Pergamon

Tetrahedron Letters 39 (1998) 5045–5048

TETRAHEDRON
LETTERS

# Potassium Vinyltrifluoroborate : A Stable and Efficient Vinylating Agent of Arenediazonium Salts using Palladium Catalysts

**Sylvain Darses, Guillaume Michaud, Jean-Pierre Genêt***

Laboratoire de Synthèse Sélective Organique, Ecole Nationale Supérieure de Chimie de Paris et CNRS,
11 rue P&M Curie, 75231 Paris cedex 05, France

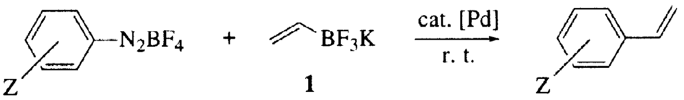
Received 3 April 1998; accepted 13 May 1998

***Abstract*** *: The air stable potassium vinyltrifluoroborate 1 was efficiently prepared in one step from vinylmagnesium chloride and used in palladium cross-coupling reactions with arenediazonium salts affording functionalized styrenes.* © 1998 Published by Elsevier Science Ltd. All rights reserved.

Carbon-Carbon bonds formation using palladium mediated cross-coupling reactions has became one of the most useful procedures[1]. One reaction, in particular, the palladium cross-coupling of organoboron derivatives has been extensively used in organic synthesis[2].

We[3], then others[4], have recently shown that arenediazonium tetrafluoroborates[5] were effective substrates in palladium-catalyzed cross-coupling reactions with aryl- and alkenylboronic acids. Further improvements in the preparation of biaryls were obtained using the very stable potassium aryltrifluoroborates[5] ($ArBF_3K$), more easily obtained[6,7] and purified than the corresponding boronic acids. A vinyl boronate protected as its pinacol ester has been recently used with aryl halides providing a mixture of the styryl boronates and styrenes depending upon the reaction conditions[8].

Here, we report a simple preparation of potassium vinyltrifluoroborate **1**. This reagent is a very efficient agent for the preparation of functionalized styrenes introducing the vinyl moiety on an aromatic ring from arenediazonium tetrafluoroborates (Scheme 1) *via* palladium catalyzed reaction.



1

**Scheme 1**

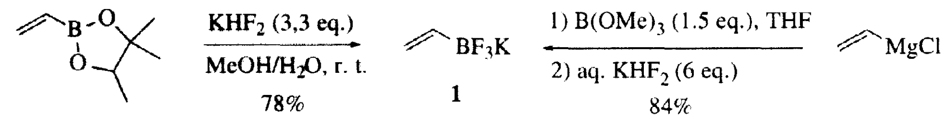
First of all, the desired potassium vinyltrifluoroborate was prepared in 78% yield by treatment of commercially available 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane, with aqueous potassium hydrogenodifluoride ($KHF_2$).

A more direct and efficient procedure for the preparation[9] of **1** involves treatment of trimethylborate with vinylmagnesium chloride, followed by the *in situ* addition of aqueous $KHF_2$.

The titled compound was obtained in 84% yield (Scheme 2). The reaction has been carried out on a 0.2 mol scale. This material is none air and water sensitive and is thermally stable.

*e-mail : genet@ext.jussieu.fr; fax : (33) 01 44 07 10 62

*PII:* S0040-4039(98)01003-X

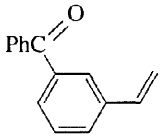
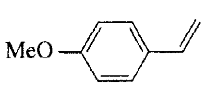
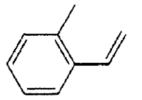
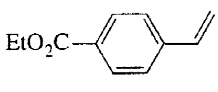
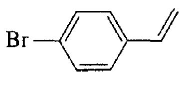
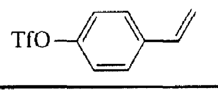


**Scheme 2**

The reagent **1** proved to be a highly efficient vinylating agent for the preparation of styrenes derivatives. The palladium-catalysed cross-coupling reaction of arenediazonium tetrafluoroborates with potassium vinyltrifluoroborate was carried out, at room temperature (Table). We noted that the efficiency of the cross-coupling depends on the correct choice of catalyst and solvent.

The data given in table (entry 1) that 5% of Pd(OAc)$_2$ in dioxane is an effective catalyst. The reaction took place in 5 minutes and 86% yield. In the presence of the palladacycle[10] Pd$_2$($\mu$-OAc)$_2$(P(*o*-tolyl)$_3$)$_2$ (5%) in methanol. The reaction was completed in less than one minute, affording cross-coupling product in 81% yield. Since the reaction rate was very high we decreased the amount of catalyst. The reaction was achieved in 10 minutes using 1% of the palladacycle in 86% yield. Under these conditions (0.1 to 1% of catalyst) we synthetized various functionalized styrenes[11] A slight excess (1.2 eq.) of the boron reagent was necessary to obtain better yields of styrenes. As described in the table, good yields of styrenes could be obtained even with low catalytic rates such as 0.1%.

Pd-catalyzed vinylation of diazonium salts with **1**

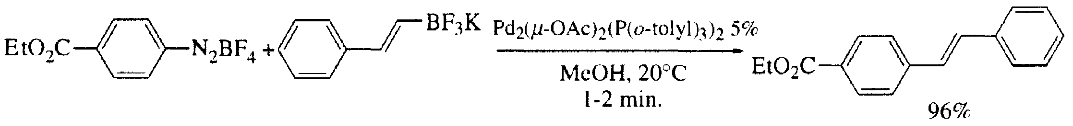
| Entry | % catalyst | Time (min) | Styrene | Yield (%) |
|---|---|---|---|---|
| 1 | $5^a$ | 5 |  | $86^c$ |
| | $5^b$ | instantaneous | | $81^c$ |
| | $1^b$ | 10 | | $86^c$ |
| 2 | $1^b$ | 20 |  | ($97^d$) $81^c$ |
| 3 | $0.5^b$ | 20 |  | $78^c$ |
| 4 | $0.1^b$ | 120 |  | ($98^d$) $88^c$ |
| 5 | $0.1^b$ | 30 |  | ($95^d$) $70^c$ |
| 6 | $0.5^b$ | 60 |  | $75^c$ |

(a) In 1.4 dioxane using Pd(OAc)$_2$. (b) In methanol/ Pd$_2$($\mu$-OAc)$_2$(P(*o*-tolyl)$_3$)$_2$.
(c) Isolated Yields. (d) Conversion Yields (G.C.).

Whatever, the nature of the substituents on the arenediazonium salt, electronwithdrawing groups (ester, ketone) or electrondonating groups (methoxy, methyl), the reaction proceeded smoothly with potassium vinyltrifluoroborate. Arenediazonium tetrafluoroborate bearing an *ortho* substituent gave also good yield of styrene (entry 3).

Next, we examined the reactivity of diazonium towards halides and triflate using arenediazonium tetrafluoroborates bearing a bromide or a triflate substituent. The reaction was chemoselective (entries 5, 6). The diazonium functionnal group proved to be far more reactive giving bromo- and (trifluoromethylsulfonyloxy)styrene in yield ranging from 70 to 75%.

This reaction is not limited to the simple potassium vinyltrifluoroborate **1**. Thus, in the described conditions, cross-coupling of 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate with potassium styryltrifluoroborate, afforded the stilbene derivative in almost quantitative yield. The reaction is instantaneous at room temperatures and a simple filtration gives the pure product.



**Scheme 3**

We have thus shown that potassium vinyltrifluoroborate proved to be an efficient vinylating agent[12] of arenediazonium salts. This reagent is one of the most stable form of vinyl derivatives and can be stored at room temperature without decomposition. Moreover, boron is non toxic and from an industrial view point, the use of diazonium salts, which derive from aromatic amines, is a better route than from conventional halides and pseudohalides. Diazonium is so reactive that very fast reactions have been conducted at room temperature. Chemoselective cross-coupling reactions have been achieved since the bromide and triflate substituents don't participate in the present coupling. Extension of this reaction in synthesis and to other potassium alkenyltrifluoroborates is in progress and will be reported in due course.

## References and Notes

1. For recent books see : (a) Tsuji, J. *Palladium Reagents and Catalysts*, Wiley & sons, **1995** ; (b) Malleron, J.L.; Fiaud, J.C.; Legros, J.Y. *Handbook of Palladium-Catalyzed Organic Reactions*, Academic Press, London, **1997**. For recent reviews see : (a) Heck, R.F. in *Comprehensive Organic Synthesis,* Oxford, Pergamon Press, **1991**; (b) De Meijere, A.; Meyer, F.E. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379-2411 ; (c) Negishi, E.; Coperet, C.; Ma S.; Liou, S.Y.; Liu, F. *Chem. Rev.* **1996**, 365-393 ; (d) Bräse, S.; De Meijere, A. *Metal-Catalyzed Cross-Coupling Reactions*, Eds. Stang, P.J.; Diederich, F. Wiley-VCH, Weiheim, **1997**.
2. Review : Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483.
3. (a) Darses, S.; Jeffery, T.; Brayer, J.L.; Demoute, J.P.; Genêt, J.P. *Tetrahedron Lett.* **1996**, *37*, 3857-3860. (b) Darses, S.; Jeffery, T.; Brayer, J.L.; Demoute, J.P.; Genêt, J.P. *Bull. Soc. Chim. Fr.* **1996**, *133*, 1095-1102.
4. Sengupta, S.; Bhattacharyya, S. *J. Org. Chem.* **1997**, *62*, 3405-3406.
5. Darses, S.; Brayer, J.L.; Demoute, J.P.; Genêt, J.P. *Tetrahedron Lett.* **1997**, *38*, 4393-4396.
6. Darses, S. PHD Thesis University P. M. Curie, December **1997**.
7. Vedejs, E.; Chapman, R.W.; Fields, S. C.; Lin, S.; Schrimpf, M.R. *J. Org. Chem.* **1995**, *60*, 3020-3027.

8. Hunt, A.R.; Stewart, S.K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599-3602.

9. ***Potassium vinyltrifluoroborate 1*** : To a solution of trimethylborate (freshly distilled over sodium, 34 ml, 1.5 eq.) in anhydrous THF (200 ml) was added dropwise a 15% solution of vinylmagnesium chloride in THF (119 ml, 0.2 mol) at -60°C. The mixture was stirred under argon for 30 min at -60°C, placed at room temperature and stirred another 30 min. Potassium hydrogen difluoride (94 g, 6 eq.) was added at once at 0°C followed by slow addition of water (200 ml) which resulted in an intense white precipitate. The suspension was stirred 30 mn at room temperature and the solvents were removed under (bath temperature : 50°C). The resulting powder was thoroughly dried under vacuum (< 1 mmHg) overnight, extracted several times with acetone (3X150 ml) and the solvent removed under vacuum. The product was purified by dissolving in the minimum amount of boiling acetone and reprecipitation by addition of diethyl ether. 22.53 g of potassium vinyltrifluoroborate were obtained as a white powder (84% yield). This material has been prepared for the first time (Stafford, S.L. *Can. J. Chem.* **1963**, *41*, 807-808) in a two step sequence from tetravinylstannane in 29% yield.

10. Herrmann, W.A.; Brossmer, C.; Öfele, K.; Reisinger, C.P.; Priermeier, T.; Beller, M.; Fisher, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844-1848.

11. *General Cross-coupling procedure* : Arenediazonium tetrafluoroborate (5 mmol), potassium vinyltrifluoroborate **1** (1.2 eq.) and $Pd_2(\mu\text{-}OAc)_2(P(o\text{-}tolyl)_3)_2$[10] (0.1 to 5 mol%) were placed in a flask under an argon atmosphere, in the dark (aluminium foil). Degassed methanol (10 ml) were then added and the resulting suspension was stirred at 20°C for the indicated time. The course of the coupling was followed by measuring gas evolution with a gas buret. After completion, the mixture was filtered off on celite and washed with diethyl ether. The organic phase was washed several times with brine and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product was purified by Kugelrohr distillation.

12. Until now the most useful, vinyltributylstannane has been developed by Stille et al.
(a) McKean, D.R.; Parrinello, G.; Renaldo, A.F.; Stille, J.K. *J. Org. Chem.* **1987**, *52*, 422-424. (b) Echavarren, A.M.; Stille, J.K. *J. Am. Chem. Soc.* **1987**, *109*, 5478-5486. (c) Roth, G.P.; Fuler, C.E. *J. Org. Chem.* **1991**, *56*, 3493-3496. (d) Badone, D.; Cecchi, R.; Guzzi, U. *J. Org. Chem.* **1992**, *57*, 6321-6323. However such coupling are generally limited to the rather expensive aryl iodide, bromide and triflate and toxic side products are formed in this reaction.