Organic Process Research & Development **2008,** *12,* 1089–1093

Green Chemistry with a Novel 5.8-GHz Microwave Apparatus. Prompt One-Pot Solvent-Free Synthesis of a Major Ionic Liquid: The 1-Butyl-3-methylimidazolium Tetrafluoroborate System

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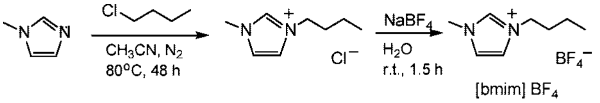
Abstract:

This article reports for the first time the rapid one-pot solvent-free synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), a major ionic liquid, in good yields (87%) after 30 min of microwave irradiation with microwaves at a frequency of 5.8 GHz in a batch-mode reactor. By contrast, the yields of [bmim]BF_4 are about 3-to-4-fold smaller when using 2.45-GHz microwave radiation and oil bath heating: 28% and 21%, respectively, under otherwise identical conditions. This further shows the advantage(s) of the 5.8-GHz microwave radiation and the accompanying apparatus as a novel synthetic tool reported in some detail elsewhere {*Org. Process Res. Dev.*. 2008, *12*, 257−263}. The three synthetic methods (viz., 5.8-GHz and 2.45-GHz microwave heating, and oil bath heating) were examined in reactors used in both the batch and reflux modes. In the latter mode, the yields of [bmim]BF_4 were less than 10% even after a 60-min reaction period. The dependence of the synthesis on the frequency of the microwave radiation is discussed in terms of the chemical yields of the product and the dielectric factors of each substrate in the synthesis mixtures composed of 1-methylimidazole, 1-chlorobutane, and sodium tetrafluoroborate.

1. Introduction

The last two decades have witnessed an increasing number of new ionic liquids (or so-called room-temperature molten salts) based mostly on the 1-alkyl-3-methylimidazolium cation and tetrafluoroborate anion that are resistant to traces of moisture and are commonly used as solvents with virtually no vapor pressure so that they are the solvents of choice and environmentally benign media to replace volatile organic solvents in many industrially relevant chemical processes. Such ionic liquids are widely used as electrolytic media in fuel cells and batteries,[1,2] in biphasic and homogeneous catalysis,[3,4] in major subdisciplines of analytical chemistry such as chromatography, extraction, electroanalytical chemistry, sensing, and spectrometry,[5,6] in microwave-assisted organic syntheses,[7] and in various supercritical fluid applications.[8] In recent years, ionic liquids have also found application as green solvents because of their nonvolatility, their chemical stability, and noninflammability and recycling.[9] However, such applications are often restrained because of the high costs of producing ionic liquids in comparison with the more common organic solvents.

The complex synthesis of ionic liquids typically necessitates long reaction times, a point that has impacted negatively on some applications. For instance, reaction times of one or more days are necessary for the synthesis of high yields of the room-temperature ionic liquid (RTIL) 1-butyl-3-methyl-imidazolium tetrafluoroborate [bmim]BF_4 [10−12] (see reaction 1). Note that



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the precursor to the synthesis of the pale-yellow[12−17] oily RTIL [bmim]BF_4 in reaction 1 is the 1-butyl-3-methylimidazolium chloride salt, a white crystalline solid.[10] Earlier syntheses of the [bmim]BF_4 ionic liquid have employed an anion exchange method, an acid ester method, and a neutralizing method, all carried out at ambient temperatures.

Earlier reports by Namboodiri and Varma[18−20] showed that the 1,3-dialkylimidazolium halide precursors can be synthesized successfully in relatively short times (from several hours to a

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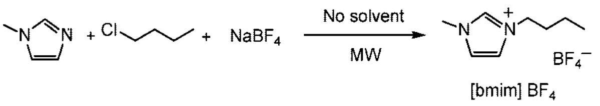
10.1021/op800135t CCC: $40.75

few minutes) by a microwave-assisted process that avoids employing large quantities of alkyl halides and organic solvents. Subsequently, using a nonmodified domestic microwave oven operated at relatively high microwave powers (240 and 360 W) these authors were also successful in preparing ionic liquids bearing tetrafluoroborate anions using microwave irradiation under solvent-free conditions by exposing a mixture of the imidazolium halides and ammonium tetrafluoroborate to microwaves. This combination of solvent-free conditions and microwave irradiation can lead to large decreases of reaction times and to enhancement in conversions and selectivity. To underline the potential of coupling a solvent-free reaction with focused microwave activation and to further examine nonthermal microwave-specific effects on comparison with the reaction carried out under conventional heating under otherwise identical conditions, Thanh and co-workers[21] were able to synthesize, for the first time, chiral ionic liquids bearing chiral ephedrinium cations using a solvent-free process under green chemistry conditions in closed and open systems. A simple and rapid method of preparing alkylpyridinium and 1-alkyl-3-methylimidazolium salts on a large scale in a closed vessel under 2.45-GHz microwave irradiation has also been reported by Khadilkar and Rebeiro.[22] Other studies and reviews have examined various syntheses in ionic liquids through the prompt heating imparted by microwave radiation and ultrasounds[23−25] along with applications of ionic liquids in organic and organometallic syntheses.[26]

In an earlier report,[27] we examined a novel 5.8-GHz microwave apparatus to characterize some properties of the most common organic solvents and its application to a Diels−Alder reaction as opposed to and compared with the more commonly used 2.45-GHz microwaves. Herein, we examine further the 5.8-GHz microwave radiation and irradiation apparatus (a) in carrying out the one-pot solvent-free synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF$_4$, in a reactor containing the three required reagents, namely 1-methylimidazole, sodium tetrafluoroborate and 1-chlorobutane, (b) in examining further the frequency dependence of the microwaves in organic syntheses using both the 5.8-GHz and 2.45-GHz radiation, and (c) in examining the temperature dependence of the process from microwave heating as opposed to conventional heating using an oil bath.

2. Experimental Section

2.1. Synthesis of 1-Butyl-3-methylimidazolium Tetrafluoroborate ([bmim]BF$_4$). The three reagents sodium tetrafluoroborate (NaBF$_4$; 17.5 g), 1-methylimidazole (11.0 mL, 0.139 mol) and 1-chlorobutane (15.0 mL, 0.144 mol) were introduced under argon-purged conditions into a high-pressure 150-mL Pyrex glass cylindrical reactor {Taiatsu Techno Co.; size, 160 mm (H) × 37 mm (i.d.); maximal pressure, 1 MPa} toward the synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate (reaction 2).The cylindrical reactor was then installed in the 5.8 GHz microwave apparatus[27] as displayed partially in Figure 1. The 5.8-GHz frequency microwave generator was a Panasonic M5801 with maximal power of 700 W. A pressure gauge and a release bulb were connected to the cover of the reactor (Figure 1). The temperature of the reacting solution was monitored using an optical fiber thermometer (FL-2000, Anritsu Meter Co. Ltd.) and a k-type sheathed thermocouple. The cylindrical reactor was sealed with a silicone O-ring and covered with a stainless steel cap; in the batch mode, the reactor was capped with a Teflon cover, whereas in the reflux mode a reflux condenser was connected to the reactor as displayed in Figure 1. The reaction mixture was continually stirred magnetically under batch and reflux conditions. We also confirmed that the magnet bar used to stir was not a heat source under microwave irradiation.



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Factors of the 5.8-GHz radiation that impact on the synthesis yields are compared with those from the 2.45-GHz microwaves and from the synthesis carried out by conventional heating with

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(13) Extensive studies by Farmer and Welton (ref 14) and by Burrell et al. (ref 15) have shown that the ionic liquid [bmim]BF$_4$ is a colorless oily liquid, contrary to the observations by Creary and Wills (ref 16) who report that [bmim]BF$_4$ is a colorless to pale-yellow viscous liquid, and the observations by Dupont et al (ref 12) who indicate the product to be a light-yellow oily liquid. Apparently, the synthesis temperature may have an effect on the quality of [bmim]-based products (ref. [17]).

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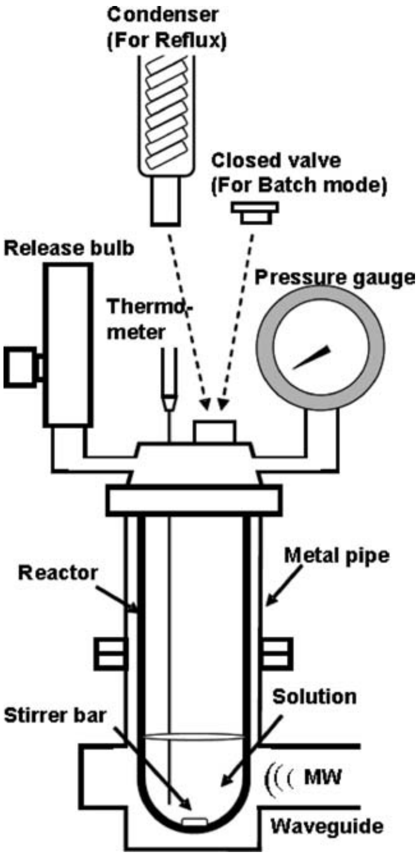

Figure 1. **Schematic illustration of the reactor that can be used in both the batch and reflux modes in the microwave system operated in the single mode.**

an oil bath. In all cases, the same experimental instruments were used as for the experiments carried out with the 5.8-GHz microwaves. For the experiment involving oil bath heating, the oil was preheated to 130 °C because the rate of temperature increase for the reacting mixture was lower than the corresponding rate obtained under microwave irradiation. Initially it was important to optimize the microwave power level for the synthesis of [bmim]BF_4. A rapid increase of the internal pressure was observed in the cylindrical reactor upon irradiating the reacting mixture with microwaves at power levels greater than 30 W. Clearly, 30 W was the safe maximum microwave power level output under our conditions, and thus was chosen to carry out the syntheses with microwave radiation. Further details of the experimental setup were described earlier.[27]

2.2. Analytical Methodology. Purification of the pale-yellow room-temperature ionic liquid (oily product; [bmim]BF_4)[12−17] resulting from the solvent-free one-pot microwave-assisted synthesis was carried out using a methodology reported earlier for similar ionic liquids.[10] Thus, the product mixture was filtered to remove the precipitated chloride salt (NaCl) and any unreacted $NaBF_4$, after which the organic phase was treated with diethyl ether repeatedly to remove any unreacted 1-chlorobutane and 1-methylimidazole. Diethyl ether was then removed *in vacuo* and the residue washed three times with small volumes of water to remove any remnant of chloride ions. A subsequent workup of drying *in vacuo* at 100 °C gave the desired product, the nature of which was ascertained by ^{1}H NMR spectrometry using a JEOL 500 MHz GX-270 ^{1}H NMR spectrometer ($CDCl_3$ was the solvent and TMS was the reference standard) and by mass spectral methods using a JEOL JMS-700 FAB-MS spectrometer.[10]

Scheme 1. **Overall reaction in the synthesis of the ionic liquid [bmim]BF_4, inferred from ^{1}H NMR spectrometry by comparison of the NMR results with those reported in ref** 10 **for various 1-butyl-3-methylimidazolium-based products with different counterions**[a]

[a] The resulting data of the product [bmim]BF_4 gave, respectively, ^{1}H NMR spectral data: δ (ppm) = 8.81 (1H, singlet, $\mathrm{NC\underline{H}N}$), 7.32 (1H, triplet, $\mathrm{CHNCHC\underline{H}N}$), 7.28 (1H, triplet, $\mathrm{CH_3NC\underline{H}CHN}$), 4.18 (2H, triplet, $\mathrm{NC\underline{H}_2(CH_2)_2CH_3}$), 3.95 (3H, singlet, $\mathrm{NC\underline{H}_3}$), 1.86 (2H, multi, $\mathrm{NCH_2C\underline{H}_2\text{-}CH_2CH_3}$), 1.37 (2H, multi, $\mathrm{NCH_2CH_2C\underline{H}_2CH_3}$), 0.93 (3H, triplet, $\mathrm{NCH_2CH_2CH_2C\underline{H}_3}$). Mass spectral data (10.0 kV) gave: *m/z* = 139 (M^+, 100%), 83 ($C_4H_7N_2^+$, 5%).

2.3. Dielectric Parameters of the Reacting Substrates and the [bmim]BF_4 Ionic Liquid. The dielectric parameters measured for the [bmim]BF_4 product and for the reacting substrates were the dielectric constant (ε'), the dissipation factor ($\tan\delta = \varepsilon''/\varepsilon'$), the dielectric loss factor (ε'') and the penetration depth. The dielectric constant (ε') and the dielectric loss factor (ε'') were analyzed with an Agilent Technologies HP—85070B Network analyzer. The dissipation factor ($\tan\delta$) was calculated from these values as $\tan\delta = \varepsilon''/\varepsilon'$. The dielectric loss factor (ε'') reflects the microwave energy converted to heat.[25] This factor is a useful index for the generation of heat because of the interaction of the reagents with the microwave radiation field. The penetration depth (cm) of the microwaves into the reacting system was calculated from equation 3.[25]

$$d = \frac{1}{2\left(\sqrt{\frac{1}{2}\omega^2\varepsilon_0\mu_0\left(\sqrt{\varepsilon'^2\varepsilon''^2} - \varepsilon'\right)}\right)} \qquad (3)$$

3. Results and Discussion

3.1. The Synthesis of [bmim]BF_4. Subsequent to microwave irradiation of the reacting mixture for 15-, 30-, and 60-min periods and the purification stages, a comparison of the proton NMR and mass spectral data of the resulting product (summarized in Scheme 1) with those reported earlier by Cammarata and co-workers[10] indicates the product to be the 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid [bmim]BF_4.

The synthesis yields of this ionic liquid under the various experimental conditions used are listed in Table 1. Results clearly demonstrate that the one-pot solvent-free synthesis of this ionic liquid is possible with microwave radiation heating and by classical heating. It is relevant to note that the reaction of Scheme 1 is not a synthesis peculiar only to the microwave radiation since conventional heating with the oil bath gave the same product. Regardless, the synthetic efficiency was significantly different as evidenced by the data of Table 1. In the batch mode, the chemical yields of [bmim]BF_4 (87% after a 30-min period) from the 5.8-GHz microwave heating were some 3-to-4-fold greater than the yields obtained with either the 2.45-GHz microwave heating (28%) or the oil-bath heating (21%).

Table 1. **Chemical yields of [bmim]BF_4 from the solvent-free one-pot synthesis under various experimental conditions; microwave power level was constant at 30 W**

		batch		reflux	
	time (min)	temperature attained (°C)	yield (%)	temperature attained °C)	yield (%)
5.8 GHz	15	125	trace	105	trace
	30	155	87	105	4
	60	169	84	105	8
2.45 GHz	15	138	trace	105	3
	30	204	28	105	8
	60	219	29	105	10
Oil bath	15	133	trace	103	trace
	30	168	21	105	5
	60	176	25	105	12

By contrast, in the reflux mode the yields were rather mute (less than 10%) with no predominance of either the 5.8-GHz or 2.45-GHz microwaves compared to oil bath heating.

3.2. Factors Impinging on the High Yields of [bmim]BF_4 by 5.8-GHz Microwave Heating. The temperature−time profiles of the mixture of reacting substrates in the synthesis of [bmim]BF_4 in the batch mode are illustrated in Figure 2a. After 10 min into the process, the 5.8-GHz microwave heating was constantly lower than either with the 2.45-GHz microwave heating or with the oil bath heating methods. The temperature increase was not monotonic under the 2.45-GHz microwave radiation. In fact, for the synthesis of [bmim]BF_4 by the batch process, unusual temperature increases were observed with the 2.45-GHz radiation after 3, 10 and 20 min (Figure 2a). This irregular increase is likely caused by the formation of the [bmim]BF_4 ionic liquid. That is, the heating efficiency with the 2.45-GHz microwaves changed because the composition of the reacting mixture changed by formation of [bmim]BF_4. Evidently, the synthesis of this ionic liquid proceeded in various stages (herein examined no further) when using the 2.45-GHz microwaves. Contrary to the latter, the temperature profile observed for the 5.8-GHz microwave radiation was somewhat noisy beyond 20 min of irradiation, but otherwise of no consequence with regard to the smooth formation of the product.

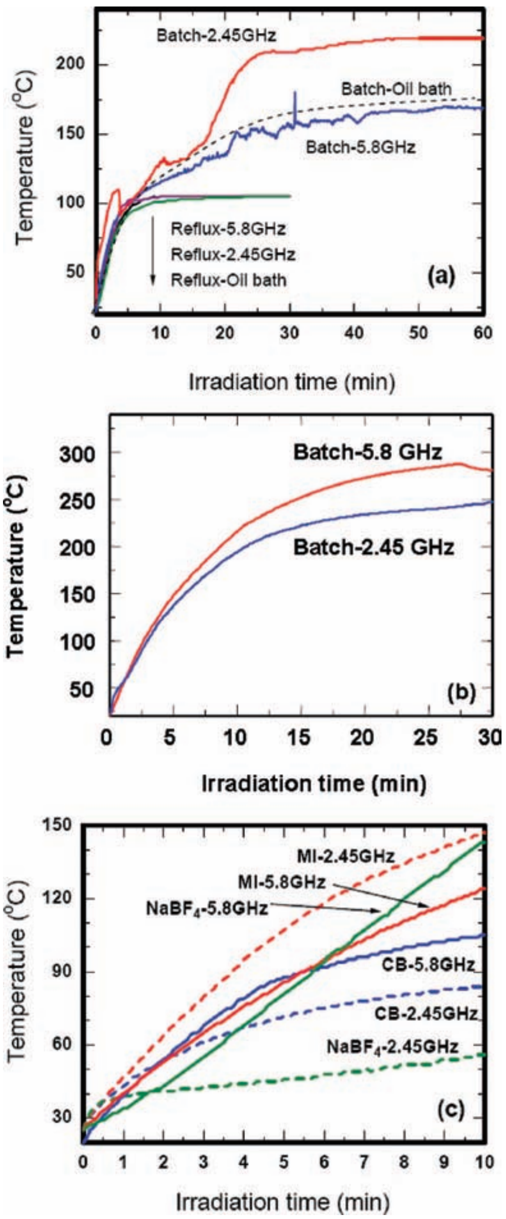

Figure 2. **(a) Temperature−time profiles in the synthesis of [bmim]BF_4 on using the 5.8 and 2.45 GHz microwave radiation and oil bath heating for both batch and reflux modes. (b) Temperature−time profiles of pure [bmim]BF_4 subjected to 5.8 and 2.45 GHz microwave irradiation in the batch mode. (c) Temperature−time profiles of the individual reacting substrates $NaBF_4$, 1-methylimidazole (MI), and 1-chlorobutane (CB) under 5.8 and 2.45 GHz microwave irradiation in the batch mode. In all cases the mixtures were stirred during the temperature measurements (microwave power level, 30 W). Note that the temperature was measured every 30 s.**

The temperature−time profiles of pure [bmim]BF_4 subjected to 5.8-GHz and 2.45-GHz microwave radiations in an open system reactor are shown in Figure 2b. Rapid heating of [bmim]BF_4 was observed: ∼180−200 °C within about 10 min at both microwave frequencies, although the temperature rise in the case of the 5.8-GHz microwaves was somewhat higher (by ∼25 °C after 30 min) than under the 2.45-GHz radiation. Figure 2c reports the temperature−time profiles of the individual reacting substrates (1-chlorobutane (CB), 1-methylimidazole (MI), and the solid $NaBF_4$) in the batch mode. Significant differences in the temperature profiles of the reacting substrates are evident on irradiation with the 2.45-GHz microwaves: 84, 147, and 56 °C, respectively, after a 10-min irradiation period. The rather inefficient microwave heating of the 1-chlorobutane substrate, relative to that of 1-methylimidazole, was also evidenced by the small dielectric loss factor ($\varepsilon'' = 0.51$ versus 1.4) and penetration depth (336 cm vs 165 cm; see Table 2). Differences in the temperature profiles of the reacting materials subjected to the 5.8-GHz microwave radiation were smaller (105, 124 and 143 °C, respectively, after 10 min) than with the 2.45-GHz microwaves (Figure 2c). Moreover, the temperature profile of CB on irradiation with the 5.8-GHz microwaves was notably greater in contrast to the profile observed for CB with the 2.45-GHz microwaves. Of particular significance is the crossover observed in the temperature profiles of the CB and MI liquid substrates after ∼5.5 min of irradiation with the 5.8-GHz microwaves. This confirms the occurrence of temperature-dependent changes in the dielectric factors.[28] Although $NaBF_4$ is a solid material, the temperature profile under the 5.8-GHz

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Table 2. **Dielectric parameters at a microwave frequency of 5.8 and 2.45 GHz for the ionic liquid [bmim]BF_4, 1-methylimidazole (MI), and 1-chlorobutane (CB) at ambient temperature**

	dielectric constant (ε')		dissipation factor (tan δ)		dielectric loss factor (ε'')		penetration depth (cm)	
	5.8 GHz	2.45 GHz	5.8 GHz	2.45 GHz	5.8 GHz	2.45 GHz	5.8 GHz	2.45 GHz
[bmim]BF_4	8.9	10.5	0.66	1.0	5.9	10.5	44	21
1-methyl imidazole (MI)	21.5	32.3	0.75	0.35	16.1	11.2	25	32
1-chlorobutane (CB)	7.6	7.7	0.18	0.07	1.4	0.51	165	336

microwave irradiation was nonetheless significantly greater than under the 2.45-GHz microwaves.

The dielectric constants (ε'), the dissipation factors (tan δ), the dielectric loss factors (ε''), and the penetration depth (cm) of pure [bmim]BF_4, 1-methylimidazole (MI), and 1-chlorobutane (CB) at the two microwave frequencies of 5.8 and 2.45 GHz at ambient temperature are listed in Table 2. These data show a correlation with the temperature−time profiles of the [bmim]BF_4 ionic liquid with the profile being greater for the 2.45-GHz microwave radiation. No similar correlation is evident for 1-methylimidazole.

Closer examination of the results reported in Figure 2a shows that the temperature rise in the synthesis of [bmim]BF_4 with 2.45-GHz microwave heating was more effective than with the 5.8-GHz microwaves, even though the temperature increase was not uniform. The profiles in Figure 2c indicate that the 1-methylimidazole was promptly heated by the 2.45-GHz microwave radiation, and subsequently aided in the temperature rise of the CB and $NaBF_4$ substrates with MI becoming a secondary heat source. Accordingly, the necessary temperature for the synthesis of [bmim]BF_4 was achieved by the 2.45-GHz radiation. In the absence of mixing the substrates (see Figure 3) localized temperature hot spots can form on the MI, CB, and $NaBF_4$ reacting materials. Even under mixing conditions with a magnetic stirrer, however, such localized hot spots can nonetheless still form at the macro- and nanoscale since complete intimate mixing of the substrates is not likely to occur. By contrast, the greater synthetic efficiency, as evident by the 3-to-4-fold greater yields of product when using microwave radiation at the 5.8-GHz frequency, must be due to an equally efficient heating of the three substrates; note for instance the similar temperature rise in Figure 2c of all three substrates when using the 5.8-GHz microwaves.

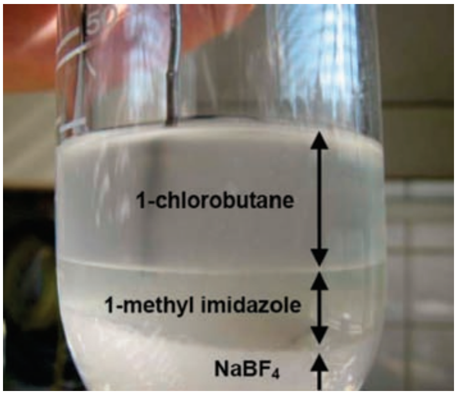

Figure 3. **Actual picture of the reacting materials 1-chlorobutane, 1-methylimidazole, and $NaBF_4$ in the cylindrical reactor.**

4. Concluding Remarks

Together with the earlier report,[27] the present study has demonstrated several features and advantages of using the novel 5.8-GHz microwave irradiation methodology in organic syntheses that avoids organic solvents and minimizes reaction times. In summary, the advantages can be summarized thusly: (i) a major room temperature and ecofriendly ionic liquid, namely 1-butyl-3-methylimidazolium tetrafluoroborate, could be synthesized in matters of minutes, rather than hours or days, by a one-pot solvent-free process, thereby avoiding the prior synthesis of the 1-methylimidazolium halide precursors; (ii) usage of the 5.8-GHz microwaves gave product yields that were significantly greater (3−4 times) than using the more common 2.45 GHz microwave frequency for heating the reacting mixture or by the conventional heating method with an oil bath; and finally (iii) the organic synthesis was microwave frequency-dependent. Clearly, the 5.8-GHz microwave frequency has displayed significant advantages not only from the chemical yield standpoint but also from the usage of small microwave power levels needed to induce syntheses of practical products such as the room-temperature ionic liquids.

Acknowledgment

We are grateful to the Sophia University-wide Collaborative Research Fund, the Foundation of Research for Promoting Technological Seeds from the Japan Science and Technology Agency, to S.H. One of us (N.S.) is grateful to Prof. Albini and his group for their gracious hospitality during the several winter semesters in Pavia since 2002. We also greatly appreciate the expert technical assistance of the personnel at the Hitachi Kyowa Engineering Co., Ltd.

Received for review June 10, 2008.

OP800135T