SHORT PAPER

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Formation of (*Z*)-allylboronates *via* ruthenium-catalysed hydroboration of propargyl ethers with pinacolborane†

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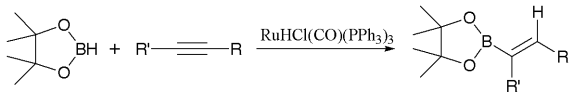
Hydroboration of propargyl ethers with pinacolborane in the presence of a catalytic amount of $RuHCl(CO)(PPh_3)_3$ involved a carbon–carbon double bond isomerisation to afford γ-alkoxyallylboronate, predominantly in the *Z* form, in good yields.

Keywords: pinacolborane, Z-allyboronates, ruthenium

Considerable attention has recently been paid to pinacolborane **1** in view of its excellent chemoselectivity, and **1** is utilised in the synthesis of pinacol boronates *via* hydroboration of unsaturated compounds[1] or the palladium-catalysed borylation of organic halides.[2] The catalytic hydroboration of alkynes with pinacolborane in the presence of several metals, such as zirconium, rhodium, and nickel, has been reported.[1] Recently, we have reported that a dehydrogenative borylation of alkenes in the presence of a rhodium or ruthenium catalyst proceeded predominantly over the hydroboration.[3] During the course of our studies, we found a new catalytic system for hydroboration of alkynes **2** by using a ruthenium hydride complex (Scheme 1).[4] Very recently, a similar catalytic system has been reported, but only the result for phenylacetylene has been shown.[5] We herein describe a ruthenium-catalysed hydroboration of **2** by using pinacolborane **1**, including a notable result obtained in the reaction of propargyl ethers as **2**.

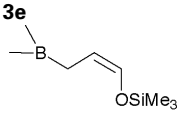
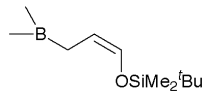


1 **2a** R=Ph, R'=H **3a–f**
2b R=^{t}Bu, R'=H
2c R=4-$MeCOC_6H_4$, R'=H
2d R=Ph, R'=Ph
2e R=CH_2OSiMe_3, R'=H
2f R=$CH_2OSiMe_2{}^t$Bu, R'=H

Scheme 1

Initially, we investigated a simple hydroboration of alkynes **2**. The representative results examined are listed in Table 1. At room temperature, the reaction of phenylacetylene **2a** with 1.1 equiv of **1** in the presence of $[RuHCl(CO)(PPh_3)_3]$ provided the corresponding (*E*)-alkenylboronate **3a** in a 99% yield (entry 1). Among the catalysts we examined, $[RuHCl(CO)(PPh_3)_3]$ gave the best result, and other ruthenium complexes such as $[RuCl_2(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $[RuCpCl(PPh_3)_2]$, and $[Ru_3(CO)_{12}]$ were less effective. Four solvents, including toluene, benzene, CH_2ClCH_2Cl, and dioxane, were tested, but it was observed that these did not play an important role. Although the above reaction of terminal alkynes took place smoothly (entries 1–3), in the case of diphenylacetylene **2d**, the reaction required a higher reaction temperature to obtain a satisfactory yield (entry **4**).

Table 1 Hydroboration of representative **2** with **1**

Entry	Alkyne **2**	Product **3**	Yield/%[a]	Isomeric purity/%[b]
1	**2a**	**3a**	99	98
2	**2b**	**3b**	92	99
3	**2c**	**3c**	78	97
4	**2d**	**3d**	77	97
5	**2e**	**3e**	(25)	99
				
		(4e)	(75)	94
6	**2f**	**3f**	(33)	99
				
		(4f)	(67)	90

[a] GLC yields of **3** were based on **2**. NMR yields were shown in parentheses. [b] Determined by GLC and ^{1}H NMR analysis of isolated products. [c] The reaction was carried out at 50°C for 16 h.

Interestingly, in the use of propargyl ethers **2e–f** as substrate, the above $[RuHCl(CO)(PPh_3)_3]$-catalysed hydroboration involved carbon–carbon double bond isomerisation of the adduct **3**. That of trimethylsilyl propargyl ether **2e** with **1** afforded a 75% yield of γ-alkoxyallylboronate **4e** along with a 25% yield of **3e** (entry 5). Stereochemically, ^{1}H NMR analysis of **4e** indicated a predominant formation of its (*Z*)-isomer (*Z*/*E* = 94/6). The stereoselectivity was affected by the protective group of ethers used; *i.e.*, the hydroboration of *t*-butyldimethylsilyl ether **2f** resulted in a 67% yield of **4f** with lower isomeric ratio (entry 6). This (*Z*)-stereoselectivity in the present reaction is unique, because Miyaura has demonstrated the iridium-catalysed isomerisation of isolated 3-alkoxy-1-propenylboronate to (*E*)-allylboronate.[6]

For the present hydroboration, the use of the ruthenium hydride complex was essential. In analogy with early transition metal-catalysed reactions,[1] the reaction mechanism may involve insertion of **2** into the Ru–H bond to provide a vinylruthenium intermediate[7] and σ-bond metathesis between an Ru–C bond and 1.[8] The ^{1}H NMR analysis of the solution of the vinylruthenium complex, prepared *in situ* from $[RuHCl(CO)(PPh_3)_3]$ (0.02 mmol) and **2a** (0.03 mmol) at room temperature in $CDCl_3$ (0.6 ml), observed two doublets at 5.61 and 8.41 ppm. When **1** (0.04 mmol) was added to the solution, ^{1}H NMR signals of the vinylic proton of **3a** (6.17 ppm) and that of the hydride of $[RuHCl(CO)(PPh_3)_3]$ (–7.20 ppm) were exhibited, thus supporting the catalytic cycle.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

In conclusion, pinacolborane **1** was one of the most accessible hydroboration reagents of alkynes **2** in the presence of the ruthenium hydride catalyst and the reaction of propargyl ethers provides (*Z*)-allylboronates directly.

Experimental

A typical procedure for the ruthenium-catalysed hydroboration is as follows. A flask was charged with $RuHCl(CO)(PPh_3)_3$ (0.03 mmol) and toluene (4 ml) under an argon flow. After **1** (1.1 mmol) and terminal alkynes **2** (1.0 mmol) were added, the mixture was stirred at room temperature for 4 h. The reaction mixture was extracted with ether, the extract was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on a silica gel to give the corresponding alkenylboronate.

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