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

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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 procedures¹. One reaction, in particular, the palladium cross-coupling of organoboron derivatives has been extensively used in organic synthesis².

We³, then others⁴, have recently shown that arenediazonium tetrafluoroborates⁵ 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 aryltrifluoroborates⁵ (ArBF₃K), 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 conditions⁸.

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.



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 (KHF₂).

A more direct and efficient procedure for the preparation⁹ 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.

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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 palladacycle¹⁰ Pd₂(μ -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 styrenes¹¹ 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%.

Entry	% catalyst	Time (min)	Styrene	Yield (%)
1	5^{a}	5	0	86 [°]
	5 ^b	instantaneous	PhC	81 ^c
	1 ^b	10		86 [°]
2	1 ^b	20	MeO -	(97 ^d) 81 ^c
3	0.5 ^b	20		78 [°]
4	0.1 ^b	120	EtO ₂ C	(98 ^d) 88 ^c
5	0.1 ^b	30	Br	(95 ^d) 70 ^c
6	0.5 ^b	60	TfO-	75°

Pd-catalyzed vinylation of diazonium salts with 1

(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 (trifluoro-methylsulfonyloxy)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 agent¹² 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

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