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Copper(I)-Catalyzed Efficient and Stereoselective Synthesis of (*E*)-Vinyl Selenides and Tellurides by the Reaction of Potassium Vinyltrifluoroborates with Diphenyl Dichalcogenides

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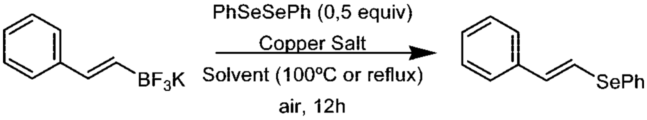
Summary: A mild, stereoselective, and effective strategy has been developed for the synthesis of (E)-vinyl selenides and (E)-vinyl tellurides by reaction of potassium vinyltrifluoroborates with the respective dichalcogenides using a copper salt as catalyst.

Vinylic selenides and tellurides are of current interest, due to the reactivity of their $C=C$ bonds and their use as sources of vinylic groups.[1] Of special interest are their applications in the preparation of vinylic lithium,[2] copper,[3] and aluminum[4] reagents by transmetalation reactions. Furthermore, vinylic selenium and tellurium transfer their vinylic substituents stereospecifically, with retention of geometric configuration of the vinyl groups, to diverse organic substrates in metal-assisted cross-coupling reactions.[1d,5]

In recent years, a number of methods have been developed for the synthesis of (*E*)- and (*Z*)-vinyl selenides and tellurides.[1a,b,e] The leading synthetic methods for vinyl tellurides and selenides fall broadly under two categories: (a) use of the chalcogen as an electrophile and (b) use of anionic chalcogen species. In the former category are reactions of vinylic Grignard reagents with chalcogen halides[6] and addition of selenium and tellurium electrophiles to acetylenes.[7] Under the latter category are the Wittig−Horner reactions of selenium and tellurium phosphonates followed by addition of aldehydic species[8] and reactions of vinylic bromides with organotelluride and -selenide anions.[9] Another methodology for synthesis of vinyl tellurides and selenides utilizes transmetalation reactions through vinylic metal intermediates such as vinylic zirconium intermediates.[10]

Table 1. Effect of Copper Salt/Solvent on the Reaction of (*E*)-Styryltrifluoroborate Salt with Diphenyl Diselenide



entry	Cu salt (amt (mol %))	DMSO/H_2O (1:1)	yield (%)[a]
1	CuI (5)	DMSO	90
2	CuCl (5)	DMSO	32
3	$CuCl_2$ (5)	DMSO	66
4	CuCN (5)	DMSO	68
5	CuI (10)	DMSO	92
6	CuI (2.5)	DMSO	76
7	CuI (1)	DMSO	54
8	CuI (5)	DMF	83
9	CuI (5)	THF	65
10	CuI (5)	MeCN	58
11	CuI (5)	1,4-dioxane	15
12	CuI (5)	CH_2Cl_2	
13	CuI (5)	H_2O	15
14	CuI (5)	DMSO/H_2O (1/1)	35
15	CuI (5)	DMSO/H_2O (8/2)	72
16	none	DMSO	

[a] Isolated yields.

Unfortunately, almost all of the above strategies result in the formation of *Z* isomeric vinylic chalcogenides as the sole product

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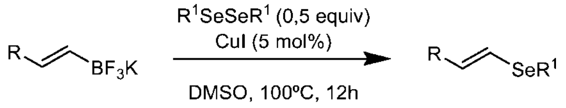
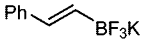
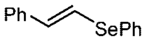
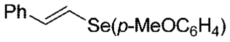
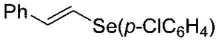
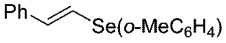
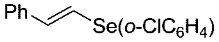
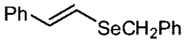
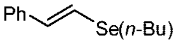
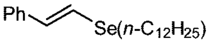
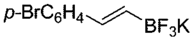
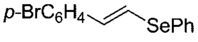
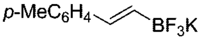
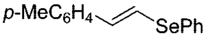
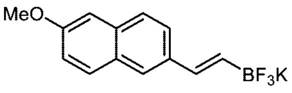
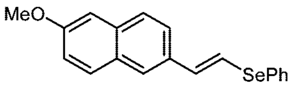
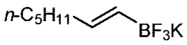
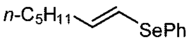
Table 2. CuI-Catalyzed Reactions of (*E*)-Vinyltrifluoroborate Salts with Diorganyl Diselenides



Entry	Vinyltrifluoroborate	$(R^1Se)_2$	Vinylic Selenide	Yield (%)[a]
1	 **1a**	$(PhSe)_2$	 **2a**	**90**
2	**1a**	$(p\text{-}MeOC_6H_4Se)_2$	 **2b**	**98**
3	**1a**	$(p\text{-}Cl\ C_6H_4Se)_2$	 **2c**	**84**
4	**1a**	$(o\text{-}Me\ C_6H_4Se)_2$	 **2d**	**72**
5	**1a**	$(o\text{-}Cl\ C_6H_4Se)_2$	 **2e**	**44**
6	**1a**	$(PhCH_2Se)_2$	 **2f**	**48**
7	**1a**	$(n\text{-}BuSe)_2$	 **2g**	**53**
8	**1a**	$(n\text{-}C_{12}H_{25}Se)_2$	 **2h**	**45**
9	 **1b**	$(PhSe)_2$	 **2i**	**78**
10	 **1c**	$(PhSe)_2$	 **2j**	**80**
11	 **1d**	$(PhSe)_2$	 **2l**	**70**
12	 **1e**	$(PhSe)_2$	 **2m**	**80**

[a] Isolated yields.

or at least the major product. There have been few studies directly aimed at the preparation of (*E*)-vinyl chalcogenides. Among these for (*E*)-vinyl selenides and tellurides are reactions of acetylenic chalcogenides with various reducing agents.[11] (*E*)-Vinyl tellurides have been prepared by the reaction of vinyl bromides with organotellurate anions[6a] and of tellurophosphonate with aldehydes[8e] and by vinyl transfer from (*E*)-vinylzirconates[10a] or vinylalanes to tellurenyl halides.[12]

Recently, the synthesis of (*E*)-vinyl chalcogenides from vinylic boron precursors such as vinylboranes and vinylboronic acids or esters has been reported.[13]

Concurrently, potassium organotrifluoroborate salts have been developed as a superior class of nucleophilic coupling reagents in terms of their stability and functional group tolerance as compared to those of the corresponding boronic acids or

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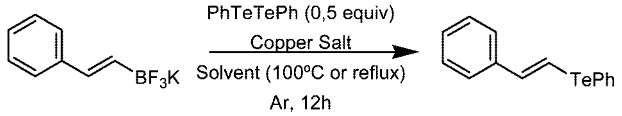
Table 3. Effect of Copper Salt/Solvent on the Reaction of Potassium (*E*)-Styryltrifluoroborate Salt with Diphenyl Ditelluride



entry	Cu salt (amt (mol %))	solvent	yield (%)[a]
1	CuI (10)	DMSO	77
2	CuI (5)	DMSO	76
3	CuI (2.5)	DMSO	77
4	CuI (1)	DMSO	70
5	CuCN (2.5)	DMSO	66
6	CuCl (2.5)	DMSO	78
7	$CuCl_2$ (2.5)	DMSO	59
8	CuCl (2.5)	CH_2Cl_2	12
9	CuCl (2.5)	THF	50
10	CuCl (2.5)	DMF	41

[a] Isolated yields.

boronate esters.[14,15] They have been successfully employed as useful synthetic intermediates in palladium-catalyzed cross-coupling,[16] in rhodium-catalyzed conjugate addition,[17] and in the allylation of aldehydes[18] and *N*-toluenesulfonylimines.[19] Vinyltrifluoroborate salts have the inherent advantages of being commercially available, quite air stable, and easily isolated. They show enhanced reactivity in some cases compared to that of other organoboron compounds.[20]

With these potential advantages in mind, we report here a new, mild, and efficient synthesis of vinyl selenides and tellurides from potassium vinyltrifluoroborates using copper(I) iodide as a catalyst.

Results and Discussion

In an initial experiment the reaction of diphenyl diselenide with potassium (*E*)-*s*tyryltrifluoroborate in the presence of 5 mol % of CuI in DMSO gave (*E*)-phenyl styryl selenide in 90% yield. The reaction required no auxiliary or base, as required in the reported methods. In subsequent work optimized conditions were developed (Table 1).

Only copper(I) iodide provided optimum yields of the product (entry 1, Table 1). In other experiments, the catalyst loading was varied from 2.5 to 10 mol %; 5 mol % of CuI gave the best results. When the amount of CuI was less than 2.5 mol %, only trace amounts of product were formed. No reaction occurred in the absence of copper salt (entry 16, Table 1).

Among the solvents examined, only DMF gave somewhat near the performance of DMSO. No reaction occurred in CH_2Cl_2, even after the reaction mixture had been heated for more than 19 h (entry 12). The reactions in the presence of 5 mol % of CuI in DMSO at 100 °C provided optimum results.

The scope of the reaction was examined using various substituted organotrifluoroborate salts on one hand and changing the organic moiety of the diselenide on the other. The results are shown in Table 2. It is clear that there is no considerable substituent effect in the case of aryl diselenides (entries 1–4, Table 2), except in the case of bis(*o*-chlorophenyl) diselenide (entry 5, Table 2), where the yield of the product was only 44%. However, when dialkyl diselenides were employed, there was a noticeable drop in the yield of the products (entries 6–8, Table 2), possibly due to an electronic effect. On the other hand, there was no significant substituent effect observed in the organorifluoroborate (entries 9–12, Table 2).

The same methodology was extended to diphenyl ditelluride compounds. Here, the yields of the product were not as high upon reaction of **1a** with diaryl ditellurides in the presence of 5 mol % of catalyst. In order to improve the product yields, the amount of catalyst was varied, but no change in product yield was observed for 2.5–10 mol % of the catalyst (entries 1–3, Table 3). CuCl gave slightly better results than CuI, (entry 6, Table 3), and in further experiments CuCl was used. DMSO continued to be the best solvent (Table 3, entries 8–10).

Further studies were carried out with various substituted organotrifluoroborates and diaryl ditellurides. As seen in Table 4, except for diphenyl ditelluride (entry 1, Table 4), the yield of product decreased significantly for both electron-donating and electron-withdrawing substituents alike (entries 2–6, Table 4).

Again as in the case of selenides, bis(*o*-chlorophenyl) ditelluride gave the lowest yield (entry 3, Table 4). Similarly, both electron-donating and electron-withdrawing substituents on the organotrifluoroborate salts adversely affected the yield of the products (entries 7 and 8, Table 4) as did alkyl-substituted organotrifluoroborate (entry 10, Table 4). Naphthyltrifluoroborate provided the highest product yield (entry 9, Table 4).

Experimental Section

General Procedure for the Synthesis of Substituted (*E*)-Vinyl Selenides. Representative Procedure for (*E*)-Phenylvinyl Phenyl Selenide (Table 2, Entry 1). Potassium *trans*-styryltrifluoroborate (105 mg, 0.5 mmol), diphenyl diselenide (78 mg, 0.25 mmol), CuI (4.8 mg, 0.025 mmol), and DMSO (3 mL) were added to a 25 mL flask under an inert atmosphere. The reaction mixture was stirred and heated in an oil bath at 100 °C for 12 h. After the reaction was complete, the resulting mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The crude product was purified by columm chromatography on silica gel with hexanes, which gave a yellowish viscous oil (90%, 117 mg). This procedure was followed for the synthesis of all products listed in Table 2. The known compounds were

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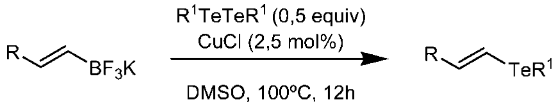
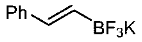
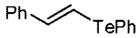
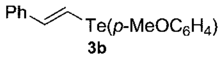
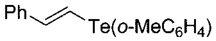
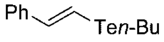
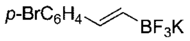
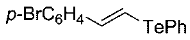
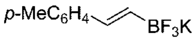
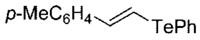
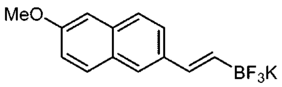
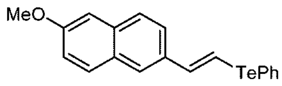
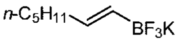
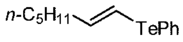
Table 4. CuCl-Catalyzed Reactions of Potassium (*E*)-Vinyltrifluoroborate Salts with Diorganyl Ditellurides



Entry	Vinyl trifluoroborate	(R'Te)$_2$	Vinylic telluride	Yield (%)[a]
1	 **1a**	(PhTe)$_2$	 **3a**	**78**
2	**1a**	(p-MeOC$_6$H$_4$Te)$_2$	 **3b**	**43**
3	**1a**	(p-Cl C$_6$H$_4$Te)$_2$	 **3c**	**49**
4	**1a**	(o-Me C$_6$H$_4$Te)$_2$	 **3d**	**56**
5	**1a**	(o-Cl C$_6$H$_4$Te)$_2$	 **3e**	**23**
6	**1a**	(n-BuTe)$_2$	 **3f**	**53**
7	 **1b**	(PhTe)$_2$	 **3i**	**63**
8	 **1c**	(PhTe)$_2$	 **3j**	**64**
9	 **1d**	(PhTe)$_2$	 **3i**	**81**
10	 **1e**	(PhTe)$_2$	 **3j**	**28**

[a] Isolated yields.

identified by comparison of their spectral data with those reported (Table 2), and the new compounds were properly characterized by their IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data and mass analysis and elemental analysis.

General Procedure for the Synthesis of Substituted (*E*)-Vinyl Tellurides. Representative Procedure for (*E*)-Phenylvinyl Phenyl Telluride (Table 4, Entry 1). In a flask (25 mL) under an argon atmosphere were added potassium *trans*-styryltrifluoroborate (105 mg, 0.5 mmol), diphenyl ditelluride (102 mg, 0.25 mmol), CuCl (1.2 mg, 0.012 mmol), and dry DMSO (3 mL). The reaction mixture was stirred and heated in an oil bath at 100 °C for 12 h. After the reaction was complete, the resulting mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The crude product was purified by columm chromatography on silica gel with hexanes, which gave a yellow viscous oil (78%, 120 mg). This procedure was followed for the synthesis of all products listed in Table 2. The known compounds were identified by comparison of their spectral data with those reported (Table 4), and the new compounds were properly characterized by their IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data and mass analysis and elemental analysis.

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Supporting Information Available: Text and figures giving experimental details and characterization data (^{1}H NMR, ^{13}C NMR, mass analysis, and elemental analysis) for all new compounds listed in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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