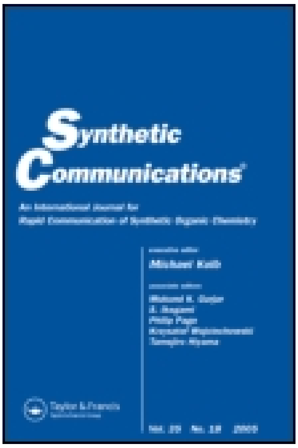

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Green, One-Pot, Solvent-Free Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles Using a Brønsted Acidic Ionic Liquid as Novel and Reusable Catalyst

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GREEN, ONE-POT, SOLVENT-FREE SYNTHESIS OF 1,2,4,5-TETRASUBSTITUTED IMIDAZOLES USING A BRØNSTED ACIDIC IONIC LIQUID AS NOVEL AND REUSABLE CATALYST

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3-Methyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate [$(CH_2)_4SO_3HMIM$] [HSO_4], a Brønsted acidic ionic liquid, has been used as an efficient, green, and reusable catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles using benzil, an aromatic aldehyde, and a primary amine in the presence of ammonium acetate under solvent-free conditions. The catalyst could be recycled and reused several times without noticeably decreasing the catalytic activity.

Keywords: Brønsted acidic ionic liquids; multicomponent reactions; one-pot synthesis; solvent-free conditions; tetrasubstituted imidazole

INTRODUCTION

Multicomponent reactions (MCRs) have emerged as efficient and powerful tools in modern synthetic organic chemistry because the synthesis of complex organic molecules from simple and readily available substrates can be achieved in a very fast and efficient manner without the isolation of any intermediate.[1–3] Therefore, developing new MCRs and improving known MCRs are popular areas of research in current organic chemistry. One such reaction is the synthesis of imidazoles. In recent years, imidazoles have attracted attention because the compounds with the imidazole ring system have many pharmacological properties and play important roles in biochemical processes.[4] Different substituted imidazoles show variable biological activities such as anti-inflammatory,[5] anti-allergic,[6] analgesic,[7] antibacterial,[8] and antitumor[9] activities. Also, some of them are known as inhibitors of P38 kinase.[10] Recent advances in green chemistry and organometallic catalysis has extended the application of imidazoles as ionic liquids[11] and N-heterocyclic carbenes.[12]

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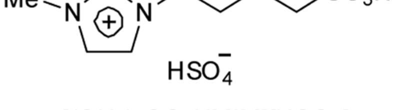
Despite the availability of a wide variety of synthetic routes toward imidazoles, few studies exist on the synthesis of 1,2,4,5-tetrasubstituted imidazoles. These compounds are generally synthesized in a four-component condensation of aldehydes, 1,2-diketones, amines, and ammonium acetate in the presence of several catalysts such as HY zeolite,[13] silica gel/$NaHSO_4$,[14] molecular iodine,[15] $K_5CoW_{12}O_{40} \cdot 3H_2O$,[16] heteropolyacids,[17] $HClO_4$-SiO_2,[18] $InCl_3 \cdot 3H_2O$,[19] BF_3-SiO_2, $AlCl_3$, and $MgCl_2$.[20] In addition, they can also be accessed by the cycloaddition reaction of mesoionic 1,3-oxazolium-5-olates with N-(arylmethylene)-benzenesulfonamides, hetero-Cope rearrangement, condensation of a 1,2-diketone with an aryl nitrile and primary amine under microwave irradiation, and N-alkylation of trisubstituted imidazoles.[21,22] However, some of these synthetic methods have limitations such as harsh reaction conditions, use of hazardous and often expensive acid catalysts, long reaction times, and moderate yields. Moreover, the synthesis of these compounds is usually carried out in polar solvents such as ethanol, methanol, acetic acid, dimethylformamide (DMF), and dimethylsulfoxide (DMSO), leading to complex isolation and recovery procedures. Therefore, the development of simple, efficient, clean, high-yielding, and environmentally friendly approaches using new catalysts for the synthesis of these compounds is an important task for organic chemists.

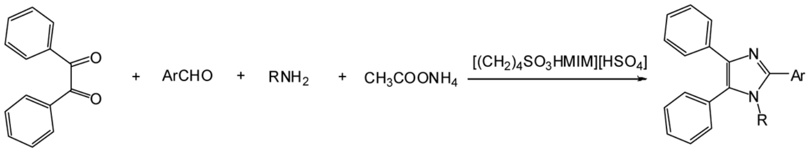
Ionic liquids (ILs), which are recognized as environmentally benign media, have been widely applied in many reactions as catalysts or dual catalyst–solvents because of their low vapor pressure, reusability, and high thermal and chemical stability.[23,24] The introduction of Brønsted acidic functional groups into cations or anions of the ILs, especially the SO_3H functional groups, obviously enhanced their acidities and water solubilities.[25–28] Therefore, Brønsted acidic ILs can be used as highly efficient acid catalysts. Moreover, their polar nature makes them suitable for use under solvent-free conditions. In fact, the use of Brønsted acidic ILs as catalysts is an area of ongoing activity; however, development and exploration of Brønsted acidic ILs are currently in the preliminary stage. To the best of our knowledge, there are no examples of the use of Brønsted acidic ILs as catalysts for the synthesis of tetrasubstituted imidazoles.

In continuation of our previous work on the applications of reusable acid catalysts in the synthesis of heterocyclic compounds,[29–31] here we report the eco-friendly synthesis of tetrasubstituted imidazoles **5a–j** by 3-methyl-1-(4-sulfonic acid)-butylimidazolium hydrogen sulfate $[(CH_2)_4SO_3HMIM][HSO_4]$ (Fig. 1), a Brønsted acidic IL, using a one-pot, four-component condensation of benzil **1**, benzaldehyde derivatives **2**, primary amines **3**, and ammonium acetate **4** under solvent-free conditions (Scheme 1).



$[(CH_2)_4SO_3HMIM][HSO_4]$

Figure 1. Brønsted acidic IL structure.

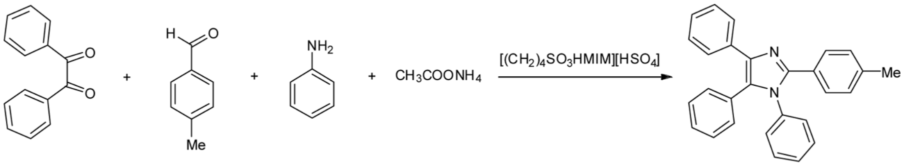


Scheme 1. Synthesis of 1,2,4,5-tetrasubstituted imidazoles.

RESULTS AND DISCUSSION

For our investigations, $[(CH_2)_4SO_3HMIM][HSO_4]$ was prepared according to the literature procedure.[32] Initially, to optimize the reaction conditions, the reaction of benzil, 4-methyl benzaldehyde, aniline, and ammonium acetate was used as a model reaction (Scheme 2).

The efficiency of the reaction is mainly affected by the amount of $[(CH_2)_4SO_3HMIM][HSO_4]$ (Table 1). It showed that no product could be detected in the absence of this catalyst (entry 1), which indicated that the catalyst should be absolutely necessary for this condensation reaction. When the amount of $[(CH_2)_4SO_3HMIM][HSO_4]$ was increased, a ramp in the yield of the product **5c** was observed. The optimal amount of $[(CH_2)_4SO_3HMIM][HSO_4]$ was 15 mol%; greater amounts of the catalyst did not increase the yield noticeably (entries 5, 6).



Scheme 2. Synthesis of 2-(4-methylphenyl)-1,4,5-triphenyl-1*H*-imidazole **5c** as model reaction.

Table 1. Effect of the amounts of $[(CH_2)_4SO_3HMIM][HSO_4]$ on the reaction[a]

Entry	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	None	3	0
2	5	2.5	71
3	10	2	82
4	15	2	94
5	20	2	94
6	30	2	95

[a] 2 mmol benzil, 2 mmol 4-methyl benzaldehyde, 2 mmol aniline, and 2 mmol ammonium acetate at 140 °C.

[b] Isolated yields.

Table 2. Synthesis of 2-(4-methylphenyl)-1,4,5-triphenyl-1*H*-imidazole **5c** in the presence of [$(CH_2)_4SO_3HMIM$][HSO_4] (15 mol%) in different solvents

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1	MeOH	64	9	56
2	EtOH	78	7	62
3	CH_3CN	81	9	60
4	CH_2Cl_2	40	10	Trace
5	$CHCl_3$	61	10	Trace
6	Solvent-free	140	2	94

[a] Isolated yields.

Also, the reaction was carried out in various solvents and also under solvent-free conditions. As shown in Table 2, in comparison to conventional methods, the yields of the reaction under solvent-free conditions are greater and the reaction time is shorter.

The effect of temperature was studied by carrying out the same model reaction in the presence of 15 mol% of this catalyst and at different temperatures in solvent-free conditions. It was observed (Table 3) that yield is a function of temperature, so the yield increased as the reaction temperature was raised, and at 140 °C the product **5c** was obtained in excellent yield. In other studies, all reactions were carried out at 140 °C in the presence of 15 mol% of [$(CH_2)_4SO_3HMIM$][HSO_4] under solvent-free conditions.

To show the generality of this method, the optimized system was used for the synthesis of other imidazoles derivatives with various aromatic aldehydes and primary amines (Table 4). The yields obtained were good to excellent without formation of any side products such as 2,4,5-trisubstituted imidazoles.

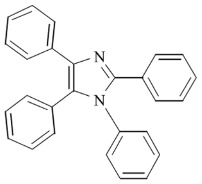
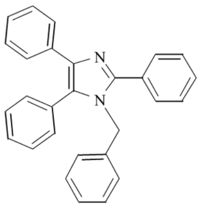
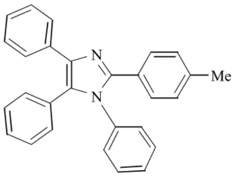
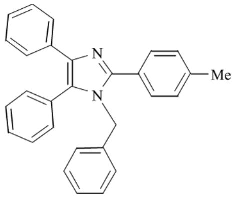
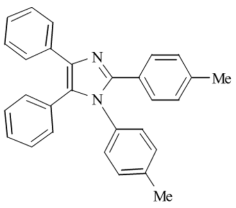
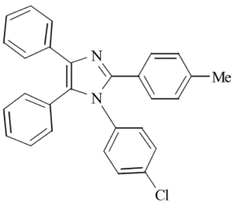
Although we did not investigate the reaction mechanism, based on Sharma et al.'s suggestion,[19] a plausible mechanism for the present reaction may proceed as depicted in Scheme 3. The addition of nucleophiles to the aldehydes and ketones is promoted by protonation of the carbonyl group using a Brønsted acid, enhancing the electrophilicity of this moiety. Therefore, it may be proposed that the [$(CH_2)_4SO_3HMIM$][HSO_4] ≡ HA catalyst facilitates the formation of diamine intermediate **I** by increasing the electrophilicity of the carbonyl group of the aldehyde. This intermediate condenses with the activated benzil to form

Table 3. Synthesis of 2-(4-methylphenyl)-1,4,5-triphenyl-1*H*-imidazole **5c** in the presence of [$(CH_2)_4SO_3HMIM$][HSO_4] (15 mol%) at different temperatures in solvent-free conditions

Entry	Temperature (°C)	Time (h)	Yield (%)[a]
1	25	12	21
2	50	7	41
3	100	3	53
4	140	2	94

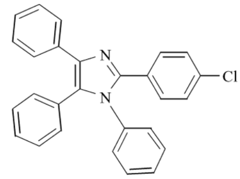
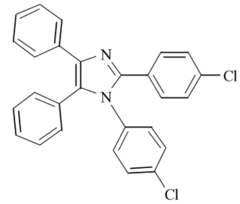
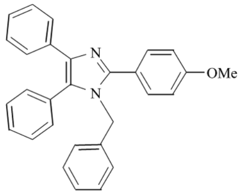
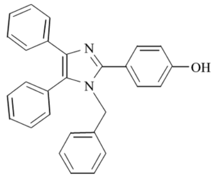
[a] Isolated yields.

Table 4. Synthesis of 1,2,4,5-tetrasubstituted imidazoles **5a**–**j**

Entry	Ar	R	Products[a]	Time (h)	Yield[b] (%)	Mp (°C)		Ref.
						Found	Reported	
1	C_6H_5	C_6H_5	**5a** 	2.5	88	213–215	216–218	20
2	C_6H_5	$CH_2C_6H_5$	**5b** 	2	90	161–163	163–165	20
3	$4\text{-}CH_3C_6H_4$	C_6H_5	**5c** 	2	94	183–184	185–188	20
4	$4\text{-}CH_3C_6H_4$	$CH_2C_6H_5$	**5d** 	2	91	163–165	165–166	20
5	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	**5e** 	2	91	190–192	188–191	16
6	$4\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_4$	**5f** 	2	94	168–170	167–169	16

(*Continued*)

Table 4. Continued

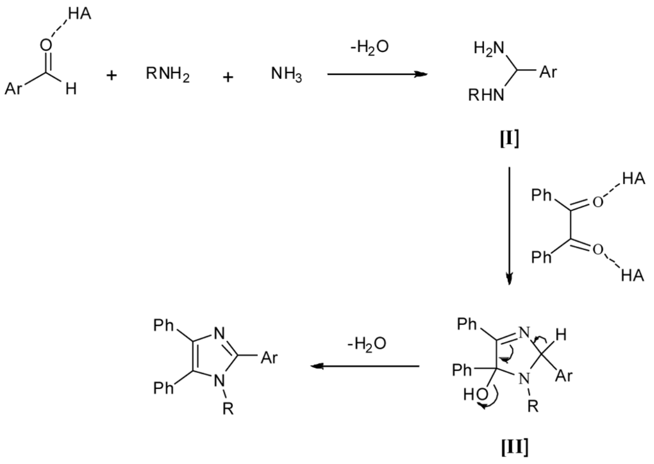
Entry	Ar	R	Products[a]	Time (h)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported	Ref.
7	4-ClC_6H_4	C_6H_5	**5g** 	2	87	146–148	149–151	20
8	4-ClC_6H_4	4-ClC_6H_4	**5h** 	2	95	188–190	187–189	16
9	4-$CH_3OC_6H_4$	$CH_2C_6H_5$	**5i** 	2.5	85	155–157	157–160	18
10	4-HOC_6H_4	$CH_2C_6H_5$	**5j** 	2.5	87	131–132	134–135	20

[a] All the products were characterized by ^{1}H NMR and IR spectral data and comparision of their melting points with those of authentic samples.

[b] Isolated yields.

the intermediate **II**, which can be converted to the desired product by dehydration. In the absence of a primary amine and using the greater amount of ammonium acetate, 2,4,5-trisubstituted imidazoles can be formed by a similar mechanism.[19]

Reusability of the catalyst was also investigated. For this purpose, the model reaction was again studied in the optimized conditions. After the completion of the reaction, the catalyst was recovered (Experimental section) and reused for the similar reaction. This process was carried out over three runs without appreciable reduction in the catalytic activity of the catalyst.



Scheme 3. Plausible mechanism for the formation of 1,2,4,5-tetrasubstituted imidazoles in the presence of $[(CH_2)_4SO_3HMIM][HSO_4] \equiv HA$ as catalyst.

CONCLUSION

In conclusion, we have reported here a new efficient catalyst for the synthesis of tetrasubstituted imidazoles through the four-component condensation of benzil, benzaldehyde derivatives, primary amines, and ammonium acetate using $[(CH_2)_4SO_3HMIM][HSO_4]$, a Brønsted acidic IL. No organic solvent was used, resulting in an ecofriendly process. The catalyst can be reused after a simple workup, with a gradual decline of its activity being observed. Good yields, relatively short reaction times, simplicity of operation, and easy workup are some advantages of this protocol.

EXPERIMENTAL

All chemicals were commercially available and used without further purification. The Brønsted acidic ionic liquid $[(CH_2)_4SO_3HMIM][HSO_4]$ was synthesized according to the literature. Melting points were recorded on an Electrothermal type 9100 melting-point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrophotometer as KBr disks. The ^1H NMR (100-MHz) spectra were recorded on a Bruker AC 100 spectrometer.

Preparation of Brønsted Acidic Ionic Liquid $[(CH_2)_4SO_3HMIM][HSO_4]$

A mixture of 1-methylimidazole (200 mmol) and 1,4-butane sultone (200 mmol) was charged into a 150-mL conical flask. The mixture was stirred at room temperature for 4 days until it turned into solid. The white solid zwitterion that formed was washed repeatedly with ether, filtered to remove nonionic residues, and dried in vacuum. Then, a stoichiometric amount of concentrated sulfuric acid (98%, 10.9 mL) was added dropwise to the white solid zwitterion at 0 °C. The mixture was stirred at 80 °C for 6 h. Product was washed with diethyl ether and dried in vacuo at 50 °C for 2 h to get the viscous clear $[(CH_2)_4SO_3HMIM][HSO_4]$.

General Procedure for the Synthesis of Tetrasubstituted Imidazoles

A mixture of benzil (2 mmol), primary amine (2 mmol), aromatic aldehyde (2 mmol), ammonium acetate (2 mmol), and $[(CH_2)_4SO_3HMIM][HSO_4]$ (15 mol%) was heated on the oil bath at 140 °C for 2–2.5 h. The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature, and then water was added. The precipitate was filtered off and recrystallized from ethanol to give compounds **5a–j** in good to excellent yields. All products were known and characterized by comparison of their physical and spectroscopic data with those already reported.[16,18,20]

Selected ^{1}H NMR Data

Compound 5b. ^{1}H NMR (DMSO-d_6) δ: 5.15 (s, 2H, CH_2), 6.65–7.65 (m, 20H, ArH).

Compound 5c. ^{1}H NMR (DMSO-d_6) δ: 2.23 (s, 3H, CH_3), 6.90–7.60 (m, 19H, ArH).

Compound 5d. ^{1}H NMR (DMSO-d_6) δ: 2.35 (s, 3H, CH_3), 5.14 (s, 2H, CH_2), 6.60–7.65 (m, 19H, ArH).

Compound 5i. ^{1}H NMR (DMSO-d_6) δ: 3.76 (s, 3H, CH_3), 5.13 (s, 2H, CH_2), 6.65–7.70 (m, 19H, ArH).

Compound 5j. ^{1}H NMR (DMSO-d_6) δ: 5.12 (s, 2H, CH_2), 6.65–7.60 (m, 19H, ArH), 9.80 (br, 1H, OH).

Recycling of the Catalyst

The catalyst is soluble in water and therefore could be recycled. The catalyst was recovered by evaporation of the water, washed with diethyl ether, and dried at 50 °C under vacuum for 1 h.

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