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LETTERS

Preparation of (*Z*)- and (*E*)-vinyl selenides utilizing vinylboronic acids and vinylboronic esters in ionic liquids

George W. Kabalka* and Bollu Venkataiah

Departments of Chemistry and Radiology, The University of Tennessee, Knoxville, TN 37996-1600, USA

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Abstract—Vinylboronic acids and vinylboronic esters react with phenylselenyl chloride in ionic liquids to generate vinyl selenides stereospecifically. © 2002 Elsevier Science Ltd. All rights reserved.

Vinyl selenides have attracted considerable attention in recent years as synthetic precursors.[1] Many selenide preparations involve the use of expensive catalysts or starting materials that are not readily available.[2] Recently, Ogawa and his co-workers reported that organic selenols react with acetylenes to generate vinyl selenides.[3] However, they were unsuccessful in generating stereochemically pure products, although (*Z*)-isomers formed preferentially.

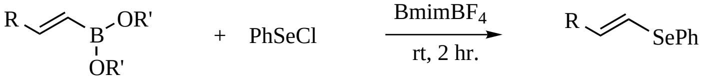
Since the hydroboration of alkynes proceeds stereoselectively to generate (*E*)-vinylboranes,[4] the stereospecific displacement of the boron moiety by selenium reagents would then afford (*E*)-vinyl selenides. We wish to report that vinylboronic acids and vinylboronic esters readily react with phenyl selenenyl chloride in ionic liquids such as butylimidazolium tetrafluoroborate ($BmimBF_4$) and BmimBr to generate the corresponding phenyl vinyl selenides. Since $BmimBF_4$ is a liquid at room temperature and it is easily prepared,[5] we decided to utilize $BmimBF_4$ in the initial phase of the study.

Fortunately, good yields are obtained in $BmimBF_4$ at room temperature. In addition, after completion of the reaction, the products are simply extracted into ether and the ionic liquid recycled.

Several vinylboronic acids[4,6] and esters were treated with phenyl selenyl chloride. Substituents such as bromo and hydroxy are tolerated quite well. Both (*E*)- and (*Z*)-vinylboronates react (Table 1). Pinacolate esters are also reactive but catechol esters are not suitable substrates due to the electrophilic substitution reactions of the phenyl selenium cation on the catechol moiety.[7]

The synthesis of 1-hexenylselanylbenzene is representative: 1-Hexenylboronic acid (1 mmol) and $BmimBF_4$ (400 mg) were placed in a 10 mL round-bottomed flask. Phenyl selenenyl chloride (1 mmol) was added and the mixture was allowed to stir at room temperature for 2 h. The mixture was washed with ether (4×5 mL) and the combined organic extracts were dried ($MgSO_4$), filtered, the solvent removed under reduced pressure and the product purified by silica gel column chromatography (pentane) to yield 82% of the desired product.

In conclusion, we have developed a simple and efficient method for the preparation of geometrically pure vinyl selenides from vinylboronic acids and esters in ionic liquids. The solvent can be recycled without significant loss in yields.



Keywords: selenides; boronic acids; boronic esters; ionic liquids.

* Corresponding author. Tel.: (865) 974-3260; fax: (865) 974-3260; e-mail: kabalka@utk.edu

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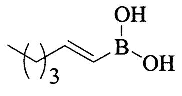
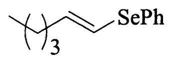
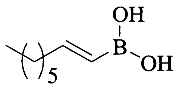
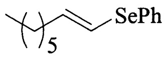
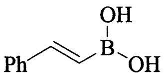
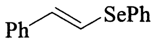
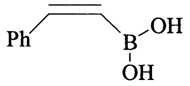
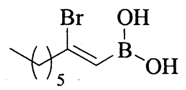
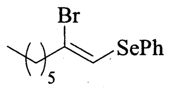
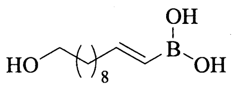
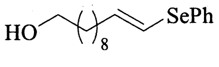
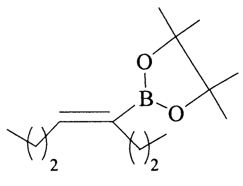
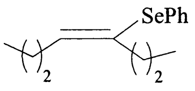
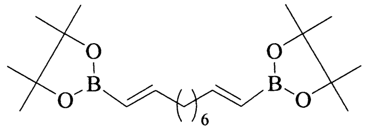
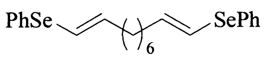
Table 1. Preparation of vinyl selenides from alkenyl boronates

Alkenyl Boronate	Product[a]	Yield[b](%)
		82
		84
		75
		74
		78
		79
		76
		71

[a] All products exhibited satisfactory spectroscopic and analytical data. [b] Isolated yield.

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