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Microwave-assisted direct esterification of cyclic phosphinic acids in the presence of ionic liquids

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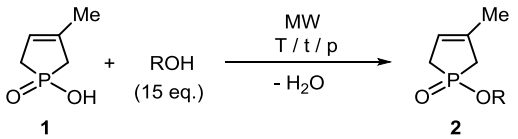
ABSTRACT

The efficiency of the microwave-assisted direct esterification of cyclic phosphinic acids was significantly enhanced by adding 10% of an ionic liquid to the reaction mixture prior to irradiation. In the presence of [bmim][PF_6] most of the esterifications were complete within 30 min at 180 °C.

The most frequent method for the synthesis of phosphinates involves the reaction of phosphinic chlorides with alcohols.[1–3] However, the use of acid chlorides introduces cost, and the hydrochloric acid formed needs to be removed by a base. On the whole, this esterification is not atom efficient. It is known that phosphinic acids typically do not undergo direct esterification with alcohols, and this reaction is possible only in special cases.[4,5] We have found that under microwave (MW) irradiation, phosphinic acids react with alcohols when used in a 15–20-fold molar excess to afford the corresponding phosphinates in variable yields.[6–8] The use of less volatile alcohols (bp ≥ 118 °C) was more efficient, as in these cases, the optimum temperature of 200–220 °C could be ensured considering the pressure limit of the MW reactor of *ca.* 20 bar. According to our theory, MW irradiation is helpful in overcoming the relatively high enthalpy barrier[9,10] because of the beneficial effect of the local overheating[11] appearing statistically in the bulk of the mixture.[12]

The obvious disadvantage of our MW-assisted esterification was the relatively high reaction temperature (optimally 200–235 °C) required. In a few cases, the reaction times reached 4 h. When alcohols with low boiling points were used, the yields of the phosphinates remained low. We wished to develop a more efficient esterification method utilizing ionic liquids (ILs) as additives. It has recently been found that certain organic chemical transformations became more efficient in the presence of ILs.[13–18] In a few cases, ILs were applied together with MW irradiation.[13,17,18]

Our model reaction was the MW-assisted esterification of 1-hydroxy-3-phospholene 1-oxide (**1**) which was carried out in the presence of 15 equivalents of various C_1–C_{12} alcohols at 160–230 °C in a closed vessel under MW irradiation (Scheme 1). The data whose major part was published earlier[6,8,9] are listed in Table 1. The esterifications with C_1–C_4 alcohols were not efficient, and a maximum conversion of *ca.* 38–62% could be obtained in five out of the six cases (Table 1, entries 1–6). The main reason was that the volatility of these alcohols prevented the application of temperatures >200 °C. Using *n*-pentanol, isopentanol, *n*-octanol, 2-ethylhexanol and dodecyl alcohol, quantitative conversions could be obtained as a consequence of the higher (220–235 °C) reaction temperature. However, with one exception, there was a need for 2–3 h irradiation. The corresponding phosphinates **2g**, **2h** and **2j-l** were prepared in yields of 82%, 76%, 71%, 76% and 95%, respectively (Table 1, entries 7, 8, 10–12). The esterification of phosphinic acid (**1**) with 3-pentanol could only be attempted at a maximum temperature of 210 °C allowed by its volatility. This temperature, together with the steric hindrance resulted in a rather low conversion of 36% after 4 h irradiation (Table 1, entry 9).



1 **2**

R = Me (**a**), Et (**b**), ^{n}Pr (**c**), ^{i}Pr (**d**), ^{n}Bu (**e**), ^{i}Bu (**f**), ^{n}Pent (**g**), ^{i}Pent (**h**), 3-Pent (**i**), ^{n}Oct (**j**), ^{i}Oct (**k**), Dodecil (**l**)

Scheme 1.

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