

RESEARCH ARTICLE

Alcoholysis Versus Fission of the Ester Group During the Reaction of Dialkyl Phenylphosphonates in the Presence of Ionic Liquids

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Abstract: In the microwave-assisted alcoholysis of dialkyl phenylphosphonates performed in the presence of suitable ionic liquids, such as [bmim][BF₄] or [bmim][PF₆], affording the phosphonate with mixed alkoxy groups and the fully transesterified product, the fission of the phosphonate function to the ester-acid or diacid moiety was inevitable. Moreover, in the presence of [emim][HSO₄], the reaction could be performed to afford the phosphonic ester-acid with a selectivity of 66% and the diacid with a selectivity of 97%. The ester-acids provided by the new protocol may be valuable intermediates.



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ARTICLE HISTORY

Received: October 23, 2020
Revised: December 23, 2020
Accepted: January 05, 2021

DOI:
10.2174/1385272825666210212115649

Keywords: Dialkyl phosphonates, microwave, alcoholysis, ionic liquid, phosphonic ester-acid, phosphonic acid

1. INTRODUCTION

The *P*-esters, including phosphinates and phosphonates, are important starting materials or intermediates in organic syntheses [1, 2] that may be prepared by the reaction of the corresponding phosphinic chloride or phosphonic dichloride, respectively, with alcohols [2, 3]. An up-to-date option is a microwave (MW)-assisted, ionic liquid (IL)-catalyzed direct esterification of phosphinic or phosphonic acid with alcohols [4, 5]. An alternative possibility for the preparation of *P*-esters is the Arbuzov reaction [1]. Modification of the *P*-esters by alcoholysis (transesterification) may also be a good choice [6-8], which is an analogous process with biodiesel production [9]. Both the alcoholysis of phosphinates [10] and that of phosphonates [11] have been studied by the senior author of this paper and Kosolapoff, respectively. The transesterification of dialkyl phosphites (*H*-phosphonates) was investigated by different groups headed, among others, by Aitken and Lewkowski [11-14]. The two-step transformations of dialkyl phosphites were also performed under MW conditions [15, 16]. The dialkyl phosphites with two different alkyl groups are the intermediates of these processes that are valuable species due to the asymmetric *P*-center. Moreover, continuous flow accomplishments were also elaborated [17, 18]. The transesterification of dialkyl phosphites

with di-, tri- and tetrahydroxy compounds, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, resorcinol, hydroquinone, glycerol, or pentaerythritol is of importance, as these polycondensations lead to *P*-functionalized polymers [19-22]. The potential of MW irradiation in the synthesis of polymers was also underlined [23].

The hydrolysis of *P*-esters (phosphinates and phosphonates) is mostly carried out under acidic conditions and is of immense importance [24-26]. Till date, the hydrolysis of phosphonates cannot be performed selectively to afford the ester-acid [26].

In this paper, we summarize the results of our investigations on the MW-assisted, IL-catalyzed alcoholyses and related reactions of dialkyl phenylphosphonates. The beneficial effect of ILs as catalyst/additives is well-known in a wide range of reactions [27].

2. RESULTS AND DISCUSSION

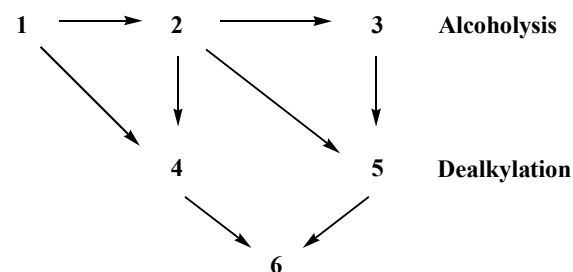
The first model for the attempted alcoholyses was the reaction of diethyl phenylphosphonate (**1**) with *n*-butanol. The alcoholyses were performed under MW irradiation, applying the alcohol in a 15 fold quantity. The results obtained by ³¹P NMR spectral and LC-MS analysis are summarized in Table 1. There was no reaction after a 2 h irradiation at 200 °C (Table 1/Entry 1). In search of promoting the reaction, the catalytic effect of different ionic liquids (ILs) was tested. After reacting the components at 200 °C for 3.5 h in the presence of 10% of [bmim][BF₄], the mixture contained unreacted starting material (**1**) together with the phosphonate with different

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alkoxy groups (**2**) and the fully transesterified product **3** (the three components all together: 39%), along with phosphonic ester-acids **4** and **5** (all together: 55%), as well as 6% of the phosphonic acid (**6**) (Table 1/Entry 2). The ^{31}P NMR shifts of the different dialkyl phosphonates (starting material (**1**), intermediate (**2**) product (**3**)), as well as, that of ester-acids **4** and **5** were overlapped. Although the effect of ILs to cleave the phosphinate function to the acid moiety is not unknown [6], the drastic effect of [bmim][BF₄] to result in the formation of 55% of ester-acids **4** and **5** was surprising. Performing the reaction at 220 °C for 2 h, the proportion of phosphonates **2** and **3**, phosphonic ester-acids **4** and **5**, as well as phosphonic acid **6** was 8%, 19%, 3%, 56% and 14%, respectively, that was almost comparable with the previous results (Table 1/Entry 3). Allowing a longer reaction time of 3.5 h at 220 °C, there was practically no change in the product composition (Table 1/Entry 3/footnote “d”). The effect of [bmim][PF₆] at 200 °C for 2 h was rather similar to that of [bmim][BF₄] at 200 °C for 3.5 h (the quantity of **2+3** was 38%, that of **4+5** was 54%, while that of **6** was 8%; entries 4 and 2 of Table 1 are to be compared). After a longer reaction time of 3.5 h, the proportion of the esters (**2** and **3**) decreased to 27%, while that of ester-acids **4** and **5**, as well as diacid **6** increased to 61% and 12%, respectively (Table 1/Entry 5). [Emim][HSO₄] was the third additive tested. Irradiating the components at 200 °C for 2 h, the fraction comprising **1-3** was formed in 43% (unreacted starting material **1**: 38%, mixed ester **2** and **3**: 5%), the ester-acids **4+5** in 51% (**4**: 5% and **5**: 46%), while acid **6** in 5% (Table 1/Entry 6). Prolongation of the reaction time to 3.5 h led to a composition of 23%, 66%, 11% for fractions **1-3**, ester-acid **5**, and acid **6**, respectively (Table 1/Entry 7). The predominating formation of the phosphonic ester-acid **5** is noteworthy. At 220 °C after 2 h, the composition was 37%, 58%, 5% for the fractions **1-3**, **4/5** and **6**, respectively

(Table 1/Entry 8). After a longer irradiation time of 3.75 h, only 29% of the ester-acids **4** and **5**, along with 71% of the diacid **6** formed the mixture (Table 1/Entry 9). It is worth noting that we worked under anhydrous conditions. One may see that it is possible to fine-tune the outcome of the reaction by selecting the appropriate IL, temperature and reaction time.

To summarize our findings, the phenylphosphonate (**1**) was converted to phosphonate **3** via intermediate **2**. However, intermediate **2** may be transformed to ester-acids **4** and **5**, while ester **3** to ester-acid **5**. Further alkoxy fission of ester-acids **4** and **5** afforded phosphonic acid **6**. The fission of the alkoxy group of the phosphonic derivative (**2**, **4**, or **5**) may be caused by the attack of the BF₄[−], PF₆[−], or HSO₄[−] anion of the IL. The formed salt is converted to the acid (**4**, **5** or **6**) on workup. The dry “hydrolysis” is a known procedure [28]. Ester-acid **4** may also be formed directly from the starting phosphonate (**1**) (Scheme 1).



Scheme 1. Possible routes for the formation of the intermediates/products

In order to simplify the previous reaction leading to the mixture of five products, we wished to focus only on the fission of the alkoxy group(s); therefore, the next experiments were carried out in

Table 1. The alcoholysis of diethyl phenylphosphonate (**1**) with butanol accompanied by dealkylation in the presence of ionic liquids.

Entry	IL	T (°C)	t (h)	Composition (%) ^{a,b}					
				1	2	3	4	5	6
				M + H = 215 ^c	M + H = 243 ^c	M + H = 271 ^c	M + H = 187 ^c	M + H = 215 ^c	M + H = 159 ^c
1	-	200	2	100 ^a	0			0	0
2	[bmim][BF ₄]	200	3.5	39 ^a			55 ^a		
3	[bmim][BF ₄]	220	2 ^d	0	8 ^b	19 ^b	3 ^b	56 ^b	14 ^b
4	[bmim][PF ₆]	200	2	0	16 ^b	22 ^b	43 ^b	11 ^b	8 ^b
5	[bmim][PF ₆]	200	3.5	27			61		
6	[emim][HSO ₄]	200	2	38 ^b	4 ^b	1 ^b	5 ^b	46 ^b	6 ^b
7	[emim][HSO ₄]	200	3.5	14 ^b	6 ^b	3 ^b	0	66 ^b	11 ^b
8	[emim][HSO ₄]	220	2	37			58		
9	[emim][HSO ₄]	220	3.75	0			29		

^a On the basis of relative ^{31}P NMR integrals

^b On the basis of combined ^{31}P NMR and LC-MS analysis

^c Confirmed by LC-MS

^d Practically, there was no change after further irradiation (Σ 3.5 h)

the alcohol having an identical alkyl group as the phosphonate. In the first series of experiments, diethyl phenylphosphonate (**1**) was irradiated at 160 °C in ethanol in the presence of 10% of [bmim][BF₄] and [emim][HSO₄] (Table 2/Entries 1 and 2). In the first case, there was no reaction, however, the second run took place in a conversion of 42%, furnishing PhP(O)(OEt)(OH) (**4**) and PhP(O)(OH)₂ (**6**) in 38% and 4%, respectively. After a prolonged reaction time of 6 h, there was only a little increase in the conversion (49%) (Table 2/Entry 3). It can be concluded that the PhP(O)(OEt)₂/EtOH model is not suitable due to the limit in the temperature that is the consequence of the volatility of ethanol.

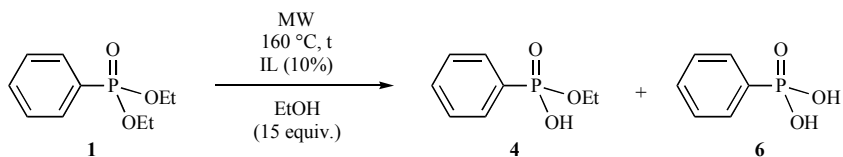
The PhP(O)(OBu)₂/BuOH system allowed a higher temperature of 200 °C. However, using [bmim][BF₄], there was again no reaction after an irradiation time of 2 h (Table 3/Entry 1). [Emim][HSO₄] was again more efficient as an additive after a reaction time of 2 and 2.5 h (Table 3/Entries 2 and 3). After running the reaction for 3.5 h, no starting material remained in the mixture, and the proportion of the monoacid (**5**) and diacid (**6**) was 37% and 63%, respectively (Table 3/Entry 4).

There is also a possibility that ester-acids **4** and **5**, as well as diacid **6** are also formed in the presence of [bmim][BF₄]/EtOH or BuOH, but under the conditions of 160/200 °C, species **4-6** are esterified back. Earlier studies revealed that [bmim][BF₄] was the best additive for direct esterification [5].

The above experiments were carried out under anhydrous conditions. The following question emerged: what would happen if the reactions were performed in the presence of a small amount of water. Hence, dibutyl phenylphosphonate **3** was irradiated in the presence of 10% IL and 1 equivalent of water at 200 °C for 2 h. The fission of the hydroxy groups was inhibited, as only 24% of ester-acid **5** and 8% of diacid **6** were formed (Table 3, footnote “c” to Entry 2). This proves that no hydrolysis is involved.

In the next stage, the fission of dialkyl phenylphosphonates was attempted in a solvent-free manner. The results obtained in the experiments with diethyl phenylphosphonate **1** are shown in Table 4. Applying 10% of [bmim][BF₄] at 200 °C for 3.5 h, the conversion was only 30% (Table 4/Entry 1). Irradiation at 220 °C for 4 h allowed the conversion of 79% with a 21-58% ratio of the ester-acid (**4**) and diacid (**6**) (Table 4/Entry 2). After a 6.5 h reaction time, the conversion was complete, and the mixture contained 27% of the ester-acid (**4**) and 73% of the diacid (**6**) (Table 4/Entry 3). The use of [emim][HSO₄] as an additive was more efficient. After a treatment at 200 °C for 2 h, the composition of the mixture was 19% (**1**), 36% (**4**), and 45% (**6**) (Table 4/Entry 4). Following a 5 h reaction time, there was no starting material (**1**) in the mixture that contained 13% of ester-acid **4** and 87% of diacid **6** (Table 4/Entry 5). Increasing the temperature to 220 °C, but decreasing the reaction time to 1.5 h and 4.5 h, the compositions were comparable with the previous variations. Entry 4 to 6, and entry 5 to 7 in Table 4 are to

Table 2. The reaction of diethyl phenylphosphonate (**1**) with ionic liquids in ethanol.

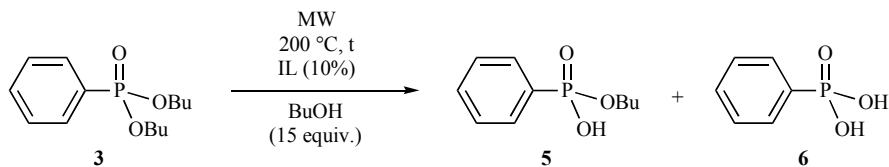


Entry	IL	t (h)	Composition (%) ^a		
			1 M + H = 215 ^b	4 M + H = 187 ^b	6 M + H = 159 ^b
1	[bmim][BF ₄]	3.5	100	0	0
2	[emim][HSO ₄]	3.5	58	38	4
3	[emim][HSO ₄]	6	51	44	5

^a On the basis of relative ³¹P NMR integrals

^b Confirmed by LC-MS

Table 3. The transformation of dibutyl phenylphosphonate (**3**) with ionic liquids in butanol.

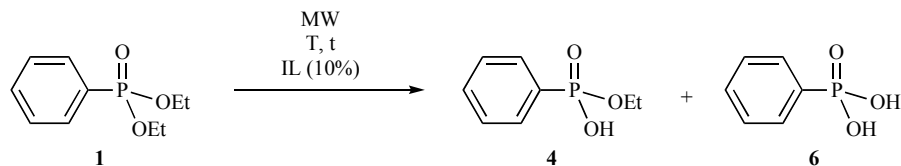


Entry	IL	T(°C)	t (h)	Composition (%) ^a		
				3 M + H = 271 ^b	5 M + H = 215 ^b	6 M + H = 159 ^b
1	[bmim][BF ₄]	200	2	100	0	0
2 ^c	[emim][HSO ₄]	200	2	12	53	36
3	[emim][HSO ₄]	200	2.5	4	40	56
4	[emim][HSO ₄]	200	3.5	0	37	63

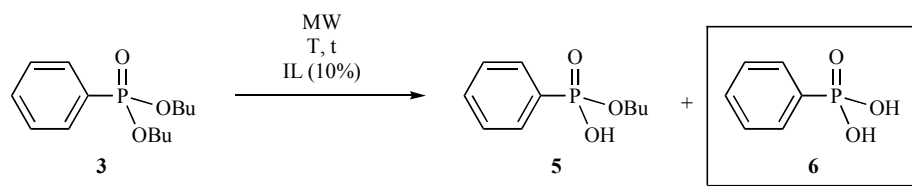
^a On the basis of relative ³¹P NMR integrals

^b Confirmed by LC-MS

^c Performing the reaction in the presence of 1 equiv. of water, the mixture contained 68% of **3**, 24% of **5** and 8% of **6**.

Table 4. The dealkylation of diethyl phenylphosphonate (**1**) with ionic liquids in the absence of solvent.

Entry	IL	T (°C)	t (h)	Composition (%) ^a		
				1 M + H = 215 ^b	4 M + H = 187 ^b	6 M + H = 159 ^b
1	[bmim][BF ₄]	200	3.5	70	24	5
2	[bmim][BF ₄]	220	4	21	21	58
3	[bmim][BF ₄]	220	6.5	0	27	73
4	[emim][HSO ₄]	200	2	19	36	45
5	[emim][HSO ₄]	200	5	0	13	87
6	[emim][HSO ₄]	220	1.5	15	26	59
7	[emim][HSO ₄]	220	4.5	0	20	80

^a On the basis of relative ³¹P NMR integrals^b Confirmed by LC-MS**Table 5.** The dealkylation of dibutyl phenylphosphonate (**3**) with ionic liquids in the absence of solvent.

Entry	IL	T (°C)	t (h)	Composition (%) ^a		
				3 M + H = 271 ^b	5 M + H = 215 ^b	6 M + H = 159 ^b
1	[bmim][BF ₄]	200	2	92	8	0
2	[bmim][BF ₄]	200	3.5	40	50	10
3	[bmim][BF ₄]	220	4	7	21	72
5	[bmim][BF ₄]	220	7	2	9	89
6 ^c	[emim][HSO ₄]	200	2	13	22	65
7	[emim][HSO ₄]	200	4	0	3	97

^a On the basis of relative ³¹P NMR integrals^b Confirmed by LC-MS^c Performing the reaction in the presence of 30% of the IL, the composition was 9% of **3**, 3% of **5** and 88% of **6**.

be compared. The double fission of the -P(O)(OEt)₂ moiety of ester **1** to afford the diacid (**6**) took place in a selectivity of 80-87%.

Dibutyl phenylphosphonate **3** was also subjected to MW irradiation in the presence of different ILs in the absence of any solvent. The experimental data were summarized in Table 5. The irradiation of PhP(O)(OBu)₂ at 200 °C for 2 h in the presence of 10% of [bmim][BF₄] took place in only a low conversion, affording 8% of the ester-acid **5** (Table 5/Entry 1). However, after a 3.5 h heating, the conversion was 60%, indicating the presence of 50% of the ester-acid **5** and 10% of the acid (**6**) (Table 5/Entry 2). The treatment at 220 °C for 4 h resulted in a mixture of 7% (**3**), 21% (**5**), 72% (**6**) (Table 5/Entry 3). After a 7 h reaction time, the conversion was almost complete leading to a mixture containing only 9% of the ester-acid (**5**), along with 89% of diacid **6** (Table 5/Entry 5). Applying [emim][HSO₄], the fissions were again more efficient. After the

treatment at 200 °C for 2 h, the relative quantity of species **3**, **5** and **6** was 13%, 22% and 65%, respectively (Table 5/Entry 6). An irradiation of 4 h led practically selectively to the diacid (**6**) (Table 5/Entry 7). The conversions took place in the absence of water, even traces of water could not be present. After purification, phenylphosphonic acid (**6**) was obtained in a yield of 82%. Combination of the shorter reaction time of 2 h with a larger amount (30%) of the IL, catalyst led to the formation of phosphonic acid **6** in 88% (Table 5/footnote “c” to Entry 6). The latter experiments exemplify a novel conversion of a phosphonate to phosphonic acid. [Emim][HSO₄] proved to be more efficient than [bmim][BF₄].

Finally, the mixture of dibutyl phenylphosphonate (**3**), 15 equivalents of *n*-pentanol and 10% of [bmim][BF₄] was irradiated at 220 °C in the hope of attaining a more selective reaction. After 2 h, the fraction of diesters represented 7% of **3**, 11% of **7** and 30% of

Table 6. The alcoholysis of dibutyl phenylphosphonate (**3**) with pentanol in the presence of ionic liquids in the absence of solvent.

Entry	t (h)	Composition (%) ^a					
		3 M + H = 271 ^b	7 M + H = 285 ^b	8 M + H = 299 ^b	5 M + H = 215 ^b	9 M + H = 229 ^b	6 M + H = 159 ^b
1	2	7	11	30	0	52	0
2	4.5	0	5	31	1	57	6

^a On the basis of combined ³¹P NMR and LC-MS analysis^b Confirmed by LC-MS

8, while among the ester-acids **5** and **9**, only the latter (**9**) was present in 52% (Table 6/Entry 1). Following a reaction time of 4.5 h, the starting ester (**3**) disappeared from the mixture. The esters formed by alcoholysis (**7** and **8**) were present in a portion of 5% and 31%, respectively. Ester-acid **9** was formed with a noteworthy selectivity of 57% along with 6% of diacid **6** (Table 6/Entry 2). The monopentyl ester (PhP(O)(OPent)(OH)) (**9**) was prepared in a yield of 38% (Supplementary Material).

3. EXPERIMENTAL

3.1. General

The ³¹P, ¹³C, ¹H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7 and 500 MHz, respectively. The couplings are given in Hz. HPLC-MS measurements were performed using a Shimadzu LCMS-2020 device equipped with a Reprospher 100 C18 (5 mm; 100 × 3 mm) column and positive-negative double ion source (DUIS) with a quadrupole MS analyzer in a range of 50-1000 m/z. The sample was eluted with gradient elution using eluent A (0.1% formic acid in water: acetonitrile 19: 1) and eluent B (0.1% formic acid in water: acetonitrile 1: 19). The flow rate was set to 1 mL min⁻¹. The initial condition was 0% B eluent, followed by a linear gradient to 100% B eluent by 1 min; from 1 to 3.5 min 100% B eluent was retained and from 3.5 to 4.5 min, back to the initial condition with 5% B eluent and retained to 5 min. The column temperature was kept at room temperature. High resolution mass spectrometric measurements were performed using a Waters Q-TOF Premier hybrid mass spectrometer in positive electrospray mode (Waters, Manchester, UK).

The experiments were carried out under anhydrous conditions. Unopened original bottles of the two IL-s were used. According to the supplier, the water content of the IL-s that we used in only microliters was 0.5-1%. To check the situation, we heated the samples of IL-s at 80 °C under vacuum, but no measureable weight losses were experienced. The MW experiments were carried out in close vials.

3.2. Use of the ³¹P NMR Spectra in Quantitative Analysis

The composition of the reaction mixtures was determined on the basis of the relative ³¹P NMR integrals of the signals of the starting material and products.

3.3. General Procedure for the Attempted Alcoholysis of Diethyl Phenylphosphonate (**1**) with Butanol in the Presence of Ionic Liquids

To 0.50 mmol (0.10 g) of diethyl phenylphosphonate (**1**), 0.64 mL (7.0 mmol) of butanol and 0.050 mmol (10 μl [bmim][PF₆], 7 μl [emim][HSO₄], 9 μl [bmim][BF₄]) of ionic liquid were added. The mixture was irradiated in a CEM MW reactor at 200-220 °C for 2-3.5 h. After evaporation, the reaction mixture was analyzed by ³¹P NMR spectroscopy and LC-MS. The results are shown in Table 1. The crude mixture obtained from the experiment marked by entry 7 of Table 1 was subjected to column chromatography (silica gel, DCM-MeOH 97:3) to afford ester-acid **5** in a yield of 22%.

3.3.1. Monobutyl Phenylphosphonate (**5**)

³¹P NMR: see Table 7; ¹³C NMR (CDCl₃) δ: 13.6 (s, CH₃), 18.7 (s, CH₂), 32.3 (d, *J* = 6.8, CH₂), 65.6 (d, *J* = 5.8, OCH₂), 128.3 (d, *J* = 15.2, C₃), 129.2 (d, *J*_{P,C} = 193.4, C₁), 131.4 (d, *J* = 10.1, C₂), 132.1 (d, *J* = 3.0, C₄); ¹H NMR (CDCl₃) δ: 0.84 (t, *J* = 7.6, 3H, CH₃), 1.33 (m, 2H, 2 CH₂), 1.58 (m, 2H, CH₂), 3.97 (q, *J* = 6.8, 2H, OCH₂), 7.37 - 7.47 (m, 3H, Ar), 7.78 - 7.85 (m, 2H, Ar), 12.56 (s, 1H, OH)

3.4. General Procedure for the Reaction of Diethyl Phenylphosphonates (**1**) in the Presence of Ionic Liquids and Ethanol

0.50 mmol (0.10 g) of diethyl phenylphosphonate (**1**) was added to 0.41 mL (7.0 mmol) of ethanol and 0.050 mmol 7 μl [emim][HSO₄], 9 μl [bmim][BF₄] of ionic liquid. The mixture was irradiated in a CEM MW reactor at 160 °C for 3.5 h. After evaporation, the reaction mixture was analyzed by ³¹P NMR spectroscopy. The results are shown in Table 2.

3.5. General Procedure for the Transformation of Dibutyl Phenylphosphonates (**3**) in the Presence of Ionic Liquids and Butanol

To 0.50 mmol (0.13 g), of dibutyl phenylphosphonate (**3**) 0.64 mL (7.0 mmol) of butanol and 0.050 mmol (7 μl [emim][HSO₄], 9 μl [bmim][BF₄]) of ionic liquid were added. The mixture was irradiated in a CEM MW reactor at 200 °C for 2-2.5 h. After evaporation, the reaction mixture was analyzed by ³¹P NMR spectroscopy. The results are shown in Table 3.

Table 7. ^{31}P NMR and HRMS characterization of dialkyl phenylphosphonates (**1** - **3**, **7** and **8**), monoesters (**4**, **5** and **9**) and phenylphosphonic acid (**6**).

Compounds		δ ^{31}P NMR		HRMS	
		Found	Literature	M + H _{found}	M + H _{calculated}
Esters	1	18.0 (DMSO)	18.8 [25] (CDCl ₃)	215.0842	215.0837
	2	18.0 (DMSO)	17.7 [29] (CDCl ₃)	265.0968*	265.0970*
	3	18.0 (DMSO)	18.8 [30] (CDCl ₃)	293.1278*	293.1283*
	7	17.9 (DMSO)	-	285.1631	285.1620
	8	17.9 (DMSO)	18.9 [30] (CDCl ₃)	299.1781	299.1776
Monoesters	4	15.1 (DMSO)	15.0 [25] (DMSO)	187.0527	187.0524
	5	14.9 (DMSO); 18.8 (CDCl ₃)	20.5 [29] (CDCl ₃)	215.0841	215.0837
	9	14.6 (DMSO); 19.8 (CDCl ₃)	22.2 [30] (CDCl ₃)	229.0996	229.0994
Acid	6	13.2 (DMSO)	13.0 [25] (DMSO)	159.0209	159.0211

*Identified as M + Na

3.6. General Procedure for the Dealkylation of Dialkyl phenylphosphonates (**1**, **3**) in the Presence of Ionic Liquids in the Absence of Solvent

A mixture of 0.50 mmol of dialkyl phenylphosphonate (**1**: 0.10 g, **3**: 0.13 g), and 0.050 mmol (7 μL [emim][HSO₄], 9 μL [bmim][BF₄]) was stirred under MW conditions (max 150 W) at 200–220 °C for 2–4 h. The reaction mixture was analyzed by ^{31}P NMR spectroscopy. The results are shown in Tables 4 and 5. Diacid **6** was obtained from the experiment, marked by Table 5/Entry 7, by filtration and washing with 2 x 0.5 mL of acetone in a yield of 82%.

3.6.1. Phenylphosphonic Acid (**6**)

^{31}P NMR: see Table 7; ^{13}C NMR (DMSO-*d*₆) δ : 128.6 (d, *J* = 14.2, C₃), 131.0 (d, *J* = 9.9, C₂), 131.4 (d, *J* = 3.0, C₄), 134.3 (d, *J*_{P,C} = 181.9, C₁); ^1H NMR (DMSO-*d*₆) δ : 7.41 – 7.54 (m, 3H, Ar), 7.66 – 7.73 (m, 2H, Ar), 9.60 (s, 2H, 2 OH).

3.7. General Procedure for the Alcoholysis of Dibutyl Phenylphosphonate (**3**) with Pentanol in the Presence of Ionic Liquids in the Absence of Solvent

To 0.40 mmol (0.10 g), of dibutyl phenylphosphonate (**3**) 0.60 mL (5.6 mmol) of pentanol and 0.040 mmol (7.5 μL) of [bmim][PF₆] were added. The mixture was irradiated in a CEM MW reactor at 220 °C for 2 h. After evaporation, the reaction mixture was analyzed by ^{31}P NMR spectroscopy and LC-MS. The results are shown in Table 6. Ester-acid **9** was obtained from the experiment, marked by Table 6/Entry 2 by column chromatography (silica gel, DCM - MeOH 97 : 3) in a yield of 38%.

3.7.1. Monopentyl Phenylphosphonate (**9**)

^{31}P NMR: see Table 7; ^{13}C NMR (CDCl₃) δ : 14.0 (s, CH₃), 22.2 (s, CH₂), 27.6 (s, CH₂), 30.0 (d, *J* = 6.7, CH₂), 66.0 (d, *J* = 6.0,

OCH₂), 128.3 (d, *J* = 15.2, C₃), 129.0 (d, *J*_{P,C} = 193.8, C₁), 131.4 (d, *J* = 10.2, C₂), 132.1 (d, *J* = 2.9, C₄); ^1H NMR (CDCl₃) δ : 0.88 (t, *J* = 6.7, 3H, CH₃), 1.30 (m, 4H, 2CH₂), 1.65 (m, 2H, CH₂), 4.00 (q, *J* = 6.8, 2H, OCH₂), 7.39 – 7.55 (m, 3H, Ar), 7.79 – 7.86 (m, 2H, Ar), 12.69 (s, 1H, OH).

Identification of the starting materials (**1** and **3**) and products (**2**–**9**) can be found in Table 7.

CONCLUSIONS

In summary, the alcoholysis of dialkyl phenylphosphonates could not be performed neatly. However, in the presence of 10% of [emim][HSO₄], the ester-acid formed after transesterification and mono fission of the phosphonate function was the major component. A similar reaction in the absence of alcohol could be fine-tuned to afford the phenylphosphonic diacid in a selective way. The partial or complete fission of the phosphonate moiety in the presence of suitable ionic liquids under dry conditions represents a novel transformation that is an alternative to hydrolysis.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data supporting the findings of the article is available within the article and supplementary material which is available on publishers website.

FUNDING

The research was supported by the National Research, Development and Innovation Office (K134318). N.Z.K. is grateful for the János Bolyai Research Scholarship of the Hungarian Academy of

Sciences (BO/00130/19/7) and New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund (ÚNKP-20-5-BME-329).

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

Declared none.

SUPPLEMENTARY MATERIAL

Supplementary Material contains ^{31}P , ^{13}C and ^1H NMR spectra for compounds **5**, **6** and **9**, as well as ^{31}P NMR and LC-MS spectra for a few representative mixtures.

Supplementary material is available on the publisher's website along with the published article.

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