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Novel Synthesis of Phosphinates by the Microwave-Assisted Esterification of Phosphinic Acids

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Abstract: 1-Hydroxy-3-phospholene oxides (**1** and **3**) and phenyl-H-phosphinic acid (**6**) are converted to the corresponding phosphinic esters (**2, 4**, and **7**, respectively) by reaction with simple alcohols on microwave irradiation. Under traditional heating conditions, the esterification does not take place, as in the cases of **1** and **3**, or is highly incomplete, as in the case of **6**. Steric hindrance in diphenylphosphinic acid prevents efficient microwave-assisted esterification.

Keywords: Esterification, green chemistry, microwave synthesis, phosphinates, phosphinic acids

INTRODUCTION

Phosphoric, phosphonic, and phosphinic esters are usually prepared by the reaction of the corresponding P-acid chlorides with alcohols and phenols.[1,2] Although this method is not the best from the point of view

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of environmentally friendly chemistry, it is widely applied in industry. The liberated hydrochloric acid is removed by a tertiary amine or alkali hydroxide. In a variation of this method, the phosphonic or phosphinic chlorides are prepared in situ from the corresponding acids by thionyl chloride, and the so-formed P-chlorides react with the alcohol in a one-pot procedure.[3] It is also possible to make phosphonic and phosphinic esters available by the alkylation of the corresponding acids. In this case, either alkyl halides or unsaturated species, such as olefins or acetylenes, may be the alkylating agents. In the former case, the P-acid should first be converted to the sodium or potassium salt,[4,5] or the alkylation carried out under solid–liquid phase-transfer catalytic conditions,[6] whereas the addition of unsaturated hydrocarbons should be accomplished in the presence of suitable catalysts.[7]

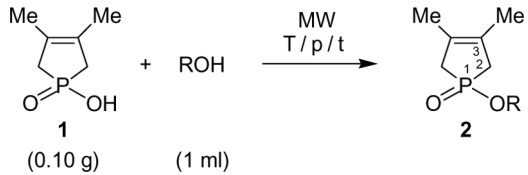
Otherwise, the esterification of phosphinic acids requires special reagents, such as orthoformates (for the preparation of hypophosphorous acid esters),[8–10] orthoacetates,[11] chloroformates,[12] orthosilicates (for the synthesis of hypoposphorous esters and H-phosphinates),[8,13,14] and trialkyl phosphites (also for the preparation of phosphonates).[15,16] Direct esterification of phosphinic acids has not been reported, but diphenylphosphinodithioate esters have been prepared by heating PhP(S)(SH)H with primary alcohols.[17]

On the basis of our recent experiences in microwave (MW)–assisted organic synthesis,[18–23] it seemed worth trying the direct esterification of phosphinic acids with simple alcohols under MW conditions. On the one hand, unexpected reactions could occur,[21] but on the other hand, we could benefit from the effect of pressure developed in closed systems.[18,19] In this article, the scope and limitations of the synthesis of simple phosphinates from the corresponding phosphinic acids and C_2–C_4 aliphatic alcohols under MW conditions are described.

RESULTS AND DISCUSSION

The first model compounds were 1-hydroxy-3-phospholene oxides **1** and **3**, which are the basic starting materials for other five- and six-membered P-heterocycles.[2,24] A variety of alkoxy-phospholene oxides was prepared earlier by the alcoholysis of 1,1,1-trihalophospholium salts.[25–27] In our experiments, reaction temperatures of $>180^{\circ}C$ were anticipated, and for this reason the not-too-volatile butanol was chosen as the reaction partner. Dimethylphospholene oxide **1** and *n*-butanol, used in a 16-fold excess, were irradiated at 200°C for 1 h in a sealed tube. After flash chromatography, the phosphinic ester **2a** was obtained in 20% yield (Table 1, entry 1). By prolonging the reaction time to 2 h, the yield of **2a** was

Table 1. Esterification of 1-hydroxy-3,4-dimethyl-3-phospholene 1-oxide (**1**) under MW conditions



R	T (°C)	p (bar)	t (h)	Yield of **2** (%)[a]	Remark	Entry
^{n}Bu	200	14	1	20 (**2a**)		1
^{n}Bu	200	14.5	2	51 (**2a**)		2
^{n}Bu	200	13.5	1	20 (**2a**)	Three times more BuOH was used	3
^{n}Bu	200	13.5	1	73 (**2a**)	Three times more BuOH and two times more **1** was used	4
^{n}Bu	200	15	2	12 (**2a**)	In the presence of 10% of PTSA	5
^{i}Bu	200	14	2	30 (**2b**)		6
^{n}Pr	180	13.5	2	15 (**2c**)		7
^{n}Pr	180	14	4	20 (**2c**)		8

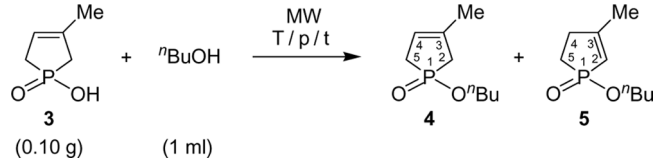
[a]After flash column chromatography (silica gel, 3% MeOH in chloroform).

increased to 51% (Table 1, entry 2). The use of three times more butanol did not lead to an increase in the yield (Table 1, entry 3). After adding twice as much phospholene oxide **1** to a similar reaction mixture, the isolated yield amounted to 73% (Table 1, entry 4). An increase in the concentration of **1** may be favorable, because as in this case the MW absorption becomes more efficient. An attempt to promote the efficiency of the esterification by the use of 10% of p-toluenesulfonic acid (PTSA) as a catalyst was not successful (Table 1, entry 5). In the cases mentioned here, a pressure of 13.5–15 bar was developed. If *n*-butanol was replaced by isobutanol, the yield of the phosphinic ester (**2b**) was 30% after irradiation at 200°C/14 bar for 2 h (Table 1, entry 6). Using propanol as the alcohol component, the reaction temperature had to be somewhat cooler because of the greater tension of this alcohol. At 180°C, the yield of propyl phosphinate **2b** was only 15% after a reaction time of 2 h (Table 1, entry 7). A prolonged irradiation led to a modest increase of the yield (Table 1, entry 8).

It is known that at temperatures greater than 200°C, the 3-methyl-3-phospholene oxide may undergo rearrangement of the double-bond.[21] For this reason, the esterification of 1-hydroxy-3-methyl-3-phospholene oxide **3** with *n*-butanol was carried out at 180°C. After irradiation for 1 and 2 h, the yields of phosphinate **4** were 31 and 36%, respectively (Table 2, entries 1 and 2). No isomerization took place in these instances. When esterification in the presence of 10% PTSA as a possible catalyst at 180 and 200°C was tried, the proportions of the 2-phospholene oxide (**5**) were 20 and 50%, respectively (Table 2, entries 3 and 4). In these cases, a pressure of 8–10 bar was developed.

After the esterification of the simplest ring phosphinic derivatives **1** and **3**, a similar reaction of phenyl-H-phosphinic acid **6** was studied. By using butanol and working at 160°C for 1 h and 180°C for 0.5 h, we obtained yields of butyl phosphinate **7a** of 85 and 90%, respectively (Table 3, entries 1 and 2). When isobutanol was used at 160°C for 1 h, the yield of phosphinate **7b** was 75% (Table 3, entry 3). The esterification with *n*-propanol and isopropanol gave **7c** and **7d** in 73% and 48% yields, respectively (Table 3, entries 4 and 5). The lower yield of 48% may be the consequence of steric hindrance due to the isopropyl group. In instances covered by entries 1–5, the accompanying pressure was 7–8.5 bar. Because phosphinic acid **6** seemed to be quite reactive, its esterification

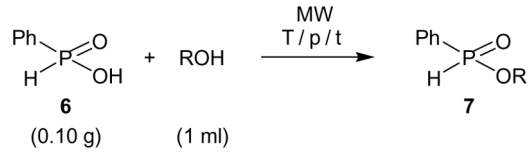
Table 2. Esterification of 1-hydroxy-3-methyl-3-phospholene 1-oxide (**3**) under MW conditions



T (°C)	p (bar)	t (h)	Proportion[a] of **4** and **5**	Yield of **4** (%)[b]	Remark	Entry
180	8	1	1:0	31		1
180	8	2	1:0	36		2
180	9	1	4:1		In the presence of 10% of PTSA	3
200	10	1	1:1		In the presence of 10% of PTSA	4

[a]On the basis of relative ^{31}P NMR intensities.
[b]After flash column chromatography (silica gel, 5% MeOH in chloroform).

Table 3. Esterification of phenyl-H-phosphinic acid (**6**) under MW conditions



R	T (°C)	p (bar)	t (h)	Yield of **7** (%)[a]	Entry
^{n}Bu	160	7	1	85 (**7a**)	1
^{n}Bu	180	8	0.5	90 (**7a**)	2
^{i}Bu	160	7	1	75 (**7b**)	3
^{n}Pr	160	8.5	1	73 (**7c**)	4
^{i}Pr	180	8.5	2	48 (**7d**)	5
Et	160	15	1	80 (**7e**)	6

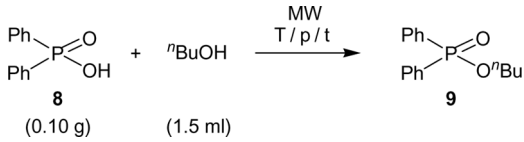
[a]After flash column chromatography (silica gel, 3% MeOH in chloroform).

with the volatile ethanol was also attempted at 160°C (15 bar) for 1 h. The yield of **7e** was 80% (Table 3, entry 6). When phenylphosphinic acid was refluxed in ethanol under thermal conditions, ethyl phenylphosphinate (**7a**) was formed in only 13%. In the literature, a preparative yield of 12% was described for this case.[28] As a comparison, octyl phenyl-H-phosphinate was prepared in 53% yield by a dicyclohexylcarbodiimide (DCC)-promoted coupling of phenylphosphinic acid with 1-octanol.[29] It is worth mentioning that the H-phosphinic esters (**7**) undergo oxidation on exposure to air; therefore they should be stored under nitrogen.

Finally, the apparently sterically hindered model compound diphenylphosphinic acid **8** was subjected to esterification. Irradiation at 180°C for 1.5 h and 200°C for 1 h did not lead to complete conversions, and the yield of butyl phosphinate **9** was only ca. 14% (Table 4, entries 1 and 2). In these cases, most of the unreacted starting material **8** precipitated from the mixture after evaporating the excess of the butanol. The esterification was, in this case, somewhat more efficient in the presence of PTSA (Table 4, entry 3).

In all, 10 phosphinates (**2a–c, 4, 7a–e,** and **9**) were prepared by the novel MW-assisted method. After flash column chromatography, the yields for **2a** and **7a–c,e** were quite good (73–90%) but were less for **2b, 2c, 4, 7d,** and **9**, (20–48%) for different reasons. Volatility of the alcohol, isomerization side reactions, and steric hindrance of the substrate may cause problems, as was shown in the example of phosphinates **2b, 4,** and **9**, respectively.

Table 4. Esterification of diphenylphosphinic acid (**8**) under MW conditions



T (°C)	p (bar)	t (h)	Yield of **9** (%)[a]	Remark	Entry
180	10	1.5	15		1
200	12	1	13		2
200	12	3	20	In the presence of 10% of PTSA	3

[a]After flash column chromatography (silica gel, 3% MeOH in chloroform).

The phosphinates (**2, 4, 7,** and **9**) obtained after flash column chromatography in 98% purity were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectroscopy. The >P(O)H function in products **7a–c** was confirmed by proton-coupled ^{31}P NMR spectra. A number of the phosphinic esters (**2b, 4, 7b, 7c**) are new, whereas others (**2a, 2c, 7a, 7d, 7e, 9**) have been described earlier (see Experimental).

In conclusion, the first direct esterification of phosphinic acids and simple alcohols was accomplished by the MW technique. This is an environmentally friendly procedure because the generally applied phosphinic chlorides can be substituted with inexpensive phosphinic acids. In the case of suitable model compounds, this simple method is obviously of synthetic importance. Because volatility of the alcohol is a limiting factor, the method developed is the most suitable for esterifications involving nonvolatile (longer-carbon-chain) alcohols. Further work on possible extensions is to be done soon.

EXPERIMENTAL

General

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were obtained on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or tetramethylsilane (TMS). The couplings are given in hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument. The starting

1-hydroxy-3-phospholene oxides (**1** and **3**) were prepared by the McCormack cycloaddition reaction followed by hydrolysis.[25,30] The esterifications were carried out in a CEM Discover microwave reactor equipped with a pressure controller at 50–80 W.

General Procedure for the Preparation of Phosphinates

A mixture of 0.10 g of phosphinic acid [**1** (0.68 mmol), **3** (0.76 mmol), or **6** (0.70 mmol)] and 1 ml of alcohol [*n*-butanol (10.9 mmol), isobutanol (10.9 mmol), *n*-propanol (13.3 mmol), isopropanol (13.3 mmol), or ethanol (17.4 mmol)] was measured in a sealed tube and irradiated in a CEM Microwave reactor equipped with a pressure controller at the temperatures and for the times shown in Tables 1–3. Then the alcohol was removed under reduced pressure, and the obtained residue was purified by flash column chromatography using silica gel and 3% methanol in chloroform as the eluant to afford phosphinates **2, 4,** and **7** as oils in a purity of ca. 98%. For the details, see Tables 1–3. The operations with phosphinic esters **7** should be carried out under nitrogen.

The following products were thus prepared:

(1-n-Butoxy)-3,4-dimethyl-3-Phospholene 1-Oxide **2a**

Optimum conditions involved irradiation of 0.20 g of **1** in 3 ml of butanol at 200°C for 1 h. Yield: 73% (Table 1, entry 4); ^{31}P NMR ($CDCl_3$) δ 68.4; ^{13}C NMR ($CDCl_3$) δ 13.6 ($CH_2\mathit{C}H_3$), 16.5 ($^3J = 15.9$, C_3–$\mathit{C}H_3$), 18.8 ($\mathit{C}H_2CH_3$), 32.7 ($^3J = 5.9$, $OCH_2\mathit{C}H_2$), 35.7 ($^1J = 90.8$, C_2), 64.5 ($^2J = 6.6$, OCH_2), 127.5 ($^2J = 12.9$, C_3); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, $J = 7.4$, 3H, $CH_2C\mathit{H}_3$), 1.37–1.44 (m, 2H, $C\mathit{H}_2CH_3$), 1.64–1.70 (m, 2H $OCH_2C\mathit{H}_2$), 1.72 (s, 6H, C_3–CH_3), 2.37–2.50 (m, 4H, PCH_2), 4.00–4.04 (m, 2H, OCH_2) [δ (lit.)[27] 1.73 (s, 6H, C_3–CH_3), 2.44 (d, $J_{PH} = 13$, 4H, PCH_2), 4.01 (m, 2H, OCH_2)]. $(M+H)^+_{found} = 203.1194$; $C_8H_{16}O_2P$ requires 203.1201.

1-Isobutoxy-3,4-dimethyl-3-phospholene 1-Oxide **2b**

Parameters: 220°C/2 h; yield: 30% (Table 1, entry 6); ^{31}P NMR ($CDCl_3$) δ 68.5; ^{13}C NMR ($CDCl_3$) δ 16.4 ($^3J = 15.8$, C_3–$\mathit{C}H_3$), 18.6 [$CH(\mathit{C}H_3)_2$], 29.1 ($\mathit{C}HMe_2$), 35.5 ($^1J = 90.9$, C_2), 70.6 ($^1J = 6.9$, OCH_2), 127.3 ($^2J = 12.9$, C_3); ^{1}H NMR ($CDCl_3$) δ 0.95 [d, $J = 6.7$, 6H, $CH(C\mathit{H}_3)_2$], 1.73 (s, 6H, C_3–CH_3), 1.91–1.98 (m, 1H, $C\mathit{H}$), 2.38–2.50 (m, 4H, PCH_2), 3.76–3.79 (m, 2H, OCH_2). $(M+H)^+_{found} = 203.1191$; $C_8H_{16}O_2P$ requires 203.1201.

(1-n-Propoxy)-3,4-dimethyl-3-phospholene 1-Oxide **2c**

Parameters: 180°C/4 h; yield: 20% (Table 1, entry 8); ^{31}P NMR ($CDCl_3$) δ 68.5; ^{13}C NMR ($CDCl_3$) δ 10.1 (CH_2CH_3), 16.5 ($^3J = 15.9$, C_3–CH_3), 23.9 (CH_2CH_3), 35.7 ($^1J = 90.8$, C_2), 66.3 ($^2J = 6.7$, OCH_2), 127.5 ($^2J = 12.9$, C_3); ^{1}H NMR ($CDCl_3$) δ 0.96 (t, $J = 7.3$, 3H, CH_2CH_3), 1.68–1.72 (m, 2H, CH_2CH_3), 1.72 (s, 6H, C_3–CH_3), 2.38–2.51 (m, 4H, PCH_2), 3.96–4.00 (m, 2H, OCH_2) [δ (lit.)[27] 0.94 (t, $J = 7$, 3H, CH_2CH_3), 1.72 (s, C_3–CH_3) overlapped by 1.40–2.05 (m, CH_2CH_3), total intensity 8H, 2.42 (d, $J = 12$, 4H, PCH_2), 3.97 (m, 2H, OCH_2)]. $(M+H)^+_{found} = 189.1036$; $C_9H_{18}O_2P$ requires 189.1044.

(1-n-Butoxy)-3-methyl-3-phospholene 1-Oxide **4**

Parameters: 180°C/2 h; yield: 36% (Table 2, entry 2); ^{31}P NMR ($CDCl_3$) δ 74.6; ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_2CH_3), 18.9 (CH_2CH_3), 20.9 ($^3J = 12.9$, C_3–CH_3), 30.9 ($^1J = 88.2$, C_2), 32.7 ($^3J = 6.0$, OCH_2CH_2), 33.6 ($^1J = 92.3$, C_6), 64.7 ($^2J = 6.8$, OCH_2), 120.4 ($^2J = 10.8$, C_4), 136.4 ($^2J = 16.8$, C_3); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, $J = 7.4$, 3H, CH_2CH_3), 1.38–1.43 (m, 2H, CH_2CH_3), 1.64–1.69 (m, 2H OCH_2CH_2), 1.80 (s, 3H, C_3–CH_3), 2.39–2.52 (m, 4H, PCH_2), 4.01–4.06 (m, 2H, OCH_2), 5.52 (d, $J = 35.9$, 1H, CH). $(M+H)^+_{found} = 189.1038$; $C_9H_{18}O_2P$ requires 189.1044.

n-Butyl Phenyl-H-phosphinate **7a**[31,32]

Parameters: 160°C/1 h; yield: 85% (Table 3, entry 1); ^{31}P NMR ($CDCl_3$) δ 24.9, $^1J_{P,H} = 566.7$ [(δ (lit.)[33] 25.3, $^1J_{P,H} = 563$)]; ^{13}C NMR ($CDCl_3$) δ 13.2 (CH_3), 18.4 (CH_2CH_3), 32.1 ($^3J = 6.4$, OCH_2CH_2), 65.4 ($^2J = 6.6$, OCH_2), 128.4 ($J = 13.8$, $C_{3'}$),* 129.6 ($^1J = 131.9$, $C_{1'}$), 130.5 ($J = 11.7$, $C_{2'}$),* 132.7 ($^4J = 2.6$, $C_{4'}$) (*may be reversed); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, $J = 7.3$, 3H, CH_2CH_3), 1.39–1.51 (m, 2H CH_2CH_3), 1.68–1.78 (m, 2H, OCH_2CH_2), 4.06–4.15 (m, 2H OCH_2), 7.6 (d, $J = 562.3$, 1H, PH), 7.54–7.84 (m, 5H, Ar). $(M+H)^+_{found} = 199.0881$; $C_{10}H_{15}O_2P$ requires 199.0888.

Isobutyl Phenyl-H-phosphinate **7b**[28,34,35]

Parameters: 160°C/1 h; yield: 75% (Table 3, entry 3); ^{31}P NMR ($CDCl_3$) δ 25.0, $^1J_{P,H} = 562.3$; ^{13}C NMR ($CDCl_3$) δ 18.4 [$CH(CH_3)_2$] 28.8 [$J = 6.6$, $CH(CH_3)_2$], 71.4 ($^2J = 6.8$, OCH_2), 128.3 ($J = 13.8$, $C_{3'}$), 128.7 ($^1J = 132.6$, $C_{1'}$), 130.5 ($J = 11.7$, $C_{2'}$), 132.7 ($^4J = 2.8$, $C_{4'}$); ^{1}H NMR

($CDCl_3$) δ 0.97 [d, $J = 6.6$, 6H, $CH(CH_3)_2$], 1.90–2.08 (m, 1H, OCH_2CH), 3.79–3.92 (m, 2H, OCH_2), 7.59 (d, $J = 562.6$, 1H, PH), 7.52–7.83 (m, 5H, Ar). $(M+H)^+_{found} = 199.0881$; $C_{10}H_{15}O_2P$ requires 199.0888.

n-Propyl Phenyl-H-phosphinate **7c**

Parameters: 160°C/1 h; yield: 73% (Table 3, entry 4); ^{31}P NMR ($CDCl_3$) δ 24.9, $^1J_{P,H} = 562.9$; ^{13}C NMR ($CDCl_3$) δ 10.1 (CH_3), 23.6 ($^3J = 6.5$, CH_2CH_3), 67.3 ($^2J = 6.6$, OCH_2), 128.5 ($J = 13.8$, $C_{3'}$),* 129.8 ($^1J = 132.0$, $C_{1'}$), 130.7 ($J = 11.8$, $C_{2'}$)*133.0 ($^4J = 2.9$, $C_{4'}$) (*may be reversed); ^1H NMR ($CDCl_3$) δ 0.98 (t, $J = 7.4$, 3H, CH_2CH_3), 1.74–1.81 (m, 2H CH_2CH_3), 4.01–4.09 (m, 2H OCH_2), 7.59 (d, $J = 562.5$, 1H, PH), 7.50–7.82 (m, 5H, Ar). $(M+H)^+_{found} = 185.0725$; $C_9H_{13}O_2P$ requires 185.0731.

Isopropyl Phenyl-H-phosphinate **7d**[28,34,35]

Parameters: 180°C/2 h; yield: 48% (Table 3, entry 5); ^{31}P NMR ($CDCl_3$) δ 22.3, $^1J_{P,H} = 559.0$ [δ (lit.)[36] 23.4)]; ^{13}C NMR ($CDCl_3$) δ 23.7 [$J = 4.1$, $CH(CH_3)$], 24.1 [$J = 4.6$, $CH(CH_3)$], 71.2 [$J = 6.5$, $CH(CH_3)_2$], 128.5 ($J = 13.8$, $C_{3'}$),* 130.3 ($^1J = 133.4$, $C_{1'}$), 130.7 ($J = 11.8$, $C_{2'}$),* 132.8 ($^4J = 2.9$, $C_{4'}$) (*may be reversed); ^1H NMR ($CDCl_3$) δ 1.35 (d, $J = 6.0$, 3H, CH_3), 1.43 (d, $J = 6.0$, 3H, CH_3) 4.66–4.79 (m, 1H, OCH), 7.62 (d, $J = 559.2$, 1H, PH), 7.51–7.83 (m, 5H, Ar). $(M+H)^+_{found} = 185.0726$; $C_9H_{13}O_2P$ requires 185.0731.

Ethyl Phenyl-H-phosphinate **7e**

Parameters: 160°C/1 h; yield: 80% (Table 3, entry 6); ^{31}P NMR ($CDCl_3$) δ 24.7, $^1J_{P,H} = 563.0$ [δ (lit.)[33] 25.7, $^1J_{P,H} = 562$)]; ^{13}C NMR ($CDCl_3$) δ 16.2 ($^3J = 6.5$, CH_2CH_3), 61.9 ($^2J = 6.3$, OCH_2), 128.6 ($J = 13.9$, $C_{3'}$),[a] 129.7 ($^1J = 132.2$, $C_{1'}$), 130.7 ($J = 11.8$, $C_{2'}$),[a] 133.0 ($^4J = 2.9$, $C_{4'}$) [δ (lit.)[27] 16.4 ($^3J = 6$, CH_2CH_3), 62.0 ($^2J = 6$, OCH_2), 130.0 ($^1J = 132$, $C_{1'}$), 128.8 ($J = 14$, $C_{3'}$),[b] 130.9 ($J = 12$, $C_{2'}$),[b] 133.1 ($^4J = 3$, $C_{4'}$)], ([a,b]may be reversed); ^1H NMR ($CDCl_3$) δ 1.39 (t, $J = 7.0$, 3H, CH_2CH_3), 4.11–4.24 (m, 2H, OCH_2), 7.60 (d, $J = 562.5$, 1H, PH), 7.52–7.83 (m, 5H, Ar). $(M+H)^+_{found} = 171.0569$, $C_8H_{11}O_2P$ requires 171.0575.

n-Butyl Diphenylphosphinate **9**

Process: 0.10 g (0.46 mmol) of **8** and 1.5 ml (16.3 mmol) of butanol were used, and 7.9 mg (0.05 mmol) of PTSA was also measured in;

conditions: 200°C/3 h; yield: 20% (Table 4, entry 3); ^{31}P NMR ($CDCl_3$) δ 31.2; ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 18.9 (CH_2CH_3), 32.6 ($^3J = 6.6$, OCH_2CH_2), 64.7 ($^2J = 6.1$, OCH_2), 128.4–128.5 ($J = 13.1$, $C_{3'}$),* 127.8–129.7 ($^1J = 144.6$, $C_{1'}$), 131.5–131.7 ($J = 10.0$, $C_{2'}$),* 132.0 ($^4J = 2.8$, $C_{4'}$) (*may be reversed); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, $J = 7.3$, 3H, CH_2CH_3), 1.35–1.48 (m, 2H, CH_2CH_3), 1.68–1.74 (m, 2H, OCH_2CH_2), 3.99–4.07 (m, 2H, OCH_2), 7.44–7.55 (m, Ar), 7.78–7.85 (m, Ar), total intensity 10H, [δ (lit.)[37] 0.85 (t, 3H, CH_3), 1.4 (m, 4H, $CH_2CH_2CH_3$), 3.9 (m, 2H, OCH_2), 7.5 (m, 10H, Ar)]. $(M+H)^+_{found} =$ 275.1193; $C_{16}H_{19}O_2P$ requires 275.1201.

The isomerized 1-butoxy-3-methyl-2-phospholene 1-oxide (**5**) was identified on the basis of the following data: ^{31}P NMR ($CDCl_3$) δ 75.0; ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_2CH_3), 18.9 (CH_2CH_3), 21.4 ($^3J = 19.3$, C_3–CH_3), 23.0 ($^1J = 93.5$, C_5), 32.7 ($^3J = 6.0$, OCH_2CH_2), 64.7 ($^2J = 6.8$, OCH_2), 118.3 ($^1J = 128.4$, C_2), 163.4 ($^2J = 33.3$, C_3).

Attempted Esterification Under Traditional Heating

Phenyl-H-phosphinic acid (0.50 g, 3.50 mmol) in 10 ml (0.17 mol) of ethanol was refluxed for 4 h in the nitrogen atmosphere. Then solvent was evaporated, and the crude product was analyzed by ^{31}P NMR spectroscopy. The mixture contained 13% of ethyl phenyl-H-phosphinate **7e** (δ_P 24.3) and 87% of unreacted phenylphosphinic acid (δ_P 20.6).

In a similar treatment of 1-hydroxy-3,4-dimethyl-3-phospholene oxide **1** with n-butanol, not even traces of the expected ester **2a** could be detected.

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