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A Greener Method Towards the Synthesis of 1,3-Diarylimidazolium Tetrafluoroborates

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ABSTRACT

A new strategic method for the synthesis of 1,3-diarylimidazolium tetrafluoroborate salts is illustrated herein. A solvent-free approach was employed in the synthesis of the diimines which are precursors in the preparation of the imidazolium salts. The reaction proceeds faster, cleaner and in a better yield than previously reported methods.

KEYWORDS

Diimines, imidazolium salts, NHC-metal ligand precursors, solvent-free, synthesis.

1. Introduction

The organic compounds 1,3-diarylimidazolium tetrafluoroborates are imidazolium salts (IMSs), which have received much attention[1–3] due to their wide applications, notably in medicine.[4] Zhao and coworkers[5] have successfully used IMSs as mild reducing agents in the production of ultrafine gold nanoparticles and as radical scavenger antioxidants to counter the damage caused by reactive oxygen species in the body. They have also found wide application in biofuel chemistry[6] and the petroleum industry,[6] as an alternative source of energy. Their use as ionic liquids[7] and as solvents[8] for many organic reactions is also an advantage. In addition, IMSs are precursors to *N*-heterocyclic carbenes (NHCs)[9], which today have become ubiquitous ligands in organometallic chemistry after the isolation of the first stable NHCs by Arduengo.[10] Numerous studies have confirmed NHC-metal complexes as highly efficient catalysts when compared to the corresponding phosphine-metal analogues.[11] From established data on the electronic and steric influence of a broad range of NHC ligands, their catalytic performance may be systematically studied and optimized by ligand tuning.[12–17] In addition, superior properties of NHCs when compared with traditional phosphine ligands, which amongst others include: ease of preparation, non-toxicity, air and moisture stability, low loading and high efficiency in catalysis have further established the chemistry of NHC compounds.[18]

Since the deprotonation of imidazolium salts[9] has been established as the easiest and the most commonly utilised method for the synthesis of NHCs, it is therefore essential that new, simple and high yielding methods for the synthesis of the salts are developed.[19–21] Towards this effort, Arduengo and coworkers'[22] method of reacting glyoxal, formaldehyde, substituted aniline, and an acid in a one-pot synthesis, is arguably the most adopted method, but it is only possible for the synthesis of some imidazolium salts and also requires extensive washing to obtain an analytically pure sample, which usually resulted in low product yields.[23,24]

In an effort to improve the one-pot procedure, both the groups of Arduengo[23] and Nolan[25] have modified it so that it can be extended to more imidazolium salts especially the sterically hindered ones, in order to improve product yields and reduce tedious product purification procedures.[22] To obtain their imidazolium salts they started with glyoxal imines and used chloromethyl ether and HCl/dioxane as a source of counter-ions. In addition to obtaining a low yield, the toxicity of the reagents and long reaction times are key disadvantages of this method.[25,26]

Later on, Leuthaußer and coworkers[27] have modified Nolan's method by introducing electron withdrawing/donating groups to two of the most commonly applied NHC ligands (*N,N'*-bis(2,6-dimethylphenyl)imidazol-2-ylidene and *N,N'*-bis(2,6-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene); thus, allowing the systematic tuning of the electron density of the metal bonded to the NHC ligands. The diimines were obtained by reaction of the corresponding anilines and glyoxal in ethanol as the solvent, which was stirred overnight. This was then followed by ring closure with HCl/dioxane to obtain their imidazolium salts. The HCl/dioxane mixture is a very hazardous/toxic and expensive counter ion source.

The synthesis of 1,3-diarylimidazolium salts possessing only halides substituted at the *para*-position has been reported by a few authors.[9,28] The salts were prepared by reacting glyoxal, formaldehyde, substituted aniline and an acid (in most cases HCl) as the source of counter-ions. Recently, Garden *et al.*[29] were the first to elucidate the crystal structure of 1,3-bis(4-bromophenyl)imidazolium chloride which was isolated as a dihydrate. A slight modification of Hintermann's method[30] was employed in their synthesis.

Here we report a novel method for the synthesis of 1,3-diarylimidazolium tetrafluoroborates by employing a solvent-free approach for the synthesis of the precursor diimines, which proceeds faster, cleaner and in a better yield than the aforementioned procedures. This reaction (without solvent) can be deemed 'green', simple and occurs readily under mild conditions. To our knowledge, the solvent-free approach has not been applied before for the synthesis of diimines, which are precursors to imidazolium salts. To obtain the 1,3-diarylimidazolium tetrafluoroborates from the diimines, the ring closure reaction was conducted in the presence of a solvent due to experimental challenges encountered with the solvent-free method for this step. However, we used a milder tetrafluoroboric acid as the source of counter-ions.

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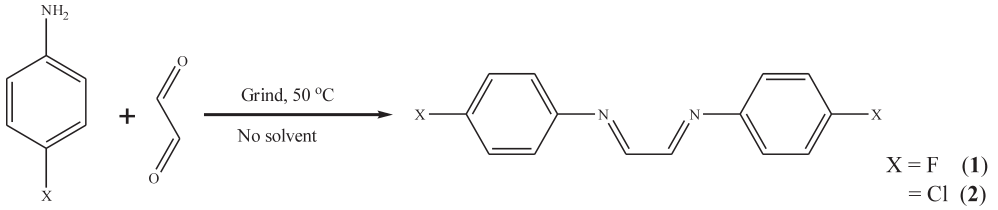
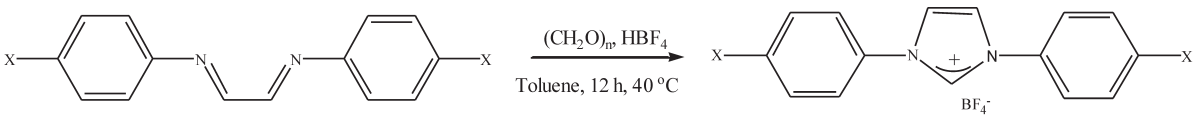


X = F (**1**)
= Cl (**2**)
= Br (**3**)
= I (**4**)

Scheme 1
Synthesis of diimines by the solvent-free method.



X = F (**5**)
= Cl (**6**)
= Br (**7**)
= I (**8**)

Scheme 2
Synthesis of the 1,3-diaryl imidazolium tetrafluoroborates.

2. Results and Discussion

Diimines as precursors to imidazolium salts are usually prepared by heating a solution of the corresponding aniline and glyoxal in anhydrous methanol[30] or ethanol.[27] We utilized this method with dry methanol as the solvent, but did not obtain a very good yield of the desired product. This is due to the thermal and moisture sensitivity of the diimines. To overcome the problem and in keeping with the principles of green chemistry,[31] a solvent-free approach was employed in the synthesis of the diimines.[32] The compounds were synthesized via the route shown in Scheme 1. This involves reacting the corresponding aniline (2 equiv.) with glyoxal (1 equiv.) using a solvent-free reaction technique. In this method, the corresponding aniline and glyoxal mixture was ground in a mortar, placed in a flask and heated to about 50 °C to melt the mixture. This was left under vacuum until it solidified at room temperature. The reactions proceeded very fast and were completed within a few minutes. The only exception was for compound **1** which took longer time to complete. This is due to the *para* substituent on the aniline utilized in the synthesis of compound **1**. Fluorine being the most electronegative halide, it exhibits the highest negative inductive effect on the aniline. Hence, it decreases its susceptibility to nucleophilic attack, and thus the reaction time is relatively longer compared to other *para*-haloanilines.

This new method avoids the problem of decomposition associated with heating/reflux and the sensitivity of diimines to moisture/impurities from solvents such as methanol or ethanol normally used in the majority of cases for their synthesis. The products (compounds **1**–**4**) were purified by minimal washing with cold anhydrous diethyl ether in order to remove unreacted aniline used in the reaction. Other solvents such as ethanol, which is considered relatively 'green', were also tried in the purification of the diimines, but diethyl ether gave the best result.

The solidified melt was analysed by infrared spectroscopy to ascertain the formation of the diimines. The strong band associated with glyoxal (CO) which usually resonates around 1700 cm^{-1} was absent and was replaced by a strong absorption band at 1596 cm^{-1}, which corresponds to the normal peak region for an imine bond (C=N).[33] Further confirmation of the formation of compounds **1**–**4**, was obtained by ^{1}H and ^{13}C NMR

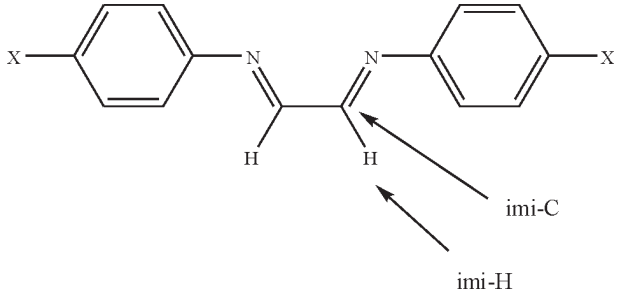


Figure 1 The positions of the imine proton and carbon, denoted as imi–H and imi-C, respectively.

spectroscopic analysis. The appearance of resonances at 8.34, 8.37, 8.32, 8.32 ppm in the ^{1}H NMR spectra for compounds **1**–**4**, respectively, correspond to the imine protons (imi-H) (Fig. 1). This was further confirmed by the ^{13}C NMR peak at around 159 ppm assigned to the imine carbon (imi-C) (Fig 1).

The reaction of the corresponding diimines (**1**–**4**) with paraformaldehyde and tetrafluoroboric acid (Scheme 2) was used as the source of counter ions in the ring closure reaction to form the corresponding 1,3-diarylimidazolium salts (**5**–**8**). Compounds **5**–**8** were found to be solids at room temperature with sharp melting points (see Experimental section for details).

^{1}H NMR analyses for compounds **5**–**8** (the general structure is shown in Fig. 2) were performed and data on the imidazole proton (imd-H) chemical shift is recorded in Table 1. The gradual

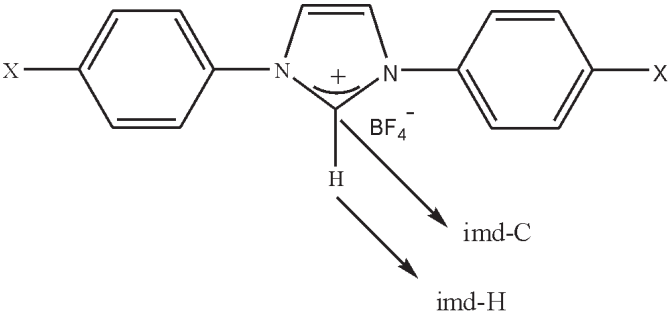


Figure 2 The positions of the imidazole proton and carbon, denoted as imd-H and imd-C, respectively.

Table 1 The effect of variations in the *para*-halogen substituent on the imidazolium salts.

Compounds	Melting point /°C	% Yield	^{1}H-NMR (imd-H*)/ppm
5	205	76	10.28
6	186	71	10.35
7	180	67	10.36
8	160	62	10.51

* Chemical shift of imidazole proton as indicated alongside.

downfield increase of the imd-H chemical shifts may be associated with the gradual decrease in the electron withdrawing ability and hence inductive effect of the halide substituents. Thus, the chemical shift of the iodine bearing compound **8** has the most downfield chemical shift at 10.51 ppm for the imd-H as compared to 10.28 ppm for the fluoride bearing compound **5**. The use of tetrafluoroboric acid as a source of counter ions instead of the expensive HCl/dioxane[18,19] mixture leads to a reliable synthetic procedure for the synthesis of compounds **5**–**8**.

3. Conclusion

A new synthetic strategy has been devised for the preparation of 1,3-diarylimidazolium tetrafluoroborates from diimines in excellent yields. The diimines were synthesized by solvent-free conditions and purified by solvent washing. This approach is faster, simpler and more atom economical as compared to other previously reported methods. The four novel imidazolium tetrafluoroborate salts were synthesized from starting materials that are readily available, especially the substituted aniline.

4. Experimental

4.1. General Procedures

The syntheses of the 1,3-diarylimidazolium tetrafluoroborates were performed under a nitrogen atmosphere and the solvents were dried by using standard literature methods. In the case of the solvent-free reactions, grinding and all work-up procedures were done open to air. Reagents were purchased from Aldrich and were used as received. Infrared spectra were recorded with a PerkinElmer Universal ATR Spectrum 100 FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a 400 MHz Bruker Ultrashield spectrometer and samples were dissolved in deuterated chloroform or deuterated dimethylsulpfoxide. Mass spectra were recorded with an Agilent Technologies, 1100 series, mass spectrometer, which was equipped with an ion trap with quadrupole analyzer and electron multiplier detector. Melting points were recorded on a Bibby Stuart Scientific model SMP3 apparatus and were uncorrected.

4. 2. General Procedure for the Synthesis of Diimines

The corresponding aniline (1 equiv.) was ground in a mortar with glyoxal (0.5 equiv.). The mixture was then transferred to a round-bottom flask and heated to 50 °C until it had melted and left under vacuum to solidify. It was then washed with dry cold diethyl ether to remove unreacted aniline.

4.2.1. *1,3-Bis(4-fluorophenyl)ethylenediimine* (**1**)

Starting materials used were 4-fluoro aniline (10.0 g, 90.0 mmol) and glyoxal (2.61 g, 45.0 mmol). Yield: 10.2 g; 93 %, m.p. 81.6 °C; IR (ATR cm^{-1}): 3337, 3009, 2952, 1506, 1402, 1295, 1223, 1120, 1013, 1058, 987, 939, 819, 766, 612, 522; δ_H (400 MHz, $CDCl_3$): 7.11 (4H, d, *J* 8.5 Hz, Ar-H), 7.29 (4H, d, *J* 8.9 Hz, Ar-H) and 8.34 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 116.14, 122.83, 145.76, 159.01 and 163.41 ppm; m/z (ESI), Obtained 245.3 (M^+) Calculated for $C_{14}H_{10}N_2F_2$ 245.1 (M^+).

4.2.2. *1,3-Bis(4-chlorophenyl)ethylenediimine* (**2**)

Starting materials used were 4-chloro aniline (10.0 g, 78.0 mmol) and glyoxal (2.26 g, 39.0 mmol). Yield: 9.40 g, 88 %; m.p. 119.7 °C; IR (ATR cm^{-1}): 3338, 3009, 2952, 1596, 1492, 1402, 1254, 1080, 988, 828, 766, 611, 522; δ_H (400 MHz, $CDCl_3$): 7.27 (4H, d, *J* 8.4 Hz, Ar-H), 7.42 (4H, d, *J* 8.6 Hz, Ar-H) and 8.37 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 122.60, 129.59, 133.81, 148.38 and 159.85 ppm; m/z (ESI), Obtained 277.3 (M^+) Calculated for $C_{14}H_{10}N_2Cl_2$ 277.2 (M^+).

4.2.3. *1,3-Bis(4-bromophenyl)ethylenediimine* (**3**)

Starting materials used were 4-bromo aniline (1.00 g, 5.80 mmol) and glyoxal (0.170 g, 2.90 mmol) Yield: 0.900 g, 85 %; m.p. 120.6 °C; IR (ATR cm^{-1}): 3338, 3009, 2952, 1596, 1492, 1402, 1254, 1080, 988, 828, 766, 611, 522; δ_H (400 MHz, $CDCl_3$): 7.16 (4H, d, *J* 8.6 Hz, Ar-H), 7.52 (4H, d, *J* 8.8 Hz, Ar-H) and 8.32 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 116.70, 122.91, 132.77, 148.88 and 159.94 ppm; m/z (ESI), Obtained 365.2 (M^+) Calculated for $C_{14}H_{10}N_2Br_2$ 365.4 (M^+).

4.2.4. *1,3-Bis(4-iodophenyl)ethylenediimine* (**4**)

Starting materials used were 4-iodo aniline (10.0 g, 45.7 mmol) and glyoxal (1.33 g, 22.9 mmol). Yield: 8.51 g, 81 %; m.p. 157.1 °C; IR (ATR cm^{-1}): 3337, 2952, 1585, 1486, 1395, 1294, 1121, 1059, 987, 959, 8278, 766, 614, 522; δ_H (400 MHz, $CDCl_3$): 7.02 (4H, d, *J* 8.5 Hz, Ar-H), 7.74 (4H, d, *J* 8.7 Hz, Ar-H) and 8.32 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 93.16, 123.12, 138.56, 149.54 and 159.98 ppm; m/z (ESI), Obtained 461.1 (M^+) Calculated for $C_{14}H_{10}N_2I_2$ 461.0 (M^+).

4.3. General Procedures for the Synthesis of Imidazolium Tetrafluoroborates

The diimines synthesized above were dissolved in 10 mL of toluene at 10 °C. To each of these was added 1 molar equivalent of paraformaldehyde with vigorous stirring. After 30 min, the solutions were cooled to 0 °C and an aqueous solution of HBF_4 (40 %, 1.0 equiv.) was added dropwise to each. The resulting solutions were stirred at room temperature for further 30 min and then heated to 40 °C for 12 h. After cooling to room temperature, diethyl ether (10 mL) was added and the slurries filtered, washed with ethyl acetate and tetrahydrofuran and vacuum dried.

4.3.1. *1,3-Bis(4-fluorophenyl)imidazolium tetrafluoroborate* (**5**)

The starting materials used were 1,3-bis(4-fluorophenyl)ethylenediimine (3.00 g, 12.3 mmol), paraformaldehyde (0.357 g, 12.3 mmol) and aqueous solution of HBF_4 (40 %, 12.3 mmol, 1.08 g, 0.82 mL). Light brown powder, in a .yield of 4.20 g, 75 %; m.p. 204.8 °C; IR (ATR cm^{-1}): 3163, 1562, 1511, 1255, 1242, 1161, 1082, 1036, 943, 831, 751, 520; δ_H (400 MHz, [D_6]DMSO): 7.60 (4H, d, *J* 8.7 Hz, Ar-H), 7.96 (4H, d, *J* 9.0 Hz, Ar-H), 8.52 (2H, s, NCH) and 10.28 ppm (1H, s, CH); δ_C (100 MHz, [D_6]DMSO): 117.97, 122.13, 124.72, 131.13, 135.04 and 163.64 ppm; m/z (ESI): Obtained 257.3 ($M^+ - BF_4^-$) Calculated for $C_{15}H_{11}N_2F_2BF_4$ 257.1 ($M^+ - BF_4^-$).

4.3.2. *1,3-Bis(4-chlorophenyl)imidazolium tetrafluoroborate* (**6**)

The starting materials used were 1,3-bis(4-chlorophenyl)ethylenediimine (2.00 g, 7.20 mmol), paraformaldehyde (0.210 g,

7.20 mmol) and aqueous solution of HBF_4 (40 %, 7.20 mmol, 0.630 g, 0.5 mL). Light yellow powder in a yield of 3.20 g, 76 %; m.p.186.2 °C; IR (ATR cm^{-1}): 3326, 2957, 1590, 1491, 1401, 1295, 1122, 1059, 1015, 988, 960, 827, 617, 592, 523; δ_H (400 MHz, [D_6]DMSO): 7.82 (4H, d, *J* 8.7 Hz, Ar-H), 7.93 (4H, d, *J* 8.8 Hz, Ar-H), 8.55 (2H, s, NCH) and 10.35 ppm (1H, s, CH); δ_C (100 MHz, [D_6]DMSO): 121.94, 123.87, 130.14, 133.46, 134.60 and 135.05 ppm; m/z (ESI): Obtained 289.3 ($M^+ - BF_4^-$). Calculated for $C_{15}H_{11}N_2Cl_2BF_4$ 289.0 ($M^+ - BF_4^-$).

4.3.3. *1,3-Bis(4-bromophenyl)imidazolium tetrafluoroborate* (**7**)

The starting materials used were 1,3-bis(4-bromophenyl)ethylenediimine (0.200 g, 0.546 mmol), paraformaldehyde (0.016 g, 0.546 mmol) and aqueous solution of HBF_4 (40 %, 0.546 mmol, 0.048 g, 0.034 mL). Light brown powder in a yield of 0.134 g, 67 %; m.p. 180 °C; IR (ATR cm^{-1}): 3455, 3397, 3323, 3079, 2925, 1706, 1553, 1423, 1220, 1002, 821, 749, 620, 519, 435; δ_H (400 MHz, [D_6]DMSO): 7.87 (4H, d, *J* 8.9 Hz, Ar-H), 7.93 (4H, d, *J* 8.9 Hz, Ar-H), 8.55 (2H, s, NCH) and 10.36 ppm (1H, s, CH); δ_C (100 MHz, [D_6]DMSO): 121.89, 123.07, 124.07, 133.07, 133.88 and 134.94 ppm; m/z (ESI), Obtained 379.2 ($M^+ - BF_4^-$). Calculated for $C_{15}H_{11}N_2Br_2BF_4$ 379.1 ($M^+ - BF_4^-$).

4.3.4. *1,3-Bis(4-iodophenyl)imidazolium tetrafluoroborate* (**8**)

The starting materials used were 1,3-bis(4-iodophenyl)ethylenediimine (0.300 g, 0.655 mmol), paraformaldehyde (0.019 g, 0.655 mmol) and aqueou solution of HBF_4 (40 %, 0.655 mmol, 0.058 g, 0.04 mL). Light brown powder in a yield of 0.22 g, 62 %; m.p. 160 °C; IR (ATR cm^{-1}): 3327, 2954, 1588, 1486, 1399, 1295, 1122, 1015, 1059, 939, 988, 829, 767, 616, 592, 523; δ_H (400 MHz, [D_6]DMSO): 7.84 (4H, d, *J* 8.7 Hz, Ar-H), 8.24 (4H, d, *J* 8.7 Hz, Ar-H), 8.70 (2H, s, NCH) and 10.51 ppm (1H, s, CH); δ_C (100 MHz, [D_6]DMSO): 96.36, 121.78, 123.91, 134.33, 134.67 and 138.85 ppm; m/z (ESI): Obtained 473.2 ($M^+ - BF_4^-$). Calculated for $C_{15}H_{11}N_2I_2BF_4$ 473.1 ($M^+ - BF_4^-$).

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