Copper-Catalyzed Synthesis of Unsymmetrical Diorganyl Chalcogenides (Te/Se/S) from Boronic Acids under Solvent-Free Conditions ‡

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‡ Dedication: A.L.B., S.S. and J.R. dedicate this paper with gratitude to Joao Valdir Comasseto for his notable contributions in organochalcogen chemistry over the past 40 years.

Received: 4 July 2017; Accepted: 16 August 2017; Published: 18 August 2017

Abstract: The efficient and mild copper-catalyzed synthesis of unsymmetrical diorganyl chalcogenides under ligand- and solvent-free conditions is described. The cross-coupling reaction was performed using aryl boric acids and 0.5 equiv. of diorganyl dichalcogenides (Te/Se/S) in the presence of 3 mol % of CuI and 3 equiv. of DMSO, under microwave irradiation. This new protocol allowed the preparation of several unsymmetrical diorganyl chalcogenides in good to excellent yields.

Keywords: selenide; telluride; boronic acid; solvent-free; cross-coupling; CuI; selenium; tellurium

1. Introduction

Transition metal-catalyzed coupling reactions are among the most commonly applied protocols for the preparation of various target molecules under mild conditions [1,2]. In this regard, the construction of new carbon-carbon and carbon-heteroatom bonds have been described, notably through catalytic processes employing a metal as the catalyst [3–7].

In addition, catalytic transformations have been widely applied in organochalcogen chemistry for the preparation of diorganyl-tellurides, -selenides and -sulfides, which are interesting target molecules and valuable synthetic intermediates for several transformations in modern organic synthesis [8–10]. Besides the synthetic applications, these types of molecules have shown relevant biological properties, such as antitumor, antioxidant, antiviral, antimicrobial and neuroprotective effects [11–19]. Organochalcogen compounds also have noteworthy applications in materials science [20–22].

Due to their considerable importance, the development of new and greener methods for the preparation of organochalcogenides (S, Se and Te) has been widely investigated by several research groups, and a number of methodologies have been reported [23–30]. The most common procedures described for the preparation of alkyl/aryl chalcogenides involve: (a) the reaction between alkyl/aryl...
dichalcogenide precursors and organometallic reagents \([31–34]\); (b) the transition metal-catalyzed reaction of halides with chalcogenols or diorganyldichalcogenides in the presence of a base or reducing agents \([35–37]\); and (c) synthesis through the C–H activation of arenes \([38–41]\).

On the other hand, organoboron acids have been used as suitable reagents for various cross-coupling reactions since they are stable, readily available and compatible with different functional groups. They can also be employed in the boron-to-metal exchange reaction using a catalytic amount of metal \([42–44]\). Thus, organoboron acids have become interesting and appropriate alternative compounds for the preparation of symmetrical and unsymmetrical diaryl organochalcogenides via cross-coupling transformations.

In this regard, Wang and Tanigushi, independently reported the preparation of diorganyldichalcogenides from organoboronic acids and diorganyldichalcogenides using copper as a catalyst, in the presence of a ligand and solvent \([45,46]\). Since their reports, modern studies have been described to improve this kind of transformation. In particular, metals have been efficiently applied as catalysts for the cross-coupling of diorganyldichalcogenides with boronic acids, for instance, employing indium \([47]\), iron \([48]\), copper \([49–55]\) and silver \([56]\).

However, most of these procedures have their particular drawbacks, such as the use of ligands, reducing agents, air sensitivity, long reaction time, and/or the use of toxic solvents. In addition, some of these methods are not applicable for the synthesis of unsymmetrical organotellurides, which are also very important from the synthetic point of view.

Alternatively, we have recently reported suitable methods for the synthesis of unsymmetrical chalcogenides, using the iodine/DMSO system under microwave irradiation to generate, in situ, electrophilic species of chalcogenyl iodide (RYI) \([57]\). Similarly, Park and coworkers reported an ultrasound-assisted synthesis of diarylditellurides \([58]\). Nonetheless, the development of new methodologies employing boronic acids and dichalcogenides as starting materials, associated with metal catalysis instead of use RYI species, is still highly desirable. Furthermore, the use of diorganyldichalcogenides avoids the use of toxic RXH compounds (X = Te, Se, S).

Thus, in connection with our continuing interest in designing and developing eco-friendly processes and cross-coupling reactions, \([59–64]\), herein we describe a straightforward method for the synthesis of unsymmetrical diorganyldichalcogenides (S, Se and Te) through the reaction of boronic acids and half equiv. of diorganyldichalcogenides, employing CuI as a catalyst, under solvent- and ligand-free conditions (Scheme 1).

\[
\begin{array}{c}
\text{Cul (cat.)} \\
\text{DMSO (equiv.)} \\
\text{MW (100 W), 100 °C (15 min)} \\
\text{R–Y–Ar} \\
\end{array}
\]

\[
\begin{align*}
1/2 \text{RYYR} & + \text{ArB(OH)}_2 \\
Y & = \text{Te, Se, S}
\end{align*}
\]

Scheme 1. Solvent- and ligand-free synthesis of unsymmetrical diorganyldichalcogenides catalyzed by CuI.

2. Results and Discussion

In order to optimize the reaction conditions, diphenyl ditelluride (1a) and 4-methoxyphenylboronic acid (2a) were used as model substrates (Table 1). Firstly, we evaluated the catalyst loading in the reaction system (entries 1–4). When the reaction was carried out with 1.0 mol % of catalyst the desired product was obtained with only 43% yield (entry 1). However, on increasing the catalyst to 2.0 mol %, the yield of the reaction increased to 71% (entry 2). Notably, when the amount of CuI was increased to 3.0 mol % the corresponding product 3a was achieved with 90% yield (entry 3). No change in the yield was observed when the catalyst loading was increased to 4.0 mol % (entry 4).

Next, we investigated the influence of the copper source on the reaction system (entries 5–10). In general, copper halides showed better catalytic activity. For instance, when we employed CuCl₂ and CuO under the same reaction conditions, the desired organotelluride was synthesized in yields of
72 and 61%, respectively (entries 7 vs. 9). Furthermore, CuO nanoparticles were less effective than copper iodide, affording the desired product in lower yield (entry 10). Considering our previous work [57], when 3% molecular iodine was used as catalyst, 3a was obtained in 69% yield (entry 11). The reaction in the absence of catalyst provided 3a in only trace amounts, which emphasizes the notable activity of Cul in this kind of transformation (entry 12).

Table 1. Optimization of reaction conditions a.

| Entry | Catalyst | Amount | Yield (%) b,c |
|-------|----------|--------|--------------|
| 1     | Cul      | 1.0 mol % | 43           |
| 2     | Cul      | 2.0 mol % | 71           |
| 3     | Cul      | 3.0 mol % | 90           |
| 4     | CulBr    | 4.0 mol % | 90           |
| 5     | CulBr    | 3.0 mol % | 56           |
| 6     | CuCl     | 3.0 mol % | 67           |
| 7     | CuCl2    | 3.0 mol % | 72           |
| 8     | Cu(OAc)2 | 3.0 mol % | 46           |
| 9     | CuO      | 3.0 mol % | 61           |
| 10    | nano-CuO | 3.0 mol % | 65           |
| 11    | I2       | 3.0 mol % | 69           |
| 12    | -        | -      | Traces       |

a Reaction conditions: 1a (0.25 mmol), 2a (2.0 equiv.), DMSO (3.0 equiv.) under MW irradiation; b Isolated yield; c This reaction works similarly in 0.125 mmol scale with less reproducibility.

With the best catalyst in hand, we investigated the influence of other reaction parameters (temperature, time and power) as well as the effect of the additive/oxidant (Table 2).

Table 2. Optimization of reaction conditions a.

| Entry | Additive (equiv.) | MW (W) | T (°C) | Time (min) | Yield (%) b |
|-------|------------------|--------|--------|------------|-------------|
| 1     | DMSO (3.0)       | 100    | 100    | 15         | 90          |
| 2     | CH3CN (3.0)      | 100    | 100    | 15         | 35          |
| 3     | EtOH (3.0)       | 100    | 100    | 15         | 25          |
| 4     | Dioxane (3.0)    | 100    | 100    | 15         | 40          |
| 5     | H2O (3.0)        | 100    | 100    | 15         | -           |
| 6     | TBHP (3.0)       | 100    | 100    | 15         | -           |
| 7     | -                | 100    | 100    | 15         | 10          |
| 8     | DMSO (3.0)       | 100    | 100    | 15         | 29          |
| 9     | DMSO (2.0)       | 100    | 100    | 15         | 78          |
| 10    | DMSO (4.0)       | 100    | 100    | 15         | 90          |
| 11    | DMSO (3.0)       | 100    | 100    | 10         | 73          |
| 12    | DMSO (3.0)       | 100    | 100    | 20         | 88          |
| 13    | DMSO (3.0)       | 100    | 80     | 15         | 68          |
| 14    | DMSO (3.0)       | 100    | 120    | 15         | 77          |
| 15    | DMSO (3.0)       | 120    | 100    | 15         | 86          |
| 16    | DMSO (3.0)       | 80     | 100    | 15         | 70          |
| 17    | DMSO (3.0)       | -      | 100    | 24 h       | 57          |

a Reaction conditions: 1a (0.25 mmol), 2a (2.0 equiv.), Cul (3.0 mol %), DMSO (3.0 equiv.) under MW irradiation; b Isolated yield; c This reaction works similarly in 0.125 mmol scale with less reproducibility.

In this regard, we initially evaluated the influence of a series of additives (CH3CN, 1,4-dioxane, EtOH, H2O and TBHP). Of these, DMSO was established as the best option, providing the desired product in very high yield in comparison with other additives (entry 1 vs. 2–6). Furthermore, a considerable decrease in the yield was observed when the reaction was carried out either in the
also, 2-naphthylboronic acid reacted very well with diphenyl ditelluride (electron donor or acceptor) and its steric hindrance did not appear to affect the performance of the transformation, and the corresponding products were obtained in very good yields. Also, 2-naphthylboronic acid reacted very well with diphenyl ditelluride (1a) under the optimized conditions, affording the corresponding product 3f in very good yield.

The electronic characteristics of the substituent of boronic acid attached to the aromatic ring (electron donor or acceptor) and its steric hindrance did not appear to affect the performance of the transformation, and the corresponding products 3a–e were obtained in very good yields. Finally, the effect of the radiation power of the microwave was investigated and increasing the power to 120 W did not change the reaction yield significantly (entry 15). However, when the level of power was decreased to 80 W the desired product 3a was delivered in lower yield (entry 16). In addition, we carried out the reaction under conventional heating and, even after a long reaction time, a decrease in the yield of the product 3a was observed (entry 17). This result indicates that microwave irradiation offers advantages over conventional heating, for this transformation.

Having determined the best reaction conditions, we explored the scope of our protocol by employing various diorganyl ditellurides 1 and arylboronic acids 2 (Scheme 2). Firstly, we evaluated the effect of different groups attached to the aryl ring of boronic acid (Scheme 2).

The electronic characteristics of the substituent of boronic acid attached to the aromatic ring (electron donor or acceptor) and its steric hindrance did not appear to affect the performance of the transformation, and the corresponding products 3a–e were obtained in very good yields. Also, 2-naphthylboronic acid reacted very well with diphenyl ditelluride (1a) under the optimized conditions, affording the corresponding product 3f in very good yield.

We further evaluated the generality of the reaction regarding the ditellurides 1, employing electron-withdrawing or electron-donating groups. In general, the reaction proceeded very well in
both cases, furnishing the corresponding unsymmetrical tellurides 3g–j in 83–87% yields. For instance, the reaction of para-chlorobenzene ditelluride with meta-substituted aryl boronic acid delivered the respective compound 3j in 83% yield. Moreover, an aliphatic ditelluride, in this case dibutyl ditelluride, was also a suitable substrate for this cross-coupling process, furnishing the product 3k in 87% yield.

The successful preparation of unsymmetrical diorganyl tellurides 3 by a copper-catalyzed transformation prompted us to expand this approach to the synthesis of unsymmetrical diorganyl selenides (Scheme 3). To evaluate the electronic effects, we first verified the influence of the substituent attached at the para position of the aromatic ring of the boronic acid. The treatment of diphenyl diselenide with different para-substituted aryl boronic acids provided the respective products 6a and 6b in 87% and 85% yields, respectively.

Similarly, the reaction was not sensitive to steric effects, since the treatment of diphenyl diselenide with aryl boronic acid containing a methyl group at the ortho position of the aromatic ring provided the respective product 6c in 89% yield. Subsequently, a series of different diselenides, including aliphatic and aromatics diselenides, were converted into the corresponding products in very good yields. For example, when we reacted p-chlorobenzene diselenide with 4-methoxyphenylboronic acid the product 6e was obtained in 89% yield.

We also evaluated the applicability of our protocol to the preparation of unsymmetrical sulfides, under the same reaction conditions. Remarkably, diphenyl disulfide and m-chlorophenyl disulfide reacted smoothly with p-methoxyphenylboronic acid, leading to the respective products 7a and 7b in 71% and 68% yields, respectively. This slight decrease in the yield values could be associated with the lower reactivity of diaryl disulfides when compared to ditellurides or diselenides analogues, which are much more easily cleaved than disulfides [65].

![Scheme 3](image)

**Scheme 3.** Synthesis of unsymmetrical organoselenides and sulfides \(^{a,b}\). \(^{a}\) Reaction conditions: 4 or 5 (0.25 mmol), 2 (0.5 mmol) in the presence of Cul (3.0 mol %) and DMSO (3.0 equiv.) for 15 min at 100 °C and 100 W of MW-irradiations; \(^{b}\) Isolated yields.

In addition, in order to investigate the synthetic utility of this methodology, we evaluated whether the reaction could be performed with boronic acid at the gram scale under the optimized conditions (Scheme 4). To our delight, the corresponding product 3a was obtained in 85% yield, which is very significant from a synthesis point of view, since this methodology can thus be used to prepare unsymmetrical diorganyl chalcogenides on a larger scale.
In order to gain further insight into the reaction mechanism, control experiments were performed (Scheme 5). Firstly, to evaluate the possibility of a radical path, we performed the standard reaction in the presence of 3.0 equiv. of 2,2,6,6-tetramethyl-1-piperidinylxoy (TEMPO) as a radical inhibitor (Scheme 5a). The presence of TEMPO did not affect the reaction yield, which suggests that radical intermediates are not involved in this protocol. Next, we verified the influence of oxidant species on this transformation. When the reaction was carried out under argon atmosphere, an abrupt decrease was noted and the telluride 3a was delivered in only 29% yield (Scheme 5b). In contrast, when diphenyl ditelluride was treated with phenyl boronic under O2 atmosphere, the corresponding product was obtained in 93% yield (Scheme 5c). These results suggest that oxygen is mainly responsible for the oxidation steps and DMSO is most likely an important additive in terms of improving the reaction yield.

On the basis of these results and in accordance with previous reports [66,67], a plausible reaction pathway is illustrated in Scheme 6. In this pathway the catalyst cycle begins with the generation of species A through the reaction between CuI and boronic acid [66]. Subsequently, this specie reacts with diorganyl dichalcogenide to afford the desired product and the intermediate B. The specie B is then oxidized to give the Cu(II) intermediate C [66,67]. In the next step, another equiv. of boronic acid would reacts with this intermediate to furnish the intermediate D. Lastly, a second equiv. of the desired product is obtained through an elimination reaction step and, consequently, the catalyst is regenerated.
3. Materials and Methods

3.1. General Information

$^1$H- and $^{13}$C-NMR spectra were obtained at 200/50 MHz on an AC-200 NMR spectrometer (Bruker, Rheinstetten, Germany) or at 400/100 MHz on an AS-400 NMR spectrometer (Varian, Palo Alto, CA, USA). Spectra were recorded in CDCl$_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl$_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: Chemical shift ($\delta$), multiplicity, coupling constant ($J$) in hertz and integrated intensity. Abbreviations to denote the multiplicity of a particular signal are: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet). The NMR spectra are found in the Supplementary Materials. The melting points were determined using a model MQRPF-301 digital apparatus (Microquimica, Palhoça, Brazil) equipped with a heating plate. Column chromatography was performed using silica gel (230–400 mesh). Thin layer chromatography (TLC) was performed using silica gel GF$_{254}$ plates with 0.25 mm thickness (Merck, Darmstadt, Germany). For visualization, TLC plates were either placed under ultraviolet light or stained with iodine vapor and acidic vanillin. Most reactions were monitored by TLC for the disappearance of the starting material.

Unless otherwise stated, all reactions were carried out in an open atmosphere. All reagents and solvents were obtained from commercial sources and used without further purification. All reactions were performed in 10 mL sealed glass tubes in a commercially available monomode microwave reactor (CEM, Matthews, NC, USA) with IR monitoring and a non-invasive pressure transducer. Reagents and solvents were handled using standard syringe techniques. The yields are based on isolated compounds after purification.

3.2. General Procedure for the Synthesis of Unsymmetrical Organochalcogenides under MW Irradiation

A mixture of aryl boronic acid (0.5 mmol), dichalcogenide (0.25 mmol), CuI (3 mol %, 1.5 mg), and DMSO (3 equiv., 59 mg) was placed in a glass tube. The tube was sealed with a pressure lock and the mixture was heated in air at 100 °C for 15 min with the aid of an initial MW irradiation of 100 W in a CEM Discover MW reactor. When the reaction was finished, the crude mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and washed with water (3 × 5 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 hexane or a mixture of ethyl hexane/acetate (99:1) as the eluent.

Analytical Data of Products 3a–k, 6a–h and 7a,b

(4-Methoxyphenyl)(phenyl)tellane (3a). Yield: 0.140 g (90%); white solid; m.p.: 59–61 °C (lit.: [48] 60–62 °C); $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta = 7.73$ (d, $J = 8.8$ Hz, 2H, H-Ar), 7.62–7.42 (m, 2H, H-Ar), 7.30–7.07 (m, 3H, H-Ar), 6.80 (d, $J = 8.8$ Hz, 2H, H-Ar), 3.80 (s, 3H, -OCH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta = 160.1$, 141.3, 136.5, 129.4, 127.4, 116.0, 115.6, 103.3, 55.3.
(4-Chlorophenyl)(phenyl)tellane (3b). Yield: 0.133 g (84%); yellow oil; [68] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.63–7.57 (m, 2H, H-Ar), 7.52–7.46 (m, 2H, H-Ar), 7.21–7.05 (m, 5H, H-Ar); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 139.3, 138.2, 134.4, 129.8, 129.7, 128.2, 114.5, 112.5.

3-(Phenyltellanyl)aniline (3c). Yield: 0.128 g (86%); yellow oil; [57] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.57 (d, J = 8.4 Hz, 2H, H-Ar), 7.56–6.99 (m, 6H, H-Ar), 6.60–6.55 (m, 1H, H-Ar), 3.62 (s, 2H, -NH₂); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 147.3, 138.0, 130.3, 129.6, 128.2, 127.8, 124.4, 115.4, 114.9, 114.8.

(3-Nitrophenyl)(phenyl)tellane (3d). Yield: 0.137 g (84%); yellow oil; [55] 1H-NMR (400 MHz, CDCl₃, ppm) δ = 8.42 (s, 1H, H-Ar), 8.06 (d, J = 8.2 Hz, 1H, H-Ar), 7.86–7.80 (m, 3H, H-Ar), 7.41–7.25 (m, 4H, H-Ar); 13C-NMR (101 MHz, CDCl₃, ppm) δ = 148.5, 142.4, 139.6, 131.1, 130.1, 130.0, 129.1, 122.5, 117.0, 113.2.

(2-Methoxyphenyl)(phenyl)tellane (3e). Yield: 0.140 g (90%); white solid; m.p.: 53–55 °C (lit.: [48] 53–54 °C); 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.89 (dd, J = 8.1, 1.4 Hz, 2H, H-Ar), 7.44–7.25 (m, 3H, H-Ar), 7.17 (ddd, J = 8.2, 7.3, 1.6 Hz, 1H, H-Ar), 6.94 (dd, J = 7.6, 1.6 Hz, 1H, H-Ar), 6.80–6.69 (m, 2H, H-Ar), 3.86 (s, 3H, -OCH₃); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 158.2, 141.3, 133.7, 129.7, 128.7, 128.2, 122.5, 112.2, 109.8, 107.8, 56.0.

Naphthalen-2-yl(phenyl)tellane (3f). Yield: 0.146 g (88%); yellow oil; [55] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 8.19–8.14 (m, 1H, H-Ar), 7.97 (ddd, J = 7.1, 1.1 Hz, 1H, H-Ar), 7.82–7.74 (m, 2H, H-Ar), 7.62–7.57 (m, 2H, H-Ar), 7.51–7.44 (m, 2H, H-Ar), 7.28–7.08 (m, 4H, H-Ar); 13C-NMR (101 MHz, CDCl₃, ppm) δ = 138.9, 137.5, 135.9, 133.8, 131.8, 129.6, 128.9, 127.1, 126.6, 126.4, 117.9, 114.9.

1-(4-((4-Methoxyphenyl)tellanyl)phenyl)ethan-1-one (3g). Yield: 0.152 g (86%); yellow oil; [57] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.78 (d, J = 8.8 Hz, 2H, H-Ar), 7.68 (d, J = 8.5 Hz, 2H, H-Ar), 7.48 (d, J = 8.5 Hz, 2H, H-Ar), 6.83 (d, J = 8.8 Hz, 2H, H-Ar), 3.82 (s, 3H, -OCH₃), 2.52 (s, 3H, -COCH₃); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 179.5, 160.4, 122.2, 121.5, 128.6, 125.5, 115.8, 102.1, 55.2, 26.4.

(3-Nitrophenyl)(p-tolyl)tellane (3h). Yield: 0.142 g (83%); yellow oil; [57] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 8.41–8.29 (m, 1H, H-Ar), 8.06–8.01 (m, 1H, H-Ar), 7.82–7.72 (m, 3H, H-Ar), 7.30 (td, J = 8.3, 2.2 Hz, 1H, H-Ar), 7.12 (d, J = 7.1 Hz, 2H, H-Ar), 2.38 (s, 3H, -CH₃); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 148.5, 141.8, 140.1, 139.5, 131.0, 130.4, 129.8, 122.2, 117.6, 109.1, 21.4.

1-(4-((4-Chlorophenyl)tellanyl)phenyl)ethanone (3i). Yield: 0.156 g (87%); yellow solid; m.p.: 67–68 °C (lit.: [57] 67–70 °C); 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.76–7.72 (m, 4H, H-Ar), 7.61 (d, J = 7.9 Hz, 2H, H-Ar), 7.24 (d, J = 8.4 Hz, 2H, H-Ar), 2.56 (s, 3H, -COCH₃); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 197.6, 140.9, 139.5, 136.3, 136.3, 136.2, 135.5, 130.3, 129.0, 123.5, 111.1, 26.6.

3-(4-Chlorophenyl)tellanyl)aniline (3j). Yield: 0.137 g (83%); brown solid; m.p.: 60–61 °C (lit.: [57] 58–60 °C); 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.58 (d, J = 8.2 Hz, 2H, H-Ar), 7.18–6.95 (m, 5H, H-Ar), 6.59 (dt, J = 7.5, 1.9 Hz, 1H, H-Ar), 3.62 (s, 2H, -NH₂); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 147.4, 139.2, 134.2, 130.4, 129.7, 128.2, 124.4, 115.0, 112.6.

1-(4-(Butyltellanyl)phenyl)ethan-1-one (3k). Yield: 0.127 g (87%); yellow oil; [69] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.67 (d, J = 8.8 Hz, 2H, H-Ar), 6.76 (d, J = 8.8 Hz, 2H, H-Ar), 3.79 (s, 3H, -OCH₃), 2.86–2.78 (m, 2H, -CH₂), 1.73 (p, J = 7.9, 7.4 Hz, 2H, -CH₂), 1.46–1.287 (m, 2H, -CH₂), 0.92–0.851 (m, 3H, -CH₃); 13C-NMR (101 MHz, CDCl₃, ppm) δ = 159.7, 141.0, 115.2, 100.7, 55.2, 34.0, 25.1, 13.5, 8.9.

(4-Methoxyphenyl)(phenyl)isolate (6a). Yield: 0.114 g (87%); yellow oil; [54] 1H-NMR (200 MHz, CDCl₃, ppm) δ = 7.51 (d, J = 8.9 Hz, 2H, H-Ar), 7.35–7.18 (m, 5H, H-Ar), 6.86 (d, J = 8.8 Hz, 2H, H-Ar), 3.81 (s, 3H, -OCH₃); 13C-NMR (50 MHz, CDCl₃, ppm) δ = 159.7, 136.5, 133.1, 130.9, 129.1, 126.4, 119.9, 115.1, 55.3.
(4-Chlorophenyl)(phenyl)seleno (6b). Yield: 0.114 g (85%); transparent oil; [68] $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.47–7.44 (m, 2H, H-Ar), 7.35 (d, $J$ = 8.3 Hz, 2H, H-Ar), 7.27–7.18 (m, 5H, H-Ar); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 134.2, 133.6, 133.3, 130.8, 129.7, 129.6, 127.7.

Phenyl(o-tolyl)seleno (6c). Yield: 0.110 g (89%); transparent oil; [70] $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.42–7.56 (m, 2H, H-Ar), 7.34–7.14 (m, 6H, H-Ar), 7.09–7.01 (m, 1H, H-Ar), 2.40 (s, 3H, -CH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 139.9, 133.8, 132.8, 131.8, 130.9, 130.3, 129.4, 127.8, 127.2, 126.8, 22.4.

Naphthalen-2-yl(phenyl)seleno (6d). Yield: 0.125 g (88%); yellow solid; m.p.: 68–70 °C (lit.: [57] 69–71 °C); $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 8.35–8.30 (m, 1H, H-Ar), 7.84–7.74 (m, 3H, H-Ar), 7.51–7.15 (m, 8H, H-Ar); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 134.2, 133.9, 131.8, 129.4, 129.3, 128.7, 127.8, 127.1, 126.9, 126.5, 126.1.

Butyl(4-methoxyphenyl)seleno (4-chlorophenyl)(o-tolyl)seleno

(4-Chlorophenyl)(4-methoxyphenyl)seleno (6e). Yield: 0.132 g (89%); yellow solid; m.p.: 56–57 °C (lit.: [48] 58–59 °C); $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.41 (d, $J$ = 8.8 Hz, 2H, H-Ar), 7.18–7.06 (m, 4H, H-Ar), 6.77 (d, $J$ = 8.8 Hz, 2H, H-Ar), 3.72 (s, 3H, -OCH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 160.0, 136.6, 132.5, 132.1, 131.6, 129.2, 119.5, 115.2, 55.3.

(4-Chlorophenyl)(o-tolyl)seleno (6f). Yield: 0.117 g (83%); transparent oil; [57] $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.36–7.03 (m, 8H, H-Ar), 2.37 (s, 3H, -CH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 140.2, 134.1, 133.8, 133.4, 131.3, 130.5, 129.4, 128.3, 127.0, 22.5.

(4-Chlorophenyl)(o-tolyl)seleno (6g). Yield: 0.130 g (89%); transparent oil; [57] $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.55 (d, $J$ = 8.8 Hz, 2H, H-Ar), 7.16–7.05 (m, 1H, H-Ar), 6.88 (d, $J$ = 8.8 Hz, 2H, H-Ar), 6.82–6.72 (m, 3H, H-Ar), 3.88 (s, 3H, -OCH$_3$), 3.81 (s, 3H, -OCH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 160.3, 156.0, 138.5, 129.1, 127.0, 123.6, 121.7, 117.4, 115.4, 110.2, 55.9, 55.4.

Butyl(4-methoxyphenyl)seleno (4-chlorophenyl)(o-tolyl)seleno (6h). Yield: 0.094 g (77%); yellow oil; [48] $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.46 (d, $J$ = 8.9 Hz, 2H), 6.81 (d, $J$ = 8.8 Hz, 2H), 3.79 (s, 3H, -OCH$_3$), 2.82 (t, $J$ = 7.6 Hz, 2H, -CH$_2$-), 1.71–1.57 (m, 2H, -CH$_2$-), 1.49–1.34 (m, 2H, -CH$_2$-), 0.89 (t, $J$ = 7.2 Hz, 3H, -CH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 159.2, 135.6, 120.4, 114.8, 55.4, 32.5, 29.0, 23.0, 13.7.

(4-Methoxyphenyl)(phenyl)sulfane (7a). Yield: 0.077 g (71%); transparent oil; [68] $^1$H-NMR (200 MHz, CDCl$_3$, ppm) $\delta$ = 7.42 (d, $J$ = 8.9 Hz, 2H, H-Ar), 7.28–7.15 (m, 5H, H-Ar), 6.90 (d, $J$ = 8.9 Hz, 2H, H-Ar), 3.82 (s, 3H, -OCH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 160.0, 138.7, 135.5, 129.0, 128.3, 125.9, 124.5, 115.1, 55.5.

(3-Chlorophenyl)(4-methoxyphenyl)sulfane (7b). Yield: 0.085 g (68%); white solid; m.p.: 59–61 °C (lit.: [57] 59–61 °C); $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ = 7.42 (d, $J$ = 8.9 Hz, 2H, H-Ar), 7.13–7.03 (m, 3H, H-Ar), 6.98 (dt, $J$ = 7.7, 1.3 Hz, 1H, H-Ar), 6.91 (d, $J$ = 8.9 Hz, 2H, H-Ar), 3.81 (s, 3H, -OCH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$, ppm) $\delta$ = 160.4, 141.4, 136.2, 134.9, 129.9, 127.2, 125.7, 125.6, 122.8, 115.4, 55.5.

4. Conclusions

In summary, we have developed a straightforward method for the preparation of unsymmetrical diorganyl chalcogenides (S, Se and Te), under solvent- and ligand-free conditions. Remarkably, copper iodide was found to be a highly efficient catalyst for this cross-coupling reaction, affording the desired products in very high yields in the absence of solvent under microwave irradiation. Of particular importance, this new metal-catalyzed process showed good potential applicability within a very broad scope, without the need for the use of ligands or solvents. It appears that the chemistry described herein characterizes a useful alternative approach to the synthesis of organochalcogen compounds through a copper-catalyzed processes.

Supplementary Materials: Copies of the $^1$H- and $^{13}$C-NMR spectra are available online.
Acknowledgments: We gratefully acknowledge the CNPq, CAPES, INCT-Catálise, FAPESP-CERSusChem (grant 2014/50249-8), GSK-CERSusChem (grant 2014/50249-8), HEC (SRGP-161), FAPESC-Pronex, and FAPERGS-Pronex, for financial support. CAPES is also acknowledged for the fellowship for J.R. under CAPES-PNPD scheme. The funding bodies had no role in the study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Author Contributions: A.L.B., S.S., J.R., G.V.B. conceived and designed the experiments; S.S., J.R., G.V.B. and T.E.A.F. performed the experiments; S.S., J.R., G.V.B., M.G., T.E.A.F. and F.Z.G. performed the spectral analysis, characterizations and contributed reagents/materials; A.L.B., S.S. and J.R. wrote the paper. All authors have approved the final version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: Samples of the compounds 3a–k, 6a–h and 7a–b are available from the authors.

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