The potential and scope of the MW tool; A case study on the synthesis of phosphinimates

György Keglevich* and Nóra Zsuzsa Kiss

Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary
E-mail: gkeglevich@mail.bme.hu
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### Recent papers:
1. Introduction

Possible synthetic routes to phosphinates

\[
P^\text{Cl} \quad \xrightarrow{\text{ROH}} \quad \text{N} \quad \text{T3P}^\text{®} \quad \text{ROH} \quad \xrightarrow{\text{MW} \quad \text{ROH}} \quad \text{MW} \quad \text{ROH} \quad \xrightarrow{\text{MW} / \text{PTC} \quad \text{RX}} \quad \text{K}_2\text{CO}_3 \quad \xrightarrow{\text{P}} \quad \xrightarrow{\text{OR}} \quad \text{PO}_\text{OR}
\]
2. The synthesis of ring phosphinates and related derivatives

2.1. Ring phosphinates via the corresponding phosphinic chlorides


2.2. The esterification of ring phosphinic acids in the presence of the T3P® reagent

\[
\begin{align*}
R^1 &= H, Me \\
25 \, ^\circ \text{C, t} \\
1) \text{T3P® (1.1 equiv.)/EtOAc} &\quad \text{2) R}_2\text{OH} \\
\end{align*}
\]

\[
\begin{align*}
R^1 = H, \text{Me} \\
R^2 = \text{Me, Et, Pr, 'Pr, Bu, 'Bu, 'Bu, 'Bu, Pent, 'Pent, 3-pentyl, 'Hexyl, Bn, menthyl} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>R^1 = H</th>
<th>t (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with primary alcohols</td>
<td>0.5</td>
<td>77 – 95</td>
</tr>
<tr>
<td>with secondary alcohols</td>
<td>2 – 3</td>
<td>76 – 91</td>
</tr>
</tbody>
</table>

**Rationalization:**
using primary alcohols, 0.67 equiv. of the T3P® is enough if the reaction is carried out at 80 °C on MW irradiation.

**Active intermediate:**
2.3. Alkylating esterification of ring phosphinic acids

in case of alkyl halides with normal reactivity
the combined use of PTC and MW is advantageous

synergic effect!

in case of alkyl halides with increased reactivity
MW is enough

2.4. **MW-assisted direct esterification of ring phosphinic acids – Reactions that are reluctant on conventional heating**

2.4.1. **Esterification of 1-hydroxy-3-phospholene 1-oxides**

**A) with BuOH**

![Reaction scheme](image)

- Conversion in %
  - R | Δ | MW
  - H | 17 | 58
  - Me | 11 | 29

**B) with longer carbon atom chain alcohols**

![Reaction scheme](image)

- R\(^1\) = H, Me
- R\(^2\) = \(^{nC}_{5}H_{11}\), \(^{iC}_{5}H_{11}\), \(^{nC}_{8}H_{17}\), \(^{iC}_{8}H_{17}\), C\(_{12}\)H\(_{25}\)

- Conversion: 80–100%
- Yield: 57–95%

---

2.4.2. Extension: Direct esterification of hydroxy-phospholane oxides and a hydroxy-1,2,3,4,5,6-hexahydrophosphinine oxide

\[
\begin{align*}
\text{P} & \quad \text{O} \quad \text{H} \\
\text{Me} & + \quad \text{ROH} \quad \xrightarrow{\text{MW}} \quad 220-235^\circ\text{C}/3-4\text{ h} \\
\text{P} & \quad \text{O} \quad \text{H} \\
\text{Me} & \quad \text{OR} \\
\text{yield: 59-86\%} \\
\text{1:1 mixture of 2 diastereomers} \\
\text{R} = \text{nC}_5\text{H}_{11}, \text{iC}_5\text{H}_{11}, \text{nC}_8\text{H}_{17}, \text{iC}_8\text{H}_{17}
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{P} & \quad \text{O} \quad \text{H} \\
\text{Me} & + \quad \text{ROH} \quad \xrightarrow{\text{MW}} \quad 220-235^\circ\text{C}/4-6\text{ h} \\
\text{P} & \quad \text{O} \quad \text{H} \\
\text{Me} & \quad \text{OR} \\
\text{Me} & \quad \text{OR} \\
\text{yield: 50-72\%} \\
\text{2:1 mixture of 2 isomers} \\
\text{a racemate} \\
\text{2 diastereomers} \\
\text{R} = \text{as above} \\
\text{68:17:15 mixture of 3 isomers}
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \\
\text{P} & \quad \text{O} \quad \text{H} \\
\text{Me} & + \quad \text{ROH} \quad \xrightarrow{\text{MW}} \quad 235^\circ\text{C}/4-6\text{ h} \\
\text{P} & \quad \text{O} \quad \text{H} \\
\text{Me} & \quad \text{OR} \\
\text{R} = \text{nC}_8\text{H}_{17}, \text{iC}_8\text{H}_{17} \\
\text{68:32 mixture of 2 diastereomers} \\
\text{yield: 54/62\%}
\end{align*}
\]

Order of reactivity:

3. Improvement and extension of the MW-assisted direct esterifications

3.1. Direct esterification in the presence of an ionic liquid

3.1.1. Esterification of 1-hydroxy-3-methyl-3-phospholene 1-oxide in the presence of 10% of [bmim][PF$_6$] as a catalyst

The IL exerts a pronounced enhancing effect on the courage of the esterification.

<table>
<thead>
<tr>
<th>R</th>
<th>[bmim][PF$_6$]</th>
<th>T (°C)</th>
<th>p (bar)</th>
<th>t (h)</th>
<th>Conversion (%)</th>
<th>MW (Δ*)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et</td>
<td>–</td>
<td>160</td>
<td>17</td>
<td>4</td>
<td>38</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Et</td>
<td>10%</td>
<td>160</td>
<td>17</td>
<td>3</td>
<td>86</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>$^n$Pr</td>
<td>–</td>
<td>180</td>
<td>15.5</td>
<td>4</td>
<td>40</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>$^n$Pr</td>
<td>10%</td>
<td>180</td>
<td>15.5</td>
<td>3</td>
<td>98</td>
<td></td>
<td>68</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>–</td>
<td>200</td>
<td>16</td>
<td>2</td>
<td>62 (11)</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>10%</td>
<td>180</td>
<td>14</td>
<td>0.5</td>
<td>90 (19)</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>$^n$Pent</td>
<td>–</td>
<td>220</td>
<td>9</td>
<td>2.5</td>
<td>100</td>
<td></td>
<td>82</td>
</tr>
<tr>
<td>$^n$Pent</td>
<td>10%</td>
<td>180</td>
<td>5</td>
<td>0.5</td>
<td>100 (52)</td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>$^i$Oct</td>
<td>–</td>
<td>220</td>
<td>3</td>
<td>1</td>
<td>100 (28)</td>
<td></td>
<td>76</td>
</tr>
<tr>
<td>$^i$Oct</td>
<td>10%</td>
<td>180</td>
<td>2</td>
<td>0.33</td>
<td>100 (75)</td>
<td></td>
<td>84</td>
</tr>
</tbody>
</table>

*Comparative thermal experiment.

3.1.2. Extension: Direct esterification of cyclic phosphinic acids A–D in the presence of \([\text{bmim}][\text{PF}_6]\) using \(n\)-pentanol

\[
\begin{align*}
\text{O=P-OH} & \quad + \quad \text{PentOH} & \quad \xrightarrow{\text{MW}} & \quad \text{O=P-O\text{Pent}} \\
\text{\includegraphics[width=0.5\textwidth]{diagram.png}}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Ring substituent</th>
<th>[bmim][PF₆]</th>
<th>T (°C)</th>
<th>p (bar)</th>
<th>t (h)</th>
<th>Conversion (%)</th>
<th>Ratio of diastereomers (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>–</td>
<td>235</td>
<td>11</td>
<td>3</td>
<td>90</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10%</td>
<td>200</td>
<td>6</td>
<td>1</td>
<td>95</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10%</td>
<td>220</td>
<td>9</td>
<td>1</td>
<td>~100</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>–</td>
<td>235</td>
<td>11</td>
<td>3</td>
<td>~85</td>
<td>50 – 50</td>
<td>79</td>
</tr>
<tr>
<td>B</td>
<td>10%</td>
<td>220</td>
<td>9</td>
<td>1</td>
<td>~100</td>
<td>52 – 48</td>
<td>89</td>
</tr>
<tr>
<td>C</td>
<td>–</td>
<td>235</td>
<td>11</td>
<td>5</td>
<td>~72</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>10%</td>
<td>220</td>
<td>9</td>
<td>2</td>
<td>~95</td>
<td>65 – 18 – 15</td>
<td>84</td>
</tr>
<tr>
<td>D</td>
<td>–</td>
<td>220</td>
<td>9</td>
<td>4</td>
<td>~45</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>10%</td>
<td>200</td>
<td>9</td>
<td>2</td>
<td>~60</td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Direct esterification of 1-hydroxy-3-methyl-3-phospholene 1-oxide with phenol derivatives in the presence of [bmim][PF$_6$]

In general, the direct esterification of phosphinic acids with substituted phenols is impossible. We could elaborate a method under MW irradiation in the presence of ILs.

3.3. Extension to phosphonic acids: direct esterification of phenyl-phosphonic acid

The efficiency is very low!
Efforts for a better accomplishment is in process.

Preparing dialkyl phenylphosphonates according to another protocol:

4. Summary of the esterification of phosphinic acids

### Comparison of the synthesis of phosphinates from “green” chemical point of view

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>best</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting materials</td>
<td>P(O)Cl means cost</td>
<td>a good combination</td>
<td>a good combination</td>
<td>RX means cost</td>
<td>C, B</td>
</tr>
<tr>
<td>Additional reagent</td>
<td>N</td>
<td>T3P</td>
<td>–</td>
<td>K₂CO₃</td>
<td>C</td>
</tr>
<tr>
<td>By-product</td>
<td>HCl/ N·HCl</td>
<td>HO-P-O-P-O-H</td>
<td>H₂O</td>
<td>KX, H₂O, CO₂</td>
<td>C</td>
</tr>
<tr>
<td>Atomic efficiency</td>
<td>medium</td>
<td>low</td>
<td>good</td>
<td>medium</td>
<td>C</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>≥ RT</td>
<td>RT</td>
<td>160–180</td>
<td>100–120</td>
<td>B, A</td>
</tr>
<tr>
<td>Reaction time (t)</td>
<td>~ 1–4</td>
<td>0.5–3</td>
<td>0.5–3</td>
<td>1–3</td>
<td>not relevant</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>~ 90</td>
<td>76–95</td>
<td>60–94</td>
<td>73–96</td>
<td>not really relevant</td>
</tr>
<tr>
<td>Advantage</td>
<td>– low reaction temperature</td>
<td>– low reaction temperature</td>
<td>– best choice of reagents</td>
<td>– catalytic method</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– industrial relevance</td>
<td></td>
<td>– no by-product (beyond water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>– good atomic efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disadvantage</td>
<td>chloro-containing reagent</td>
<td>special reactant</td>
<td>high reaction temperature</td>
<td>halogen containing reagent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>low atomic economy</td>
<td>low atomic economy</td>
<td>possible only in laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall order of preference</td>
<td>laboratory</td>
<td>4</td>
<td>1/2</td>
<td>1/2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>industry</td>
<td>1</td>
<td>2</td>
<td>3/4</td>
<td>3/4</td>
</tr>
</tbody>
</table>
A case study on the preparation of butyl methyl-phenylphosphinate

5. Theoretical aspects: mechanism, energetics, scope and limitation of the application of MWs
5.1. Possible mechanisms for the direct esterification of phosphinic acids

5.2. Energetics of selected phosphinic acid derivatizations
5.2.1. MW-assisted direct esterification of 1-hydroxy-3-methyl-3-phospholene oxide
5.2.1.1. Energy profile evaluated on the basis (B3LYP/6-31++G(d,p)) calculations

The esterification of acetic acid as a comparison

5.2.1.2. Mechanism for the esterification of 1-hydroxy-3-phospholene oxide calculated by the explicit-implicit solvent model using the B3LYP/6-31G(d,p) method

Dependence of the enthalpy of activation values on the substituents

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>$\Delta H^#$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Bu</td>
<td>135.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Me</td>
<td>Bu</td>
<td>138.8</td>
<td>0.8</td>
</tr>
<tr>
<td>H</td>
<td>$i$Oct</td>
<td>130.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Me</td>
<td>$i$Oct</td>
<td>134.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

B3LYP/6-31G(d,p)//PCM(MeOH)

5.2.2. MW-assisted esterification of 1-hydroxy-3-methyl-3-phospholene 1-oxide with a thioalcohol; Energetics calculated by the B3LYP/6-31++G(d,p) method

\[
\Delta H_0 = 3.3 \quad \Delta H^\# = 101.7
\]

Enthalpy profile for the esterification with thiobutanol

Comparison esterification with butanol

5.2.3. MW-assisted amidation of cyclic phosphinic acids; Energetics calculated by the B3LYP/6-31++G(d,p) method

\[
\Delta H (\text{kJ mol}^{-1}) = 79.4 \quad \Delta H^0 = 32.6
\]

"Phosphimides" as by-products or as exclusive products – Variation of the imide formation

5.2.4. Explanation for the effect of MWs – Scope and limitations for the use of MWs

The role of microwave is to enhance reactions with higher (≥100 kJ mol⁻¹) enthalpy of activation. The MW assistance is optimal for thermoneutral reactions. Endothermicity works against the beneficial effect of MWs.

This is possible due to the statistically occurring local overheating effect (that may be in the range of 1–60 °C) in the bulk of the reaction mixture. Assuming an overheated segment of 5–40%, the effect is significant!

6. Modelling and calculating of the effect of local overheatings
6.1. Principles

**Arrhenius equation:**

\[ k = A \cdot e^{-\frac{\Delta H^\#}{RT}} \]

\( \Delta H^\# \): activation enthalpy (kJ mol\(^{-1}\))

\( T \): reaction temperature

\( R \): universal gas constant

**The increase may be characterized by**

\[ k_{overall} = \frac{V_{bulk}}{V_0} \cdot k_{bulk} + \sum_{i=1}^{n} \frac{V_{OH}^i}{V_0} \cdot k_{OH}^i \]

\( k_{rel} = \frac{k_{overall}}{k_{bulk}} \)
Modelling the thermal effect of MWs by assuming an exponential relationship between \( \frac{V_{OH}}{V_0} \) and \( T_{OH} - T_{bulk} \) and calculating the rate enhancing effect

6.2. Modelling

The volume percentage \( \frac{V_{OH}}{V_0} \) – overheating \( T_{OH} - T_{bulk} \) relationships assumed in the overheated segments of 5–50%

\[
V_{OH}/V_0 = A \exp[-(T_{OH} - T_{bulk})/B] + C
\]

\[
\begin{array}{ccc}
A & B & C \\
95 & 0.404 & 94.6 & 1.317 \\
90 & 0.965 & 89.0 & 1.494 \\
80 & 2.054 & 77.9 & 1.865 \\
70 & 3.192 & 66.8 & 2.211 \\
60 & 3.209 & 56.8 & 3.770 \\
50 & 4.238 & 45.6 & 4.500 \\
\end{array}
\]

## 6.3 The accelerating effect of local overheatings

![Chemical structure](image)

\[ T_{\text{bulk}} = 200 \degree C; \Delta H^\# = 135.0 \text{ kJ mol}^{-1} \]

\[ k = A \cdot e^{-\frac{\Delta H^\#}{RT}} \]

Dependence of the relative rate enhancement \((k_{\text{rel}})\) on the overheated segment \((V_{\text{OH}}/V_0)\) assuming an exponential distribution of the \(T_{\text{OH}} - T_{\text{bulk}}\)

<table>
<thead>
<tr>
<th>Model ((V_{\text{bulk}}/V_0))</th>
<th>Reference</th>
<th>(A) (bulk)</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>Overall effect ((k_{\text{rel}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (95%)</td>
<td>(T_{\text{OH}} - T_{\text{bulk}} \degree C)</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>(V_{\text{OH}}/V_0 %)</td>
<td>0</td>
<td>0</td>
<td>2.5</td>
<td>1.1</td>
<td>0.6</td>
<td>0.32</td>
<td>0.2</td>
<td>0.155</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>(k_{\text{rel}})</td>
<td>1.00</td>
<td>0.95</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>II (90%)</td>
<td>(T_{\text{OH}} - T_{\text{bulk}} \degree C)</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>(V_{\text{OH}}/V_0 %)</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2.5</td>
<td>1.4</td>
<td>0.8</td>
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<td>1.00</td>
<td>0.90</td>
<td>0.06</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
<td>0.09</td>
<td>0.12</td>
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<tr>
<td>III (80%)</td>
<td>(T_{\text{OH}} - T_{\text{bulk}} \degree C)</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
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<tr>
<td></td>
<td>(V_{\text{OH}}/V_0 %)</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>4.8</td>
<td>3.3</td>
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<td>0.80</td>
<td>0.10</td>
<td>0.10</td>
<td>0.14</td>
<td>0.18</td>
<td>0.20</td>
<td>0.24</td>
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<tr>
<td>IV (70%)</td>
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<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>(V_{\text{OH}}/V_0 %)</td>
<td>0</td>
<td>0</td>
<td>9.5</td>
<td>7</td>
<td>5</td>
<td>3.5</td>
<td>2.5</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(k_{\text{rel}})</td>
<td>1.00</td>
<td>0.70</td>
<td>0.14</td>
<td>0.15</td>
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<td>0.29</td>
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<td>V (60%)</td>
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<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>(V_{\text{OH}}/V_0 %)</td>
<td>0</td>
<td>0</td>
<td>16.5</td>
<td>9.6</td>
<td>5.2</td>
<td>3.4</td>
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<td>0.20</td>
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<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td></td>
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<td>0.50</td>
<td>0.26</td>
<td>0.21</td>
<td>0.30</td>
<td>0.46</td>
<td>0.65</td>
<td>0.85</td>
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</table>

6.4. Calculation of the experimental rate enhancement

1.) pseudo first order kinetic equation

\[ k' = B \cdot \frac{\ln[(100 - x)/100]}{t} \]

where  
- \( k' \): pseudo first order rate constant
- \( x \): conversion
- \( t \): time

2.) Arrhenius equation

\[ k = A \cdot e^{\frac{-\Delta H^\#}{R \cdot T}} \]

where  
- \( k \): rate constant
- \( \Delta H^\# \): enthalpy of activation
- \( T \): temperature
- \( R \): universal gas constant

**the relationships utilized**

**the data used**

<table>
<thead>
<tr>
<th></th>
<th>( T_{set} = 200 , ^\circ C )</th>
<th>( t ) (h)</th>
<th>( x ) (%)</th>
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<tbody>
<tr>
<td>( \Delta ) reaction</td>
<td>2</td>
<td>17</td>
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<tr>
<td>( MW ) reaction</td>
<td>3</td>
<td>58</td>
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\( \Delta H^\# = 135.0 \, \text{kJ mol}^{-1} \)  
(obtained by quantum chemical calculation)

\( T^\Delta = 200 \, ^\circ C \)

\( k_{rel}^{exp} = \frac{k_{MW}^{MW}}{k^\Delta} = 3.10 \)

**the calculated parameters**

\( T^{MW} = 215.2 \, ^\circ C \)

\( A = 2.32 \)

\( k^\Delta = 2.59 \cdot 10^5 \, \text{s}^{-1} \)

\( k_{MW}^{MW} = 8.03 \cdot 10^5 \, \text{s}^{-1} \)
7. A study on the conformation of cyclic phosphinic acids and their esters (that were starting materials and products in the previous study.)

7.1. Conformational equilibrium and relative energies for 1-substituted-3,4-dimethyl-phospholane oxides

**cis**

The P-center remains unchanged!

**trans**

<table>
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<tr>
<th>R</th>
<th>A-a</th>
<th>A-b</th>
<th>conformational equilibrium</th>
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<td>H</td>
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<td>0</td>
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</tr>
<tr>
<td>Me</td>
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<table>
<thead>
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<th>B-b</th>
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<tr>
<td>Me</td>
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<table>
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<tbody>
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<tr>
<td>Me</td>
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<table>
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<tr>
<th>R</th>
<th>D-a</th>
<th>D-b</th>
<th>a shifted equilibrium</th>
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<tbody>
<tr>
<td>H</td>
<td>-8.1</td>
<td>0.9</td>
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</tr>
<tr>
<td>Me</td>
<td>-9.3</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>
Forbidden conformational/configurational changes for the cis forms of 1-hydroxy-3,4-dimethyl-phospholane oxide

The P-centers may not undergo a configurational change
7.2. Conformational situation for 1-substituted 3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxides

For isomers A and C of compound 5:

R = H (5), Me (6)
8. Summary / Conclusions

- From among the possible methods for the synthesis of phosphinates, the MW-assisted direct esterification of phosphinic acids is the most favourable. A suitable ionic liquid catalyst allows lower temperatures, shorter reaction times, and higher yields.

- Our experiences suggest that MW irradiation may be useful for thermoneutral reactions with high enthalpy of activation. Endothermicity works against complete conversion.

- The distribution of the beneficial local overheatings was modeled by an exponential function, and the extent of the rate enhancement was predicted by the Arrhenius equation.