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Microwave-Enhanced Palladium-Catalyzed Cross-Coupling Reactions of Potassium Vinyltrifluoroborates and Allyl Acetates: A New Route to 1,4-Pentadienes

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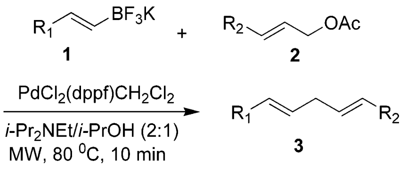
ABSTRACT



Where R_1 = Ph, alkyl
R_2 = Ph, H

A novel and straightforward microwave synthesis of 1,4-pentadienes has been developed involving the cross-coupling of potassium vinyltrifluoroborates and allyl acetates in the presence of a palladium catalyst.

Reactions involving the coupling of potassium organotrifluoroborates with organic electrophiles have received a good deal of attention in organic chemistry as a result of their efficiency in creating carbon−carbon bonds.[1] Trifluoroborates are readily prepared and remarkably stable, yet they are quite reactive. To our knowledge, of the reported couplings involving potassium vinyltrifluoroborate and electrophiles, none include straightforward allylation reactions.[2]

Although examples describing the palladium-catalyzed coupling of arylboronic acids with allyl halides[3] and allyl acetates[4] have been reported, reactions producing 1,4-dienes have not been explored.[5] The 1,4-diene framework constitutes

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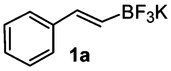
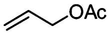
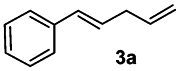
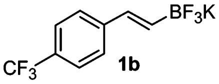
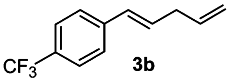
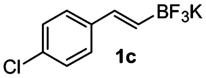
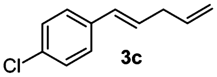
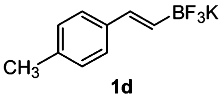
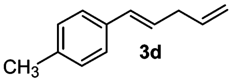
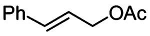
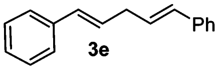
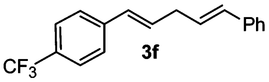
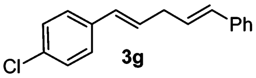
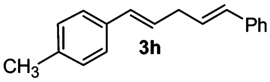
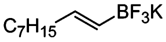
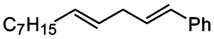
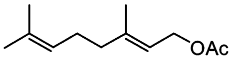
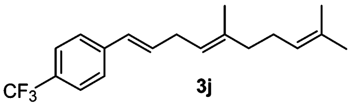
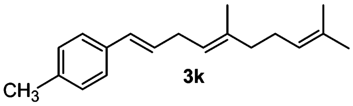
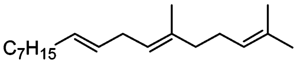
(5) In one case, a reaction between 1-hexenyl-1,3,2-benzodioxaborole and cinnamyl acetate was carried out in benzene at refluxing temperatures for 4 h using 5 mol % $Pd(PPh_3)_4$ and a 10% excess of 1-hexenyl-1,3,2-benzodioxaborole. A 12% yield of the corresponding 1-phenyl-1,4-nonadiene was reported: Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. An additional example was recently reported: Kayaki, Y.; Koda, T.; Ikariya, T. *Eur. J. Org. Chem.* **2004**, 4989.

10.1021/ol051955v CCC: $33.50

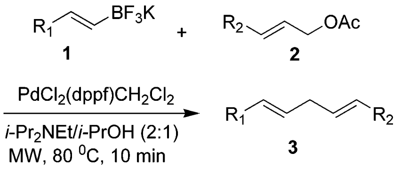
Table 1. Pd-Catalyzed Allylation of Potassium Vinyltrifluoroborates with Allyl Acetates[a]

alkenyl trifluoroborates	allylating agent	products	yields (%)[b]
 **1a**	 **2a**	 **3a**	97
 **1b**	**2a**	 **3b**	89
 **1c**	**2a**	 **3c**	94
 **1d**	**2a**	 **3d**	71
1a	 **2b**	 **3e**	76
1b	**2b**	 **3f**	90
1c	**2b**	 **3g**	81
1d	**2b**	 **3h**	97
 **1e**	**2b**	 **3i**	80
1b	 **2c**	 **3j**	93
1d	**2c**	 **3k**	56
1e	**2c**	 **3l**	74

[a] Reaction conditions: **1** (0.5 mmol), allylating agent **2** (0.5 mmol), *i*-Pr_2NEt (1.5 mmol), $PdCl_2(dppf){-}CH_2Cl_2$ (0.001 mmol), 2-propanol/water (2:1), 80 °C, MW, 10 min. [b] Isolated yields.

an important structural assembly in many molecules of biological importance[6] in addition to its application in organic synthesis.[7] Homoconjugated dienes can also be transformed into conjugated 1,3-dienes in the presence of sulfur dioxide via an ene reaction.[8] We wish to report a rapid palladium-catalyzed cross-coupling of allyl acetates with a variety of potassium vinyltrifluoroborates that furnishes 1,4-pentadienes under microwave irradiation (Scheme 1).

Scheme 1. Synthesis of 1,4-Dienes



Where R_1 = Ph, alkyl
R_2 = Ph, H

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Microwave activation has been utilized with some notable success in a variety of Suzuki−Miyaura coupling reactions.[9] This study was initiated by allowing potassium *trans*-2-[4-(trifluoromethyl)phenyl]vinyltrifluoroborate to react with allyl acetate in the presence or absence of a palladium catalyst. No carbon−carbon bond formation occurred in the absence of palladium. $PdCl_2$(dppf)·CH_2Cl_2, Pd_2dba_3·$CHCl_3$/dppf, Pd_2dba_3/(*o*-tolyl)$_3$, Pd(OAc)$_2$/dppf, and Pd(OAc)$_2$ were evaluated as potential catalysts. Diisopropylethylamine, cesium carbonate, potassium carbonate, and triethylamine were examined as bases. Of the conditions studied, the best results were obtained using 2 mol % of $PdCl_2$(dppf)·CH_2Cl_2 in the presence of 3.0 equiv of diisopropylethylamine (Hünig's base) in 2-propanol/water (2:1) at 80 °C under microwave irradiation. The required organotrifluoroborates were readily accessible from the corresponding organoboronic acids by addition of potassium hydrogen fluoride.[10] Table 1 contains the results of this initial study. Allyl acetate and cinnamyl acetate were allowed to react with various substituted potassium arylvinyltrifluoroborates to produce a variety of 1,4-dienes in good to excellent yields. Geranyl acetate also reacted as an allylating agent.

Aliphatic potassium vinyltrifluoroborates such as potassium *trans*-1-nonenyltrifluoroborate can also be utilized. The coupling reactions are stereoselective in that the *E* isomers are the only observed products and also regioselective, although traces of the isomeric products are observed in the products derived from cinnamyl acetate (presumably generated via an n^3-allylpalladium intermediate). The regioisomer is more prevalent in the products generated from geranyl acetate. The presence of the isomer is revealed by resonances near 112 ppm in the carbon-13 spectra due to the terminal methylene carbon. In conclusion, the new method provides a general and efficient synthetic method for preparing 1,4-pentadienes.[11]

Acknowledgment. We wish to thank the Department of Energy and the Robert H. Cole Foundation for support of this research. We also thank Mr. Eric Dadush and Dr. Arjun Mereddy for technical assistance.

Supporting Information Available: Experimental procedure for the syntheses; copies of the ^{13}C NMR, ^{1}H NMR, and ^{19}F NMR spectra; and combustion analyses for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **General Procedure for the Synthesis of 1,4-Pentadienes.** A dry Pyrex tube fitted with an airtight rubber cap was charged with potassium vinyltrifluoroborate (0.50 mmol) and $PdCl_2$(dppf)·CH_2Cl_2 (0.01 mmol, 9.0 mg) and was flushed with argon. The allylating agent (0.50 mmol) and Hünig's base (1.5 mmol, 265 μL) were then added, followed by argon-purged 2-propanol/water (2:1, 5.0 mL). The resulting mixture was placed in a CEM microwave unit and allowed to react at 80 °C for 10 min. The reaction mixture was then transferred to a separatory funnel and diluted with ethyl ether (2 × 15 mL) and water (15 mL). After extraction, the organic phase was separated and dried over anhydrous sodium sulfate. The ether solution was filtered and concentrated, and the product was subjected to silica gel chromatography using hexane/ethyl acetate (100/1) as eluent.