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A Superior New Route to Methyl Phosphonate-based Ionic Liquids

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In the search for new ionic liquids (ILs) for biomass processing, analytical chemistry, or modern nonvolatile fire retarding agents, alkyl phosphonate-based ILs represent very promising candidates. A very practical synthesis of such ILs, which is superior to the conventional quaternization of 1-alkylimidazoles by dimethyl phosphite (DMP), was developed. 1,3-Dialkylimidazolium halide salts serve as convenient starting materials, and various 1,3-dialkylimidazolium methyl phosphonates are thus accessible by simple, fast, and solvent-free procedures with DMP, where the anion is methylated.

Ionic liquids (ILs) have been frequently investigated for the exploitation of renewable raw materials such as biomass because of their ability to dissolve the usually insoluble lignocellulose. In this context, our attention was attracted to alkyl phosphonate-based ILs, which were reported to be excellent for use in high-performance ionic liquid chromatography and extraction of polysaccharides from bran.[1–3] The primary aim of our research was the synthesis of new alkyl phosphonate-based imidazolium salts for cellulose dissolution. The synthesis should be practical for large-scale industrial use; a technical grade of the compound is accepted in favor of a reasonably priced product. Two different synthetic routes for these compounds are known, but both seemed to be too time-consuming and tedious for bulk syntheses. In the first approach, a dialkyl phosphite is used for the quaternization of 1-alkylimidazoles to form 1,3-dialkylimidazolium alkyl phosphonate-based ILs[4] (Figure 1a), our favored class of ILs. However, processes of this type are normally very slow (up to 48 h).[5–7] In addition, the alkylation is limited by the availability of the respective dialkyl phosphites. Therefore we envisaged an alternative synthetic route with dialkylimidazolium halides as starting materials, whereupon the halide anion is removed after alkylation by dimethyl phosphite (DMP)

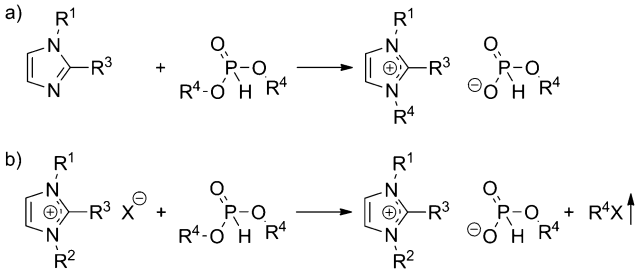

Figure 1. a) Existing procedure: quaternization of alkylimidazoles;[4] b) novel, generalized synthesis: alkylation of the halide counter ion of dialkylimidazolium salts with DMP.

(Figure 1b). This type of reaction was first reported in 2005 for the respective ion metathesis of cetyltrimethylammonium bromide using a large excess of diethyl phosphite under reflux in toluene.[8] An alternative synthesis was reported, also starting with a bromide salt and exchanging the anion first to hydroxide and then to the desired phosphonate.[1] These procedures were not suitable for our purpose due to the long reaction time and the necessary removal of excess alkylating agent and solvent. Therefore, we developed a convenient synthesis, which is fast, simple, solvent-free, and provides access to a wide range of different derivatives. Halide impurities are considered acceptable to a certain extent (<3 wt %), all the more so since chloride-based ILs are excellent solvents for biocomposites on their own (despite other drawbacks).[9]

For the practical synthesis, neat 1,3-dialkylimidazolium halide[10] (60 mmol) was placed in a flask, and a small excess (1.01 equiv) of DMP was added. The suspension was heated to 80 °C and stirred for 2 h. The methyl halide generated was allowed to escape and collected using a cold trap. The volatiles were removed, and the product was dried in vacuum at 80 °C for another 4 h. Insoluble starting material, such as 1-propargyl-2,3-dimethylimidazolium bromide (propargyl means 2-propynyl), was dissolved in a minimum amount of methanol. This was also the only case giving a solid product; all other reactions resulted in room-temperature ILs.

The products were analyzed by ^{1}H and ^{13}C NMR spectroscopy, a discrepancy was revealed between the expected and found integration of the H atoms of the methyl phosphonate CH_3-group, which showed less than three H atoms. The assumption of residual halide in the anion composition due to incomplete reaction was confirmed by ion-exchange chromatography (IEC). The results of the IEC confirmed the expected halide contents determined by calculation from H-integration values in ^{1}H NMR spectra. The results are summarized in Table 1. Chlorides (Entries 1–4) showed an average of 92 mol % conversion, whereas bromides (Entries 5–7) and iodides (Entries 8 and 9) gave only 30–40 mol % of the desired methyl phosphonates. This remarkable performance of the chloride salts can be ascribed to the high vapor pressure of the escaping CH_3Cl (490 kPa, 20 °C) and the resulting continuous removal of this by-product. In comparison, ^{1}H NMR spectra of products from classical quaternization of 1-alkylimidazoles with DMP did not show these too low H integration values.

In the case of 1-propargyl-2,3-dimethylimidazolium methyl phosphonate, the coexistence of the starting bromide could be confirmed by X-ray analysis of single crystals, which were spotted in the solid product.[10,11] By using a large excess of DMP (4 equiv) and stirring overnight at 80 °C, the conversion of 1-allyl-3-benzylimidazolium bromide (Entry 5) could be slight-

Table 1. Conversion of 1-alkylimidazolium halides with DMP

Entry	X	R^1	R^2	R^3	H integr.	Conv. /mol %[a]	X/wt % calc.[a]	X/wt % IEC[b]	CA-No. product
1	Cl	Methyl	Allyl	H	2.57	86	2.4	2.1	1239277-06-5
2	Cl	Methyl	Benzyl	H	2.82	94	0.8	1.7	81995-06-4
3	Cl	3,4,5-Tri-methoxybenzyl	Allyl	H	3.00	100	0.0	0.6	—
4	Cl	Allyl	Allyl	H	2.66	89	1.7	1.8	—
5	Br	Benzyl	Allyl	H	1.02	33	18.6	14.2	—
6	Br	Methyl	Allyl	H	1.13	38	23.9	26.5	1239277-06-5
7	Br	Methyl	Propargyl	Methyl	1.14	38	22.4	20.9	—
8	I	Methyl	Ethyl	H	0.96	32	36.0	—	81994-80-1
9	I	Methyl	Butyl	H	1.23	41	29.6	32.6	81994-81-2

[a]From ^{1}H NMR integration. [b]From IEC.

ly improved to 50 mol % (integration of 1.5 H for the methyl phosphonate CH_3-group).

Similar procedures have been published for the reaction of 1,3-dialkylimidazolium chlorides with trialkyl phosphates,[12–14] or with *O*,*O*,*O*-trimethyl thiophosphate.[15] Products of the latter reaction also showed a chloride content of 1–2 wt %, which could be significantly decreased by ultrasonication.[16] Consequently, the attempt was made to improve the dimethyl phosphite reaction using ultrasonication at 50 °C for 2 h, but the result was hardly satisfying.

In summary, 1,3-dialkylimidazolium chlorides are the best starting materials for this practical synthesis of methyl phosphonate-based ILs. These liquids exhibit superior dissolution power and low viscosity. They contain up to 2 wt % of chloride, which is perfectly acceptable for technical grade ILs intended for commercial use. Whereas the conventional quaternization is always restricted by the availability of the necessary dialkyl phosphite, this limitation is circumvented by the novel synthetic approach. Another big advantage of the present method is the utilizability of commercial, or easily accessible, very affordable 1,3-dialkylimidazolium halides. This henceforth available diversity of phosphonate-based ILs lays groundwork for further possible stimulus, especially in the fields of biomass fractionation,[17] analytical chemistry,[18] or nonvolatile fire retarding agents with high environmental benignity.[19]

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11 Crystal data for $C_8H_{11}N_2Br$ (fw = 215.1). Monoclinic, $P2_1/n$, $a = 10.3869(5)$, $b = 7.5143(3)$, $c = 11.7958(6)$ Å, $\beta = 102.662(5)°$, $V = 898.28(7)$ Å^3, $Z = 4$. $R_1 = 0.025$ for 1447 reflections with $I > 2\sigma(I)$, $wR_2 = 0.063$ for all data. Crystallographic data reported in this manuscript have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-873256. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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