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

MICROWAVE-ASSISTED ORGANIC SYNTHESIS

PhD Thesis

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1. Introduction

These days, green chemistry has become of increasing importance. Selecting atom economy reactions, racionalization of the solvent usage, applying catalytic ractions are the most important topics of the 12 principles of green chemistry.[1] Microwave-(MW-)assisted organic synthesis and catalysis could serve as one of the best methods to fulfil these principles.[2,3] Applying MW technics for the organic syntheses, the reactions are usually faster and more efficient, the yields and selectivities are much higher, compared to conventional heating. In addition, the use of solvents and catalysts can be avioded. The combination of MW with solventless conditions and phase transfer catalysis (PTC) offers also attractive possibilities.

I started my PhD work at the research group of Prof. György Keglevich at the Budapest University of Technology and Economics, Department of Organic Chemistry and Technology. During my research work I focused on the development of environmentally friendly synthetic methods, which are important for the pharmaceutical industry and pesticide chemistry. We wished to study alkylation, addition, condensation and transesterification reactions under MW conditions. In the course of alkylations, we have investigated *N*-alkylation of 5-membered *N*-heterocycles, *O*-alkylation of phenol and naphthol derivatives and alkylating esterification of cyclic phosphinic acids. Our aim was to examine what will happen, if the phase transfer (PT) catalyst and the MW technique are combined. Beside this, we have examined the phospha-Michael addition of >P(O)H species to maleic derivatives and dimethyl acetylenedicarboxylate, the alcoholysis of phosphonates and phosphinates, as well as the Kabachnik-Fields (phospha-Mannich) reaction of 2*H*-pyran-2-ones and primary amines.

Our aim was to carry out the above mentioned reactions without the use of any solvents and catalysts, and to find the optimum conditions of these reactions.

In some cases, the P-compounds obtained after deoxygenation were used as ligands in transition metal complexes that are potential catalysts.

[1] Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
[2] Sheldon, R. A.; Arends, I.; Hanefeld, U. *Green Chemistry and Catalysis*; Wiley-VCH: Weinheim, 2007.
[3] *Microwaves in Organic Synthesis*; De La Hoz, A.; Loupy, A., Eds.; Wiley-VCH: Weinheim, 2002.

2. Experimental methods

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

Purification of the crude products was carried out by column- or flash (CombiFlash Rf) chromatographic methods. The reaction mixtures were analyzed by gaschromatography (GC) or GC-MS. The compounds were identified by spectroscopic methods (^{31}P, ^{13}C and ^{1}H NMR, HRMS). The structure of the platinum complexes were confirmed by single crystal diffractometric measurements and quantum chemical calculations.

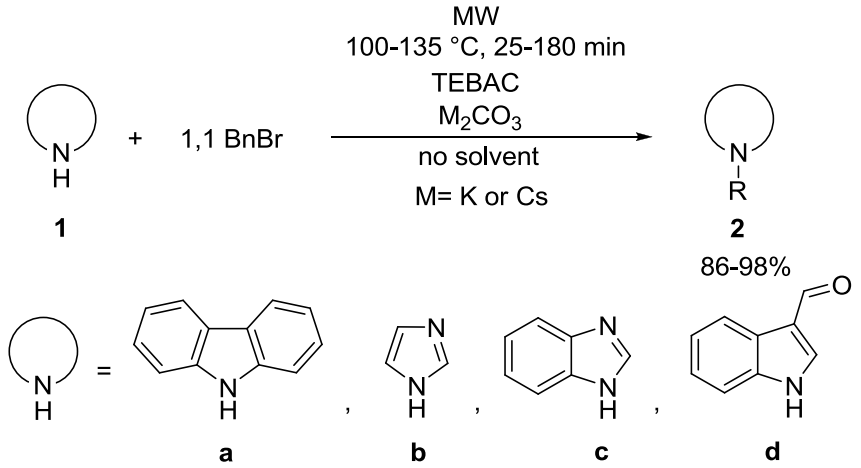
3. New scientific results

3.1. Microwave-assisted alkylations

The MW-assisted alkylations were carried out in a solid-liquid (S-L) phase system in the presence or absence of PT catalyst. We have studied and explored the optimum reaction conditions of *N*- and *O*-alkylations.

3.1.1. *N*-Alkylation of 5-membered *N*-heterocycles with benzyl bromide

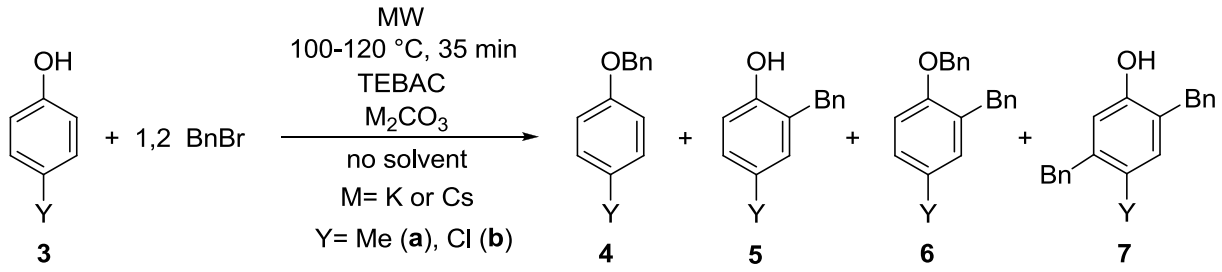
The MW-assisted solvent-free benzylation of carbazole (**1a**), imidazole (**1b**), benzimidazole (**1c**) and indol-3-carbaldehyde (**1d**) (*Scheme 1*) was accomplished with complete conversion and in short reaction times, as compared to the variations at conventional heating. Except the case of carbazole, the alkylations were complete in the absence of PT catalyst [1].



Scheme 1. *N*-Alkylation of 5-membered *N*-heterocycles with benzyl bromide under MW irradiation

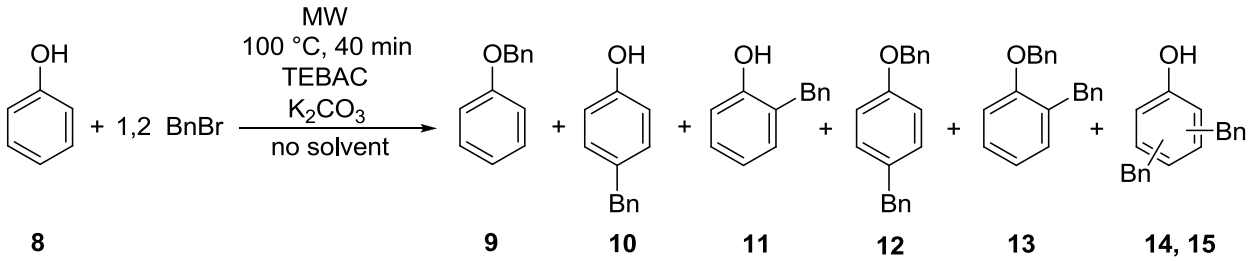
3.1.2. *O*-Alkylation of 4-methylphenol, 4-chlorophenol and phenol

The MW-enhanced solvent-free S-L phase benzylation of 4-methylphenol (**3a**) and 4-chlorophenol (**3b**) was similar (*Scheme 2*). Dependig on the conditions, the reactions resulted in an *O*-alkylated (**4**), a *C*-alkylated (**5**) and two dibenzylated products (**6** and **7**). In the presence of K_2CO_3 and TEBAC, the alkylation was complete and *O*-selective. In this case, 96% of benzyl-4-methylphenyl ether (**4a**) or benzyl-4-chlorophenyl ether (**4b**) was present in the reaction mixture at 100 or 120 °C after 35 min [2].



Scheme 2. *O*-Alkylation of 4-methylphenol, 4-chlorophenol with benzyl bromide under MW irradiation

In the *O*-alkylation of phenol, seven products (**9-15**) may be formed, three of which are monobenzylated (**9-11**) and four are dibenzylated derivatives (**12-15**) (Scheme 3). The best results (89%) for the *O*-alkylated product (**9**) were obtained in the presence of PT catalyst at 100 °C after 40 min.



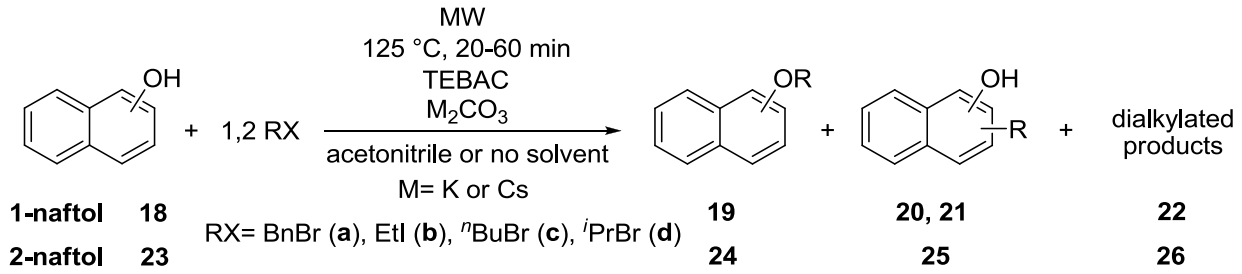
Scheme 3. *O*-Alkylation of phenol with benzyl bromide under MW irradiation

On the basis of our study, we have foud that the selectivity of *O*- versus *C*-benzylation, can be controlled by the absence or presence of K_2CO_3 and TEBAC. If neither of them is present in the reaction mixture, only the *C*-benzylated product is formed. In the presence of base, *O*- and *C*-alkylation were observed, while if both are present in the mixture, a pronounced *O*-selectivity and complete conversion can be achieved under MW conditions. The alkylations were reluctant under conventional heating. In the reactions with alkyl halides, the most appropriate is to use Cs_2CO_3 without any onium salt.

The *O*-alkylation of phenol derivatives (**3a,b** and **8**) were also carried out with quaternary ammonium salts under solventless MW conditions [4]. These alkylations took place *O*selectively and relatively fast.

3.1.3. *O*-Alkylation of 1- and 2-naphthols

We have also investigated the *O*-alkylation of 1- and 2-naphthol (**18** and **23**) under MW irradiation (*Scheme 4*) [5].

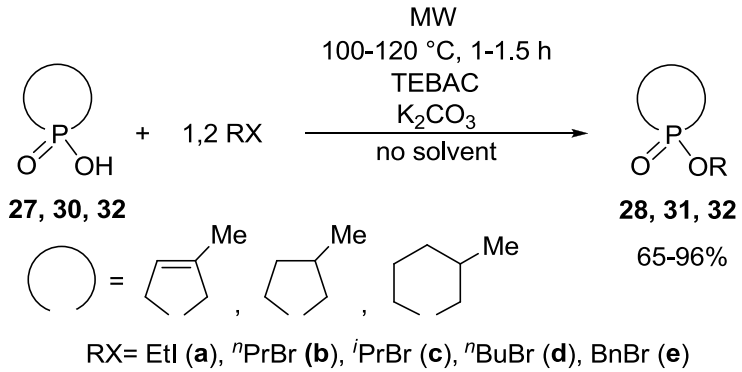


Scheme 4. *O*-Alkylation of 1- and 2-naphthol with benzyl bromide under MW irradiation

We have found, that the solvent-free MW-assisted benzylation of naphthols (**18** and **23**) are, depending on the base, chemoselective: using K_2CO_3 the benzylation is *C*-selective, while in the presence of Cs_2CO_3 the reaction is *O*-selective, but the conversions are not complete. Complete conversions were achieved only in acetonitrile after 20 min. In this case 98% of benzyl-1-naphthyl ether (**19a**) or 89% of benzyl-2-naphthyl ether (**24a**) was present in the reaction mixture. The most effective alkylating agensts were ethyl iodide and *n*-butyl-bromide. Applying them in the presence of K_2CO_3 and PT catalyst, the solvent-free alkylations were comlpletely *O*-selective [5]. Using isopropyl bromide, the reaction was *O*-selective, but reluctant. This experience is obviously the consequence of steric hindrance.

3.1.4. Alkylating esterification of cyclic phosphinic acids

The alkylating esterification of cyclic phosphinic acids (**27**, **30** and **32**) was also carried out under solvent-free MW conditions resulting in good yields (65-96%) (*Scheme 5*) [6,7].



Scheme 5. Alkylating esterification of cyclic phosphinic acids under MW irradiation

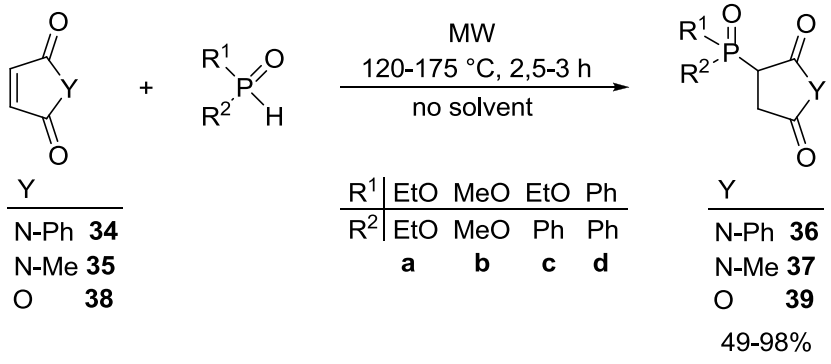
In the alkylating esterification of 1-hydroxy-3-methyl-3-phospholene 1-oxide under solvent-free MW conditions applying alkylating agents of increased reactivity (such as ethyl iodide and benzyl bromide), the MW irradiation was beneficial and there was no need for PT catalyst. The use of TEBAC is advantageous when alkyl halides of normal reactivity (such as *n*-propyl- and *n*-butyl bromide) were applied. In that case, the effect of onium salt was synergetic with the MW irradiation, and the reactions were complete. The esterification with isopropyl bromide was quite reluctant, the yield was 65% in the presence of TEBAC. The alkylating esterification of five- and six-membered derivatives (**30** and **32**) were similar with *n*-butyl bromide. The best results were also obtained in the presence of PT catalyst. We have prepared seven phosphinates whereby two of them are new.

Based on our experience of the alkylations, we can say that the MW-promoted reactions were more efficient than the thermal variations. The MW irradiation accelerates and promotes completion the reactions, the PT catalyst makes them more selective, therefore they are more favourable together.

3.2. Microwave-assisted phospha-Michael additions

3.2.1. Phospha-Michael addition to maleic derivatives

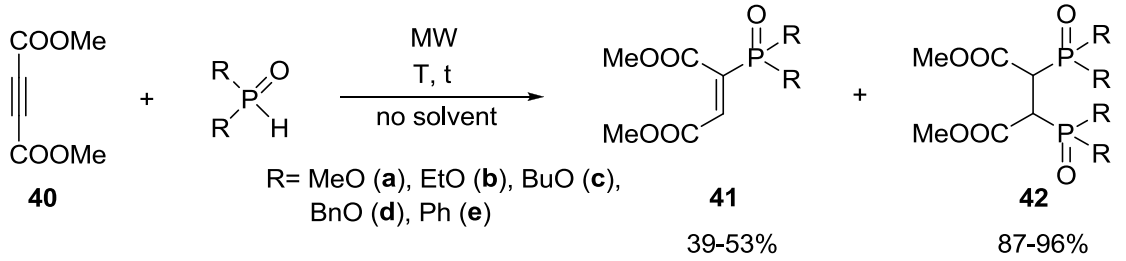
The MW-assisted phospha-Michael addition of dialkyl phosphites, ethyl phenyl-*H*-phosphinate and diphenylphosphine oxide to maleic derivatives (**34**, **35** and **38**) was performed in the absence of catalyst and, in most cases, without any solvents (*Scheme 6*) [8]. When diphenylphosphine oxide was the >P(O)H species, the reaction was carried out in acetonitrile to ensure homogenity. Applying this method, we have synthesized ten compounds in yields of 49-98% from among nine of the products are new.



Scheme 6. Phospha-Michael addition to maleic derivatives under MW irradiation

3.2.2. Phospha-Michael addition to dimethyl acetylenedicarboxylate

We have also studied the phospha-Michael addition of dialkyl phosphites or diphenylphosphine oxides to dimethyl acetylenedicarboxylate (**40**) (*Scheme 7*) [9].

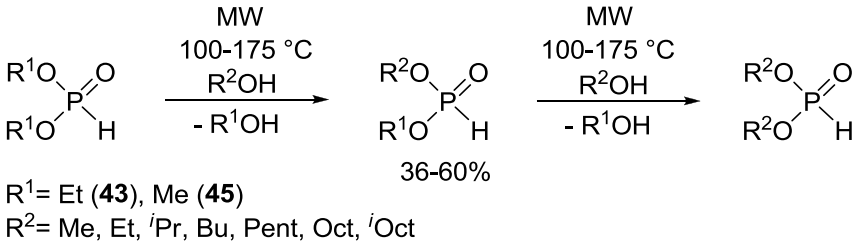


Scheme 7. Phospha-Michael addition to dimethyl acetylenedicarboxylate under MW irradiation

Mono- and bisadducts were synthesized by the above reaction. It was found that the ratio of the products could be controlled by the conditions (MW/Δ, molar ratio of the reactants, temperature, reaction time). We have prepared five maleic- (**41**) and five succinic derivatives (**42**), eight of which are new compounds. The bis(dialkyloxyphosphonoyl)-succinates were formed as a mixture of *meso* and *racemic* isomers, which were identified by a demanding NMR study [9].

3.3. Microwave-assisted alcoholysis of dialkyl phosphites (*H*-phosphonates)

The alcoholysis (transesterification) of dialkyl phosphites (*H*-phosphonates) (**43** and **45**) were efficient in the absence of base and catalyst, under MW irradiation (*Scheme 8*) [10].



Scheme 8. Alcoholysis of dialkyl phosphites under MW irradiation

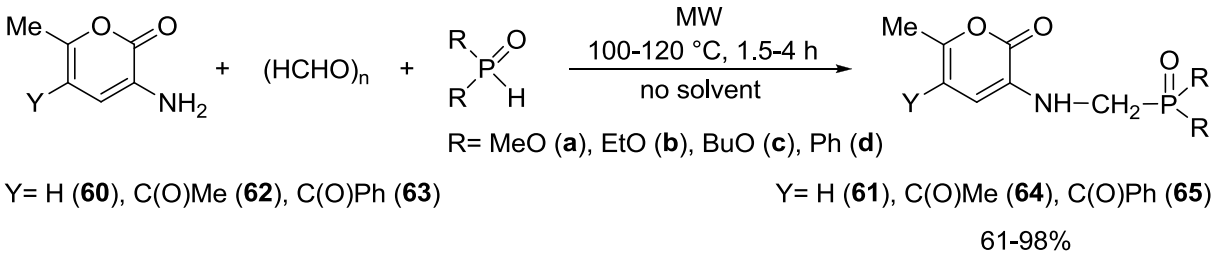
It was found that the alcoholysis of simple dialkyl phosphites under appropriate parameters (excess of the alcohol, reaction time) may lead to other dialkyl phosphites with two identical or two different alkyl groups. The symmetrical dialkyl phosphites were obtained among more forceful conditions (at 150-175 °C), while the mixed esters were prepared at lower temperature (at 100-125 °C). We have studied eight model reactions, which were optimized for the preparation of symmetrical and mixed dialkyl phosphites. In the course of these reactions, seven mixed dialkyl phosphites were isolated in yields of 36-60%, four of which are new and three of them are partially characterized. They are valuable building blocks in the synthesis of various chiral compounds.

3.4. Microwave-assisted Kabachnik-Fields reactions

Finally, we have studied the single Kabachnik-Fields (phospha-Mannich) reaction of 2*H*-pyran-2-ones (**60**, **62** and **63**) and the double Kabachnik-Fields reaction of primary amines under MW irradiation.

3.4.1. Kabachnik-Fields reactions of 3-amino-2*H*-pyran-2-ones

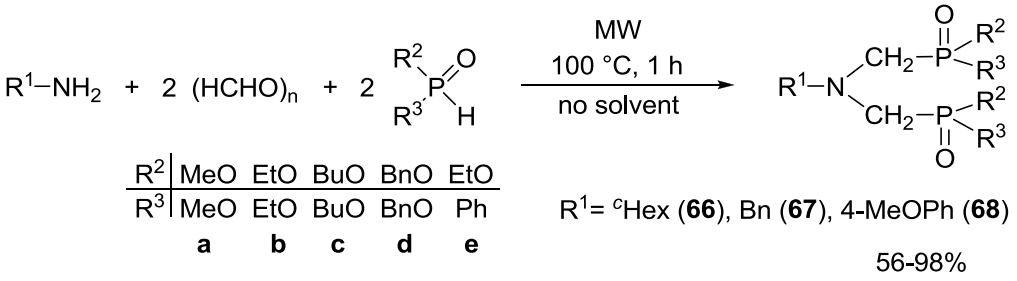
During the condensation of dialkyl phosphites or diphenylphosphine oxide and 3-amino-2*H*-pyran-2-ones (*Scheme 9*), nine new *N*-(2*H*-pyranonyl)-α-aminophosphonates or α-aminophosphine oxides were synthesized without the addition of catalyst and, in most cases, under solvent-free conditions [11].



Scheme 9. MW-assisted Kabachnik-Fields reaction of 3-amino-2*H*-pyran-2-ones

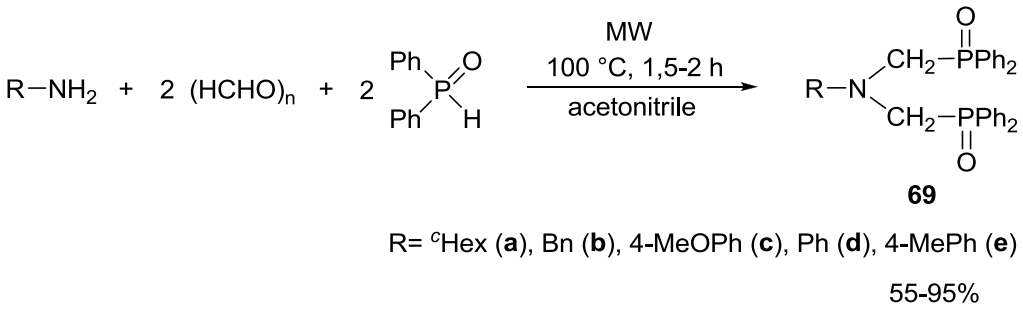
3.4.2. Kabachnik-Fields reactions of primary amines

The MW-assisted double Kabachnik-Fields reaction of cyclohexylamine, benzylamine and 4-methoxyaniline with dialkyl phosphites or ethyl phenyl-*H*-phosphinate were accomplished at 100 °C after 1 h reulting bis-pruduct (**68**) in yields of 56-98% (*Scheme 10*) [12,13]. The best results were obtained with benzylamine.



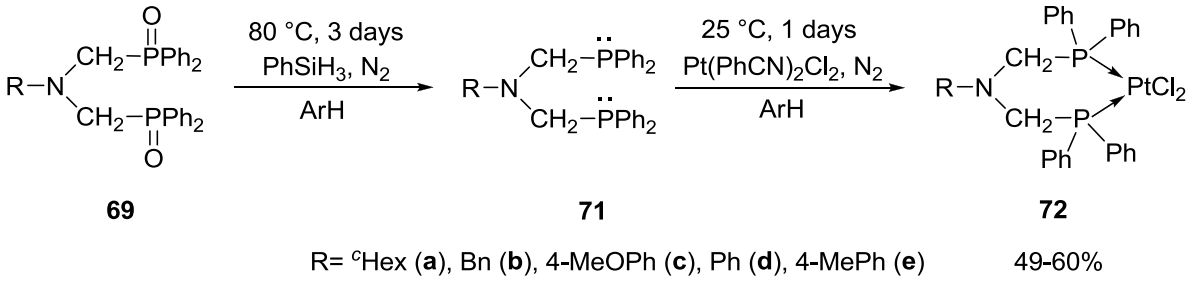
Scheme 10. MW-assisted double Kabachnik-Fields reaction of primary amines with dialkyl phosphites and ethyl phenyl *H*-phosphinate

The condensations were also carried out with diphenylphosphine oxide in acetonitrile at 100 °C for 1.5-2 h resulting in 55-95% of bis(diphenylphosphonylmethyl)amines (**69**).



Scheme 11. MW-assisted double Kabachnik-Fields reactions of primary amines with diphenylphosphine oxide

The bis(diphenylphosphonoylmethyl)amines (**69**) prepared were subjected to double deoxygenation to provide bis(phosphinomethyl)amine (**71**), from which ring platinum complexes (**72**) were synthesized (*Scheme 12*). These complexes (**72**) showed good activity and chemoselectivity, along with an unexpected regioselectivity as catalyst in the hydroformylation of styrene [13].



Scheme 12. Preparation of the *cis* chelate platinum complexes

19 bis(aminophosphonates) and aminophosphine oxides and five platinum complexes were prepared, from which 23 are new compounds.

It was proved that for the MW-assisted phospha-Michael addition, alcoholysis and Kabachnik-Fields reactions there is no need for any catalyst and, in most cases, for any solvent.

The comparative thermal experiments have demonstrated the effectiveness of the MW technique. In all cases, the reactions took place more effectively and in shorter time under MW conditions.

We can say that all four types of model reactions were accomplished in an environmentally friendly and greener way. During our experiments, more than 80 compounds were prepared and characterized, most of which are new compounds.

4. Thesis

1. The MW-assisted *N*-alkylation of carbazole, imidazole, benzimidazole and indol-3-carbaldehyde was accomplished with complete conversion in short reaction times, in the absence of solvent and, except of carbazole, without using a PT catalyst, compared to conventional heating [1].

2. During the solventless benzylation of phenol derivatives, we proved that the outcome of the reactions – regarding *O*- and *C*-selectivity – can be fine-tuned by the absence or presence of K_2CO_3 and a PT catalyst. If neither of them is present in the reaction mixture, only the *C*-benzylated product is formed, while if both are present in the mixture, a pronounced *O*-selectivity and complete conversion can be achieved under MW conditions. In the reactions with alkyl halides, the most appropriate is to use Cs_2CO_3 without any onium salt [2,3].

3. We proved that the *O*-alkylation of phenol derivatives with quaternary ammonium salts under MW and solventless conditions takes place *O*-selectively and relatively fast. This effect were modeled by measuring the heat absorbing ability of the onium salts.

4. We demonstrated that the solvent-free MW-assisted benzylation of naphthol derivatives is chemoselective depending on the base: using K_2CO_3 the benzylation shows *C*-selectivity, while in the presence of Cs_2CO_3, the reaction is *O*-selective, but the conversion is incomplete. The reactions take place completely only in the presence of solvent. With alkyl halides, the *O*-selective alkylations could be performed using an alkali carbonate under solvent-free conditions in the presence of TEBAC [5].

5. We proved that in the alkylating esterification of 1-hydroxy-3-methyl-3-phospholene 1-oxide under solvent-free MW conditions applying alkylating agents of increased reactivity, the MW irradiation was beneficial and there was no need to use PT catalyst. At the same time, using alkyl halides of normal reactivity, the presence of onium salt was synergetic with the MW irradiation, and the reactions were complete [6,7].

6. We observed that under MW conditions there is no need any catalyst and, in most cases, any solvent in the phospha-Michael addition of dialkyl phosphites, ethyl phenyl-*H*-

phosphinate and diphenylphosphine oxide to maleic derivatives. Applying this method, we prepared nine new succinimides and anhydrides [8].

7. Mono- and bisadducts were synthesized by the MW-assisted addition of dialkyl phosphites or diphenylphosphine oxide to dimethyl acetylenedicarboxylate. We found that the ratio of the products could be controlled by the molar ratio of the reactants and the conditions. We have prepared five maleic- and five succinic derivatives, eight of which are new compounds. The bis(dialkyloxiphosphonoyl)-succinates were formed as a mixture of *meso* and *racemic* isomers, which were identified by NMR spectroscopy [9].

8. Applying MW irradiation, the transesterification (alcoholysis) of dialkyl phosphites (*H*-phosphonates) took place in the absence of any catalyst. We observed that using the appropriate parameters (excess of the alcohol, reaction time), at higher temperature the symmetrical phosphites, while at lower temperature the mixed esters were formed. Seven mixed dialkyl phosphites were isolated, which may be valuable building blocks in the synthesis of chiral compounds [10].

9. Nine new *N*-(2*H*-pyranonyl)-α-aminophosphonates or α-aminophosphine oxides were synthesized by the catalyst-free and, in most cases, solvent-free Kabachnik-Fields condensation of dialkyl phosphites or diphenylphosphine oxide, paraformaldehyde and 3-amino-6-methyl-2*H*-pyran-2-ones [11].

10. We implemented the double Kabachnik-Fields reaction of primary amines, paraformaldehyde and dialkyl phosphites, ethyl phenyl-*H*-phosphinate or diphenylphosphine oxide under solvent-free and, in most cases, catalyst-free MW conditions. Applying this method, 18 new bisphosphonates were prepared [12,13].

11. After double deoxygenation, the bis(diphenylphosphinoylmethyl)amines were converted to the corresponding ring platinum complexes. This species showed good activity and chemoselectivity, along with an unexpected regioselectivity as catalyst in the hydroformylation of styrene [13].

5. Application possibilities

My work has demonstrated the effectiveness of the MW technique. Applying this technique, faster, more efficient and environmentally friendly synthetic methods have been developed for the four kinds of model reactions studied. We demonstrated that for the alkylations there is no need for any solvents. The addition, alcoholysis and condensation reactions can be carried out in the absence of any catalyst and in most cases, without solvents under MW conditions.

The platinum complexes prepared were active catalysts in the hydroformylation of styrene, which showed good catalytic activity and selectivity, along with an unexpected regioselectivity.

Usually the more expensive rhodium-containing catalysts are used in the hydroformylations, which may be replaced by our complexes. This is important from the point of view pharmaceutical industry.

6. Publications

6.1. Full scientific publications related to the PhD Thesis

[1] Milen, M.; Grün, A.; **Bálint, E.**; Dancsó, A.; Keglevich, G.: A Study on the solid–liquid phase alkylation of *N*-heterocycles; MW-assisted synthesis as an environmentally friendly alternative, *Synth. Commun.* **2010**, *40*, 2291. [IF: 0,937]

[2] Keglevich, G.; **Bálint, E.**; Karsai, É.; Grün, A.; Bálint, M.; Greiner, I.: Chemoselectivity in the microwave-assisted solvent-free solid–liquid phase benzylation of phenols: *O*- versus *C*-alkylation, *Tetrahedron Lett.* **2008**, *49*, 5039. [IF: 2,538]

[3] Keglevich, G.; **Bálint, E.**; Karsai, É.; Varga, J.; Grün, A.; Bálint, M.; Greiner, I.: Heterogeneous phase alkylation of phenols making use of phase transfer catalysis and microwave irradiation, *Lett. Org. Chem.* **2009**, *6*, 535. [IF: 0,774]

[4] **Bálint, E.**; Greiner, I.; Keglevich, G.: Microwave-assisted alkylation of phenols by quaternary onium salts, *Lett. Org. Chem.* **2011**, *8*, 22. [IF: 0,822]

[5] **Bálint, E.**; Kovács, O.; Drahos, L.; Keglevich, G.: Microwave-assisted solid-liquid phase alkylation of naphthols, *Lett. Org. Chem.* – accepted for publication. [IF (2011): 0,822]

[6] **Bálint, E.**; Jablonkai, E.; Bálint, M.; Keglevich, G.: Alkylating esterification of 1-hydroxy-3-phopsholene oxides under solventless MW conditions, *Heteroatom Chem.* **2010**, *21*, 211. [IF: 1,044]

[7] 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. [IF: 3,064]

[8] **Bálint, E.**; Takács, J.; Drahos, L.; Keglevich, G.: Microwave-assisted phospha-Michael addition of dialkyl phosphites, a phenyl-*H*-phosphinate and diphenylphosphine oxide to maleic derivatives, *Heteroatom Chem.* **2012**, *23*, 235. [IF (2011): 1,243]

[9] Keglevich, G.; **Bálint, E.**; Takács, J.; Drahos, L.; Huben, K.; Jankowski, S.: The addition of dialkyl phosphites and diphenylphosphine oxide on the triple bond of dialkyl acetylenedicarboxylate under solvent-free and microwave conditions, *Curr. Org. Synth.* – submitted for publication. [IF (2011): 3,434]

[10] **Bálint, E.**; Tajti, Á.; Drahos, L.; Ilia, G.; Keglevich, G.: Alcoholysis of dialkyl phosphites under microwave conditions, *Curr. Org. Chem.* – in press. [IF (2011): 3,064]

[11] **Bálint, E.**; Keglevich, G.; Takács, J.; Drahos, L.; Juranovič, A.; Kočevar, M.: α-Aminophosphonates and α-aminophosphine oxides by microwave-assisted Kabachnik-Fields reactions of 3-amino-6-methyl-2*H*-pyran-2-ones, *Heteroatom Chem.*– accepted for publication. [IF (2011): 1,243]

[12] **Bálint, E.**; Fazekas, E.; Pintér, G.; Szöllősy, Á.; Holczbauer, T.; Czugler, M.; Drahos, L.; Körtvélyesi, T.; Keglevich, G.: Synthesis and Utilization of the Bis(>P(O)CH2)amine Derivatives Obtained by the Double Kabachnik–Fields Reaction with Cyclohexylamine; Quantum Chemical and X-Ray Study of the Related Bidentate Chelate Platinum Complexes, *Curr. Org. Chem.* **2012**, *16*, 547. [IF (2011): 3,064]

[13] **Bálint, E.**; Fazekas, E.; Pongrácz, P.; Kollár, L.; Drahos, L.; Holczbauer, T.; Czugler, M.; Keglevich, G.: *N*-Benzyl and *N*-aryl bis(phospha-Mannich adducts): Synthesis and catalytic activity of the related bidentate chelate platinum complexes in hydroformylation, *J. Organomet. Chem.* **2012**, *717*, 75. [IF (2011): 2,384]

6.2. Proceedings related to the PhD Thesis

[14] Keglevich, G.; Kiss, N. Z.; **Bálint, E.**; Jablonkai, E.; Grün, A.; Milen, M.; Frigyes, D.; Greiner I.: Microwave-assisted esterification of phosphinic acids by alcohols, phenoles and alkyl halogenides, *Phosphorus, Sulfur, Silicon* **2011**, *186*, 802-803. [IF: 0,716]

[15] Keglevich, G.; Kiss, N. Z.; **Bálint, E.**; Kovács, R.; Jablonkai, E.; Fazekas, E.; Takács, J.; Kaszás, A.; Blastik, Z.; Grün, A.: Synthesis of Organophosphorus Compounds under Microwave Conditions, *IFMBE Proc.* **2012**, *37*, 1350.

[16] **Bálint, E.**; Fazekas, E.; Takács, J.; Tajti, Á.; Juranovic, A.; Kocevar, M.; Keglevich, G.: Microwave-assisted synthesis of organophosphorus compounds, *Phosphorus, Sulfur, Silicon* **2012**, DOI: 10.1080/10426507.2012.743544. [IF (2011): 0,716]

6.3. Other publications related to the PhD Thesis

[17] IIia, G.; Macarie, L.; **Bálint, E.**; Keglevich, G.: Phase transfer catalysis in phosphorous chemistry, *Cat. Rev. – Sci. Eng.* **2011**, *53*, 152. [IF: 7,5]

[18] Keglevich, G.; **Bálint E.**: The Kabachnik-Fields reaction: mechanism and synthetic use, *Molecules* **2012**, *17*, 12821. [IF (2011): 2,386]

[19] Keglevich, G.; Grün, A.; **Bálint, E.**: Microwave irradiation and phase transfer catalysis in *C*-, *O*- and *N*-alkylation reactions, *Curr. Org. Synth.* – in press. [IF (2011): 3,434]

[20] Keglevich, G.; Grün, A.; **Bálint, E.**; Kiss, N. Z.; Jablonkai, E.: Microwave-assisted organophosphorus synthesis, *Curr. Org. Chem.* – in press. [IF (2011): 3,064]

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6.4. Additional publications

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6.5. Oral presentations

1. **Bálint E.**, Keglevich Gy., Grün A.: *Fenol-származékok O-alkilezésének vizsgálata mikrohullámú körülmények között,* XXXII. Kémiai Előadói Napok, Szeged, 2009.
2. **Bálint E.**, Keglevich Gy., Grün A.: *Fenol-származékok O-alkilezésének vizsgálata mikrohullámú körülmények között,* Nemzetközi Vegyészkonferencia, Marosvásárhely, 2009.
3. **Bálint E.**, Jablonkai E., Grün A., Greiner I., Keglevich Gy.: *O- és N-alkilezési reakciók vizsgálata mikrohullámú körülmények között,* Vegyészkonferencia és 53. Magyar Spektrokémiai Vándorgyűlés, Hajdúszoboszló, 2010.
4. **Bálint, E.**, Fazekas E., Takács, J.: *Bisz(foszfa-Mannich) reakciók és foszfa-Michael-addíciók megvalósítása mikrohullámú körülmények között*, XXXIV. Kémiai Előadói Napok, Szeged, 2011.

5. **Bálint, E.**, Keglevich, G.: *Különféle reakciók megvalósítása mikrohullámú körülmények között,* Oláh György Doktori Iskola IX. konferenciája, Budapest, 2012.
6. **Bálint, E.**, Fazekas, E., Holczbauer, T., Czugler, T., Keglevich, G.: *Preparation and crystal structures of some bis(diphenylphosphinomethyl)-amine platinum complexes,* Twentyfirst Slovenian - Croatian Crystallographic Meeting, Slovenia, Pokljuka, 2012.
7. **Bálint, E.**; Fazekas, E.; Tajti, Á.; Kocevar, M.; Keglevich, G.: *Szerves kémiai reakciók megvalósítása mikrohullámú technika alkalmazásával.* XXXV. Kémiai Előadói Napok, Szeged, 2012.

6.6. Poster presentations

1. **Bálint E.**: *O- és N-alkilezési reakciók vizsgálata mikrohullámú körülmények között*, Oláh György Doktori Iskola VII. konferenciája, Budapest, 2010.
2. Keglevich Gy., Kiss N. Zs., **Bálint E.**, Jablonkai E., Grün A., Milen M., Frigyes D. *Microwave-assisted esterification of phosphinic acids by alkyl halogenides, alcohols and phenols,* Oláh György Doktori Iskola VIII. konferenciája, Budapest, 2011.
3. **Bálint E.**, Jablonkai E., Fazekas E., Takács J., Keglevich Gy. *Microwave-assisted reactions in the phosphorous chemistry,* 8th European Workshop on Phosphorus Chemistry, Münster, Germany, 2011.
4. **Bálint E.**, Jablonkai E., Fazekas E., Takács J., Keglevich Gy. *Synthesis of potentially biologically active phosphinates and phosphine oxides,* 4th European Conference on Chemistry for Life Science, Budapest, 2011.
5. **Bálint E.**, Jablonkai E., Takács J., Keglevich Gy. *Microwave-assisted reactions of some P- and N-heterocycles,* XIVth Conference on Heterocycles in Bio-organic Chemistry, Brno, Czech Republic, 2011.
6. **Bálint, E.**, Fazekas, E., Takács, J., Tajti, Á. Keglevich, G. *Microwave-assisted synthesis of organophosphorus compounds,* Microwave and Flow Chemstry Conference, Lanzarote, Spain, 2012.
7. **Bálint, E.**, Fazekas, E., Tajti, Á. Keglevich, G. *Microwave-assisted Double Kabachnik-Fields reactions; NMR properties and utilization of the products*, 9th European Workshop on Phosphorus Chemistry, Rennes, France, 2012.
8. **Bálint, E.;** Fazekas, E.; Takács, J.; Tajti, Á.; Kocevar, M.; Keglevich, G.: *Microwave-assisted synthesis of organophosphorus compounds,* 19th International Conference on Phosphorus Chemistry, Rotterdam, Netherlands, 2012.