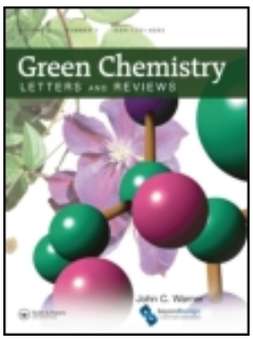

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A rapid way to synthesize Brønsted acidic ionic liquid and its application as an efficient catalyst for esterification

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A novel and time-saving method to prepare a Brønsted acidic ionic liquid, 1-carboxymethyl-3-methylimidazolium hydrogen sulfate ([CMI][HSO_4]), in high yield and purity was performed under microwave irradiation. The ionic liquid showed an incomparable catalytic efficiency in the microwave-accelerated esterification of arenecarboxylic acids. Moreover, its ability of being recovered and reused many times without loss of activity has made [CMI][HSO_4] more favorable from the viewpoint of green chemistry.

Keywords: 1-carboxymethyl-3-methylimidazolium hydrogen sulfate; ionic liquid; microwave irradiation; esterification

Introduction

In recent years, it has been witnessed that ionic liquids (ILs) have attracted more and more attention because of their diversified applications as solvents (*1*–*4*), stationary phases for chromatography (*2*, *3*), electrolytes (*5*, *6*), catalysts (*7*–*10*), and lubricants (*11*, *12*) as well as their interesting characteristics such as low volatility, low corrosiveness, low combustibility, thermal stability, and recyclability (*13*–*15*). ILs possess a unique property known as tunability which allows their chemical and physical properties to be modified as desired simply by changing the structure of component ions (*15*, *16*).

In general, there have been four typical routes to synthesize ILs including metathesis exchange of anion, neutralization of a base by a Brønsted acid, direct alkylation of alkylimidazole, and carbonate method (*17*). Among them, the metathesis exchange of anion has been the most common pathway. However, ILs prepared by this method are usually contaminated by halide impurities which may be difficult to eliminate by filtration, especially for hydrophilic ILs. It has been shown that the physical and chemical properties of ILs as well as their catalytic activity can be significantly affected by the presence of small amount of impurities (*18*, *19*). Therefore, there has been a great demand on developing new methods to prepare ILs with higher purity.

The IL, 1-carboxymethyl-3-methylimidazolium hydrogen sulfate, ([CMI][HSO_4]), consists of two Brønsted acidic sites, carboxylic acid and hydrogen sulfate. It has attracted a great deal of attention due to its versatility as both a potential acidic catalyst and a "green" solvent in organic synthesis. To date, however, there have been few papers on the synthesis of [CMI][HSO_4] as well as its applications (*20*–*27*), and unfortunately, most of them required long reaction time (10–72 h) and hazardous solvents. To overcome these defects, we proposed a new three-step process to provide [CMI][HSO_4] in a shorter time under solvent-free condition.

The new synthesized [CMI][HSO_4] will then be employed as a catalyst for the production of some benzyl arenecarboxylates. The results from this experience proved that [CMI][HSO_4] is an excellent catalyst for these reactions. This technique for the synthesis of [CMI][HSO_4] overcomes many drawbacks associated with other Brønsted acid catalyst, including corrosiveness, poor selectivity, and waste disposal (*28*). Compared with other hydrogen sulfate-based task-specific ILs in which the carboxyl group was absent (*29*), [CMI][HSO_4] showed an extraordinary catalytic activity to afford the desired products within a shorter time even when a minor quantity was employed and no extra concentrated H_2SO_4 was required.

Although the catalytic efficiency of [CMI][HSO_4] in the esterification was previously reported (*22*), this is the first time [CMI][HSO_4]-catalyzed esterification has been done under microwave irradiation. To date, there has been a great increase in the number of reports on using microwave as a means of activating

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reactions (*30*). Due to ILs' high polarity, they show good excellent ability of absorbing microwave and increase the rate of reactions as the result (*31*). Therefore, in this research, the microwave-mediated esterification in the presence of [CMI][HSO_4] was done to realize the potential of eco-friendly chemical reactions.

Results and discussion

Preparation of [CMI][HSO_4]

[CMI][HSO_4] was synthesized via a three-step pathway illustrated in Scheme 1. The first step, nucleophilic substitution between monochloroacetic acid and *N*-methylimidazole, was performed under microwave irradiation at 100°C to give the IL [CMI]Cl **1**. It can be referred from Table 1 that this intermediate was obtained in high yield from 84% to 87% only when an excess of *N*-methylimidazole was introduced to the reaction mixture (entries 6–8). Using an equimolar ratio of substrate and reagent resulted in the decrease in the yield of [CMI]Cl. It was due to the preference on the neutralization between monochloroacetic acid and *N*-methylimidazole leading to the formation of *N*-methylimidazolium chloroacetate **1'** as an undesired by-product. This hypothesis was reinforced in entry 11 in which no [CMI]Cl was detected when monochloroacetic acid was used twice as much as *N*-methylimidazole. Prolonging the reaction time from 4.5 to 6 min can improve the yield from 15% to 76% but no more significant conversion was detected for a longer time than 6 min (entries 4 and 5).

[CMI]Cl was then exposed to Ag_2O in the second step to remove nearly all chloride anions via the precipitation. Finally, the freshly prepared zwitterion **2** was treated with H_2SO_4 98% to afford pure [CMI][HSO_4] **3**. Both subsequent steps were quantitative and therefore, [CMI][HSO_4] can be obtained with the best overall yield of 81%. Ion chromatography showed that the chloride content of [CMI][HSO_4] was only 0.01%. Compared to conventional methods, this synthetic approach provided [CMI][HSO_4] in higher yield within a very short time under solvent-free condition (Table 2).

Table 1. Microwave-assisted preparation of the intermediate product [CMI]Cl.

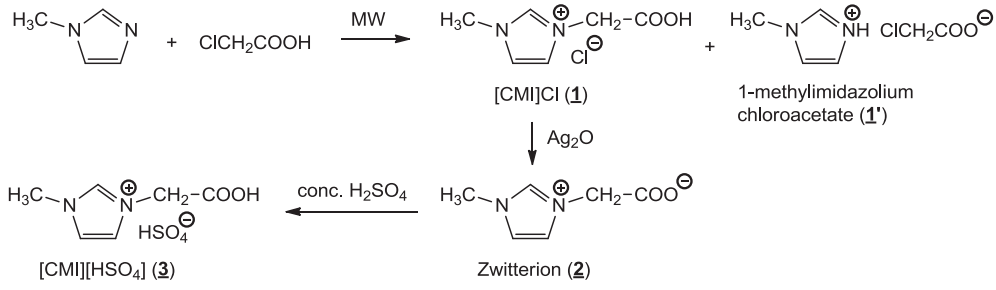
Entry	*N*-Methylimidazole: monochloroacetic acid[a]	Time (min)	Isolated yield (%)
1	1:1	4.5	15
2	1:1	5	60
3	1:1	6	76
4	1:1	7	76
5	1:1	8	78
6	2.5:1	6	87
7	2:1	6	86
8	1.5:1	6	84
9	1:1.2	6	56
10	1:1.5	6	25
11	1:2	6	0

[a]Molar ratio.

[CMI][HSO_4] as a catalyst for the esterification of arenecarboxylic acids

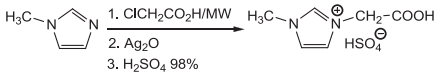
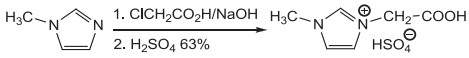
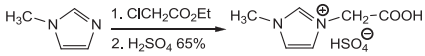
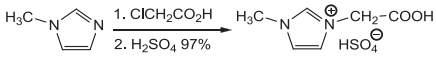
The catalytic activity of [CMI][HSO_4] was investigated using a simple esterification reaction between benzoic acid derivatives and benzyl alcohol. It was not surprising that various side products can be formed along with benzyl benzoate **6a** due to catalytic versatility of the hydrogen sulfate anion. Except for dibenzyl ether **7** whose content was considerable, the others identified by gas chromatography–mass spectrometry (GC–MS) as the Friedel–Crafts self-alkylation products of benzyl alcohol and their corresponding ester derivatives (mixture **8**) were only presented in negligible quantities. However, under appropriate conditions, these undesired products can be reduced as much as possible.

It was noted from Table 3 that only a minor change in the yield of **6a** was observed within the temperature range from 130°C to 170°C (entries 1–5). The more [CMI][HSO_4] was charged to the reaction mixture, the more desired product was obtained and the faster the reaction reached completion. The largest



Scheme 1. The three-step pathway for the preparation of [CMI][HSO_4].

Table 2. Comparison of microwave-assisted methods to prepare [CMI][HSO_4] with other conventional methods.

Entry	Method	Solvent used	Time	Total yield (%)	Ref.
1		None	51 min	81	–
2		EtOH	10.5 h	80	20
3		EtOH	Step 1: 3 days Step 2: 4 h	62	21
4		$CHCl_3$ and CH_2Cl_2	Step 1: 50 h Step 2: 48 h	76	22

increase in the desired product was observed at a 5% molar loading of the catalyst (entry 7). However, an outstanding raise in the proportion of the Friedel–Crafts alkylation products was also observed. This was because the intermediate carbocation derived from 5 responsible for the Friedel–Crafts alkylation products' formation was preferentially formed under more acidic medium. And without [CMI][HSO_4], as expected, only trace amount of these products (0.6%) were detected (entry 16). From the viewpoint of the green chemistry that favors the reduction of used catalyst, we chose the molar ratio of **5**:[CMI][HSO_4] at 1:0.02 as the most appropriate parameter for the esterification. Prolonging reaction time from 15 to 60 min can significantly induce the selectivity toward **6a** and simultaneously reduce the amount of dibenzyl ether **7** in the reaction mixture. This can be explained in terms of the difference in the polarity between ester **6a** and ether 7. For a long-time exposing to microwave (60 min) in the IL medium, the less polar compound 7 which was initially formed can be gradually hydrolyzed into the starting material **5**. This compound then reacted with benzoic acid **4a** to give the more polar product **6a** (76%) which is more compatible with microwave. The best yield of **6a** (87%) can be achieved in the case where 1.5 molar equiv. of **4a** was introduced to the reaction mixture (entry 12).

It has been well known that the Fischer esterification is mainly controlled by both steric and electronic effects of starting compounds. However, unlike the expectation that an increase in the substituent size from fluoro- to bromo- can result in a significant decrease in yield, all corresponding methyl esters **6b**–**6d** were formed in nearly same yields (entries 17–19). The electronic effect of substituents, on the contrary, intensively influenced the esterification. Such electron-withdrawing groups like fluoro-, chloro-, and bromo- which reduce the density of electrons at carboxyl carbons via the inductive effect enhanced the yield of methyl esters by 5–8% as compared with the methyl group, an electron-donating substituent (entry 21). For 2-nitrobenzoic acid, it was advisable to reduce the reaction time because long exposing to microwave irradiation led to complete decomposition. Therefore, the yield of methyl ester **6e** was not high as expected (entry 20).

Reusability of [CMI][HSO_4]

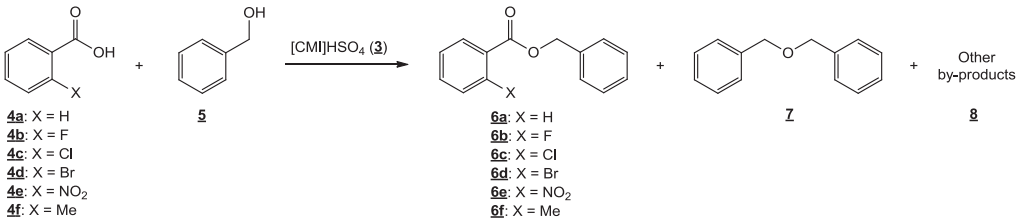
Besides its good compatibility with microwave, [CMI][HSO_4] was also well known for its reusability. Because of products' insolubility in water, they can be easily separated out of the IL which completely remained in the water. The aqueous solution of [CMI][HSO_4] was washed many times with AcOEt to remove the unreacted arenecarboxylic acid and subsequently rotary evaporated under low pressure to afford the recovered [CMI][HSO_4] whose ^1H and ^{13}C NMR spectral data were consistent with those of pure [CMI][HSO_4]. The recovered IL was then reused to catalyze the esterification and the results showed that the catalytic efficiency of [CMI][HSO_4] still remained virtually unchanged even after four runs of being recovered and reused (Figure 1).

Experimental

General

All chemicals were purchased from Sigma–Aldrich and employed without further purification. Solvents used for the reactions were the HPLC grade from Labscan. Microwave-assisted reactions were conducted in a professional microwave oven Discover (CEM). ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker 500 MHz spectrometer in dimethyl sulfoxide (DMSO) with

Table 3. [CMI][HSO_4]-catalyzed esterification of some arenecarboxylic acids.



Other by-products: 2-BnBnOH, 4-BnBnOH, 2-BnBnOBz, 4-BnBnOBz

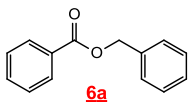
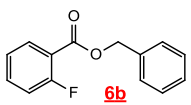
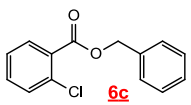
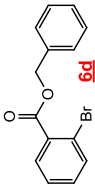
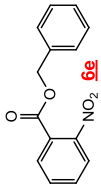
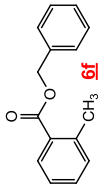
Entry	Ester	5:a–f:3[a]	Temp. (°C)	Time (min)	GC (%) 5	6a–6f	7	8	Yield[b] (%)
1		1:1:0.01	130	15	12	48	36	4	46
2		1:1:0.01	140	15	10	49	36	5	48
3		1:1:0.01	150	15	7	52	35	6	50
4		1:1:0.01	160	15	9	50	33	7	48
5		1:1:0.01	170	15	14	47	35	4	45
6		1:1:0.02	150	15	2	60	23	15	58
7		1:1:0.05	150	15	0	67	22	11	65
8		1:1:0.02	150	30	0.8	70	20	9	69
9	 6a	1:1:0.02	150	40	2	73	13	9	71
10		1:1:0.02	150	50	1	77	8	10	74
11		1:1:0.02	150	60	0.6	79	6	13	76
12		1:1.5:0.02	150	60	0.5	89	2	5	87
13		1:2.0:0.02	150	60	0.5	80	9	9	78
14		1:2.5:0.02	150	60	0.5	77	11	11	75
15[c]		1:1.5:0.02	150	60	19	55	24	2	52
16		1:1.5:0	150	60	40	59	0.3	0.6	21
17	 6b	1:1.5:0.02	150	60	1	85	0	14	85
18	 6c	1:1.5:0.02	150	60	1	84	1	14	82

Table 3 (*Continued*)

Entry	Ester	5:a–f:3[a]	Temp. (°C)	Time (min)	GC (%)				Yield[b] (%)
					5	**6a–6f**	**7**	**8**	
19	 **6d**	1:1.5:0.02	150	60	0.6	85	1	13	82
20	 **6e**	1:1.5:0.02	100	30	0	60	24	16	55
21	 **6f**	1:1.5:0.02	150	60	4	80	8	8	77

[a]Molar ratio.
[b]Calculated yield of benzyl esters **6a–6f** based on GC analyses.
[c]Under conventional heating.

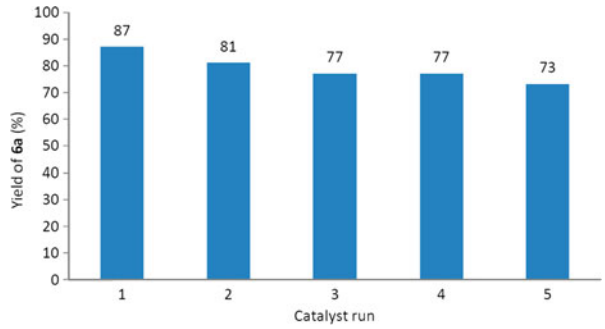


Figure 1. The reusability of [CMI][HSO_4].

tetramethylsilane as an internal standard. GC–MS analyses were performed on an Agilent GC System 7890A equipped with a mass selective detector Agilent 5973 and a capillary column HP-5MS (30 m × 0.25 mm × 0.25 μm). Ion chromatographic analyses of anions were performed on an 850 Professional IC 1 instrument equipped with a column Metrosep A Supp 7 250/4.0.

Typical procedure for the preparation of [CMI][HSO_4]

Synthesis of [CMI]Cl ***1***

A mixture of monochloroacetic acid (0.945 g, 10 mmol) and *N*-methylimidazole (1.230 g, 15 mmol) was stirred under the microwave irradiation at 100°C (20 W) for 6 min. Upon completion, the product was washed with acetone (3 × 20 mL) to remove unreacted starting materials and afforded 1.482 g of [CMI]Cl as white solid (84%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 3.91 (s, 3H), 5.08 (s, 2H), 7.74–7.75 (d, 2H), 9.25 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 35.7, 50.2, 122.9, 123.6, 137.4, 168.0.

Synthesis of zwitterion 1-carboxylatemethyl-3-methylimidazolium 2 and [CMI][HSO_4]

[CMI]Cl (1.482 g, 8.4 mmol) was dissolved in deionized water followed by the addition of Ag_2O (0.5 molar equiv.), which had been freshly prepared from $AgNO_3$ and NaOH. After being stirred at the room temperature for 15 min, the reaction mixture was filtered to remove the precipitation. The filtrate containing the zwitterion **2** was checked with $AgNO_3$ solution to ensure that no chloride anion was detected. Subsequently, concentrated sulfuric acid (1.0 molar equiv.) was added dropwise to the vigorously stirred filtrate mentioned above. After finishing the addition of H_2SO_4, the resulting solution was continuously stirred for further 30 min. Water was then removed to give 1.933 g of [CMI][HSO_4] as a yellow

viscous liquid (96%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 3.89 (s, 3H), 4.99 (s, 2H), 7.69 (d, 2H), 9.08 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 35.7, 50.3, 123.0, 123.6, 137.5, 168.0.

Typical procedure for the esterification catalyzed by [CMI][HSO$_4$]

Under microwave irradiation

A 10-mL pressurized vessel was charged with [CMI][HSO$_4$] (0.005 g, 0.02 mmol), benzoic acid **4a** (0.183 g, 1.5 mmol), and benzyl alcohol **5** (0.108 g, 1 mmol). The mixture was then exposed to microwave irradiation at 150°C (20 W) for 1 h in a CEM Discover oven. Upon completion, the resulting mixture was cooled to room temperature and diluted with Et_2O. A sufficient amount of water was added to the ethereal solution to extract [CMI][HSO$_4$]. The ethereal layer was then washed with the aqueous saturated solution of $NaHCO_3$ until the unreacted **4a** was completely removed, dried over Na_2SO_4, filtered, and concentrated under the reduced pressure to afford the mixture of products, whose constituents were identified and quantified by GC–MS and gas chromatography–flame ionization detector (GC–FID), respectively. The calculated yield of benzyl benzoate **6a** was 87%.

Under conventional heating

A 5-mL flask was charged with [CMI][HSO$_4$] (0.005 g, 0.02 mmol), benzoic acid **4a** (0.183 g, 1.5 mmol), and benzyl alcohol **5** (0.108 g, 1 mmol). The mixture was then immersed in a preheated oil bath, refluxed gently, and simultaneously stirred for 1 h at 150°C. Upon completion, the resulting mixture was worked up in the same way described for the microwave-assisted reaction to afford the mixture of products whose constituents were identified and quantified by GC–MS and GC-FID, respectively. The calculated yield of benzyl benzoate was 52%.

Conclusion

A novel pathway for the synthesis of [CMI][HSO$_4$] has been developed. This method provided an efficient approach for highly pure ILs. In addition, [CMI][HSO$_4$] prepared herein was found to be a good catalyst for the esterification. The reaction can be carried out without any solvent in a short time. Finally, the catalyst can be recycled several times without noticeable loss of reactivity.

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