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Silica Sulfuric Acid-Catalyzed One-Pot Synthesis of 1,3-Diarylimidazolium Tetrafluoroborate

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A silica sulfuric acid-catalyzed three-component one-pot synthesis of 1,3-diarylimidazolium tetrafluoroborates was undertaken *via* the reaction of aromatic amine, formaldehyde and glyoxal at room temperature in ionic liquid [BMIM][BF_4] with good yields. Up to four new bonds and one new ring were formed in one-pot with water as the only by-product in the reactions. The product **4d** was determined by X-ray diffraction. This work develops an efficient and low-cost preparation of 1,3-diarylimidazolium and N-heterocylic carbene.

Keywords: Synthesis, Silica sulfuric acid, 1,3-Diarylimidazolium tetrafluoroborate.

INTRODUCTION

Since the first isolation and characterization of N-heterocyclic carbene (NHC) by Arduengo and co-workers[1] in 1991, various stable N-heterocyclic carbenes (NHCs)[2,3] has been investigated and applied extensively. It is possible to prepare new nucleophilic reagent[4], organic catalysts[5], organic metal catalysts[6] and chiral catalysts[7] from N-heterocyclic carbenes, which promoted the revolutionary progress in the key fields of organic synthesis and polymer chemistry[8].

Imidazolium salt has been widely used in organic synthesis as precursors. It was generating great interest in their usage as versatile organocatalyst[9-12], ionic liquid[13] and key ligands[14-19] in N-heterocyclic carbene complexes. Most of all, it represents the typical architectures of stable nucleophilic singlet carbenes. Accordingly, the development of simple and efficient strategies for the construction of this molecular architecture is of considerable importance.

Generally, imidazolium salts were prepared by two steps involving the condensation of glyoxal, amine and formaldehyde and then the dehydration in the presence of strong acid[20]. However, these procedures must be processed under some harsh reaction conditions (high reaction temperature, strong acid and so on) with low total yields. Comparatively speaking, their one-step synthesis by condensation of 1,2-diamine with formaldehyde or ammonium formate or triethyl orthoformate[21] gradually became the main method with the advantages high yield and easily controlled reaction conditions. However, a long time reflux in organic solvent and absolute removal of organic solvent were necessary to ensure the final cyclization.

EXPERIMENTAL

IR spectra were recorded with a Varian FTIR-Tensor-27 spectrophotometer using KBr optics. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker DPX 400 spectrometer using TMS as an internal standard and DMSO as solvent. Mass was determined by using a Bruker TOF-MS high resolution mass spectrometer. All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Silica sulfuric acid was prepared in our lab. Organic solvents were dried and distilled prior to use.

Experimental process

Synthesis of 1,3-diarylimidazolium tetrafluoroborate: A mixture of amines (2.0 mmol), formaldehyde (1.0 mmol), glyoxal (1.0 mmol) and silica sulfuric acid (0.2 g) and [BMIM]BF_4 (3.0 mL) was stirred at room temperature for 1.5 h until complete consumption of the starting material as monitored by TLC. After completion of the reaction, the mixture was diluted with water; the crude solid was recrystallized with 95 % EtOH/DMF (1:4), and then filtered to remove silica sulfuric acid to provide the pure product **4**.

Spectral data for compounds

1,3-Di-*p*-tolylimidazolidine (4b): White crystal, m.p. > 300 °C, 0.29 g (85 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.80 (1H, q, ArH), 8.00-7.98 (4H, d, *J* = 8.4 Hz), 7.54 (s, 2H), 7.44-7.42 (4H, d, *J* = 8.0 Hz), 2.44 (s, 6H). IR (cm^{-1}): 3441, 3340, 3924, 2861, 1606, 1557, 1452, 1381, 948, 722, 633. HRMS: calcd. for $C_{17}H_{20}N_2$ [M+H]$^+$ found (expected): 252.1678 (252.1626).

1,3-*Bis*(4-methoxyphenyl)imidazolidine (4d): White crystal, m.p. > 300 °C, 0.34 g (91 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.15 (s, 1H, ArH), 8.46-8.45 (2H, d, *J* = 1.6 Hz, ArH), 7.83-7.816 (4H, d, *J* = 9.2 Hz, ArH), 7.25-7.23 (4H, d, *J* = 8.8 Hz, ArH), 3.86 (6H, s). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.16, 13.89, 127.78, 123.60, 121.955, 115.13, 55.78. IR (cm^{-1}): 3367, 3069, 2938, 2857, 1794, 1505, 985, 743, 679. HRMS: calcd. for $C_{17}H_{20}N_2O_2$ [M+H]$^+$ found (expected): 284.1583 (284.1525). $C_{17}H_{19}N_2O_3Cl$, monoclinic, P1, a = 15.6706 (19) Å, b = 9.4198 (9) Å, c = 5.0402 (64) Å, α = 90.00°, β = 90.1560 (10)°, γ = 90.00°, V = 797.50 Å^3, Z = 2, R (F) = 0.0294, wR (F2) = 0.0737, T = 298 K.

1,3-*Bis*(4-fluorophenyl)imidazolidine (4e): White crystal, m.p. > 300 °C, 0.29 g (83 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.29 (1H, s, CH), 8.53-8.52 (2H, d, *J* = 7.6 Hz), 7.99-7.95 (4H, d, Ar), 7.63-7.59 (4H, t). IR (cm^{-1}): 3151, 3024, 1614, 1590, 1512, 1483758, 650. HRMS: calcd. for $C_{15}H_{14}N_2F_2$ [M+H]$^+$ found (expected): 260.1185 (260.1125).

1,3-*Bis*(4-chlorophenyl)imidazolidine (4f): White crystal, m.p. > 300 °C, 0.31 g (82 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H, ArH), 8.58-8.58 (2H, s, ArH), 8.00 (2H, s, ArH), 7.97 (2H, s, ArH), 7.83-7.80 (3H, t, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.07, 134.61, 133.48, 130.15, 123.91, 121.97. IR (cm^{-1}): 3102, 1634, 1546, 1495, 763. HRMS: calcd. for $C_{15}H_{15}N_2Cl_2$ [M+H]$^+$ found (expected): 293.0669 (293.0607).

1,3-*Bis*(3-bromophenyl)imidazolidine (4g): White crystal, m.p. > 300 °C, 0.37 g (79 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H, ArH), 8.61 (s, 2H, ArH), 8.26 (s, 2H, ArH), 7.96-7.90 (s, 2H, ArH), 7.94-7.86 (s, 2H, ArH), 7.71-7.67 (t, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ135.71, 135.26, 132.90, 132.03, 124.86, 122.58, 121.85, 121.06. IR (cm^{-1}): 3175, 3123, 1717, 1605, 1549, 1514, 635. HRMS: calcd. for $C_{15}H_{14}N_2Br_2$ [M+H]$^+$ found (expected): 379.9575 (379.9524).

1,3-*Bis*(4-bromophenyl)imidazolidine (4h): White crystal, m.p. > 300 °C, 0.39 g (84 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 1H, ArH), 8.58 (2H, s, ArH), 7.98 (2H, s), 7.96 (2H, s, ArH), 7.89 (2H, s, ArH), 7.87 (2H, s, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.95, 133.90, 133.07, 124.12, 123.08, 121.92. IR (cm^{-1}): 1571, 1564, 1454, 1378, 1069, 751, 625. HRMS: calcd. for $C_{15}H_{14}N_2Br_2$ [M+H]$^+$ found (expected): 379.9573 (379.9524).

1,3-*Bis*(3-chloro-4-fluorophenyl)imidazolidine (4i): White crystal, m.p. > 300 °C, 0.36 g (81 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.90 (s, 1H, ArH), 8.15-8.13 (m, 2H, ArH), 8.08-8.06 (m, 2H, ArH), 7.85-7.83 (t, 3H), 7.39-7.26 (m, 2H, ArH). IR (cm^{-1}): 3080, 2942, 1621, 1565, 1424, 926, 97, 765, 651. HRMS: calcd. for $C_{15}H_{12}N_2Cl_2F_2$ [M+H]$^+$ found (expected): 328.0398 (328.0346).

RESULTS AND DISCUSSION

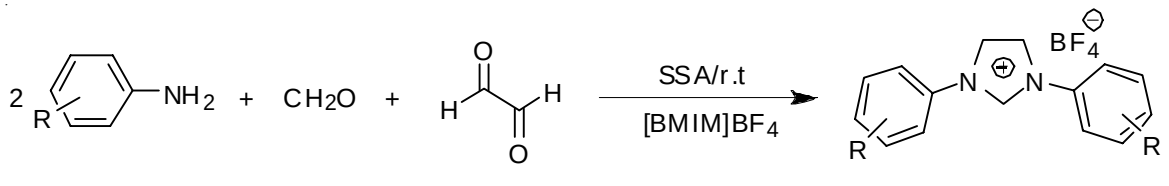
Herein we integrated the advantages of these two methods mentioned above, reported a simple and efficient method for the synthesis of 1,3-diarylimidazolium tetrafluoroborates *via* the one-pot reaction of aromatic amine, formaldehyde and glyoxal catalyzed by silica sulfuric acid at room temperature in ionic liquid [BMIM][BF_4] with good yields (**Scheme-I**).

Initially, to optimize reaction condition, some catalysts (entries **1-5**) were screened when *p*-methoxyaniline (**1d**), glyoxal and formaldehyde, were chosen as substrates (Table-1). It was shown that 0.2 g silica sulfuric acid is the most suitable one (entry **5**) which may attribute to its suitable acidity, whereas catalysts possess stronger acidity or basicity have no advantages in this reaction. Consequently, all further studies were conducted using 0.2 g silica sulfuric acid as catalyst (entry **5**).

Having established the best catalyst, the effect of solvents (Table-1, entries **5-10**) and time (entries **5** and **11-13**) on the model reaction was subsequently investigated (Table-1). The results indicated that this reaction can not proceed in common organic solvents except ionic liquids. [BMIM]BF_4 gave the highest yield (entry **5**) than ethanol, THF, DMF, [BPY]BF_4, H_2O and [BMIM]BF_4. [BPY]BF_4 can also promote the reaction but in lower yield (entry **9**) than [BMIM]BF_4 due to its slight weak acidity than that of [BPY]BF_4. It was observed that the suitable time was 1.5 h.

So, the mixture of aromatic amine (**1**), formaldehyde (**2**), glyoxal (**3**) and [BMIM]BF_4 was stirred in the presence of 0.2 g silica sulfuric acid at room temperature for 1.5 h to give the corresponding compounds (**4**) (Table-2). In all the cases, 1,3-diarylimidazolium tetrafluoroborates have been obtained in moderate to high yields in short times (1.5 h). It was important to note that the process tolerates both electrondonating groups (such as alkoxy groups, Table-2, entries **3-4**) and electron-withdrawing substituents (such as halide groups, Table-2, entries **5-9**) on aromatic amine.

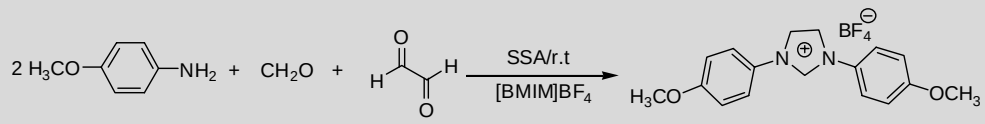
The structures of compound **4d** (Fig. 1) was determined by X-ray crystal structure analysis (CCDC 965289). The ethanol (95 %)-dimethylformamidc (DMF) solution (10:1) of the products stood at room temperature for 5-7 days to give single crystals suitable for X-ray diffraction analysis. The crystal data clearly indicated that the structures of products conform to the speculated structures completely. There are



1 **2** **3** **4**

Scheme-I: One-pot synthesis of 1,3-diarylimidazolium tetrafluoroborates

TABLE-1
OPTIMIZATION OF THE REACTION CONDITIONS[a]



1d **2** **3** **4d**

Entry	Solvent	Catalyst	Cat. (g)	Time (h)	Yield[b] (%)
1	$[BMIM]BF_4$	HCl	0.2	1.5	NR[c]
2	$[BMIM]BF_4$	NaOH	0.2	1.5	NR
3	$[BMIM]BF_4$	$NaHSO_3$	0.2	1.5	NR
4	$[BMIM]BF_4$	–	0.2	1.5	NR
5	$[BMIM]BF_4$	Silica sulfuric acid[d]	0.2	1.5	91
6	C_2H_5OH	Silica sulfuric acid	0.2	1.5	NR
7	THF	Silica sulfuric acid	0.2	1.5	NR
8	DMF	Silica sulfuric acid	0.2	1.5	NR
9	$[BPY]BF_4$	Silica sulfuric acid	0.2	1.5	87
10	H_2O	Silica sulfuric acid	0.2	1.5	0
11	$[BMIM]BF_4$	Silica sulfuric acid	0.1	1.5	50
12	$[BMIM]BF_4$	Silica sulfuric acid	0.3	1.5	85
13	$[BMIM]BF_4$	Silica sulfuric acid	0.4	1.5	70
14	$[BMIM]BF_4$	Silica sulfuric acid	0.2	0.5	33
15	$[BMIM]BF_4$	Silica sulfuric acid	0.2	1.0	80
16	$[BMIM]BF_4$	Silica sulfuric acid	0.2	2.0	91

[a]Reactions were performed in 2:1:1 (*p*-methoxyaniline: glyoxal: formaldehyde) at room temperature in different conditions; [b]Yield of isolated products; [c] No reaction; [d] Prepared in our lab.

TABLE-2
SYNTHESIS OF COMPOUND **4** CATALYZED BY SILICA SULFURIC ACID[a]

Entry	R	Product	Time (h)	Yield[b] (%)	m.p. (°C)
1	H	**4a**	1.5	87	> 300
2	4-CH_3	**4b**	1.5	85	> 300
3	2-CH_3O	**4c**	1.5	76	> 300
4	4-CH_3O	**4d**	1.5	91	> 300
5	4-F	**4e**	1.5	83	> 300
6	4-Cl	**4f**	1.5	82	> 300
7	3-Br	**4g**	1.5	79	> 300
8	4-Br	**4h**	1.5	84	> 300
9	3-Cl-4-F	**4i**	1.5	81	> 300

[a]All reactions were carried out in the scale of 0.2 g silica sulfuric acid in 3 mL of $[BMIM]BF_4$ at room temperature and starting materials (**1:2:3** = 2.0:1.0:1.0 mmol) were completely consumed; [b]Isolated yield.

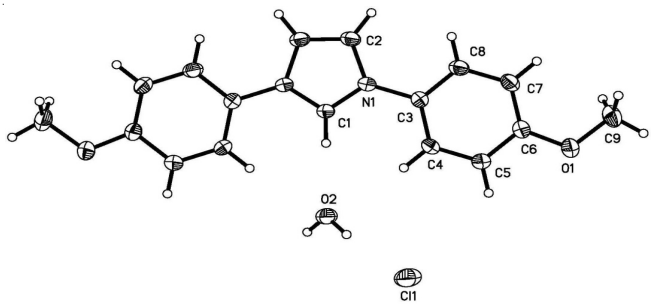
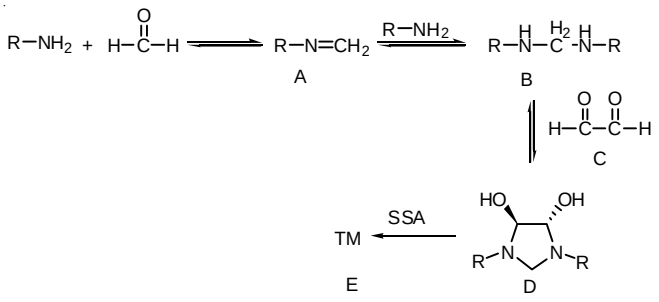


Fig. 1. X-ray crystal structure of compound **4d**

one water molecule and one chloride ion as impurities from glass container in the single crystal structure of **4d**.

The probable mechanism was shown in **Scheme-II**. The first step involved the acid-catalyzed reaction of aromatic amine (**1**) with formaldehyde (**2**), which acted as the source of methylene to give imine (**A**) as the first key intermediate.



Scheme-II

The addition of (**A**) to nucleophiles R-NH_2 then gave the intermediate (**B**). Subsequently, the intermediate (**B**) condensed with the glyoxal to form the intermediate (**D**). Then, the dehydration and rearranging of (**D**) *via* [1,5]sigmatropic shift to give the final 1,3-diarylimidazolium tetrafluoroborates (**E**).

In summary, we have developed a novel and simple silica sulfuric acid-catalyzed three-component condensation for the construction of 1,3-diarylimidazolium tetrafluoroborates from commercially available starting materials. Silica sulfuric acid showed its important role in this interesting reaction. Up to four new bonds and one new ring were formed in one-pot with water as the only by-product in the reactions. This method offers several advantages including inexpensive starting materials, low catalyst loading and no formation of by-products. This work develops an efficient and low-cost preparation of 1,3-diarylimidazolium and N-heterocylic carbene.

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