Efficient synthesis of ionic liquid-supported [bis(trifluoroacetoxy)iodo] benzene

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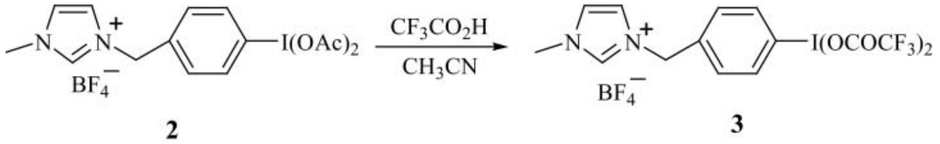
Ionic liquid-supported [bis(trifluoroacetoxy)iodo]benzene, a useful chemical reagent for organic synthesis, was synthesised in high yields using three different methods. The product was found to be stable in air and in a high humid atmosphere over a few weeks. The chemical structure of the product was characterised by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR, MS and elemental analysis.

Keywords: ionic liquids, [bis(trifluoroacetoxy)iodo]benzene, hypervalent iodine reagent

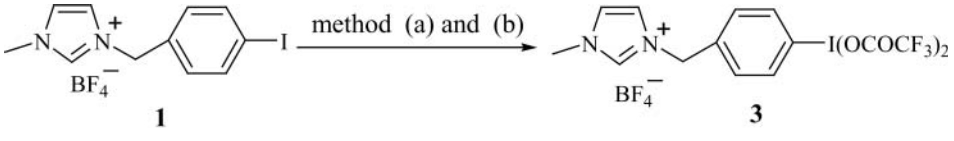
Phenyliodine bis(trifluoroacetate) (PIFA) is a hypervalent iodine reagent widely used in organic synthesis. PIFA has a higher reactivity than that of the other analogue, phenyliodine diacetate (PIDA), because of the strong electron withdrawing effect of the fluorine atom. It was demonstrated that some reactions, which failed when using PIDA, were efficiently promoted by PIFA. For example, the synthesis of a variety of bioactive natural products has been achieved using an intramolecular nucleophilic substitution reaction of phenol ethers using PIFA, while the same reactions failed in using PIDA.[1–4] Moreover, compared to PIDA, PIFA was reported to be a more effective oxidiser.[5] For example, cyclohexa-1,4-diene and its derivatives were oxidised to 1,4-benzoquinone and its derivatives by PIFA, while the same reactions failed to give the corresponding product by using PIDA and other hypervalent iodine reagents.[6] Furthermore, the cyanation reaction of heteroaromatic compounds with trimethylsilyl cyanide mediated by PIFA selectively occurred in the heteroaromatic ring, while the reactions failed when PIDA or [hydroxy(tosyloxy)iodo]-benzene were used.[7]

Although PIFA is a useful reagent, and has many potential applications in organic synthesis, its byproduct, iodobenzene produced by PIFA, cannot be easily removed from the expected product. Consequently, the recycling of iodobenzene is difficult. In addition, PIFA is quite sensitive to moisture, and should be handled under dry conditions. Obviously, this is not convenient, especially when larger scale syntheses are performed, in which larger quantities of PIFA would be used. To improve the properties and performance of PIFA, we explored a new version of PIFA, namely ionic liquid-supported PIFA. Room-temperature ionic liquids, have been used not only as reaction solvents, but also as catalysts due to their advantages such as high stability, non-toxicity, low vapour pressure, good solubility, and their easy ability to be recycled. In recent years, the exploration of task-specific ionic liquids with different functions has become an attractive research topic.[8,9] Task-specific ionic liquids have demonstrated a number of salient features, including higher reaction yields, remarkable selectivity, capability to be recycled and reused.

1-(4-Diacetoxyiodobenzyl)-3-methylimidazolium tetrafluoroborate **2**, an ionic liquid-supported PIDA, has previously been synthesised and used in organic synthesis.[10–14] Due to the electron withdrawing effect of the quaternary ammonium cations, the reactivity of iodine (III) in compound **2** was found to be increased. In addition, ionic liquid-supported PIDA has many advantages such as the ability to be recycled, good loading capacity, excellent selectivity and yields, good solubility (soluble in room temperature ionic liquids or water), and the possibility of homogeneous reactions.[10,14] Furthermore, when ionic liquids were utilised in the chemical reaction, the use of volatile organic solvent and excessive reagents could be greatly reduced, which would reduce not only the cost but also the pollution to the environment. This is especially true when reactions are carried out in a pilot plant manufacturing process. We now report the synthesis of a homogeneous supported PIFA reagent 1-[4-bis- (trifluoroacetoxy)- iodobenzyl]-3-methylimidazolium tetrafluoroborate **3**, which was based on a room-temperature ionic liquid (RTIL) support as outlined in Schemes 1 and 2.



Scheme 1 Ligand-exchange method.



Scheme 2 (a) Urea peroxide method, Reagent and conditions: $H_2O_2\cdot$urea–$(CF_3CO)_2O$–CH_2Cl_2/–40°C. (b) Sodium percarbonate method, Reagent and conditions: $2Na_2CO_2\cdot 3H_2O_2$–$(CF_3CO)_2O$–CH_3CN.

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Experimental

Melting points were determined using a WRS-1B digital thermometer and melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DRX-500 Avance spectrometer with TMS as the internal standard. IR spectra were recorded on a Nicolet Protege 460 IR spectrometer. Mass spectra were obtained on a HP5890-GCQ and Agilent 5975I instrument. Elemental analyses were performed using an EA2400 II instrument.

1-(4-Iodobenzyl)-3-methylimidazolium tetrafluoroborate **1** and **2** were prepared according to literature methods,[10] All other reagents were of analytical or chemical grade quality purchased commercially and used as received unless noted otherwise.

Method 1: Ligand-exchange method (see Scheme 1)

In a 250-mL three-neck round bottom flask equipped with a magnetic stirrer, **2** (5.04 g, 10 mmol) was added in anhydrous acetonitrile (100 mL). The resulting suspension was stirred at room temperature, followed by the addition of trifluoroacetic acid (60mmol.) until solid **2** was fully dissolved. The reaction mixture was then stirred for another 1 h. The solvent and other low boiling point organic compounds were removed under reduced pressure, dichloromethane (5 mL) was added with stirring, the CH_2Cl_2 solution was removed by pouring and the residue was dried under vacuum at 50 °C for 6 h to afford **3** (5.97 g, 97.5%) as a viscous liquid. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 3.90 (s, 3H, CH_3), 5.25 (s, 2H, CH_2), 7.10 (d, J = 10 Hz, 2H, ArH), 7.21 (s, 1H, imidazolium-H), 7.26 (s, 1H, imidazolium-H), 7.72 (d, J = 10 Hz, 2H, ArH), 8.82 (s, 1H, imidazolium-H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 36.0, 51.5, 95.3, 115.5 (q, $^1J_{CF}$ = 290 Hz), 122.5, 124.3, 130.7, 134.4, 137.9, 138.9, 158.9 (q, $^2J_{CCF}$ = 36.3 Hz); ^{19}F NMR (DMSO-d_6, ppm): δ –148.0 (4F, BF_4), –74.8 (6F, CF_3); IR (film, cm^{-1}): ν 3160.8, 1765.6 (C=O), 1488.1, 1405.5, 1163.1 (B-F); MS *m/z* (%): 298.9 (100) [M^+-BF_4^--$2CF_3CO_2^-$]. Anal. Calcd for $C_{15}H_{12}BF_{10}IN_2O_4$: C, 29.44; H, 1.98; N 4.58. Found: C, 29.49; H, 1.99; N 4.59%.

Method 2: Urea peroxide method (see Scheme 2)

The solution of $H_2O_2 \cdot$urea (2.16 g, 22.9 mmol) in de-ionised water (5mL) was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered to give a CH_2Cl_2 solution containing hydrogen peroxide. Then the solution was cooled to –40 °C and trifluoroacetic anhydride (12.7 mL, 91.7 mmol) was slowly added. The reaction mixture was stirred for 30 min. To this reaction mixture **1** (3.3 g; 8.6 mmol) was added. The mixture was stirred at –40 °C for 7 h, and then the reaction mixture was warmed up to room temperature, and stirred for another 1 h. During the course of the reaction a homogeneous, straw yellow solution was formed. The solvent and other low boiling point of organic compounds were removed under reduced pressure, acetone (3 mL) was added with stirring, the solution of acetone was poured out and the residue was dried under vacuum at 50 °C for 6 h to afford **3** (4.84 g, 92.5%) as a viscous liquid. Analytical data were identical to those reported in the first method.

Method 3: Sodium percarbonate method (see Scheme 2)

Compound **1** (1.16 g, 3 mmol), trifluoroacetic anhydride (7.2 mL) and anhydrous acetonitrile (24 mL) were added to a 50-mL three-neck round bottom flask. The solution was cooled to 0 °C. Sodium percarbonate (1.26 g, 4 mmol) was slowly added to the mixture. After the addition of sodium percarbonate was completed, the resulting solution was stirred at 0 °C for 2 h, and at room temperature for 18 h. The resulting slurry was filtered. The filtrate was concentrated under reduced pressure, acetone (1 mL) was added with stirring, the solution of acetone was poured out and the residue was dried under vacuum to afford **3** (1.43 g, 77.9%) as a viscous liquid. Analytical data were identical to those reported in the first method.

In conclusion, we have developed three different methods for the preparation of compound **3**. Method 1, using ligand-exchange, is characterised by a shortened reaction time, high yield and is easy to purify. Methods 2 and 3 used urea peroxide and sodium percarbonate as oxidisation agents. However, method 2 (urea peroxide) gave the better yield. Compound **3** was stable in air and in high humid atmospheres for a long time. It may be suitable as a new type of task-specific ionic liquid.

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