Research Article

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MW-assisted hydrolysis of phosphinates in the presence of PTSA as the catalyst, and as a MW absorber

Abstract: The hydrolysis of phosphinic esters is an important transformation that may be performed under acidic or basic conditions on conventional heating. A series of cyclic phosphinates, 1-alkoxy-3-methyl or 3,4-dimethyl-phospholane oxides, has now been hydrolyzed under microwave (MW) conditions in the presence of 0.1 or 0.5 equivalents of p-toluenesulfonic acid that served not only as the catalyst but also as a MW absorber. The later phenomenon was proved separately. The pseudo-first-order rate constants for the hydrolyses performed by the new approach were determined and a reactivity order was setup. The model reactions investigated were transplanted into flow MW accomplishment.

Keywords: phosphinate derivatives, acidic hydrolysis, MW absorber, kinetics, flow accomplishment

1 Introduction

Change of the P-function, such as esterification of P-acids, is an often-emerging task during organic syntheses [1]. Hydrolysis of P-esters, as the opposite direction, is also a typical transformation [2,3] performed, in most cases, under acidic conditions [4–9] and in other cases applying base catalysts [10–13]. Among the acid catalyst, hydrochloric acid is the most often applied agent [4–7]. However, in most cases, the hydrolyses remained un-optimized, applying the acid or base in excessive quantities and allowing too long reaction times. We rationalized and optimized the HCl-catalyzed hydrolysis of cyclic and acyclic phosphinates [14,15], as well as phosphonates [16,17] in term of catalyst quantity and reaction time. The two-step transformation of phosphonates deserved special attention.

There are only a few cases when microwave (MW) irradiation was utilized in hydrolyses. Czech authors elaborated the MW-promoted HCl-catalyzed hydrolysis of acyclic nucleoside phosphate diesters at 130–140°C [18]. During our studies on acidic hydrolyses, we described the MW-assisted hydrolysis of 1-methoxy and 1-ethoxy-3-methyl-3-phospholene oxide [14] and that of alkyl diphenylphosphinates [15]. In both cases, p-toluenesulfonic acid (PTSA) was the catalyst to avoid corrosion problems of the MW reactor caused by HCl. Now we wished to revisit this problem for two reasons: (1) to study the MW absorbing effect of the PTSA additive as a dipolar agent (in the sense that it is an acid that can be dissociated [deprotonated] or protonated) and (2) to elaborate a MW-assisted flow chemical variation. Our earlier experience showed that dipolar additives, such as quaternary ammonium and phosphonium salts, may promote MW reactions [19]. Alloying the two aims means a novel kind of accomplishment for MW-enhanced hydrolysis. To realize our proposes, we wished to study the acidic hydrolysis of a series of 1-alkoxyphospholane oxides as a new model.

2 Materials and methods

2.1 General

The $^{31}$P NMR spectra were taken on a Bruker DRX-500 spectrometer (Bruker Corporation, Billerica, Massachusetts, USA) operating at 202.4, 125.7, and 500 MHz, respectively. LC–MS measurements were performed with an Agilent 1200 liquid chromatography system coupled with a 6130 quadrupole mass spectrometer.
mass spectrometer equipped with an ESI ion source (Agilent Technologies, Palo Alto, CA, USA).

The starting phosphinates (1a, 1b, and 3) were prepared as described earlier [20]. PTSA (≥99%) was purchased from Sigma Aldrich.

2.2 General procedure for the acidic hydrolysis of 1-alkoxy-3-methylphospholane oxide (1a/b) and 1-methoxy-3,4-dimethylphospholane oxide (3) under MW conditions

A mixture of 0.68 mmol of phosphinates (1a: 0.10 g, 1b: 0.11 g, and 3: 0.11 g), 0.06 g or 0.01 g (0.35 or 0.07 mmol) of PTSA, and 1.0 mL of water was irradiated in a sealed tube placed in CEM MW reactor at 160–180°C (100 W) for 0.5–5 h. After evaporating the water, the residue so obtained was taken up in 10 mL of dichloromethane, and then washed 3× with 3 mL of water, and dried (Na₂SO₄). The product was analyzed by ³¹P NMR spectroscopy.

2.3 General procedure for the continuous flow hydrolysis of 1-alkoxy-3-methylphospholane oxide (1a/1b) and 1-methoxy-3,4-dimethylphospholane oxide (3)

A mixture of 21.0 mmol of the starting phosphate (1a: 3.0 g, 1b: 3.3 g, and 3: 3.3 g), 1.80 g of PTSA (10.5 mmol), and 30 mL of water was homogenized by stirring for 5 min at 25°C. The reactor was flushed with 20 mL of the mixture with a flow rate of 10 mL·min⁻¹ at 25°C and 17 bar. Then, the flow rate was set to 0.15 mL·min⁻¹, and the system was irradiated at 160°C for 2 h after an instationary stage of 1 h. Excess of the water of the collected fraction was removed under reduced pressure, and the residue so obtained was taken up in 30 mL of dichloromethane and then washed with 2×5 mL of water. The product obtained after drying (Na₂SO₄) and evaporating the solvent was analyzed by ³¹P NMR spectroscopy.

³¹P NMR and MS data of the starting materials (1a, 1b, and 3), and products (2 and 4) can be found in Table 1.

2.4 Use of the ³¹P NMR spectra in quantitative analysis

Composition of the reaction mixture was determined by the integration of the areas under the corresponding peaks of the starting material and product in the ³¹P NMR spectra.

2.5 Curve fitting on the time – relative quantity data pairs

The acidic hydrolysers were modeled assuming pseudo-first-order kinetics. The concentration of water and PTSA was constant during the reaction. The calculated time – composition curves were fitted on the experimental data using nonlinear least-squares method. The pseudo-first-order rate constants were optimized that the sum of squares of the residuals (i.e., the difference of the experimental and the calculated composition) to be the minimal. The approximate values of the rate constants were found iteratively, using the nonlinear generalized reduced gradient method of Microsoft Excel Solver.

3 Results and discussion

Before the synthetic work, we studied how water absorbs heat in the absence and presence of PTSA. Figure 1 shows how different amounts absorb MW: (a) 0 mg of PTSA in 3 mL of water, (b) 18 mg of PTSA in 3 mL of water, (c) 36 mg of PTSA in 3 mL of water, (d) 180 mg of PTSA in 3 mL of water, and (e) 360 mg of PTSA in 3 mL of water. Applying an irradiation of 20 W, depending on the quantity of PTSA, the temperature increased from 122°C to 152–180°C. The additive had a significant effect on the warming of the solution via its MW absorbing ability. However, it was surprising that the increase in the temperature was the highest in the presence of the less

Table 1: Characterization of cyclic phosphinates (1a, 1b, and 3) and phosphinic acids (2, 4)

| Compounds | δ ³¹P NMR | [M + H]⁺⁺ |
|-----------|-----------|-----------|
| 1a        | 81.3 (broad) | 81.1 [20] | 149 |
| 1b        | 79.0 (broad) | 79.4 [20] | 163 |
| 3         | Isomers: 74.9 | Isomers: 74.7 | 163 |
|           | 80.9       | 80.6      |       |
| 2         | 81.5       | 81.3 [20] |       |
| 3         | 80.1 (broad) | 80.2 [21] | 135 |
| 4         | Isomers: 73.3, | Isomers: 72.9, | 149 |
|           | 80.0       | 79.5 [21] |       |

*Obtained by LC-MS.
amount (18 mg per 3 mL) of PTSA. With the increasing amount of the PTSA additive \([b \rightarrow c \rightarrow d \rightarrow e]\) the warming somewhat decreased. It means that the concentration has an optimum regarding the maximum heat absorbing ability that is in our case is 6 mg·mL\(^{-1}\) or 0.034 mmol·mL\(^{-1}\). The small, but significant difference between cases “b” and “c” was confirmed by parallel measurements.

In our case, PTSA/H\(_2\)O mixtures of \(c = 0.07\) and 0.35 mmol·mL\(^{-1}\) corresponding to 0.1 and 0.5 equivalents, respectively, were applied in the MW-assisted hydrolyses in a volume of 1 mL for 0.68 mmol of the phosphinate.

The first model reaction was the hydrolysis of 1-methoxy-3-methylphospholane oxide (1a). The MW-assisted hydrolysis was carried out at 160°C in the presence of 0.5 equivalents of PTSA. Monitoring the transformation

### Table 2: Acidic hydrolysis of 1-methoxy-3-methylphospholane oxide (1a) under MW conditions

| Entry | Temperature (°C) | Heating | Time (h) | PTSA (equiv.) | Conversion (%) |
|-------|------------------|---------|----------|----------------|----------------|
| 1     | 160              | MW      | 0.25     | 0.5            | 28             |
| 2     | 160              | MW      | 0.5      | 0.5            | 55             |
| 3     | 160              | MW      | 1        | 0.5            | 85             |
| 4     | 160              | MW      | 2        | 0.5            | 90             |
| 5     | 160              | MW      | 3        | 0.5            | 93             |
| 6     | 160              | Δ       | 3        | 0.5            | 28             |
| 7     | 180              | MW      | 0.33     | 0.5            | 100*           |
| 8     | 180              | Δ       | 0.33     | 0.5            | 25             |
| 9     | 180              | MW      | 0.25     | 0.1            | 20             |
| 10    | 180              | MW      | 0.5      | 0.1            | 59             |
| 11    | 180              | MW      | 1        | 0.1            | 78             |
| 12    | 180              | MW      | 2        | 0.1            | 88             |
| 13    | 180              | MW      | 3        | 0.1            | 95             |

*Isolated yield: 94%.
by $^{31}$P NMR spectroscopy showed that the conversion was 93% after 3 h (Table 2, entries 1–5). Completion takes 3 h 15 min. Concentration profile of the components may be seen in Figure 2. The pseudo-first-order rate constant was 1.57 h$^{-1}$. In the comparative thermal experiment carried out at 160°C per 3 h, the conversion was only 28% (Table 2, entry 6). The hydrolysis was much faster at 180°C applying 0.5 equivalents of PTSA: complete conversion was attained after 20 min (Table 2, entry 7). In the comparative thermal experiment, the conversion was only 25% (Table 2, entry 8). Comparing the results of the MW-assisted and conventionally heated hydrolyses, one may conclude the significant difference. To be more eco-friendly, the hydrolysis of phosphinate 1a was also performed using only 0.1 equivalents of the catalyst and MW absorber at 180°C. In this case, again ca 3 h 10 min was the reaction time (Table 2, entries 9–13 and Figure 3) confirmed by a k value of 1.42 h$^{-1}$ similar to the previous one.

Then, we studied the PTSA-catalyzed hydrolysis of 1-ethoxy-3-methylphospholane oxide (1b) under similar conditions (Table 3). Using 0.5 equivalents of the catalyst at 160°C, the hydrolysis was complete after 5 h (Table 3, entry 7). The similar reaction at 180°C took place in a reaction time of 1.5 h (Table 3, entry 10). A decrease in the quantity of the additive to 0.1 equivalents had to be compensated by a reaction time of 5 h (Table 3, entry 11).

**Table 3:** Acidic hydrolysis of 1-ethoxy-3-methylphospholane oxide (1b)

| Entry | Temperature (°C) | Heating | Time (h) | PTSA (equiv.) | Conversion (%) |
|-------|------------------|---------|----------|--------------|----------------|
| 1     | 160              | MW      | 0.25     | 0.5          | 14             |
| 2     | 160              | MW      | 0.5      | 0.5          | 31             |
| 3     | 160              | MW      | 1        | 0.5          | 37             |
| 4     | 160              | MW      | 2        | 0.5          | 65             |
| 5     | 160              | MW      | 3        | 0.5          | 83             |
| 6     | 160              | MW      | 4        | 0.5          | 88             |
| 7     | 160              | MW      | 5        | 0.5          | 100*           |
| 8     | 160              | Δ       | 5        | 0.5          | 30             |
| 9     | 180              | MW      | 1        | 0.5          | 93             |
| 10    | 180              | MW      | 1.5      | 0.5          | 100            |
| 11    | 180              | MW      | 5        | 0.1          | 100            |

*Isolated yield: 96%.
One can see that the hydrolysis of the ethoxyphospholane oxide (1b) was significantly slower than that of the methoxy derivative (1a); otherwise, the tendencies were exactly the same.

Data of the kinetic study (Table 3, entries 1–7 and Figure 4) suggested a pseudo-first-order rate constant of 0.56 h⁻¹. The low conversion of 30% for the comparative thermal experiment (Table 3, entry 8) is again noteworthy. This may suggest a relatively high enthalpy of activation for the hydrolyses investigated, similarly to the direct esterifications [22].

The next model for the MW-assisted PTSA-catalyzed hydrolysis was 1-methoxy-3,4-dimethylphospholane oxide (3) comprising three diastereomers. The hydrolyzed product (4) consisted of two diastereomers. The experimental results are listed in Table 4. Completion of the hydrolysis at 160°C in the presence of 0.5 equivalents of catalyst required a somewhat longer reaction time than 4.5 h (Table 4, entry 7). At 180°C, the hydrolysis took place in 1.5 h (Table 4, entry 9). Decreasing the quantity of PTSA to 0.1 equivalents, complete conversion could be attained after 5.5 h (Table 4, entry 11). All results, including the pseudo-first-order rate constant of 0.58 h⁻¹ obtained at 160°C using 0.5 equivalents of the additive (Table 4, entry 1–7 and Figure 5) were rather similar to the data collected with the 1-ethoxy-3-methylphospholane oxide 1b that is not surprising if the substitution patterns are compared.

Then, we wished to realize the PTSA-catalyzed hydrolysis of an unsaturated P-cycle, 1-methoxy-3-methyl-3-phospholene oxide (5) under the above-applied conditions. However, it was found that under MW irradiation at 160°C for 1 h, or at 180°C for 1 h, in the presence of 0.5 equivalents of PTSA, decomposition took place, especially at 180°C (Scheme 1), and the expected phosphinic acid 6

Table 4: MW-assisted hydrolysis of the 1-methoxy-3,4-dimethylphospholane oxide

| Entry | Temperature (°C) | Time (h) | PTSA (equiv.) | Conversion (%) | Ratio of the diastereomers (%) |
|-------|------------------|----------|---------------|---------------|-------------------------------|
| 1     | 160              | 0.25     | 0.5           | 17            | 59:41                         |
| 2     | 160              | 0.5      | 0.5           | 21            | 86:14                         |
| 3     | 160              | 1        | 0.5           | 41            | 68:32                         |
| 4     | 160              | 2        | 0.5           | 71            | 70:30                         |
| 5     | 160              | 3        | 0.5           | 79            | 70:30                         |
| 6     | 160              | 4        | 0.5           | 93            | 70:30                         |
| 7     | 160              | 4.5      | 0.5           | 96            | 70:30                         |
| 8     | 180              | 1        | 0.5           | 88            | 70:30                         |
| 9     | 180              | 1.5      | 0.5           | 100*          | 67:33                         |
| 10    | 180              | 4        | 0.1           | 88            | 70:30                         |
| 11    | 180              | 5        | 0.1           | 93            | 70:30                         |

*Isolated yield: 91%.
formed after isomerization was only a minor by-product, along with 1,3-dihydroxy-4-methylphospholane oxide (7) formed by the addition of one molecule of water on the double bond (Scheme 1). Species 6 and 7 were identified by 31P NMR, LC-MS, and HRMS: 6: δp (DMSO) 69.7, δp [14] (CDCl3) 79.7, [M + H]+ = 133, [M + H]+[Found] = 133.0422, C9H12O3P requires 133.0418; 7: δp (DMSO) 43.3, [M + H]+ = 151, [M + H]+[Found] = 151.0526, C9H12O3P requires 151.0524. It is noted that according to our earlier examination, the 5 → 6 conversion took place neatly on irradiation at 140°C for 1 h in the presence of three equivalents of PTSA. In this case, phosphinic acid 6 was formed in 88%, along with 12% of the 1-hydroxy-3-methyl-3-phospholene oxide [14].

Only two other examples can be found in the literature for MW-assisted hydrolysis of P-esters. Earlier, we described the MW-promoted hydrolysis of a few phosphinates in the presence of three equivalents of PTSA at a lower temperature of 120–140°C [14]; however, this was not “green” due to the excess amount of the acid applied. However, the HCl-catalyzed hydrolysis of acyclic nucleoside phosphonate diesters was disclosed [18]; however, no data were provided on the possible corrosion problems. The method described in this study may be the superior protocol.

In the final stage of our study, we wished to utilize the results of the batch experiments in developing the MW flow variation. The equipment is shown in Figure 6, whereas the results were summarized in Table 5. In all experiments, a mixture containing 0.5 equivalents of PTSA was fed in the MW reactor at a flow rate of 0.15 mL·min⁻¹ at a temperature of 160°C. Regarding the hydrolysis of the methoxyphospholane oxide 1a, the conversion was 63%. Recycling the mixture collected from

![Figure 5](image-url)

**Figure 5:** Concentration profile for the components during the hydrolysis of methoxy-3,4-dimethylphospholane (3) at 160°C using 0.5 equivalents of PTSA. The R² measure of goodness of fit is 0.9758.

![Scheme 1](image-url)

**Scheme 1:** The inefficient hydrolysis of 1-methoxy-3-methyl-3-phospholene 1-oxide (5).

![Table 5](image-url)

**Table 5:** Continuous flow hydrolysis of saturated cyclic phosphinates (1a, 1b, and 3).

| Entry | R¹ | R² | Conversion (%) | Yield (%) |
|-------|-----|-----|----------------|-----------|
| 1     | Me  | H  | Round 1: 63   | —         |
|       |     |    | Round 2: 100  | 89 (2)    |
| 2     | Et  | H  | Round 1: 59   | —         |
|       |     |    | Round 2: 77   | —         |
|       |     |    | Round 3: 90   | 82 (2)    |
| 3     | Me  | Me | Round 1: 61   | —         |
|       |     |    | Round 2: 82   | —         |
|       |     |    | Round 3: 92   | 86 (4)    |

![Figure 6](image-url)

**Figure 6:** The flow MW equipment used for the hydrolysis of cyclic phosphinates (1a, 1b, and 3).
the first run, the conversion was complete (Table 5, entry 1). Based on our earlier results, it was obvious that the hydrolysis of the monomethyl P-ethoxy and the dimethyl P-methoxy models (1b and 3, respectively) led to similar results. However, there was a need for three runs due to the somewhat lower reactivity of these phosphinates (1b and 3). In the first round, the conversion was 59/61%, in the second run it was 77/82%, whereas in the third cycle 90/92% was reached (Table 5, entries 2 and 3). The phosphinic acids 2 and 4 were obtained in yields of 82–89%.

4 Conclusion

After proving the MW absorbing effect of PTSA in separate experiments, batch MW-assisted hydrolysis of a series of 1-alkoxyphospholane oxides was elaborated. Hence, PTSA had a double role serving also as the acid catalyst. The hydrolyses of the 1-methoxy- and ethoxy derivatives, as well as the 3-methyl- and 3,4-dimethyl model compounds were characterized by pseudo-first-order rate constants, and a reactivity order was set up. Finally, the hydrolyses were transplanted into a MW-assisted flow system allowing a more productive hydrolysis.

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Conflict of interest: The corresponding author (György Keglevich) is a member of the Editorial Board of Green Processing and Synthesis.

Supplementary material: $^{31}$P NMR spectra of the best experiments including those of the pure phosphinic acids. Representative LC-MS spectra were also included.

References

[1] Quin LD. A guide to organophosphorus chemistry. New York: Wiley; 2000.
[2] Virieux D, Volle J-N, Bakalara N, Pirat J-L. Synthesis and biological applications of phosphinates and derivatives. In: Montchamp JL, editor. Phosphorus chemistry I. Topics in current chemistry. Vol 360. Cham: Springer; 2014. p. 39–114. doi: 10.1007/128_2014_566.
[3] Harsági N, Keglevich G. The hydrolysis of phosphinates and phosphonates – a review. Molecules. 2021;26(10):2840. doi: 10.3390/molecules26102840.
[4] Gavande N, Yamamoto I, Salam NK, Al TH, Burden PM, Johnston GAR, et al. Novel cyclic phosphinic acids as GABA_C receptor antagonists: design, synthesis, and pharmacology. ACS Med Chem Lett. 2011;2(1):11–6. doi: 10.1021/ml1001344.
[5] Dennis EA, Westheimer FH. The rates of hydrolysis of esters of cyclic phosphonic acids. J Am Chem Soc. 1966;88(14):3431–2. doi: 10.1021/ja00966a045.
[6] Froestl W, Mickel SJ, von Sprecher G, Diel PJ, Hall RG, Maier L, et al. Phosphinic acid analogues of GABA. 2. Selective, orally active GABA_B antagonists. J Med Chem. 1995;38(17):3313–31. doi: 10.1021/jm00017a016.
[7] Wang Y, Wang Y, Yu J, Miao Z, Chen R. Stereoselective synthesis of α-aminophenyl)methyl)methyl)methylphosphonic acids with O-pivaloylated D-galactosamine as chiral auxiliary. Chem Eur J. 2009;15(37):9290–3. doi: 10.1002/chem.200901419.
[8] Reiter LA, Jones BP. Amide-assisted hydrolysis of β-carboxa-mido-substituted phosphonic acid esters metal ions, and appropriately substituted phosphinic responsible for promoting the cleavage of the phosphonic acid esters. J Org Chem. 1997;62(9):2808–12. doi: 10.1021/jo962275w.

9) Bunnell JF, Edwards JO, Wells DV, Brass HJ, Curci R. The hydrolysis of methyl methanlyphosphinates in perchloric acid solution. J Org Chem. 1973;38(15):2703–7. doi: 10.1021/jo00955a028.
[10] Cook RD, Diebert CE, Schwarz W, Turley PC, Haake P. Mechanism of nucleophilic displacement at phosphorus in the alkaline hydrolysis of phosphinate esters, J Am Chem Soc. 1973;95(24):8088–96. doi: 10.1021/ja00805a023.
[11] Clarke FB, Westheimer FH. Substituted 1-oxophosph PHONE. J Am Chem Soc. 1971;93(18):4541–5. doi: 10.1021/ja00747a034.
[12] Hong HJ, Lee J, Bae AR, Um IH. Kinetics and reaction mechanism for alkaline hydrolysis of Y-substituted-phenyl diphenylphosphinates. Bull Korean Chem Soc. 2013;34(7):2001–5. doi: 10.5012/bkcs.2013.34.7.2001.
[13] Cevasco G, Thea S. The Quest for carbanion-promoted disso-ciative pathways in the hydrolysis of ary phosphinates. J Chem Soc Perkin Trans. 1993;2(6):1103–6. doi: 10.1039/P29930001103.
[14] Keglevich G, Rádai Z, Harsági N, Szigetvári Á, Kiss NZ. A study on the acidic hydrolysis of cyclic phosphates: 1-Alkoxy-3-phospholene 1-oxides, 1-ethoxy-3-methylphospholene 1-oxide, and 1-ethoxy-3-methyl-1,2,3,4,5,6-hexamethylphosphinine 1-oxide. Heteroat Chem. 2017;28(5):e21394. doi: 10.1002/hc.21394.
[15] Harsági N, Szilősí B, Kiss NZ, Keglevich G. MW irradiation and ionic liquids as green tools in hydrolyses and alcoholyses. Green Process Synth. 2021;10(1):1–10. doi: 10.1515/gpss-2021-0001.
[16] Harsági N, Rádai Z, Kiss NZ, Szigetvári Á, Keglevich G. Two step acidic hydrolysis of dialkyl arylphosphonates. Mendeleev Commun. 2020;30(1):38–9. doi: 10.1016/j.mencom.2020.01.012.
[17] Harsági N, Rádai Z, Szigetvári Á, Kóti J, Keglevich G. Optimization and a kinetic study on the acidic hydrolysis of dialkyl α-hydroxybenzylphosphonates. Molecules. 2020;25(17):3793. doi: 10.3390/molecules25173793.

[18] Jansa P, Baszczyński O, Procházková E, Dračínský M, Janeba Z. Microwave-assisted hydrolysis of phosphonate diesters: an efficient protocol for the preparation of phosphonic acids. Green Chem. 2012;14(8):2282–8. doi: 10.1039/c2gc35547g.

[19] Hohmann E, Keglevich G, Greiner I. The effect of onium salt additives on the Diels-Alder reactions of a 1-phenyl-1,2-dihydrophosphine oxide under microwave conditions. Phosphorus Sulfur Silicon. 2007;182(10):2351–7. doi: 10.1080/10426500701441473.

[20] Jablonkai E, Henyecz R, Milen M, Kóti J, Keglevich G. T3P®-assisted esterification and amidation of phosphinic acids. Tetrahedron. 2014;70(44):8280–5. doi: 10.1016/j.tet.2014.09.021.

[21] Keglevich G, Bálint E, Kiss NZ, Jablonkai E, Hegedűs L, Grün A, et al. Microwave-assisted esterification of phosphinic acids. Curr Org Chem. 2011;15(11):1802–10. doi: 10.2174/138527211795656570.

[22] Keglevich G, Kiss NZ, Mucsi Z, Körtvélyesi T. Insights into a surprising reaction: The microwave-assisted direct esterification of phosphinic acids. Org Biomol Chem. 2012;10(10):2011–8. doi: 10.1039/C2OB06972E.