Microwave assisted synthesis of 1-allyl-3-methylimidazolium chloride

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Abstract

The ionic liquid 1-allyl-3-methylimidazolium chloride was prepared in a fast and efficient way by solventless microwave irradiation of allyl chloride and N-methylimidazole in a sealed vessel.

Ionic liquids (IL's) have appealed consideration of researchers in the last decade, due their particular properties and applications in synthesis, catalysis, biocatalysis, liquid-liquid separations, extraction processes, nanomaterials, polymerization and electrochemistry. IL's are an excellent alternative to substitute volatile organic solvents in more environmental friendly technologies ("green technologies"), since their very low vapor pressures, thermal and chemical stability, ability to act as catalyst, and non-flammability and non-corrosive properties.[1]

Conventional synthesis of ionic liquids required usually a large excess of alkyl halides and organic solvent under refluxing for several hours at relatively high temperature, to afford reasonable yields.

Microwave activation occurs via polarization of dielectric material when the distribution of an electron cloud is distorted and physical rotation of molecular dipoles occurs or through conduction mechanism in solutions that contain ionic material, the ions start to move under the influence of the electric field of the microwave irradiation. This results in an outflow of energy because of an increased collision rate, converting kinetic energy into heat.

Ionic liquids have an ionic structure and usually consist of an organic cation and an inorganic or organic anion. This convert these compounds as ideal susceptors for microwave heating, which joined to their special properties as solvents has converted the microwave assisted synthesis in ionic liquids a useful component in the chemist's toolbox. The synthesis of ionic liquids assisted by microwaves is also benefited by its nature as is demonstrated by a wide literature.[2]

In the field of ionic liquid syntheses, the preparation of a reproducible method for obtaining a large scale is very important. In this communication we improve the preparation of 1-allyl-3-methylimidazoliym chloride due its interest, since it constitutes a monomer for the preparation of polymeric ionic liquids and it has been widely used in the removal of lignin from cellulose.[3]

The previous communication by Fu and Liu [4] on the synthesis of 1-allyl-3-methylimidazolium chloride using microwave irradiation for 30 seconds at 180ºC under reflux conditions, inspired us to carry out the reaction following these conditions. But, due to the very low boiling point of allyl chloride (45ºC) we choose to carry out the procedure in a closed reaction vessel. Under these conditions we observed a not very clean ^{1}H-NMR spectrum (Figure 1).

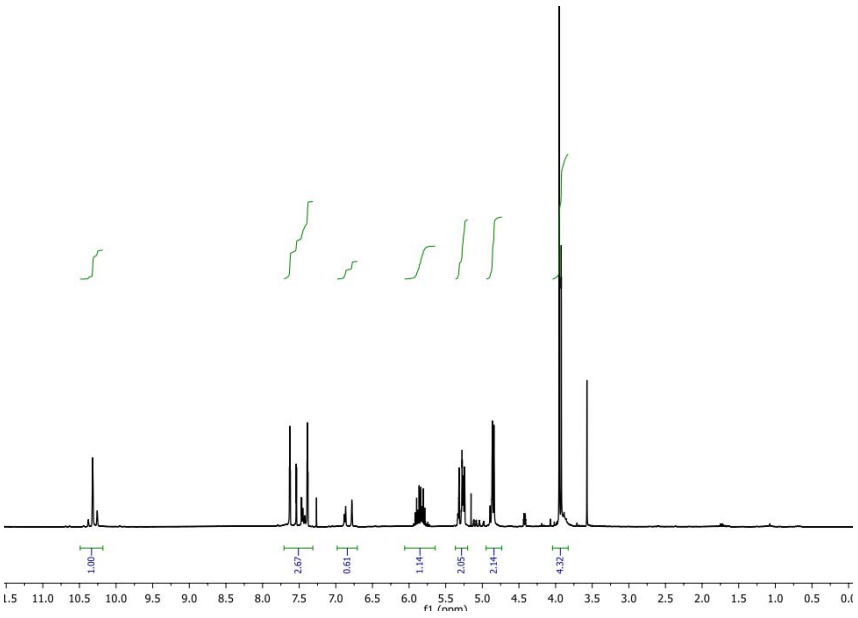


Figure 1. ^{1}H-NMR from Irradiation with microwaves at 180ºC, 30 seconds, 185W

Longer reaction times in these conditions did not improve the cleanliness of the reaction. Thus, 3 minutes irradiation gave a similar NMR spectrum (Figure 2). Irradiation at 180ºC for reaction times longer than five minutes led to decomposition.

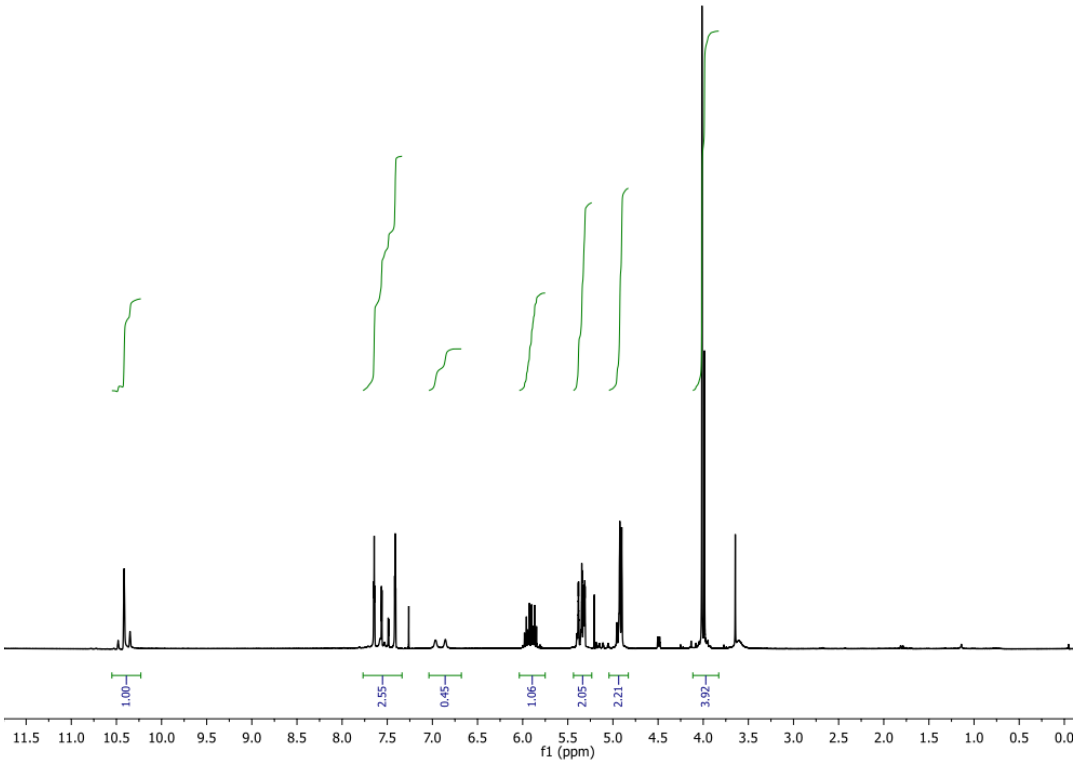


Figure 2. ^{1}H-NMR from Irradiation with microwaves at 180ºC for 3 min.

In order to improve the method, different temperatures and ratios of N-methylimidazole and allylchloride were checked. After several assays at 160ºC, the temperature was settled at 100ºC. Thus, using a proportion of imidazole-allylchloride 1:1.2, and irradiating during 10 minutes there was still a small amount of unreacted imidazole (IL:imidazole, 100:2.47, Figure 3). For a ratio of 1:1.5 the quantity of unreacted imidazole decreased (100:0.28) and for 1:2 the results were better (100:0.07). This last was considered a good compromise between completeness of the reaction and excess of allyl halide used.

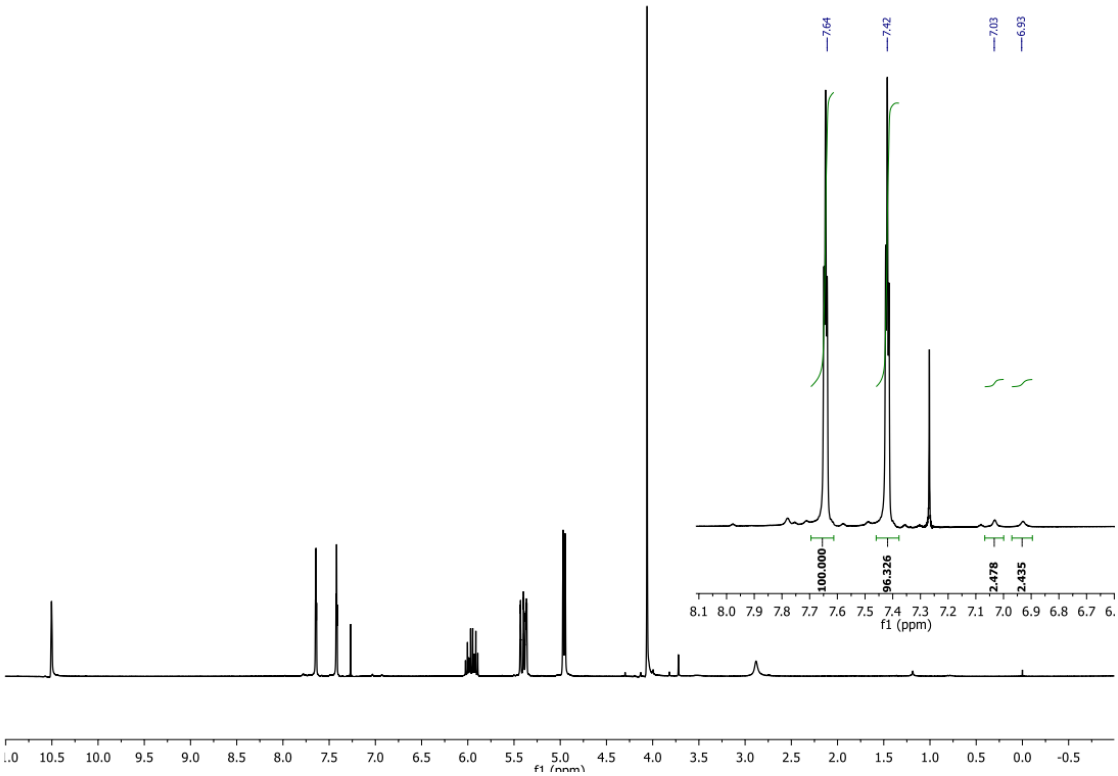
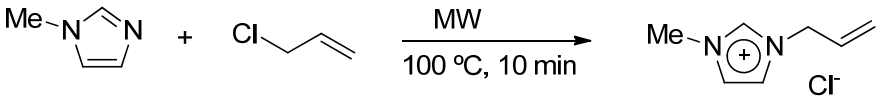


Figure 3. [1]H-NMR from microwave Irradiation at 100ºC for 10 min, using 1.2 equivalents of allyl chloride.

Then, the improved method consists in irradiating a mixture of 2 equivalents of allychloride with imidazole at 100 ºC during 10 min in a sealed vessel (Scheme 1). This rendered a 75% yield of the IL pure by [1]H-NMR (Figure 4).



Scheme 1

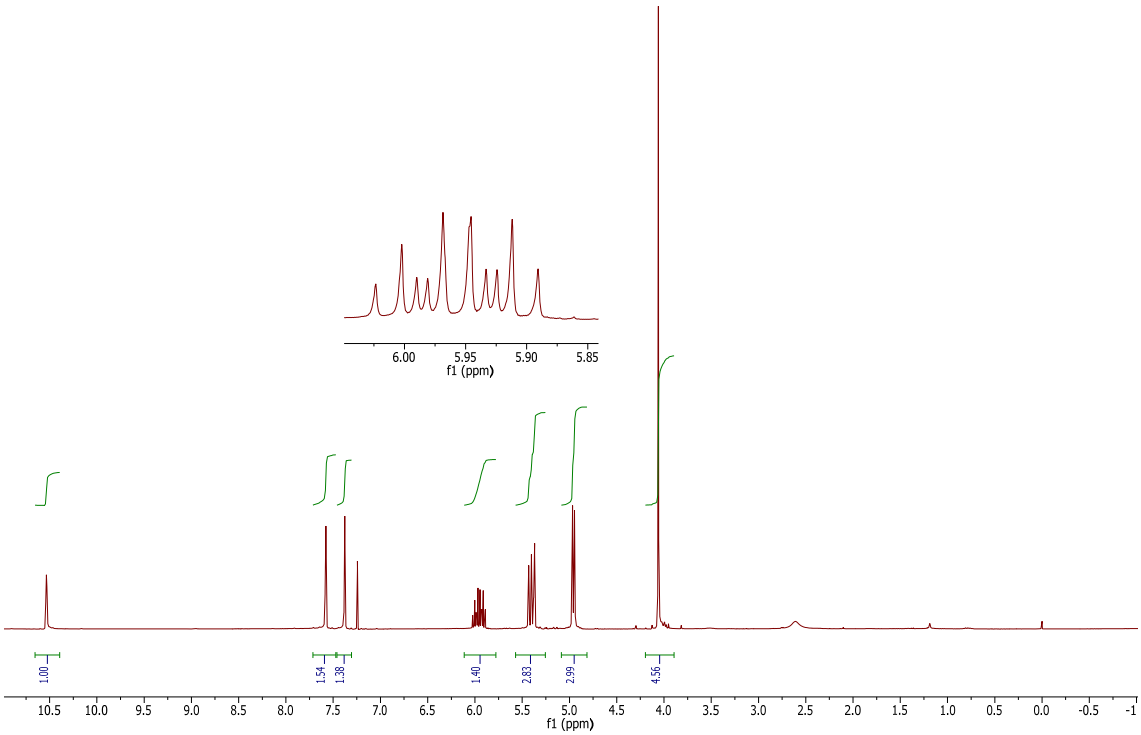


Figure 4. ^{1}H-NMR spectrum of 1-allyl-3-methylimidazoliym chloride.

Experimental procedure

Imidazole (2g, 24.4 mmol) and allylchloride (3.728g, 48.7 mmol) were irradiated in a closed vessel, for 10 minutes at 100 ºC (300W) in a Discovery microwave oven (CEM). The reaction mixture was kept under vacuum to remove the excess of allylchloride, and washed with dichloromethane (2 x 10 mL) to remove the unreacted imidazole. After storing one night under vacuum 1-allyl-3-methylimidazoliym chloride was obtained as a pale yellow oil (2.896 g, 75%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.58 (t, 1H, J= 1.7 Hz), 7.38 (t, 1H, J= 1.7 Hz), 5.96 (ddt, 1H, J= 16.5, 10.2, 6.4 Hz), 5.40 (m, 2H), 4.96 (d, 2H, J= 6.4 Hz), 4.06 (s, 3H, CH_3).

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References and Notes

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