

Palladium-catalyzed cross-coupling of vinylic tellurides and potassium vinyltrifluoroborate salt: synthesis of 1,3-dienes

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Abstract—Here we report an ultrasound-assisted synthesis of stereodefined 1,3-dienes by Suzuki–Miyaura cross-coupling reactions of vinylic tellurides and potassium β -styryl trifluoroborate salt.
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A main goal of transition metal-catalyzed organic synthesis is carbon–carbon bond formation, being the Suzuki–Miyaura reaction one of the most efficient methods for construction of C–C bonds.¹ In this regard, the use of organoboron compounds offers some advantages when compared with other organometallic reagents like Grignard reagent, organozinc and organotin compounds. For example, they are easily prepared and in several cases are commercially available. Moreover, the cross-coupling reaction conditions² are mild and the inorganic byproducts are environmentally safe, being easily removed by simple workup procedure.

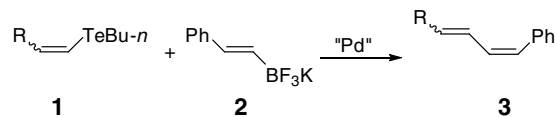
In the last years, the use of potassium organotrifluoroborate salts in Suzuki–Miyaura reactions have largely been investigated.³ These reagents are readily prepared by addition of inexpensive KHF_2 salt to organoboron intermediates⁴ to afford crystalline solids indefinitely stable in the air, providing solutions to the problems inherent to other organoboron partners (instability, cyclic trimerization).

Organotellurium compounds have successfully and widely been used in many metal-catalyzed cross-coupling reactions.^{5,6} We have previously demonstrated the use of some organotellurium compounds in Suzuki–

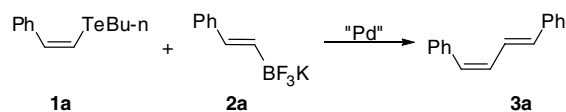
Miyaura reactions using the organotrifluoroborates as nucleophilic partners.⁷ Tellurium compounds containing halide moieties in their structures exhibited high chemoselectivity, since reactions occurred exclusively at the telluride moiety.^{7b,c}

In one of these cases^{7c} we used ultrasound waves as an energy source. This alternative energy source is very effective in many organic reactions.^{8,9} The ultrasound effects are attributed to a physical process called cavitation.^{8a}

The stereoselective synthesis of dienes has been represented as one of the long-standing challenges in organic synthesis. The Wittig and Julia reactions are classical processes to obtain *E*- or *Z*-alkenes.¹⁰ Recently, olefin



Scheme 1. Suzuki–Miyaura reaction.



Scheme 2. Standard reaction.

Keywords: Suzuki–Miyaura; Tellurium compounds and ultrasound.

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Table 1. Study of catalyst effect on cross-coupling reaction using vinylic telluride **1a** and β -styryl trifluoroborate **2a** (Scheme 2)

Entry	Catalyst ^a	Yield ^b (%)
1	PdCl ₂	58
2	Pd(Acac) ₂	30
3	Pd ₂ (dba) ₃	51
4	PdCl ₂ (BzCN) ₂	59
5	Pd(AcO) ₂	52
6	PdCl ₂ (dppf)·CH ₂ Cl ₂	51
7	Pd(PPh ₃) ₄	65

^a 10 mol % of catalyst was used.^b Isolated yields.

metathesis¹¹ and transition metal-catalyzed cross-coupling reactions^{1a,12} have been efficiently used to generate stereodefined alkenes. Herein we wish to report an ultrasound-assisted synthesis of stereodefined dienes by Suzuki–Miyaura reactions of vinylic tellurides

Table 2. Study of additive and base effect on cross-coupling reaction using vinylic telluride **1a** and β -styryl trifluoroborate **2a** (Scheme 2)

Entry	Base	Additive	Pd(PPh ₃) ₄ (mol %)	Yield ^a (%)
1	K ₂ CO ₃	Ag ₂ O	Pd(PPh ₃) ₄ (10)	65
2	Cs ₂ CO ₃	Ag ₂ O	Pd(PPh ₃) ₄ (10)	67
3	Et ₃ N	Ag ₂ O	Pd(PPh ₃) ₄ (10)	66
4	—	Ag ₂ O	Pd(PPh ₃) ₄ (10)	43
5	Cs ₂ CO ₃	—	Pd(PPh ₃) ₄ (10)	nr ^a
6	Cs ₂ CO ₃	CuI	Pd(PPh ₃) ₄ (10)	15 ^a
7	Cs ₂ CO ₃	AgOAc	Pd(PPh ₃) ₄ (10)	75
8	Cs ₂ CO ₃	AgOAc	Pd(PPh ₃) ₄ (5)	73
9	Cs ₂ CO ₃	AgOAc	Pd(PPh ₃) ₄ (15)	74
10	Cs ₂ CO ₃	AgOAc	Pd(PPh ₃) ₄ (20)	81
11	Et ₃ N	AgOAc	Pd(PPh ₃) ₄ (20)	84
12	Et ₃ N	AgOAc	Pd(PPh ₃) ₄ (20)	75 ^b

^a Isolated yields.^b Conventional condition.

(**1**) and potassium organotrifluoroborate salt (**2**), Scheme 1.

Table 3. Reaction of vinylic tellurides with β -styryl trifluoroborate **2a**

Entry	Telluride (1)	Product (3)	Yield ^a (%)
1			84
2			85
3			67
4			82
5			48
6			57
7			79
8			70
9			82

Initially, attention was focused on determination of the optimal conditions for the Suzuki–Miyaura reaction of vinylic tellurides (**1**) and alkenyltrifluoroborates (**2**). Toward this end, *Z*-vinylic telluride **1a** and β -styryl trifluoroborate **2a** (Scheme 2) were chosen as model substrates and a variety of conditions were screened (Tables 1 and 2). The reactions were monitored by TLC or GC.

First of all, we determined the palladium catalyst, the Pd(II) and (0) species were used in the coupling reactions and the best result was reached with Pd(PPh₃)₄ (Table 1, entry 7). It was used Ag₂O, K₂CO₃, and methanol were used as solvents and the reaction was irradiated for 20 min in ultrasound bath. The product was obtained in 65% isolated yield.

The next step was the determination of the best base and the necessity or not of an additive in the reaction (Table 2). We tested inorganic bases in the presence of Ag₂O (Table 2, entries 1 and 2). Cesium carbonate afforded the best result with 67% isolated yield. An organic base (triethylamine) was also used, but a lower yield was obtained (Table 2, entry 3). When no base was used a great decrease on the yield was observed (Table 2, entry 4).

In agreement with previous results,⁷ no reaction occurred when no additive was used (Table 2, entry 5). When CuI and AgOAc were tested, the product **3a** was obtained in 15% and 75% isolated yields, respectively (Table 2, entries 6 and 7).

The catalyst loadings were analyzed (Table 2, entries 8–10) and the best result was obtained with 20 mol % of Pd(PPh₃)₄ (Table 2, entry 10). When this condition was employed using triethylamine a better result was obtained, 84% isolated yield (Table 2, entry 11). Under conventional conditions (5 h of reflux and magnetic stirring) a lower yield was observed, 75% (Table 2, entry 12).

Thus, the optimized condition¹³ was the use of vinylic telluride **1a**, 1.1 equiv of β -styryl trifluoroborate **2a**, 10 mol % of Pd(PPh₃)₄, 2 equiv of AgOAc, 2 equiv of triethylamine in methanol as solvent and ultrasound irradiation for 20 min. Once the best conditions were established, the protocols were extended to other vinylic tellurides (**1**). In all the cases studied, the dienes (**3**) were obtained from moderate to good yields by using the optimized conditions described above for the preparation of **3a** (Table 3, entry 1).

The *E,E*-1,4-diphenyl-1,3-butadiene **3b** was obtained from the cross-coupling between the *E*-vinylic telluride **1b** and **2a** in 85% yield. As previously reported by us,^{7b,c} when vinylic tellurides (**1**) containing halides attached to an aromatic ring or attached at the double bond (Table 3, entries 4 and 9) were used as substrates in the cross-coupling reaction, they demonstrated high chemoselectivity, where only the telluride moiety reacted and no reaction was observed in the halide moiety and the respective products were obtained in good yields.

The reaction demonstrated to be effective with a wide variety of vinylic tellurides. The silyl group attached in a hydroxyl resisted to the reaction condition and the product was obtained in 79% yield (Table 3, entry 7). A vinylic telluride holding the *t*-butyl group attached at double bond reacted with **2a** in a good yield (Table 3, entry 8).

In summary, a wide variety of 1,3-dienes was obtained taking advantages the use of ultrasonic energy and Suzuki–Miyaura reaction. The reaction demonstrated to be chemoselective and stereodefined. The products were obtained in moderate to good yields in a mild and quick method.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.05.088.

References and notes

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 - General experimental procedure:** A suspension of *Z*-vinyllic telluride (**1a**) (0.144 g, 0.5 mmol), potassium β -styryl trifluoroborate (**2a**) (0.116 g, 0.55 mmol), Pd(PPh₃)₄ (0.115 g, 0.1 mmol), triethylamine (0.101 g, 1 mmol) and silver(I) acetate (0.167 g, 1 mmol) in 3 mL of methanol was irradiated in a water bath of an ultrasonic cleaner for 20 min. Then, the reaction was diluted with ethyl acetate (30 mL). The organic layer was washed with saturated solution of NH₄Cl (2 × 10 mL) and water (2 × 10 mL), dried over MgSO₄ and concentrated under vacuum. Purification by silica gel chromatography (eluting with hexane) yielded (*Z,E*)-1,4-diphenylbuta-1,3-diene (**3a**) in 84%.