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Stereospecific Synthesis of Vinyl(phenyl)iodonium Tetrafluoroborates *via* Boron-Iodane Exchange of Vinylboronic Acids and Esters with Hypervalent Phenyliodanes

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Abstract: Reaction of vinylboronic acids and esters with hypervalent phenyliodanes in the presence of BF_3-Et_2O undergoes boron-iodane exchange at 0 °C in dichloromethane yielding vinyl(phenyl)-iodonium tetrafluoroborates stereoselectively with retention of configuration.
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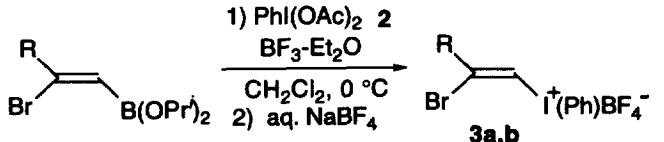
Because of an excellent leaving group ability of a phenyliodanyl group,[1] vinyl(phenyl)iodonium salts undergo nucleophilic vinylic substitutions under mild conditions, thus providing a useful route for the synthesis of various kinds of olefins including α-cyano and α-nitro olefins, vinyl sulphides and sulphones, and vinyl halides.[2,3] The base-induced α-elimination generates alkylidenecarbenes, which undergo 1,5-carbon-hydrogen insertion yielding cyclopentenes.[4] The efficient methods available for the synthesis of vinyl(phenyl)iodonium salts, however, are limited. Reaction of vinylsilanes or stannanes with hypervalent organoiodanes produces vinyliodonium salts stereoselectively.[2] Michael addition[5] or Diels-Alder reaction[6] of alkynyl(phenyl)iodonium salts constitutes an alternative method for the synthesis of functionalized vinyliodonium salts. We report herein a new, general, and practical method for the synthesis of vinyl(phenyl)iodonium salts, which involves boron-iodane exchange of vinylboronic acids or esters with hypervalent phenyliodanes in the presence of a Lewis acid.

Reaction of vinylboranes with (diacetoxyiodo)benzene (**2**) has been reported to give internal olefins *via* migration of an alkyl group attached to boron to the adjacent vinylic carbon atom; for instance, treatment of (*E*)-1-hexenyl(dicyclohexyl)borane with (diacetoxyiodo)benzene (**2**) in chloroform gives a 92:8 mixture of (*E*)- and (*Z*)-1-cyclohexyl-1-hexene in a good yield.[7-9] In marked contrast to vinyl(dialkyl)boranes, vinylboronic esters undergo a boron-iodine(III) exchange by the reaction with **2**. Exposure of (*Z*)-diisopropyl vinylboronate **1a**[10] to (diacetoxyiodo)benzene (**2**) (1.2 equiv.) in dichloromethane at 0 °C under nitrogen gave, after ligand exchange by an aqueous $NaBF_4$ solution, (*Z*)-vinyl(phenyl)iodonium tetrafluoroborate **3a**,[11] albeit in low yield



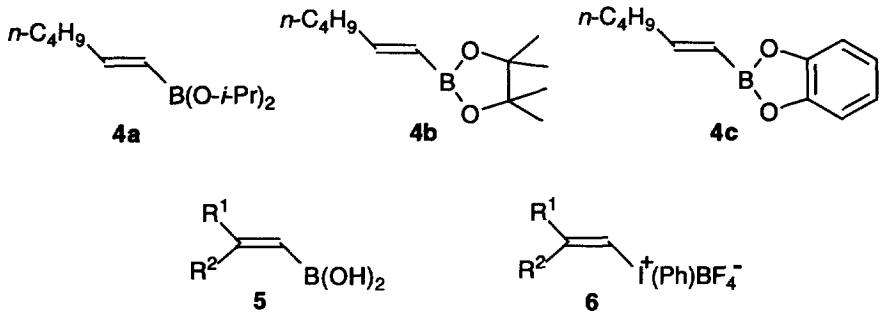
1a,b

a; R = *n*-C_8H_{17}, **b**; R = *n*-C_4H_9

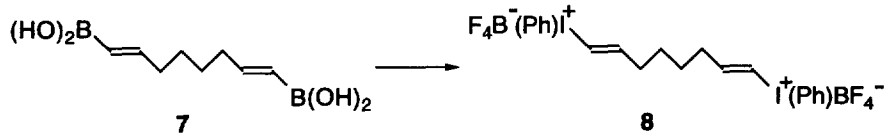
Scheme 1

(17%). Formation of a small amount of (*Z*)-2-bromodec-2-enal (9%), 2,2-dibromodecanal (3%), and (*Z*)-1,2-dibromodec-1-ene[11] (5%) was also detected in this reaction. Use of a Lewis acid as an additive was found to be essential for the selective boron-iodane exchange of the vinylboronate **1a**;[10] thus, when the reaction was carried out in the presence of BF_3-Et_2O (1.2 equiv.) at 0 °C in dichloromethane, a clean boron-iodane exchange reaction was observed and the vinyliodonium salt **3a** was obtained in 85% yield (Scheme 1). This BF_3-catalyzed reaction of diisopropyl vinylboronates **1** is relatively insensitive to the nature of the solvents. When the reaction of **1b** was carried out in dichloromethane, benzene, ethyl acetate or methanol as a solvent, (*Z*)-vinyliodonium tetrafluoroborate **3b** was isolated in more than 80% yield. Reduced yields of **3b** were obtained in acetonitrile (53%) and diethyl ether (69%).

Other commercially available phenyliodanes such as iodosylbenzene and [hydroxy(tosyloxy)iodo]benzene (Koser's reagent) react with the diisopropyl vinylboronate **1b** under similar conditions yielding the iodonium salt **3b** in 82 and 87% yields, respectively, whereas [bis(trifluoroacetoxy)iodo]benzene afforded a 10:1 mixture of **3b** and [(*Z*)-2-bromohex-1-enyl]phenyliodonium trifluoroacetate in 77% yield. These reactions are exclusively stereoselective to the limits of ^1H NMR (400 MHz) detection with retention of olefin geometry. Stereochemistry of the iodonium salt **3** was determined by a measurement of an NOE enhancement between the vinylic and allylic protons.



BF_3-Catalyzed reaction of (*E*)-diisopropyl β-alkylvinylboronate **4a** with (diacetoxyiodo)benzene (**2**) gave (*E*)-vinyliodonium salt **6a** stereoselectively, but rather in a low yield (47%), and formation of a small amount of hexanal (12%) was detected as a by-product. Using the pinacol **4b** and catechol derivatives **4c**, no improvements on the yield of **6a** was observed. The vinylboronic acid **5**[12] was found to be a choice of substrates; the reaction of **5a** with **2** in dichloromethane at 0 °C under nitrogen afforded an 82% yield of **6a**. A variety of vinylboronic acids **5** react with **2** to afford the vinyliodonium tetrafluoroborates **6** in high yields under mild conditions (generally at 0 °C within 1 h) and the results of BF_3-catalyzed boron-iodane exchange are summarized in Table 1. Functionalized vinyliodonium tetrafluoroborates **6d,e** with a chlorine atom or a cyano group were prepared by this method in high yields. (*E*)-β-Styrylboronic acid (**5i**) gave (*E*)-vinyliodonium salt



Scheme 2

Table 1 BF_3-Catalyzed boron-iodane exchange of vinylboronic acid **5** with **2**[a]

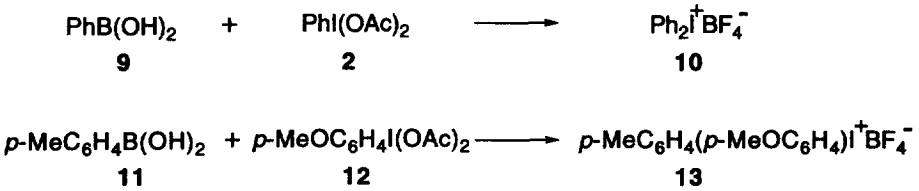
Vinylboronic acid				Product	
5	R^1	R^2	*t*/h	**6**	Yield (%)[b]
5a	*n*-C_4H_9	H	1	**6a**	82
5b	*n*-C_8H_{17}	H	0.2	**6b**	84
5c	$Ph(CH_2)_3$	H	0.2	**6c**	95
5d	$Cl(CH_2)_3$	H	0.2	**6d**	88
5e	$NC(CH_2)_3$	H	0.2	**6e**	82
5f	c-$C_5H_9CH_2$	H	0.2	**6f**	91
5g	$Me_2CH(CH_2)_2$	H	0.2	**6g**	96
5h	*t*-Bu	H	0.2	**6h**	96
5i	Ph	H	0.2	**6i**	73
5j	*n*-C_4H_9	Me	1	**6j**	92
5k	*n*-C_4H_9	Ph	1	**6k**	84

[a] Reactions were carried out in the presence of BF_3-Et_2O (1.2 equiv.) in dichloromethane at 0 °C under nitrogen. [b] Isolated yields.

6i (73%). The reaction of β,β-dialkyl- and β,β-alkylarylvinylboronic acids **5j,k**[10] proceeds smoothly with retention of configuration. It is to be noted that the bis(vinyliodonium) salt **8** could be prepared from the vinylboronic acid **7** by this new method in 40% yield (Scheme 2).

The following procedure for the synthesis of (*E*)-vinyliodonium salt **6a** from boronic acid **5a** is representative. To a solution of (*E*)-vinylboronic acid **5a** (0.1 mmol) in dichloromethane (1 mL) was added BF_3-Et_2O (0.12 mmol) at 0 °C under nitrogen and the mixture was stirred for 15 min. A solution of (diacetoxyiodo)benzene (**2**) (0.12 mmol) in dichloromethane (1 mL) was added at 0 °C and the mixture was stirred for 1 h. After the addition of a saturated aqueous solution (5 mL) of sodium tetrafluoroborate, the mixture was stirred for 15 min. Extraction with dichloromethane, filtration and then concentration gave an oil, which was washed several times with hexane by decantation. Further purification by decantation using hexane-diethyl ether gave the (*E*)-vinyliodonium salt **6a** (82%) as a colorless oil.

In addition to vinylboronic acids with various substitution patterns, the reaction also works with arylboronic acids and affords diaryliodonium salts.[13] As shown in Scheme 3, diphenyliodonium salt **10** and unsymmetrical diaryliodonium salt **13** were prepared from the arylboronic acids **9** and **11** in 90 and 86% yields, respectively.



Scheme 3

Since the alkenylboronic acids are readily available from alkynes in geometrically pure form and stable to air and water,[14] this new BF_3-catalyzed boron-iodane exchange provides a practical route for the synthesis of vinyl(phenyl)iodonium tetrafluoroborates.

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