

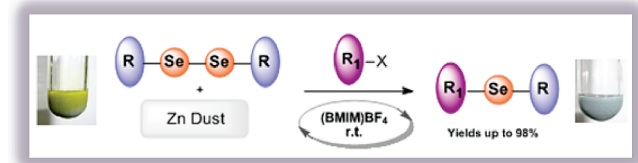
Synthesis of Diorganyl Selenides Mediated by Zinc in Ionic Liquid

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A new approach for the synthesis of diorganyl selenides is described. By using economically attractive zinc dust in BMIM-BF₄, a series of diorganyl selenides were efficiently achieved in excellent yields, under neutral reaction conditions. Compared to the usual organic solvents, BMIM-BF₄ exhibited higher performance with the advantage to be reused up to five successive runs.

Research on organoselenides has been driven by the potential applications of selenium compounds in modern organic synthesis and catalysis.¹ The biological and medicinal properties of selenium and organoselenium compounds are also becoming increasingly appreciated, mainly due to their antioxidant, antitumor, antimicrobial, and antiviral properties.² Also, the synthesis of peptides containing selenocysteine is rapidly gaining interest with the discovery of an increasing number of proteins containing this amino acid.³

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Diorganyl selenides are versatile tools in organic chemistry, and have found wide application as radical precursors, in elimination reactions, and as selenium-stabilized carbanions.⁴ Chiral diorganyl selenides are also used as efficient ligands in asymmetric reactions.⁵

These compounds are generally prepared by reductive cleavage of Se–Se bonds, employing common reducing agents such as NaBH₄, LiAlH₄, and other expensive metal sources such as La, In, Yb, Sm, etc.^{6,7} Most of the procedures require handling of unstable reagents, strongly acidic or basic conditions, or two-step procedures. Thus, there is still considerable interest in the development of highly efficient methods for this transformation.⁸

Ionic liquids are versatile and novel reaction media, for organic transformations, and have also found application as flexible “platforms” to establish highly effective and easily separable systems.⁹ Room temperature ionic liquids, especially those based on the 1,3-dialkylimidazolium cation, have attracted considerable attention due to their negligible vapor

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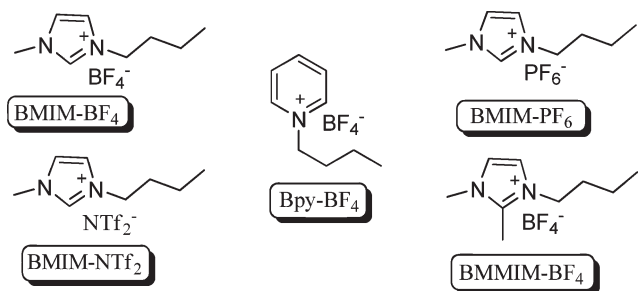


FIGURE 1. Room temperature ionic liquids.

pressure, nonflammability, reasonable thermal stability, ease of handling, and potential for recycling.¹⁰ Ionic liquids were used as solvent in many organic transformations and have shown enhanced reaction rates when compared with conventional organic solvents. Thus, development of ionic liquid mediated organic transformation is gaining prominence.¹¹

In connection with our insights about the synthesis of diorganyl selenides and their application in biological and asymmetric transformations,^{12,13} we describe herein a simple, efficient, and versatile approach to the preparation of diorganyl selenides. Employing zinc dust and ionic liquid, to promote the direct coupling of diselenides and organic halides, the respective selenides were achieved in good to excellent yields in a short time at room temperature. To optimize the protocol, we performed the reaction of benzyl chloride with PhSeSePh and 1.6 equiv of zinc dust with respect to diselenide, in five different ionic liquids (Figure 1). The formation of the product could be easily observed by the change of the reaction color from yellow to gray.

The results for BMIM-BF₄ were found to be better than those for the other ionic liquids (Table 1, entries 1–5). Similar protocols have appeared in the literature for reduction of PhSeSePh with zinc followed by reaction with benzyl chloride with use of other organic solvents. In a mixture of MeCN/H₂O at 65 °C the desired product was obtained in 64% yield after 3 h,^{7h} in CH₂Cl₂ at rt, 57% of the yield was obtained after 5 h.^{7j} Although the improved capability of ionic liquid to accelerate many organic reactions compared to other organic solvents has been extensively reported, the origin of its behavior is still an intriguing subject of study. Properties such as strong dipolar and dispersion forces,

TABLE 1. Reaction Optimization

| entry | ionic liquid ^a | X | time (min) | yield (%) ^b |
|----------------|---------------------------|----|------------|------------------------|
| 1 | Bpy-BF ₄ | Cl | 40 | 55 |
| 2 | BMMIM-BF ₄ | Cl | 40 | 65 |
| 3 | BMIM-NTf ₂ | Cl | 40 | 29 |
| 4 | BMIM-PF ₆ | Cl | 35 | 86 |
| 5 | BMIM-BF ₄ | Cl | 30 | 93 |
| 6 | BMIM-BF ₄ | Br | 25 | 95 |
| 7 | BMIM-BF ₄ | I | 20 | 98 |
| 8 ^c | BMIM-BF ₄ | Br | 25 | 96 |
| 9 ^d | BMIM-BF ₄ | Br | 25 | 92 |

^aPrepared according literature procedure.^{10e} ^bYields refer to pure isolated products. ^c1.2 equiv of zinc dust. ^d1.0 equiv of zinc dust.

hydrogen bond acidity (related to the cationic portion), and hydrogen bond basicity (related to the anionic portion) would account for the complex solvent interactions exhibited by ILs.¹⁴ In previous reports hydrogen bonds have been evoked as a pivotal interaction in the formation of a given product in reactions performed in ILs.¹⁵ Our experimental results (Table 1) suggest that perhaps the scale of hydrogen bond acidity of the tested ILs may be a distinguished property for the formation of products. If one assumes that this characteristic would facilitate the reaction through the coordination of the acid hydrogen attached to C-2 in the imidazolium ring with the leaving group (chloride) in an S_N2 like reaction, the formation of products would be in the same range of yield for BMIM-BF₄, BMIM-PF₆, and BMIM-N(Tf)₂ due to the similarity of their hydrogen bond donor (HBD) parameters.¹⁶ With the exception of BMIM-N(Tf)₂, 29% yield (entry 3), BMIM-BF₄ and BMIM-PF₆ furnished the desired product in 93% and 86% yields, respectively (entries 5 and 4). Moreover, if the extent of hydrogen bond interactions really accounts for an effective formation of products, reactions carried in Bpy-BF₄ and BMMIM-BF₄ which have a much lower (HBD) value compared to the above-mentioned ionic liquids would result in the formation of products in lower yields. Actually, these ILs exhibited poorer activity compared to BMIM-BF₄ and BMIM-PF₆ (entries 1 and 2). A reasonable explanation to the lower yield observed for BMIM-N(Tf)₂ is the influence of the anion N(Tf)₂. We speculate that it would interfere in the formation and/or in the reactivity of zinc selenolate, PhSeZnSePh.¹⁷ On the basis of these results, we investigated the influence of halide in the substrate. When benzyl iodide was used a higher

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TABLE 2. Synthesis of Diorganyl Selenides

| | Halide | Product | Time (min) | Yield (%) ^a |
|-----------------|--------|---------|------------|------------------------|
| 1 | | | 30 | 80 |
| 2 | | | 35 | 73 |
| 3 | | | 20 | 82 |
| 4 | | | 20 | 84 |
| 5 | | | 15 | 89 |
| 6 | | | 25 | 92 |
| 7 | | | 30 | 94 |
| 8 | | | 20 | 98 |
| 9 | | | 20 | 98 |
| 10 | | | 25 | 79 |
| 11 | | | 35 | 80 |
| 12 | | | 40 | 88 |
| 13 | | | 35 | 89 |
| 14 | | | 30 | 82 |
| 15 | | | 45 | 52 |
| 16 | | | 40 | 77 |
| 17 | | | 10 | 89 |
| 18 | | | 20 | 84 |
| 19 ^b | | | 180 | 61 |

^aYields refer to pure isolated products. ^bBromo ester (1 equiv), Zn (0.6 equiv), PhSe₂ (0.6 equiv), BMIM-BF₄ (1 mL).

yield was obtained as compared with that of benzyl bromide and chloride, which can be explained by the leaving group ability of the halogens (entries 5–7). However, the difference was not significant and all the halogens afforded the desired product in excellent yields. The amount of zinc required to promote the completion of the reaction was also evaluated. Reactions with 1.2 and 1.0 equiv of zinc showed similar results, leading to the product in excellent yields (entries 8 and 9).

After optimization, the coupling of different substrates and diselenides was applied to check the versatility of the protocol. A diverse range of alkyl halides were reacted with diphenyl diselenide under standard reaction conditions to provide the corresponding alkyl phenyl selenides in excellent yields. The results are summarized in Table 2 (entries 1–6) and indicate that the chain length has a positive effect on the reaction course, affording improved yields in longer chains (entries 2, 4, and 6). Reactive allylic halides allowed the corresponding allyl phenylselenide in near quantitative

yields, for both allyl chloride and iodide (entries 7 and 8). Substituted benzylic halides and diaryl diselenides were also applied to this protocol in order to check the steric and electronic effects in the course of the reaction. When 4-methylbenzyl bromide was applied, the product was achieved in 98% yield, while 2-methylbenzyl bromide gave the selenide in 79% yield (entries 9 and 10). In the diselenide moiety, a lower yield was observed by using 2-methoxy diphenyl diselenide as a selenium source compared with 4-methoxy diphenyl diselenide (entries 14 and 15). These observations can be explained by the steric dependence in this coupling reaction, driving better yields to the less sterically hindered para-substituted aryl halides and diselenides.

Electronic effects had no significant influence on the reaction course and the coupling of diaryl diselenides, with electron-donating or electron-withdrawing groups attached to the aromatic ring, afforded the products with a similar level of efficiency (entries 12–14). We also employed other diselenide sources in this reaction, e.g. benzylic and alkylic. For instance, dibenzyl diselenide and diethyl diselenide were reacted with benzyl chloride, allowing the preparation of the desired products in good yields (entries 11 and 16).

An important feature of our methodology is the tolerance of different functional groups, such as protected aminoester, ester, and nitrile, giving the corresponding products in good yields (entries 17, 18, and 19). Exploiting the versatility of our current methodology, the synthesis of the biologically important selenocysteine^{2,3,18} derivative was accomplished from the corresponding bromo amino ester derivative¹⁹ in 61% yield, employing our standard reaction conditions (entry 19). This result demonstrates the potential wide-ranging utility of this methodology by the preparation of various chiral organoselenium compounds.

Furthermore, our approach allows the preparation of the desired products in really smooth reaction conditions in a shorter time. Although in the other related procedures with Zn the products were successfully obtained,^{7h–k,8} these protocols require severe reaction conditions such as long reaction time under higher temperature. It is noteworthy to highlight that, when the solvent for the synthesis of diorganyl selenides was changed from conventional organic solvents to ionic liquid (BMIM-BF₄) excellent conversion rates and yields were obtained under room temperature with very short reaction times and mild conditions with BMIM-BF₄ as a reusable solvent.

After completion of the reaction, the desired products can be conveniently obtained by extraction with diethyl ether (3 × 15 mL). After the workup of the first run, the remaining ionic liquid (BMIM-BF₄) was diluted in ethanol, filtered through a Celite pad to remove inorganic materials, followed by concentration to remove the organic solvents. Then, it was subjected to the vacuum for 1 h to eliminate the moisture and trace organic solvents. For the following runs, the recovered ionic liquid was used after addition of 1 equiv of Zn (33 mg, 0.5 mmol), diphenyl diselenide (156 mg, 0.5 mmol), and benzyl chloride (127 mg, 1 mmol) for each run (Figure 2). The yields were almost constant for the first three runs, followed by a slight decrease for the following two runs.

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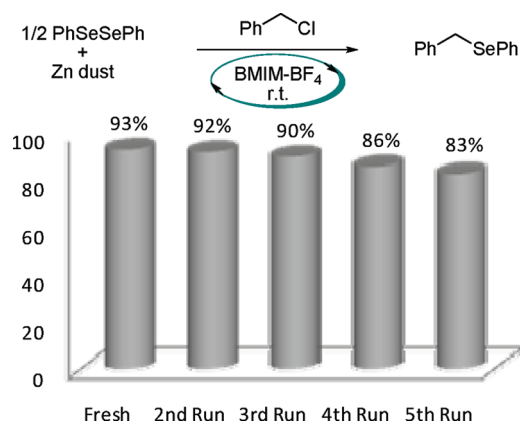


FIGURE 2. Reuse of BMIM-BF₄.

In conclusion, the present method has the following noteworthy features: (1) good to excellent yields were obtained in a short time; (2) ease of handling and better safety aspects as compared with metal hydrides; (3) neutral reaction conditions; (4) from an industrial point of view, the use of commercially available and inexpensive Zn is an interesting option to processes which use La, Yb, Sm, or In salts to promote the reduction of selenium–selenium bound; and (5) the solvent/ionic liquid is reused in up to five successive runs without loss of its efficiency and when compared to usual organic solvents, BMIM-BF₄ exhibited higher performance. Continued investigations into the utility of this novel methodology are underway in our laboratory aiming at the synthesis of seleno aminoacids and derivatives.

Experimental Section

Typical Procedure. Commercially available Zn dust (33 mg, 0.5 mmol) and PhSeSePh (156 mg, 0.5 mmol) were added to

BMIM-BF₄ (0.5 mL) at room temperature under nitrogen. The mixture was allowed to stir for 2–3 min. Then benzyl bromide (171 mg, 1 mmol) was slowly added. The reaction mixture was stirred for another 25 min (monitored by TLC and assisted by visual observation). The mixture was then extracted with ether (3 × 15 mL), and the combined ether extract was washed with brine, dried (MgSO₄), and evaporated to leave the crude product. Purification by column chromatography over silica gel (hexane/ethyl acetate 98:2) furnished the pure benzyl phenyl selenide as a yellow oil (231 mg, 92%).

Benzyl phenyl selenide:^{6f} 92% yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.50–7.42 (m, 2H), 7.28–7.14 (m, 8H), 4.10 (s, 2H); ¹³C (CDCl₃, 100 MHz) δ 138.6, 133.5, 130.4, 128.9, 128.8, 128.4, 127.3, 126.8, 32.2.

Ethyl phenyl selenide:^{6h} 80% yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.50–7.45 (m, 2H), 7.27–7.20 (m, 3H), 2.91 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ¹³C (CDCl₃, 100 MHz) δ 132.6, 130.3, 129.0, 126.7, 21.3, 15.5.

Representative Experimental Procedure To Reuse BMIM-BF₄. After the workup of the first run, BMIM-BF₄ is diluted in ethanol, filtered through a Celite pad, and then subjected to the vacuum for 1 h. For the following run the recovered ionic liquid was used after addition of 1 equiv of Zn (33 mg, 0.5 mmol), diphenyl diselenide (156 mg, 0.5 mmol), and benzyl chloride (127 mg, 1 mmol) followed by the procedure described above.

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Supporting Information Available: Synthetic procedures and compound characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.