Copper Catalyzed Cross-Coupling Reactions of Diaryl Ditellurides with Potassium Aryltrifluoroborate Salts

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Apresentamos aqui resultados das reações de acoplamento de diteluretos de diarila com sais de ariltrifluoroborato de potássio, usando quantidades catalíticas de Cu(OAc)2 e bipyridina, em uma mistura de DMSO/H2O, sob ar atmosférico. Estas reações de acoplamento são gerais e são realizadas com diteluretos de diarila e sais de ariltrifluoroborato de potássio contendo substituintes neutros, retiradores e doadores de elétrons, fornecendo os correspondentes teluretos de diarila não simétricos em rendimentos de bons a excelentes.

We present here results of the cross-coupling reaction of diaryl ditellurides with potassium aryltrifluoroborate salts using a catalytic amount of Cu(OAc)2 and bipyridine in DMSO/H2O under air atmosphere. This cross-coupling reaction is general and was performed with diaryl ditellurides and potassium aryltrifluoroborate salts bearing electron-withdrawing, electron-donating and neutral substituents, affording the corresponding unsymmetrical diaryl tellurides in good to excellent yields.

Keywords: tellurium, trifluoroborate salts, copper catalysis

Introduction

Chalcogenide compounds have become attractive synthetic targets because of their chemo-, regio-, and stereoselective reactions,1-4 used in a wide variety of functional groups, thus avoiding protection group chemistry and resulting in useful biological activities.5-7 Therefore, many classes of organotellurium compounds have been prepared and studied to date and aryl- or vinylic tellurides are certainly the most useful and promising compounds in view of their usefulness in organic synthesis.5-11 A large number of methodologies have been reported to prepare these compounds.4,9-11 However, limited synthetic methods are reported to synthesize unsymmetrical diaryl tellurides. In recent years, a transition-metal-catalyzed reaction of diaryl dichalcogenides with aryl halides or boronic acids has become a versatile tool for synthesis of unsymmetrical diaryl chalcogenides.12-17 Recently, Taniguchi18 described the preparation of numerous unsymmetrical organotellurides by reaction of organoboronic acids with ditellurides via cleavage of Te-Te bond by a copper catalyst.

In the context of organoboron reagents, significant advances have been made in the use of these compounds as coupling partners in a number of transition-metal mediated reactions.18,19 The organoboron compounds most frequently employed are boronic acids and boronate esters, but these compounds have some drawbacks: among them, we can mention the low stability, very high price of some reagents and high sensitivity to air and moisture. To solve these problems, the use of potassium organotrifluoroborates, as the organoboron coupling partner, has some advantages in comparison to boronic acids and boronic esters, such as being more nucleophilic, stable on air, crystalline as solids and easily prepared.20-22

The use of potassium aryltrifluoroborate salts in the synthesis of unsymmetrical diaryl chalcogenides was reported by Wang and co-workers.15 However, only one example of unsymmetrical diaryl telluride was obtained in moderated yield, under conditions optimized to arylboronic acids. Our continuing interest in the synthesis and reactivity

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of potassium organotrifluoroborate salts prompted us to explore in detail a general procedure to access various unsymmetrical diaryl tellurides by a copper catalyzed cross-coupling reaction of diaryl ditellurides with potassium aryltrifluoroborate salts (Scheme 1).

We observed that the influence of the solvent was important for the coupling success. The reaction mixture of diaryl ditelluride 1a and trifluoroborate 2a using Cu(OAc)₂/bpy (5 mol%) was refluxed with different solvents and the results are summarized in Table 2. Optimal results were achieved using a mixture of DMSO/H₂O (2:1) as solvent (Table 2, entry 1). When using DMSO, toluene and a mixture of toluene/H₂O (Table 2, entries 2-4) moderate yields were obtained, while other solvents such as 1,4-dioxane, DMF and CH₃CN (Table 2, entries 5-7) gave poor yields of the desired product 3a.

When the reaction was carried out with other ligands such as 1,10-phenanthroline, TMEDA and 1,3-diaminopropane or without ligand, a decrease in the yield of product 3a was observed (Table 2, entries 8-11).

Careful analysis of the optimized reactions revealed that the optimum conditions for this coupling reaction were found to be the use of Cu(OAc)₂/bpy (1 mol%) as the catalytic system, diaryl ditelluride 1a (0.25 mmol), potassium aryltrifluoroborate salt 2a (0.5 mmol), and a

Results and Discussion

Our initial studies have focused on the development of an optimum set of reaction conditions. In this way, di-(p-tolyl) ditelluride 1a and potassium p-methoxyphenyltrifluoroborate 2a were used as standard substrates. Thus, a mixture of diaryl ditelluride 1a (0.25 mmol) and trifluoroborate 2a (0.5 mmol), utilizing DMSO/H₂O (2:1) as a solvent, was refluxed with different copper catalysts, using bipyridine (bpy) as ligand, in air (Table 1). As shown in Table 1, different catalysts of copper(I) and copper(II) were tested, displaying a moderated to good catalytic activity, and the best result was obtained using Cu(OAc)₂/bpy (5 mol%), giving the desired product 3a in excellent yield (Table 1, entry 6). When the reaction was performed in absence of catalyst and ligand, only traces of the desired product 3a were obtained (Table 1, entry 10).

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The use of catalyst in an amount of 10 mol% yielded 98% of 3a (Table 2, entry 12). Fortunately, when the amount of catalyst was reduced from 5 to 1 mol%, excellent yields of product 3a were obtained (Table 2, entries 13 and 14).

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mixture of DMSO/H₂O (2:1, v/v) as a solvent. The reaction mixture was refluxed for 12 h under air atmosphere, affording the desired diaryl telluride 3a with 90% yield.³⁰

In order to demonstrate the efficiency of this protocol, we explored the generality of our method reacting others potassium aryltrifluoroborate salts 2a-m with diaryl ditelluride 1a and these results are summarized in Table 3. Table 3 shows that the reaction worked well for a range of potassium aryltrifluoroborate salts. These results revealed that the reaction is sensitive to the electronic effect of the aromatic ring in the potassium aryltrifluoroborate salt. For example, trifluoroborate salts 2a-e, bearing electron-donating and electron-neutral groups at the aromatic ring, gave better yields than the trifluoroborates bearing electron-withdrawing groups (Table 3, entries 1-5 versus 6-10). When we used potassium heteroaryltrifluoroborate salts 2k-m, the desired products were obtained in good yields (Table 3, entries 11-13).

In an attempt to broaden the scope of our methodology, the possibility of performing the reaction with other diaryl ditellurides was also investigated (Table 4). Potassium trifluoroborate 2a was cross-coupled efficiently with a variety of ditellurides 1b-h. A decrease in the reaction yield was observed using hindered or heteroaryl ditellurides 1f-h (Table 4, entries 5-7).

We believe that the mechanism of this cross-coupling reaction is in accordance with the proposed by Tanigushi,¹² using organoboronic acids analogues. It seems that the reaction requires DMSO/H₂O and oxygen of air to oxidize the copper intermediates and promote the reaction.

The compounds obtained by this protocol appear highly promising as intermediates in the preparation of more complexes molecules. In the last decade, Uemura¹¹ described the use of symmetrical diaryl tellurides utilizing Heck palladium catalyzed cross-coupling and the two symmetrical aryl groups of telluride were transferred to various alkenes. For instance, the resulting unsymmetrical diaryl tellurides should be particularly useful intermediates in this type of reaction. In this way, compound 3a was coupled with ethyl acrylate, using the conditions described by Uemura¹¹ (Scheme 2).

In this reaction, unsymmetrical diaryl telluride 3a transfers the two different aryl groups to ethyl acrylate, giving two products of cross-coupling 4a and 4b in excellent yields.³²

Conclusions

We have explored in details the cross-coupling reaction of diaryl ditellurides with potassium aryltrifluoroborate salts using a catalytic amount of Cu(OAc)₂/bpy in a mixture of DMSO/H₂O (2:1, v/v) as a solvent. The reaction mixture was refluxed for 12 h under air atmosphere, affording the desired diaryl telluride 3a with 90% yield. To demonstrate the efficiency of this protocol, we explored the generality of our method reacting others potassium aryltrifluoroborate salts 2a-m with diaryl ditelluride 1a and these results are summarized in Table 3. Table 3 shows that the reaction worked well for a range of potassium aryltrifluoroborate salts. These results revealed that the reaction is sensitive to the electronic effect of the aromatic ring in the potassium aryltrifluoroborate salt. For example, trifluoroborate salts 2a-e, bearing electron-donating and electron-neutral groups at the aromatic ring, gave better yields than the trifluoroborates bearing electron-withdrawing groups (Table 3, entries 1-5 versus 6-10). When we used potassium heteroaryltrifluoroborate salts 2k-m, the desired products were obtained in good yields (Table 3, entries 11-13).

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Table 3. Coupling products using diaryl ditelluride 1a and potassium aryl trifluoroborate salts 2a-m

<table>
<thead>
<tr>
<th>Entry</th>
<th>ArBF₃K</th>
<th>Product Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeO-BF₃K</td>
<td>MeO-Te-CH₃ (90%)</td>
</tr>
<tr>
<td>2</td>
<td>H₂C-BF₃K</td>
<td>H₂C-Te-CH₃ (94%)</td>
</tr>
<tr>
<td>3</td>
<td>BF₃K</td>
<td>BF₃K-CH₃ (89%)</td>
</tr>
<tr>
<td>4</td>
<td>MeO-BF₃K</td>
<td>MeO-Te-CH₃ (88%)</td>
</tr>
<tr>
<td>5</td>
<td>BF₃K</td>
<td>BF₃K-CH₃ (91%)</td>
</tr>
<tr>
<td>6</td>
<td>Cl-BF₃K</td>
<td>Cl-Te-CH₃ (84%)</td>
</tr>
<tr>
<td>7</td>
<td>F-BF₃K</td>
<td>F-Te-CH₃ (68%)</td>
</tr>
<tr>
<td>8</td>
<td>F₂C-BF₃K</td>
<td>F₂C-Te-CH₃ (66%)</td>
</tr>
<tr>
<td>9</td>
<td>F₂C-BF₃K</td>
<td>F₂C-Te-CH₃ (68%)</td>
</tr>
<tr>
<td>10</td>
<td>O-BF₃K</td>
<td>O-Te-CH₃ (72%)</td>
</tr>
<tr>
<td>11</td>
<td>S-BF₃K</td>
<td>S-Te-CH₃ (81%)</td>
</tr>
<tr>
<td>12</td>
<td>S-BF₃K</td>
<td>S-Te-CH₃ (83%)</td>
</tr>
<tr>
<td>13</td>
<td>N-BF₃K</td>
<td>N-Te-CH₃ (78%)</td>
</tr>
</tbody>
</table>

*a Yields are given for isolated products.*
of DMSO/H₂O under air atmosphere and established a new route to obtain unsymmetrical diaryl tellurides in good to excellent yields. Subsequent Heck cross-coupling reactions of compound 3a with alkenes proceed smoothly in excellent yields and transfer the two different aryl groups from diaryl tellurides. Studies of the Heck reactions are under investigation and will be reported in due course.

**Supplementary Information**

Supplementary information, with extra experimental and characterization data, is available free of charge at http://jbcs.sbq.org.br, as PDF file.

**Acknowledgments**

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**References**


**Table 4. Coupling products using diaryl ditellurides 1b-h and potassium aryltrifluoroborate salt 2a**

<table>
<thead>
<tr>
<th>Entry</th>
<th>ArTe-TeAr</th>
<th>Product Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeO-Te-TeMe</td>
<td>MeO-Te-TeMe-OMe (89%)</td>
</tr>
<tr>
<td>2</td>
<td>CH₃-Te-TeCH₃</td>
<td>CH₃-Te-Te-OMe (91%)</td>
</tr>
<tr>
<td>3</td>
<td>CH₃-Te-TeCH₃</td>
<td>CH₃-Te-Te-OMe (91%)</td>
</tr>
<tr>
<td>4</td>
<td>Cl-Te-TeCl</td>
<td>Cl-Te-Te-OMe (91%)</td>
</tr>
<tr>
<td>5</td>
<td>H₂C-Te-TeH₂C</td>
<td>H₂C-Te-Te-OMe (79%)</td>
</tr>
<tr>
<td>6</td>
<td>H₂C-Te-TeH₂C</td>
<td>H₂C-Te-Te-OMe (87%)</td>
</tr>
<tr>
<td>7</td>
<td>S-Te-TeS</td>
<td>S-Te-Te-OMe (79%)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yields are given for isolated products.

**Scheme 2.** Application of compound 3a in a Heck cross-coupling reaction.
Copper Catalyzed Cross-Coupling Reactions of Diaryl Ditellurides  


30. General procedure for the cross-coupling reaction of diaryl ditellurides with potassium aryltrifluoroborates: To a round-bottomed flask containing diaryl ditelluride (0.25 mmol), potassium aryltrifluoroborate salt (0.5 mmol), Cu(OAc)$_2$ (1 mol%) and bpy (1 mol%), DMSO (1 mL) and H$_2$O (0.5 mL) were added. The reaction mixture was allowed to stir at reflux for 12 h. After this time, the solution was cooled to room temperature, diluted with dichloromethane (20 mL) and washed with saturated aqueous NH$_4$Cl (3 × 20 mL). The organic phase was separated, dried over MgSO$_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. Selected spectral and analytical data for $p$-Methoxyphenyl-$p$-tolyltelluride (3a): Yield: 0.146 g (90%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.69 (d, $J$ 8.5 Hz, 2H), 7.53 (d, $J$ 7.8 Hz, 2H), 7.02 (d, $J$ 7.8 Hz, 2H), 6.79 (d, $J$ 8.5 Hz, 2H), 3.80 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 159.64, 140.36, 137.25, 137.02, 130.10, 115.26, 111.21, 103.48, 54.96, 20.96. MS (relative intensity) m/z: 328 (28), 198 (100), 183 (74), 155 (25), 91 (23), 65 (17). HRMS calc. for C$_{14}$H$_{14}$OTe: 328.0107. Found: 328.0111.
32. General procedure for the Heck cross-coupling reaction of unsymmetrical diaryl telluride (3a) with ethyl acrylate: Into a two-necked 25 mL round-bottomed flask containing PdCl$_2$ (0.05 mmol), AgOAc (2.00 mmol) and unsymmetrical diaryl telluride 3a (0.50 mmol), dry methanol (10 mL), Et$_3$N (2.00 mmol) and ethyl acrylate (1.00 mmol) were added. After stirring for 8 h at 25 °C, the heterogeneous reaction mixture was filtered. The filtrate was poured into brine (60 mL) and extracted with ethyl acetate (3 × 20 mL). The organic phase was separated, dried over MgSO$_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. Selected spectral and analytical data for $p$-Methoxyphenyl-$p$-tolyltelluride (3a): Yield: 0.146 g (90%).

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