

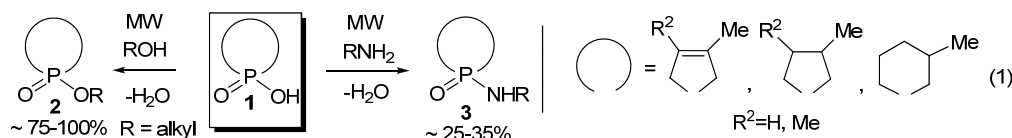
Synthesis and Use of Cyclic Phosphinic Acid Derivatives

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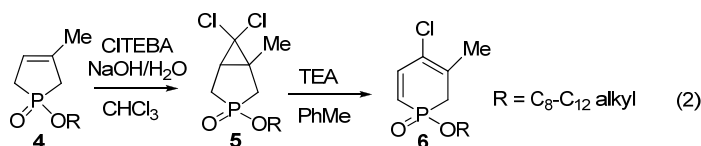
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Phosphinic acids (**1**) do not undergo direct esterification and other related derivatizations. To our surprise, the phosphinic acids (**1**) could be converted to phosphinates (**2**) and phosphinic amides (**3**) by reaction with alcohols and primary amines, respectively, under microwave (MW) irradiation (eq. 1).^[1]

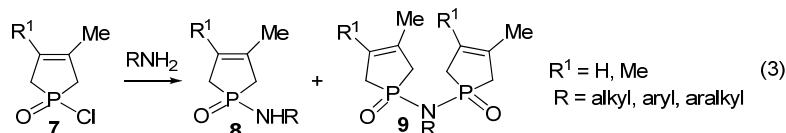


Based on high level quantum chemical calculations, we could explain the experimental observations and conclusions were drawn in respect of the scope and limitation of the MW technique.^[2]

1-Alkoxy-3-phospholene 1-oxides (**4**), obtained as shown above, could be used in ring enlargement involving the addition of dichlorocarbene to the double-bond of the phospholene oxide (**4**) followed by cyclopropane ring opening of the intermediate (**5**) so obtained (eq. 2).^[3]



The formation of 1-amino-3-phospholene 1-oxides (**8**) in the reaction of the corresponding phosphinic chloride (**7**) with amines was accompanied by the appearance of bis-phosphinoyl derivative **9** as the by-product (eq. 3).



The product composition could be fine-tuned and thus, either phosphinic amide **8**, or the bis-product (**9**) could be obtained selectively as the exclusive product.^[4] The *N,N*-bis phosphinoylated derivatives (**9**) form a new family of compounds showing interesting NMR properties and being potential *P*-ligands in catalysts.

References:

- [1] (a) G. Keglevich, N. Zs. Kiss, Z. Mucsi, T. Körtvélyesi, *Org. Biomol. Chem.* **2012**, *10*, 2011; (b) G. Keglevich, N. Zs. Kiss, L. Drahos, T. Körtvélyesi, *Tetrahedron Lett.* **2013**, *54*, 466; (c) N. Zs. Kiss, Z. Mucsi, É. Böttger, L. Drahos, G. Keglevich, *Curr. Org. Synth.* **2014**, in press.
- [2] Z. Mucsi, N. Zs. Kiss, G. Keglevich, *RSC Adv.*, **2014**, *4*, 11948.
- [3] N. Zs. Kiss, R. Örkényi, Z. Mucsi, G. Keglevich, *Heteroatom Chem.*, **2014**, submitted.
- [4] N. Zs. Kiss, A. Simon, L. Drahos, K. Huben, S. Jankowski, G. Keglevich, *Synthesis*, **2013**, *45*, 199.