Addition and Coupling Reactions of Bis(pinacolato)diboron Mediated by CuCl in the Presence of Potassium Acetate

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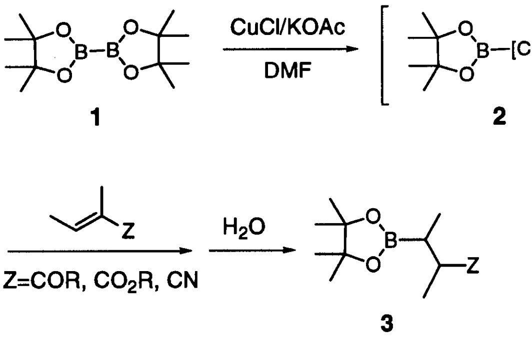
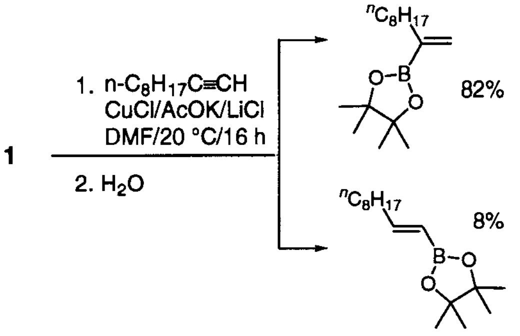
The addition of bis(pinacolato)diboron [$(Me_4C_2O_2)B-B(O_2C_2Me_4)$] to α,β-unsaturated ketones, esters, nitriles, or terminal alkynes and the coupling with allyl chlorides were carried out in DMF at room temperature in the presence of CuCl and AcOK. The transmetalation from boron to copper generating a B–Cu species was proposed as the key step of the reactions.

The addition of diborons to alkenes and alkynes is an attractive and straightforward method to introduce boryl groups into organic molecules.[1] Although tetra(alkoxo)diborons such as bis(pinacolato)diboron **1** are highly inert to ionic reactions, they oxidatively add to a low-valent transition metal with the B–B bond cleavage, thus allowing the catalyzed addition of the diboron to unsaturated organic substrates. The platinum(0) complexes were recognized to be the most efficient catalyst for such diboration of alkenes,[2] alkynes,[3] and conjugate dienes.[4] Here, we wish to report the addition reaction of bis(pinacolato)diboron (**1**) to α,β-unsaturated ketones, esters, or nitriles, and terminal alkynes (eqs 1 and 2), and the coupling reaction with allyl chloride (eq 3) mediated by CuX and AcOK. The reaction may involve the transmetalation of **1** to CuX giving a B–Cu species (**2**). A boryl nucleophile which couples with MeI, CF_3I, and RCOCl was first synthesized by the reaction of dialkylchloroborane R_2BCl with a sodium/potassium alloy yielding R_2BK.[5] The reaction suffered from poor reproducibility due to the lability of R_2BK, but the present B–Cu species is stable at room temperature and undergoes the addition and coupling reaction characteristic for copper compounds. An analogous conjugate addition of **1** to enones catalyzed by $(CuOTf)_2 \cdot C_6H_6$ was recently reported by Hosomi and coworkers.[6]



(1)



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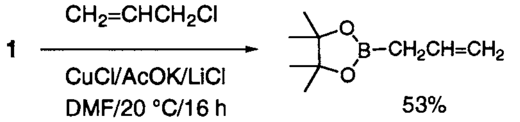


(3)

Table 1. Conjugate Addition of Diboron (**1**)[a]

Entry	Acceptor	Conditions	Yield/%[b]
1	2-cyclohexenone	AcOK	6[c]
2		CuCl/AcOK	67[c]
3		CuCl/AcOK/LiCl	68[c]
4	$CH_2=CHCOCH_3$	CuCl/AcOK	86[c]
5		CuCl/AcOK[d]	90
6	$CH_2=CHCO_2Et$	CuCl/AcOK/LiCl	59
7	$CH_2=C(Me)CO_2Me$	CuCl/AcOK/LiCl[e]	65
8	$MeCH=CHCO_2Et$	CuCl/AcOK/LiCl[e]	54
9	$CH_2=CHCN$	CuCl/AcOK/LiCl	57
10	$MeCH=CHCN$	CuCl/AcOK/LiCl[e]	49

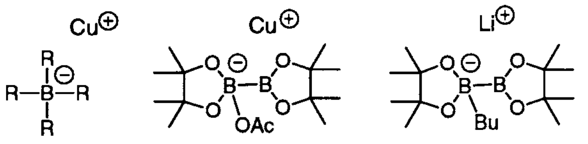
[a]A mixture of an α,β-unsaturated ketone, ester, or nitrile (1.0 mmol), diboron **1** (1.1 mmol), CuCl (1.1 mmol), LiCl (1.1 mmol), and AcOK (1.1 mmol) in DMF (6 ml) was stirred at room temperature for 16 h, unless otherwise noted. [b]Isolated yields by chromatography over silica gel. [c]GC yields. [d]The catalyzed reaction in the presence of CuCl (0.1 mmol) and AcOK (0.1 mmol). [e]The reaction was conducted at 50 °C for 16 h.

The conjugate addition of **1** to the representative Michael acceptors is summarized in Table 1. The addition of **1** to 2-cyclohexen-1-one failed in the absence of either a copper(I) halide or a base (Entry 1), but the yields were improved significantly by the addition of both CuCl and AcOK (Entry 2). The effect of a base under the conditions used for Entry 2 revealed the following order of yields, suggesting the superiority of small, more basic potassium salts; CF_3COOK (trace), PhCOOK (15%), CH_3COOK (67%), $Me_2CHCOOK$ (55%), and PhOK (54%). Various copper(I) halides or pseudohalides accelerated the reaction; for example, CuI (52%), CuBr (50%), and CuCl (67%), and CuCN (44%). The reaction was fast in polar solvents such as DMF (67%) and DMSO (55%), but it was very slow in THF (3%) and toluene (17%). The reaction smoothly proceeded catalytically both for CuCl and KOAc which was demonstrated in the addition to methyl vinyl ketone (Entries 4 and 5). Under analogous reaction conditions used for the ketones, α,β-unsaturated esters and nitriles afforded the corresponding addition products in moderate yields (Entries 6–10). Like other related reactions mediated by copper(I) halides,[7] the addition of LiCl as the ligand of the copper(I) species improved the yields.

A preliminary result for the addition of **1** to alkynes is shown in eq 2. The addition to 1-decyne afforded a mixture of internal and terminal addition products in a ratio of 91 : 9. The reactions of alkyl-,[8] silyl-,[9] and stannylcuprates[10] with terminal alkynes alter the regioselectivity depending on the elements in the copper metal center. Both lower-order and higher-order stannyl or alkyl cuprates such as $Me_3SnCu{\cdot}SMe_2$, $Me_3Sn(n\text{-}Bu)Cu(CN)Li_2$, $n\text{-}BuCu{\cdot}MgBr_2$, and $(n\text{-}Bu)_2CuLi$ selectively afford the internal products whereas $(PhMe_2Si)_2Cu(CN)Li_2$ yield the terminal addition products for aliphatic terminal alkynes. The origin of regioselectivity is not well understood, but the present results suggest the generation of a borylcopper species (**2**) which exhibits the internal selectivity for terminal alkynes.

Another indirect evidence for the formation of a B–Cu species was obtained by the coupling reaction with allyl chloride yielding pinacol allylboronate (eq 3).

We previously reported that copper(I) tetraalkylborate (**4**) has a quite analogous reactivity to that of organocopper(I) compounds undergoing the conjugate addition to α,β-unsaturated carbonyl compounds and the coupling with allyl and benzyl halides (Figure 1).[11] Although no spectral evidence is available for the present B–Cu species, the results imply the formation of a boron ate-complex (**5**) or the equilibrium dissociation of a free B–Cu species (**2**) from **5**. The addition of BuLi to **1** in toluene at –78 °C also afforded a nucleophilic boron species, presumably a B–Li complex (**6**), that reacted with cinnamyl bromide at 50 °C giving a mixture of 3-phenyl-2-propenylborate (43%) and 1-phenyl-2-propenylborate (23%) at 50 °C.[12] Thus, available information suggests that the quarternalization of one boron atom with a negatively charged base generates a nucleophilic boron species which is synthetically equivalent to the boryl anion.



4 **5** **6**

Figure 1. Nucleophilic Boron Species

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6 During the course of our study, the copper-catalyzed addition of diboron **1** to enones was reported. We thank Professor Akira Hosomi for sending a manuscript prior to publication: H. Ito, H. Yamanaka, and A. Hosomi, 78th Annual Meeting of Chemical Society of Japan, March 2000, 1F534. *Tetrahedron Lett.*, in press.

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