A Simple Copper Salt-Catalyzed Synthesis of Unsymmetrical Diaryl Selenides and Tellurides from Arylboronic Acids with Diphenyl Diselenide and Ditelluride

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Received 7 June 2005

Abstract: In the presence of a catalytic amount of simple copper salt, the reaction of arylboronic acids with diphenyl diselenide and ditelluride was accomplished without any additive to afford the corresponding unsymmetrical diarylselenides and tellurides in good yields.

Key words: copper salt, diaryl selenides, diaryl tellurides, arylboronic acids, diphenyl diselenide, diphenyl ditelluride

Organoselenium and tellurium compounds have received much attention not only as synthetic reagents or intermediates in organic synthesis but also as promising donor molecules for conductive materials, anticancer and antioxidant agents.¹ A number of synthetic methods have been reported to prepare organoselenium and tellurium derivatives. A convenient and general method to introduce a selenium or tellurium moiety into organic molecules is the reaction of a metal selenolate or tellurolate with appropriate electrophiles such as organic halides, acyl chlorides, epoxides, and α , β -enones.² However, it is more difficult to synthesize the unsymmetrical diaryl selenides and tellurides through the reaction of selenide and telluride anions with aryl halides because of the less reactivity of halides. The reaction of halobenzenes with phenylselenol or benzeneselenolate anion was generally carried out in the presence of catalyst, ligand and strong base for accomplishing this transformation.³ In addition, the reaction often needs long time and harsh reaction conditions and sometimes generates the products in moderate yields. Therefore, it is desirable to develop more simple and efficient method to synthesize unsymmetrical diaryl selenides and tellurides in the absence of additional ligand and base.

Organoboronic acids are widely used as reagents in organic synthesis because they are commercially available, stable, generally non-toxic, and compatible with a variety of functional groups. Over the past years, the coupling reactions of boronic acids with organic halides,⁴ phenols,⁵ amines,⁶ allyl alcohols,⁷ imidazoles,⁸ alkynes,⁹ alkynes and imines,¹⁰ allenic alcohols,¹¹ aryl arenesulfonates and arylsulfonyl chlorides¹² have been demonstrated. However, to the best of our knowledge, the reaction of boronic acids with diphenyl diselenide and ditelluride has not been disclosed. In this communication, we describe a simple copper salt catalyzed the reaction of arylboronic acids with diphenyl diselenide and ditelluride in the absence of additional ligand and base, which generates the corresponding unsymmetrical diaryl selenides and tellurides in good yields under mild reaction conditions (Scheme 1).

PhZZPh	+	ArB(OH) ₂	Cul (10 mol%)	_	
Z = Se, Te		-	DMSO, air		Pnzar
			Without anv addi	tive!	

Scheme 1

Transition metal-catalyzed cross-coupling reactions represent an extremely versatile tool in organic synthesis.¹³ However, only Taniguchi and his co-worker reported a copper-catalyzed synthesis of unsymmetrical diaryl-selenides from aryl iodides and diphenyl disenide (accompanied with cleavage of the diselenide bond) in the presence of magnesium metal and bipyridine.¹⁴ With the aim of providing an important procedure for the preparation of unsymmetrical diaryl selenides and tellurides, we began to explore the reaction of organoboronic acids with diphenyl diselenide and ditelluride in the presence of copper salt.

In our initial studies, we observed that the reaction of diphenyl diselenide with p-tolylboronic acid in the presence of CuI (10 mol%, in DMSO, at 100 °C) went smoothly to generate phenyl *p*-tolyl selenide in excellent yield (91%) without the addition of any ligand and base. The results are summarized in Table 1. Of the simple copper salts we tested in the reaction, CuCl, CuBr, CuSO₄, Cu(OAc)₂, and CuCl₂ also gave the corresponding products in 64%, 56%, 70%, 67% and 61% yields, respectively (entries 1–5, Table 1). The amount of cuprous iodide was also examined. When the amount of cuprous iodide was less than 1 mol%, only trace product was formed. The satisfactory results were obtained when the amount of cuprous iodide was in the range of 5-15 mol%. It is important to note that the reaction in the absence of copper salt did not result in the formation of product.

SYNLETT 2005, No. 13, pp 2007–2010 Advanced online publication: 12.07.2005 DOI: 10.1055/s-2005-871936; Art ID: U17705ST © Georg Thieme Verlag Stuttgart · New York

To select proper solvent is very important in this reaction. We conducted the reaction of diphenyl diselenide with *p*-tolylboronic acid in the presence of cuprous iodide under different solvents. Among the solvents we investigated, DMSO proved to be the best solvent of choice. None of the desired products was obtained when the reaction was carried out in DMF, THF, acetonitrile, benzene, methylene chloride and toluene.

The effect of reaction temperature and reaction time on the reaction was also surveyed. High yield was obtained when the reaction was carried out in DMSO at 100 $^{\circ}$ C for seven hours. The reaction at room temperature for 48 hours only gave trace amount of the product.

$ B(OH)_2 +$ $ SeSe -$						
Entry	Copper salt (amount)	Yield (%) ^b				
1	CuCl (10 mol%)	64				
2	CuBr (10 mol%)	56				
3	CuSO ₄ (10 mol%)	70				
4	$Cu(OAc)_2$ (10 mol%)	67				
5	$CuCl_2$ (10 mol%)	61				
6	CuI (10 mol%)	91				
7	CuI (20 mol%)	90				
8	CuI (15 mol%)	91				
9	CuI (7.5 mol%)	92				
10	CuI (5 mol%)	89				
11	CuI (2.5 mol%)	45				
12	CuI (1 mol%)	15				
13	None	N.r.				

^a Reaction conditions: *p*-tolylboronic acid (1.00 mmol), diphenyl diselenide (0.50 mmol), Cu salt (its amount indicated in Table 1) in DMSO (3 mL) at 100 °C for 7 h.
^b Isolated yields.

In order to enhance the utility of the reaction, a variety of substrates (diaryl diselenides and diphenyl ditelluride) and organoboronic acids (aryl and vinyl) were evaluated. The results are listed in Table 2. The data indicated that, only in the presence of catalytic amount of cuprous iodide and in DMSO at 100 °C, the reaction of boronic acids with diaryl diselenides and diphenyl ditelluride went smoothly to generate the corresponding products. Substituent effects were also screened. An electron-donating group on the benzene ring of arylboronic acid enhanced the reaction and led to the desired products in excellent yields (entries 1, 3, 4, 8, 11, 12 and 14). Strong electron-withdrawing groups led to slower reaction and moderate yields of prod-

ucts were observed (entries 6 and 13). This reaction was tolerant of ortho-substitution in arylboronic acids (entries 4, 8 and 14). More remarkable was our observation that extremely sterically hindered 2,6-dimethoxyphenylboronic acid reacted cleanly with diphenyl diselenide and ditelluride under this reaction conditions (entries 8 and 14). Fortunately, dialkyl diselenide $(n-C_4H_9SeSeC_4H_9-n)$ also reacted with p-methoxyphenylboronic acid and ptolylboronic acid to generate the corresponding products in 62% and 68% yields, respectively (entries 16 and 17). It should be noted that diaryl tellurides are not stable in the air and they are easily to be oxidized by oxygen (diphenylditelluride and diarylselenides are more stable). The reaction of arylboronic acids with diphenyl ditelluride should be performed under inert atmosphere (generally under nitrogen or argon).

Table 2	CuI-Catalyzed the Reaction of Boronic Acids with
Diphenyl	Diselenide and Ditelluride ^a

Entry	ArB(OH) ₂	RZZR	Yield (%) ^b
1	p-CH ₃ C ₆ H ₄ B(OH) ₂	$(C_6H_5Se)_2$	91
2	C ₆ H ₅ B(OH) ₂	$(C_6H_5Se)_2$	88
3	<i>p</i> -CH ₃ OC ₆ H ₄ B(OH) ₂	$(C_6H_5Se)_2$	84
4	o-CH ₃ C ₆ H ₄ B(OH) ₂	$(C_6H_5Se)_2$	95
5	p-ClC ₆ H ₄ B(OH) ₂	$(C_6H_5Se)_2$	82
6	p-CH ₃ COC ₆ H ₄ B(OH) ₂	$(C_6H_5Se)_2$	63
7	α -C ₁₀ H ₇ B(OH) ₂	$(C_6H_5Se)_2$	80
8	2,6-(CH ₃ O) ₂ C ₆ H ₃ B(OH) ₂	$(C_6H_5Se)_2$	89
9	(E)-C ₆ H ₅ CH=CHB(OH) ₂	$(C_6H_5Se)_2$	60
10	(E)-Cl(CH ₂) ₃ CH=CHB(OH) ₂	$(C_6H_5Se)_2$	87
11	p-CH ₃ C ₆ H ₄ B(OH) ₂	$(C_6H_5Te)_2$	71 ^c
12	p-CH ₃ OC ₆ H ₄ B(OH) ₂	$(C_6H_5Te)_2$	80 ^c
13	p-CH ₃ COC ₆ H ₄ B(OH) ₂	$(C_6H_5Te)_2$	61°
14	2,6-(CH ₃ O) ₂ C ₆ H ₃ B(OH) ₂	$(C_6H_5Te)_2$	81°
15	p-ClC ₆ H ₄ B(OH) ₂	$(C_6H_5Te)_2$	68 ^c
16	p-CH ₃ OC ₆ H ₄ B(OH) ₂	$(n-C_4H_9Se)_2$	62
17	p-CH ₃ C ₆ H ₄ B(OH) ₂	$(n-C_4H_9Se)_2$	68

 $^{\rm a}$ Reaction conditions: organoboronic acid (1.00 mmol), diaryl diselenide or ditelluride (0.50 mmol), CuI (0.10 mmol) in DMSO (3 mL) at 100 $^{\circ}{\rm C}$ for 7 h.

^b Isolated yields.

^c In the presence of N₂.

As an alternative to organoboronic acids and esters, organotrifluoroborate salts have emerged as a new class of airstable boron derivatives, facile to prepare in high yields and purities, easy to handle, and feasible to utilize in a number of useful synthetic processes.¹⁷ When the reaction of potassium aryltrifluoroborates with diphenyl diselenide and ditelluride was performed under the present reaction conditions, as expected, good yields of the desired products were isolated (Scheme 2).

Ionic liquids, especially ambient-temperature ionic liquids consisting of 1,3-dialkylimidazolium cations, have shown great promise as alternating green solvents (reaction medium) for organic transformations in recent years, because of their non-volatile, chemically and thermally stable, non-flammatory nature.¹⁵ However, there is only one report on the stereospecific synthesis of vinyl selenides through the reaction of vinylboronic acids and vinylboronic esters with phenylselenyl chloride in BmimBF₄.¹⁶ When 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) was used as solvent instead of DMSO for the reaction of *p*-methoxyphenylboronic acid with diphenyl diselenide in the presence of CuI (10 mol%), only 16% yield of phenyl p-tolyl selenide was isolated. In an effort to improve the yield of the reaction, we next tried $Cu(OAc)_2$ and $CuSO_4$ as copper sources (better solubility than CuI in $BmimBF_4$). We were pleased to discover that when 15% mol of Cu(OAc)₂ and CuSO₄ were used as catalyst for the reaction in BmimBF₄, the desired products were obtained in 92% and 83% yields, respectively (Scheme 2). The recyclability of the BmimBF₄ and cupric acetate was also examined. After carrying out a reaction, isolating the product from the reaction mixture, washing with solvents, and drying, BmimBF₄ and cupric acetate were used for the next trial directly and the reaction repeated. Only minor decreases in product yields were observed through five repetitive cycles.



Scheme 2

In conclusion, we have developed a novel and high efficient method for synthesizing unsymmetrical diaryl selenides and tellurides in good to excellent yields through the reaction of arylboronic acids, vinylboronic acids and potassium aryltrifluoroborates with diaryl diselenides and diphenyl ditelluride in the presence of a catalytic amount of simple copper salt in DMSO, as well as in ionic liquid (BmimBF₄), without any additive. Furthermore, ionic liquid and copper salt can be recycled without significant loss of the yields. The further work and the investigation on the mechanism are being in progress in our laboratory.

General Procedure for the Synthesis of Unsymmetrical Diaryl Selenides and Tellurides in DMSO

Organoboronic acid or potassium aryltrifluoroborate (1.00 mmol), diphenyl diselenide or ditelluride (0.50 mmol), cuprous iodide (0.10 mmol) were added in a round-bottomed flask contained DMSO (3 mL). The resulting mixture was stirred at 100 °C for 7 h. After completion of the reaction, the mixture was vacuum filtered using a sintered glass funnel and purified by flash chromatography to give the desired products.

Acknowledgment

We gratefully acknowledge financial support by the National Natural Science Foundation of China (No. 20372024), the Excellent Scientist Foundation of Anhui Province, China (No. 04046080), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, China (No. 2002247), the Excellent Young Teachers Program of MOE, China (No. 2024), and the Key Project of Science and Technology of State Education Ministry, China (No. 0204069).

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