyl (1-Acetoxyvinyl) Phosphonate (**2a**)

^{1}H NMR ($CDCl_3$), δ 5.94–5.60 (2H, m=CH_2), 3.68 (6H, d OCH_3, $^{3}J_{HP}$ 12 Hz), 2.14 (3H, s $OOCCH_3$); ^{13}C NMR ($CDCl_3$), δ 159.70 (s, C=O), 138.48 (d, $^{1}J_{CP}$ 224 Hz, (P)C=), 117.36 (td, $^{2}J_{CP}$ 25 Hz, $^{1}J_{CH}$ 164 Hz, =CH_2), 55.22 (qd, $^{2}J_{CP}$ 5 Hz, $^{1}J_{CH}$ 149 Hz, OCH_3), 25.67 (q, $^{1}J_{CH}$ 130 Hz, (OOC)CH_3); ^{31}P NMR (CCl_4), δ 7.6; IR, 1277 cm^{-1} (P=O), 1640 cm^{-1} (C=C), 1780 cm^{-1} (COO).

Diethyl Acetylphosphonate (**1b**)

IR, 1260 cm^{-1} (P=O), 1695 cm^{-1} (C=O).

Diethyl (1-Acetoxyvinyl) Phosphonate (**2b**)

^{1}H NMR ($CDCl_3$), δ5.95–5.58 (2H, m=CH_2), 4.15–3.99 (4H, m OCH_2, $^{3}J_{HH}$ 7 Hz), 2.16 (3H, s $OOCCH_3$), 1.31 (6H, m CH_3, $^{3}J_{HH}$ 7 Hz); ^{13}C NMR ($CDCl_3$), δ 159.49 (s, C=O), 139.26 (d, $^{1}J_{CP}$ 223 Hz, (P)C=), 116.53 (td, $^{2}J_{CP}$ 24 Hz, $^{1}J_{CH}$ 164 Hz, =CH_2), 63.90 (td, $^{2}J_{CP}$ 15 Hz, $^{1}J_{CH}$ 146 Hz, OCH_2), 25.56 (q, $^{1}J_{CH}$ 130 Hz, (OOC)CH_3), 21.43 (qd, $^{3}J_{CP}$ 6 Hz, $^{1}J_{CH}$ 128 Hz, (CH_2)CH_3); ^{31}P NMR (CCl_4), δ 6.7; IR, 1260 cm^{-1} (P=O), 1635 cm^{-1} (C=C) 1775 cm^{-1} (COO).

Dipropyl Acetylphosphonate (**1c**)

IR, 1260 cm^{-1} (P=O), 1700 cm^{-1} (C=O).

Dipropyl (1-Acetoxyvinyl) Phosphonate (**2c**)

^{1}H NMR ($CDCl_3$), δ6.04–5.64 (2H, m=CH_2), 4.09–3.95 (4H, m OCH_2, $^{3}J_{HH}$ 7 Hz), 2.18 (3H, s $OOCCH_3$), 1.79–1.65 (4H, m CH_2), 0.96 (6H, t CH_3, $^{3}J_{HH}$ 7 Hz); ^{13}C NMR ($CDCl_3$), δ 159.40 (s, C=O), 139.32 (d, $^{1}J_{CP}$ 224 Hz, (P)C=), 116.73 (td, $^{2}J_{CP}$ 24 Hz, $^{1}J_{CH}$ 165 Hz, =CH_2), 69.16 (td, $^{2}J_{CP}$ 5 Hz, $^{1}J_{CH}$ 150 Hz, OCH_2), 28.58 (td, $^{3}J_{CP}$ 6 Hz, $^{1}J_{CH}$ 150 Hz, CH_2), 25.52 (q, $^{1}J_{CH}$ 130 Hz, (OOC)CH_3, 16.10 (q, $^{1}J_{CH}$ 132 Hz, CH_3); ^{31}P NMR (CCl_4), δ 6.6; IR, 1265 cm^{-1} (P=O), 1630 cm^{-1} (C=C), 1770 cm^{-1} (COO).

Bis-(isopropyl) Acetylphosphonate (**1d**)

IR, 1260 cm^{-1} (P=O), 1700 cm^{-1} (C=O).

Bis-(isopropyl) (1-Acetoxyvinyl) Phosphonate (**2d**)

^{1}H NMR ($CDCl_3$), δ5.97–5.60 (2H, m=CH_2), 4.81–4.53 (2H, m OCH), 2.15 (3H, s $OOCCH_3$), 1.27 (12H, s CH_3); ^{13}C NMR ($CDCl_3$), δ 159.35 (s, C=O), 139.42 (d, $^{1}J_{CP}$ 224 Hz, (P)C=), 116.85 (td, $^{2}J_{CP}$ 24 Hz, $^{1}J_{CH}$ 165 Hz, =CH_2), 25.46 (q, $^{1}J_{CH}$ 130 Hz, (OOC)CH_3); ^{31}P NMR (CCl_4), δ 6.7; by IR, 1268 cm^{-1} (P=O), 1630 cm^{-1} (C=C), 1775 cm^{-1} (COO).

Dibutyl Acetylphosphonate (**1e**)

IR, 1265 cm^{-1} (P=O), 1700 cm^{-1} (C=O).

Dibutyl (1-Acetoxyvinyl) Phosphonate (**2e**)

^{1}H NMR ($CDCl_3$), δ5.95–5.57 (2H, m=CH_2), 4.10–3.91 (4H, m OCH_2); 2.16 (3H, s (OOC)CH_3), 1.69–1.61 (4H, m CH_2), 1.49–1.40 (4H, m $CH_2(CH_3)$), 1.00–0.94 (6H, t CH_3); ^{13}C NMR ($CDCl_3$), δ 159.50 (s, C=O), 139.42 (d, $^{1}J_{CH}$ 225 Hz, (P)C=), 116.63 (td, $^{2}J_{CP}$ 25 Hz, $^{1}J_{CH}$ 165 Hz, =CH_2), 25.46 (q, $^{1}J_{CH}$ 130 Hz, (OOC)CH_3); ^{31}P NMR (CCl_4), δ 6.5; IR, 1265 cm^{-1} (P=O), 1635 cm^{-1} (C=C), 1770 cm^{-1} (COO).

General Procedure of Acylation of Acylphosphonates

In a 100 mL round bottom Schlenk type flask connected with a vacuum-argon line and condenser were placed 30 mL of acetonitrile freshly distilled in an argon stream, 5 mol % of catalyst, and 20 mL (0.2 mol) of acetic anhydride. The mixture was stirred until dissolution of the catalyst was complete and 0.1 mol of dialkyl acetylphosphonate was added. Then the solution was degassed and the apparatus was filled with argon. The flask was placed in an oil bath (100°C). After a period of 24 h the mixture was cooled, pentadecane as an internal standard was added, and a sample of the reaction mixture was withdrawn and analyzed by GLC. The yields of acylation product (**2**) varied from 25 to 60%. Formation of other products was not detected.

Acetonitrile, acetic acid, and excess of acetic anhydride were removed by distillation and the residue was fractionally distilled in vacuo. Physical constants, elemental analysis, and spectra of the obtained compounds were identical with those of the products **2** synthesized by reaction (2).

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