BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF CHEMICAL AND BIOENGINEERING
GEORGE OLAH DOCTORAL SCHOOL

THE SYNTHESIS OF PHOSPHINATES AND PHOSPHINIC AMIDES;

ENVIRONMENTALLY FRIENDLY APPROACHES

PhD Thesis

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1. Introduction

Green chemistry has become more and more important. According to the twelve principles of green chemistry,[1] synthetic methods should be designed to use and generate substances with little or no toxicity to human health and the environment, while maximizing the incorporation of all the materials used into the final product. Atom and energy efficiency, as well as sustainability are also important aspects. Unnecessary derivatizations should be minimized or avoided if possible, thus, the shortest reaction path should be chosen. In the context of green chemistry, microwave (MW)-assisted organic synthesis is a challenging field. Every minor contribution to these principles can make a difference.

I started my PhD work under the supervision of *Prof. György Keglevich* at the Budapest University of Technology and Economics, Department of Organic Chemistry and Technology. Our research group is engaged with environmentally friendly and organophosphorus chemistry, with a history of more than thirty years, performing reactions of industrial use and producing new, potentially bioactive organophosphorus compounds of fine chemical and pharmaceutical importance.

During my research work, the goal was to study transformations which cannot be carried out by conventional heating, yet could be accomplished by MW irradiation. In such cases, the MW technique enables us to omit harmful reagents by implementing solvent- and catalyst-free methods. I focused on the development of environmentally friendly synthetic methods for the preparation of phosphinic acid derivatives.

Another objective was to understand and interpret how microwaves promote organic reactions, as so-called "magic" effects are attributed frequently to MW chemistry, and the existing interpretations are highly debated.[2]

[1] Anastas, P. T.; Warner, J. C. O. *In Green Chemistry: Theory and Practice*; University Press: Oxford, **1998**.
[2] Kappe, C. O.; Pieber, B.; Dallinger, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 1088.

2. Literature

The classical method for the synthesis of phosphinic acid derivatives (esters or amides), involves the reaction of phosphinic chlorides with alcohols/phenols or amines, respectively. Despite its drawbacks in terms of environmentally friendly chemistry and costs, it is widely applied in the industry, since organophosphorus compounds find applications as agrochemicals and medicines. The Arbuzov reaction may also result in a wide range of phosphinates.

The direct derivatization of phosphinic acids could be a green approach, however, direct esterification and amidation are not possible on conventional heating. The alkylating esterification of phosphinic acids by alkyl halides is a realistic route to afford phosphinates and this protocol can be carried out under phase transfer catalytic (PTC) conditions.

Following another strategy, phosphinic acids can be converted to more active intermediates (for example by coupling reagents or the T3P® reagent) which then react with the *O*- and *N*-nucleophile more efficiently. Other methods, including the fragmentation-related phosphinylations can be found in the literature.

Although phosphinic derivatives are useful starting materials and intermediates utilized commonly in synthetic organic chemistry, the possibilities for their preparation have not been covered by any recent reviews.

3. Experimental methods

The MW-assisted reactions were carried out in a CEM Discover [300 W] microwave reactor equipped with a pressure controller.

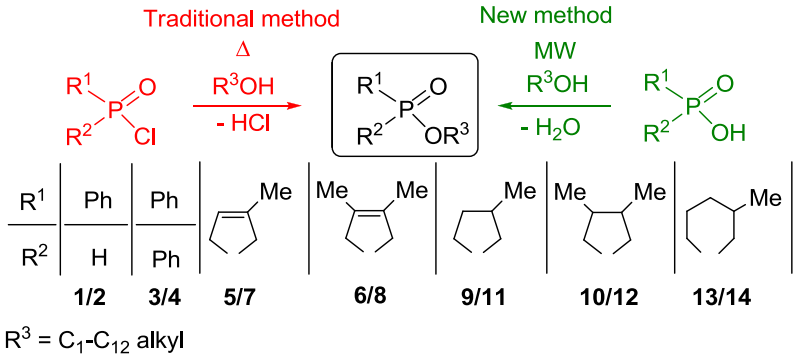
The crude reaction mixtures were analyzed by ^{31}P NMR spectroscopy. Purification of the products was carried out by flash column chromatography using silica gel. Purity of the compounds was checked by gas chromatography (GC). The compounds were identified by spectroscopic methods (^{31}P, ^{13}C and ^{1}H NMR, HRMS).

Quantum chemical investigations were carried out using the Gaussian09 program package (G09) by the B3LYP/6-31++G(d,p) and B3LYP/6-31G(d,p) methods.

4. New scientific results

4.1. Microwave-assisted direct esterification of phosphinic acids

However, phosphinic acids usually do not undergo direct esterification under conventional conditions, we observed that in case of MW irradiation at 160-235 °C, applying the alcohol in a 15-fold excess, the corresponding phosphinates can be obtained – in most cases – in ~60-100% conversion.



We have intensively studied and explored the optimal reaction conditions of the direct esterifications. The use of longer carbon atom chain, and hence less volatile alcohols, as the reagents proved to be more advantageous.

In some cases, comparative thermal experiments were performed under similar conditions and proved that the esterifications are indeed possible by MW irradiation.

Thus, we have developed an environmentally friendly method for the preparation of phosphinates that, depending on the model compound, can even be quantitative.

Applying this new method, nearly fifty phosphinates were prepared in the course of the direct esterification of phenylphosphinic acids (**1** and **3**) and cyclic phosphinic acids (**5**, **6**, **9**, **10** and **13**).

4.2. Energetics of the direct esterification

The energetics of the esterification of phosphinic acids was evaluated by B3LYP/6-31++G(d,p) calculations which showed that the esterification has a high activation barrier and the transformation is slightly endothermic (*Fig. 1*). We assume that the statistically occurring local overheating effect can overcome the barrier corresponding to the high values of the enthalpy of activation.

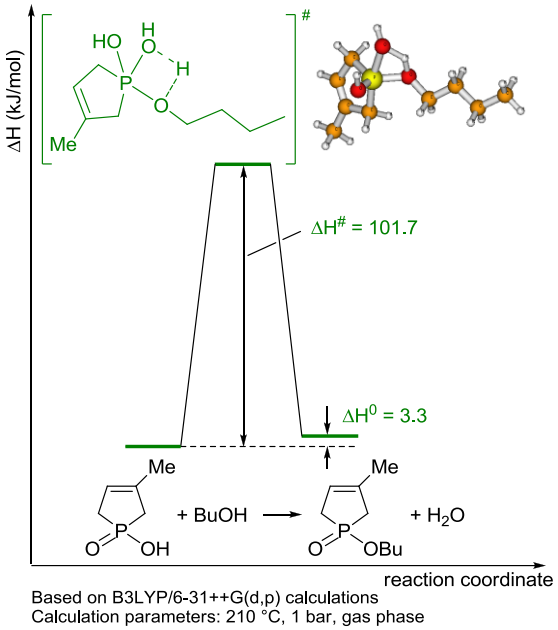
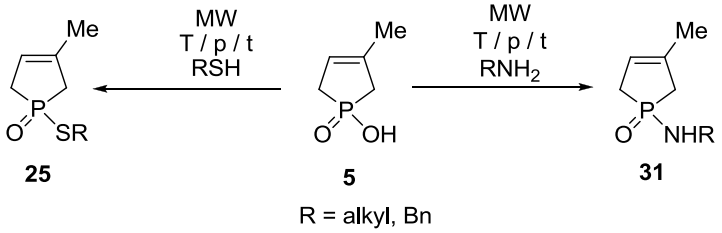


Fig. 1: The enthalpy profile of the esterification of 1-hydroxy-3-methyl-3-phospholene oxide with butyl alcohol

4.3. Direct thioesterification and amidation of phosphinic acids

The direct thioesterification of phosphinic acids was accomplished using thiols, and the derivatization was also extended to direct amidations. However, the synthesis of thiophosphinates and phosphinic amides was not efficient enough and led to conversions of only 33-50% due to the unfavourable endothermicity of these derivatizations, as suggested by quantum chemical calculations.



4.4. Comparison of the direct esterification, thioesterification and amidation

Our assumption was that the studied esterifications has a rather high enthalpy of activation and is almost thermoneutral. While the esterification of phosphinic acids is controlled kinetically, the amidations are governed by thermodynamic factors according to the rather high endothermicity (*Fig. 2*).

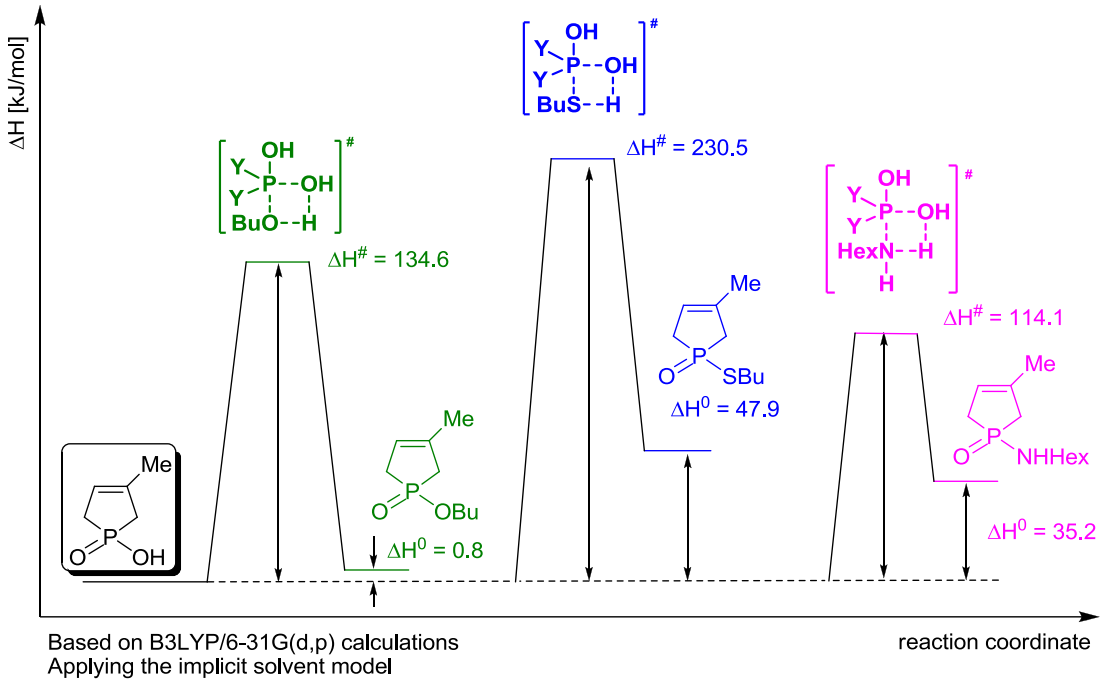


Fig. 2: Comparison of the enthalpy profiles

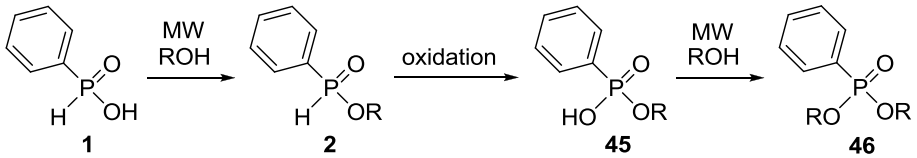
Comparing the experimental observations with the calculated energetics, we concluded that thermoneutral reactions having a high enthalpy of activation may be promoted efficiently by MW irradiation. Endothermicity works against the reaction and in such cases, the conversions will remain incomplete even under MW conditions.

The possible mechanism for the reactions concerned was also evaluated. Quantum chemical calculations corroborated the $A_{AC}2$ (phosphinylation) mechanism suggested by our experimental observations. It is a noteworthy finding that the discussed acylation reactions involve a four-membered ring transition state.

4.5. Direct esterification of phenylphosphonic derivatives

Phenyl-*H*-phosphinates (**2**) prepared by the MW-assisted direct esterification from phenyl-*H*-phosphinic acid (**1**) were oxidized to the corresponding phosphonic ester-acid derivatives (**45**).

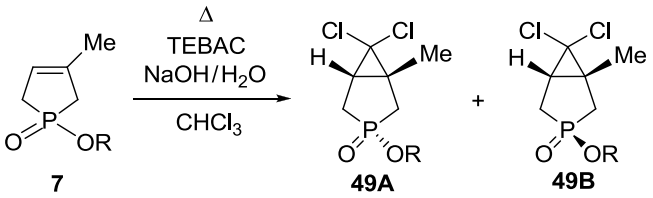
In the next step the compounds so obtained (**45**) could also be esterified by alcohols under MW conditions to furnish dialkyl phenylphosphonates.



This is the first example for the MW-assisted direct esterification of phosphonic acid derivatives.

4.6. The use of 1-alkoxy-phospholene oxides in ring enlargement

1-Alkoxy-3-phospholene 1-oxides (**7**), obtained directly from the corresponding phosphinic acid (**5**) by MW-assisted direct esterification, can be used in ring enlargement involving the addition of dichlorocarbene on the double-bond of the phospholene oxide (**7**). The longer carbon chain acting as an electron-donating group enhanced the reactivity and hence resulted in better yields. Based on this experience, an efficient one-step method has been developed for the dichlorocyclopropanation of lipophilic alkoxy-phospholene oxides.

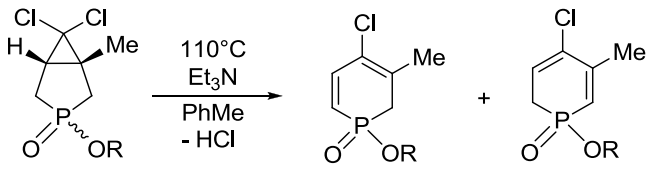


7 **49A** **49B**

R = 3-Pent (**e**), ^{i}Pent (**f**), ^{n}Oct (**g**), ^{i}Oct (**h**), Dodecyl (**i**)

Compound **49** was formed as a *ca.* 1:1 mixture of two diastereomers. In two cases (**49e** and **49f**), the crude mixtures were refined by repeated column chromatography to afford the separated isomers in a pure form.

In the next step, the 2-phosphabicyclo[3.1.0]hexane oxides (**49**) were subjected to thermal ring expansion to give 1,2-dihydrophosphinine oxides **50** as a 3:1 mixture of two isomers (**A** and **B**).



49 **50A** **50B**

R = 3-Pent (**e**), ^{i}Pent (**f**), ^{n}Oct (**g**), ^{i}Oct (**h**), Dodecyl (**i**)

1,2-Dihydrophosphinine oxides are versatile intermediates that can be utilized in the synthesis of other phosphinine derivatives.

The relative energetics of the two isomers of compounds **49** and **50** were evaluated by B3LYP/6-31G(d,p) calculations.

4.7. Reaction of phosphinic chlorides with amines

1-Alkylamino-3-phospholene oxides (**31** or **53**) can be obtained by the MW-assisted direct amidation of 1-hydroxy-3-phospholene 1-oxide (**5** or **6**) however, due to the low efficiency, a better choice for the preparation of these compounds is the reaction of the corresponding phosphinic chloride (**51** or **52**) with amines. We observed that the reaction with primary amines

resulted in a mixture of the corresponding 1-amino-3-phospholene 1-oxide (**31** or **53**) and its *N*-phosphinoyl derivative (**54** or **55**) as a by-product. Depending on the molar ratio of the reactants and on the order of mixing, the product composition could be influenced (fine-tuned) and either the *mono*- (blue), or the *bis*-product (red) could be obtained almost exclusively in high yields (*Fig. 3*).

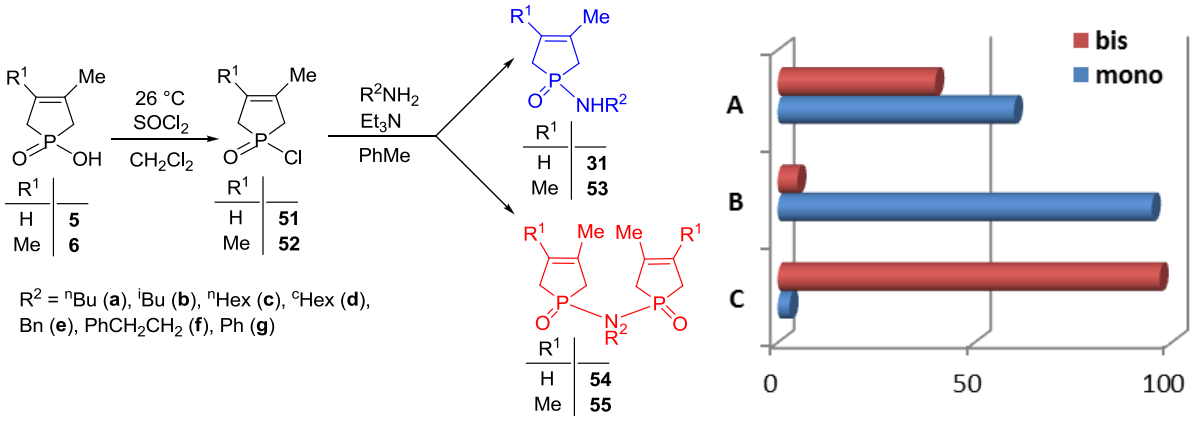
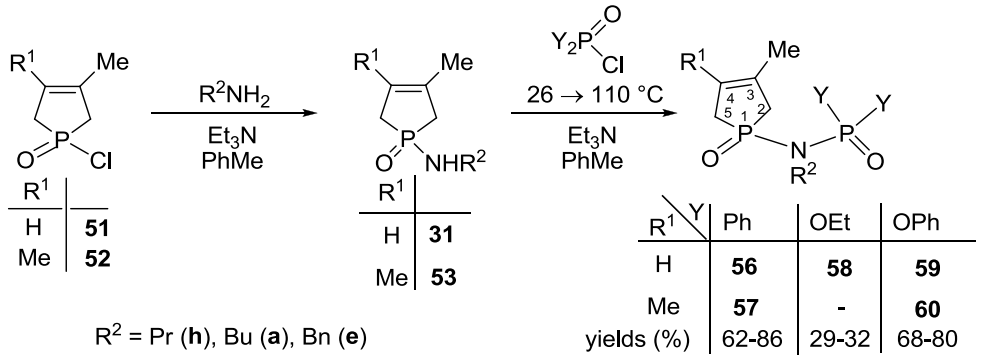


Fig. 3: Possible outcomes of the reaction of **51/52** with primary amines

Following the consecutive pathway 1-alkylamino-3-phospholene oxides (**31**/**53**) could be transformed into different bis(phosphinoyl)amines (**56** and **57**) or phosphinoyl-phosphorylamines (**58**–**60**) via phosphorylation reactions.



R1 \ Y	Ph	OEt	OPh
H	**56**	**58**	**59**
Me	**57**	-	**60**
yields (%)	62-86	29-32	68-80

The >P(O)NR(O)P< type “imides” form a new family of compounds.

5. Theses

1. We found a model reaction, namely the esterification of phosphinic acids that practically does not take place under conventional conditions yet can be carried out on MW irradiation. We developed a new method for the synthesis of phosphinates by the MW-assisted direct esterification. Applying this new method, various cyclic and acyclic phosphinic acids were subjected to direct esterification. We observed that the most suitable reaction partners are longer carbon atom chain (less volatile) alcohols that are sterically not too hindered. In some cases, comparative thermal experiments were performed under similar conditions proving that the esterifications are indeed made possible by the MW irradiation. [1,2,7]

2. On the basis of quantum chemical calculations, we demonstrated that the high activation barrier limits the direct esterification and that the statistically occurring local overheating effect can overcome the barrier corresponding to the high values of the enthalpy of activation. [3,8]

3. We explored the mechanism of the direct esterification of phosphinic acids. Quantum chemical calculations confirmed the A_{AC}^2 (phosphinylation) mechanism. We found that the rate-determining step of the acylation reactions under discussion involve a four-membered ring transition state. Similar transition states were found in the course of the esterification of carboxylic acids. [8]

4. We extended the method elaborated for the direct esterification of phosphinic acids to thioesterifications and direct amidations. However, the synthesis of thiophosphinates and phosphinic amides led to incomplete conversions of only 33-50%. We demonstrated that the unfavourable endothermicity of these derivatizations prevents the reactions to complete. [4,5]

5. Phenyl-*H*-phosphinates prepared by the MW-assisted direct esterification from phenyl-*H*-phosphinic acid were oxidized to the corresponding phosphonic ester-acid derivatives that could also be esterified by alcohols under MW conditions to furnish dialkyl phenylphosphonates. We implemented the first MW-assisted direct esterification of phosphonic acid derivatives. [9]

6. The lipophilic alkoxy-phospholene oxides obtained by the MW-assisted direct esterification were converted to 1,2-dihydrophosphinine oxides via a two-step ring enlargement reaction.

We have developed an efficient, one-step method for the dichlorocyclopropanation step involved. [10]

7. The efficient synthesis of 1-alkylamino-3-phospholene oxides involved the reaction of phosphinic-chlorides with primary amines. We observed that the reaction afforded a mixture of the corresponding 1-amino-3-phospholene 1-oxide and its *N*-phosphinoyl derivative. It was found that selecting the appropriate conditions the product composition could be influenced and thus we developed a selective method for the *mono*- or *bis*-phosphorylation of primary amines. The >P(O)NR(O)P< type "imides" form a new family of compounds. [6,11]

6. Application possibilities

The environmentally friendly method developed for the esterification of a specific family of compounds is of a more general value and thus other phosphinic acids can be esterified under similar conditions.

During our experiments, more than 100 compounds were prepared and characterized, most of which are new compounds. In addition to their potential biological activity, the target organophosphorus compounds are useful intermediates in the synthesis of new *P*-heterocycles.

Inspired by the above-mentioned results, further transformations being impossible under conventional conditions are to be searched and studied. We have shown the potential of MW technique, however, certain limitations also apply. Scaling-up is one of the most serious problems yet to address. Developing continuous-flow methods seems to be a plausible solution. The adaptation of our new method to continuous-flow reactor appears to be feasible.

7. Publications

7.1. Full scientific publications related to the PhD Thesis

[1] **Kiss, N. Z.**; Ludányi, K.; Drahos, L.; Keglevich, G.: Novel Synthesis of Phosphinates by the Microwave Assisted Esterification of Phosphinic Acids; *Synthetic Commun* **2009**, *39*, 2392-2404. [IF: **0,961**; KNZ: **100**%; C: 3]

[2] Keglevich G., Bálint E., **Kiss N. Z.**, Jablonkai E., Hegedűs L., Grün A., Greiner I.: Microwave-Assisted Esterification of Phosphinic Acids; *Curr Org Chem* **2011**, *15*, 1802-1810. [IF: **3,064**; KNZ: **34**%]

[3] Keglevich, G.; **Kiss, N. Z.**; Mucsi, Z.; Körtvélyesi, T.: Insights into a surprising reaction: The microwave-assisted direct esterification of phosphinic acids; *Org. Biomol. Chem.* **2012**, *10*, 2011-2018. [IF: **3,568**; KNZ: **100**%, C: 2]

[4] Keglevich, G.; **Kiss, N. Z.**; Körtvélyesi, T.: Microwave-Assisted Functionalization of Phosphinic Acids; Amidations versus Esterifications; *Heteroatom Chem.* **2013**, *24*, 91-99. [IF: **1,257**; KNZ: **100**%]

[5] Keglevich, G.; **Kiss, N. Z.**; Drahos, L.; Körtvélyesi, T.: Direct esterification of phosphinic acids under microwave conditions; extension to the synthesis of thiophosphinates and new mechanistic insights; *Tetrahedron Lett.* **2013**, *54*, 466-469. [IF: **2,391**; KNZ: **100**%, C: 1]

[6] **Kiss, N. Z.**; Simon, A.; Drahos, L.; Huben, K.; Jankowski, S.; Keglevich, G.: Synthesis of 1-Amino-2,5-dihydro-1*H*-phosphole 1-Oxides and their *N*-Phosphinoyl Derivatives, Bis(2,5-dihydro-1*H*-phoshol-1-yl)amine *P*,*P'*-Dioxides; *Synthesis*, **2013**, *45*, 199-204. [IF: **2,443**; KNZ: **100**%]

[7] **Kiss, N. Z.**; Böttger, É. V.; Drahos, L.; Keglevich, G.: Microwave-assisted direct esterification of cyclic phosphinic acids; *Heteroatom Chem*, **2013**, *24*, 283-288. [IF: **1,257**; KNZ: **70**%, C: 1]

[8] Mucsi, Z.; **Kiss, N. Z.**; Keglevich, G.: A quantum chemical study on the mechanism and energetics of the direct esterification, thioesterification and amidation of 1-hydroxy-3-methyl-3-phospholene 1-oxide; *RSC Adv.*, **2014**, *4*, 11948-11954. [IF: **3,708** (2013); KNZ: **100**%]

[9] **Kiss, N. Z.**; Mucsi, Z.; Böttger, É., Drahos, L.; Keglevich, G.: A Three-Step Conversion of Phenyl-1*H*-phosphinic Acid to Dialkyl Phenylphosphonates Including Two Microwave-Assisted Direct Esterification Steps *Curr. Org. Synth.* **2014**, *11*, 767-772.

[IF: **2,439** (2013); KNZ: **70**%]

[10] **Kiss, N. Z.**; Örkényi, R.; Mucsi, Z.; Keglevich, G.: The Synthesis of 3-Phosphabicyclo[3.1.0]hexane 3-Oxides and 1,2-Dihydrophosphinine 1-Oxides with Lipophilic P-Alkoxy Substituents by Ring Enlargement; *Heteroatom Chem*, **2014**, *25*, 265-273. [IF: **1,257** (2013); KNZ: **70**%]

[11] **Kiss, N. Z.**; Rádai, Z.; Mucsi, Z.; Keglevich, G.: The Synthesis of Bis(phosphinoyl)amines and Phosphinoyl–Phosphorylamines by the *N*-Phosphinoylation and *N*-Phosphorylation of 1-Alkylamino-2,5-dihydro-1*H*-phosphole 1-Oxides; **2014**, *in press.* [IF: **1,257** (2013); KNZ: **70**%]

7.2. Proceedings and short publications related to the PhD Thesis

[12] Keglevich, G.; **Kiss, N. Z.**; Bálint E.; Jablonkai E.; Grün A.; Milen M.; Frigyes D.; Greiner I.: Microwave-Assiested Esterification of Phosphinic Acids by Alcohols, Phenols, and Alkyl Halogenides; *Phosphorus, Sulfur, Silicon* **2011**, *186*, 802-803. [IF: **0,716**; KNZ: **34**%]

[13] Keglevich, G.; **Kiss, N. Z.**; Körtvélyesi, T.; Mucsi Z.: Direct esterification and amidation of phosphinic acids under microwave conditions; *Phosphorus, Sulfur, Silicon* **2013**, 188, 29-32. [IF: **0,827**; KNZ: **100**%]

[14] **Kiss, N. Z.**; Mucsi, Z.; Rádai, Z.; Böttger, É. V.; Keglevich, G.: The Synthesis and Potential Use of Cyclic Phosphinic Acid Derivatives; *Phosphorus, Sulfur, Silicon*, **2014**, *submitted for publication.* [IF: …; KNZ: **70**%]

[15] **Kiss, N. Z.**: The synthesis of phosphinates in an environmentally friendly manner; *Period. Polytech.* **2011**, *55*, 39. [IF: **0,269**; KNZ: **100**%]

[16] Keglevich, G.; **Kiss, N. Z.**; Bálint, E.; Kovács, R.; Jablonkai, E.; Fazekas, E.; Tóth, J.; Kaszás, A.; Blastik, Zs.; Grün, A.: Synthesis of Organophosphorus Compounds under Microwave Conditions. In: 5th European Conference of the International Federation for Medical and Biological Engineering. Budapest, 2011.09.14-2011.09.18. New York: Springer, pp. 1350-1353.

7.3. Review and mini-review articles related to the PhD Thesis

[17] Keglevich, G.; Grün A.; Bálint E.; **Kiss, N. Z.**; Kovács, R.; Greiner, I.; Molnár I.; Blastik, Zs.; Tóth, V. R.; Fehérvári, A.; Csontos, I.: Green Chemical Tools in Organophosphorus Chemistry – Organophosphorus Tools in Green Chemistry; *Phosphorus, Sulfur, Silicon*, **2011**, *186*, 613-620. [IF: **0,716**; KNZ: **20**%, C: 1]

[18] Keglevich, G.; Grün, A.; Bálint, E.; **Kiss, N. Z.**; Jablonkai, E.: Microwave-Assisted Organophosphorus Syntheses; *Curr. Org. Chem.* **2013**, *17*, 545-554. [IF: **2,537**; KNZ: **50**%]

[19] Keglevich, G.; **Kiss, N. Z.**; Mucsi, Z.; Jablonkai, E.; Bálint, E.: *Green Proc. Synth.* **2014**, *3*, 103–110. [IF: – KNZ: **50**%]

[20] Keglevich, G.; Grün, A.; Bagi, P.; Bálint, E.; **Kiss, N. Z.**; Kovács, R. Jablonkai, E.; Kovács, T.; Fogassy, E.; Greiner, I.: *Period. Polytech.* **2014**, *in press* [IF: **0,13** (2013); KNZ: **20**%]

[21] Keglevich, G.; **Kiss, N. Z.**; Mucsi, Z.: Synthesis of phosphinic acid derivatives; Traditional versus up-to-date accomplishments, Encyclopedia of Physical Organic Chemistry, Vol. 5.; Ed. Wang, Z.; Wiley & Son, **2014**. *Book chapters prepared by invitation, submitted.* [KNZ: **100**%]

[22] **Kiss, N. Z.**; Keglevich, G.: An overview of the synthesis of phosphinates and phosphinic amides; *Curr. Org. Chem.* **2014**, *in press.* [IF: **2,537** (2013); KNZ: **100**%]

[23] Keglevich, G.; **Kiss, N. Z.**; Jablonkai, E.; Bálint E.: The Potential of Microwave in Organophosphorus Syntheses; *Phosphorus, Sulfur, Silicon,* **2014**, *submitted for publication.* [IF: **0,827** (2013); KNZ: **50**%]

7.4. Additional publications

[24] Keglevich, G.; **Kiss, N. Z.**; Menyhárd G. K.; Fehérvári A.; Csontos I.: A Study on the Kabachnik-Fields Reaction of Benzaldehyde, Cyclohexylamine and Dialkyl Phosphites; *Heteroatom Chem* **2012**, *23*, 171-178. [IF: **1,577**; KNZ: **70**%, C: 5]

[25] **Kiss, N. Z.**; Kaszás A.; Drahos, L.; Mucsi, Z.; Keglevich, G.: A neighbouring group effect leading to enhanced nucleophilic substitution of amines at the hindered α-carbon atom of an α-hydroxyphosphonate; *Tetrahedron Lett.* **2012**, 53, 207–209. [IF: **2,397**; KNZ: **70**%, C: 2]

7.5. Oral presentations

1. **Kiss N. Z.**, Keglevich G.: *Foszfinsavak észteresítése mikrohullámú körülmények között*, Elméleti Szerves Kémiai Munkabizottság Előadói ülése, 29th November 2010, Budapest
2. **Kiss N. Z.** *Foszfinsavak direkt észteresítése – egy új és környezetbarát megközelítés*, Kémiai Előadói Napok, 2-4th November 2011, Szeged

3. **Kiss N. Z.**, Kaszás A., Keglevich G.: *Novel Reactions under MW Conditions in Organophosphorus Chemistry,* 9th European Workshop on Phosporus Chemistry, 22-23rd Marct 2012, Rennes, France
4. **Kiss N. Z.**, Körtvélyesi T., Keglevich G.: Foszfinsavak észteresítése és amidálása; Kémiai Előadói Napok, 29-31st October 2012, Szeged
5. **Kiss N. Z.**, Keglevich G.: *Foszfinsavak észteresítése és amidálása*, Oláh György Doktori Iskola X. konferenciája, 7th February 2013, Budapest
6. **Kiss N. Z.**, Böttger É., Mucsi Z., Keglevich G.: *Foszfinsavak funkcionalizálása*, Kémiai Előadói Napok, 28-30th October 2013, Szeged

7.6. Poster presentations

1. **Kiss N. Z.**, Keglevich G.: The synthesis of phosphinates in an environmentally friendly manner; 8th European Workshop on Phosporus Chemistry, 28-29th March 2011, Münster, Germany
2. **Kiss N. Z.**, Keglevich G.: The synthesis of phosphinates in an environmentally friendly manner; Oláh György Doktori Iskola Konferenciája, 17th May 2012, Budapest
3. **Kiss N. Z.**, Örkényi R., Rádai Z., Keglevich G.: *The synthesis and use of 1-alkoxy- and 1-amino-3-phospholene 1-oxides*, Heterocycles in Bio-organic Chemistry, 27-30th May 2013, Riga, Latvia
4. **Kiss N. Z.**, Mucsi Z., Körtvélyesi T., Keglevich G.: *Microwave-assisted direct esterification and amidation of cyclic phosphinic acids*, Heterocycles in Bio-organic Chemistry, 27-30th May 2013, Riga, Latvia
5. **Kiss N. Z.**, Örkényi R., Rádai Z., Keglevich G.*: 1-Alkoxi- és 1-amino-3-foszfolén-1-oxidok szintézise és hasznosítása*, Vegyészkonferencia, 26-28th June 2013, Hajdúszoboszló
6. **Kiss N. Z.**, Mucsi Z., Körtvélyesi T., Keglevich G.: *Gyűrűs foszfinsavak direkt észteresítése és amidálása mikrohullámú körülmények között*, Vegyészkonferencia, 26-28th June 2013, Hajdúszoboszló
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