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Synthesis of symmetrical 1,3-butadiynes by homocoupling reactions of alkynylboronates mediated by a copper salt

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Abstract—Alkynylboronates are employed as a practical and versatile precursor for a variety of π-conjugated organic compounds. In the presence of a Cu(I) or Cu(II) salt, transformation of alkynylboronates into the corresponding 1,3-diynes upon exposure to air takes place readily in aprotic polar solvents such as DMI.

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Compounds containing chains of conjugated triple bonds[1,2] have been of paramount importance as versatile and useful building blocks in organic synthesis. Among these 1,3-butadiynes[3] have been prominently utilized as substructures in the formation of valuable intermediates for natural products[4,5] and pharmaceuticals such as antitumor,[6] antibacterial,[7] antiinflammatory,[8] and antifungal[9] agents. Especially noteworthy is that 1,3-diynes have been recently recognized as a core functional group in organic molecular materials such as linearly σ-conjugated acetylenic oligomers and polymers,[10] macrocycles,[11] and supramolecular scaffolds.[12]

Recognized as the most commonly used synthetic methodology for symmetrically substituted 1,3-butadiynes is oxidative dimerization between sp hybridized terminal alkynes mediated by Cu(I) or Cu(II) salts under either catalytic or stoichiometric conditions; Glaser's coupling,[13] Eglinton's coupling,[14] and Hay's coupling.[15] In these reactions the generation of alkynylcopper species by transmetalation of an alkynyl group to copper is proposed to occur[16] and subsequent oxidative dimerization gives the corresponding 1,3-butadiynes.[17]

On the other hand, catalytic systems mediated by Pd(0) or Pd(II) are arguably the most mild, efficient, and selective for the oxidative homocoupling reactions of terminal alkynes.[18] In these reactions, however, common side products, *E*,*Z*-enynes, are formed. The former is produced through head-to-head coupling and the latter through head-to-tail coupling.[19]

To avoid the formation of undesired enynes, approaches using metalated alkynes such as alkynylantimony,[20] and alkynyltin[21] have recently been adopted for exclusive synthesis of 1,3-diyne. We have previously reported that alkynylsilanes also homocouple in the presence of a stoichiometric amount of CuCl in aprotic solvents such as DMF under aerobic conditions.[22,23] In the course of our research interest, we focused on the organoboron reagents, since they are stable in air and environmentally benign. Although homocouplings of aryl-, alkenyl-, and alkylboron compounds were well studied,[24] alkynylboron compounds,[25] in particular, alkynylboronates[26] have attracted less attention.

Herein, we describe a convenient protocol for the synthesis of symmetrical 1,3-butadiynes from homocoupling of alkynylboronates, which were easily prepared from the known literature procedures,[27] mediated by a copper salt in DMI.

Our initial studies of this process focused on developing an optimum set of reaction conditions for the copper-mediated homocoupling of alkynylboronates. The reaction was optimized by using alkynylboronate **1a** as a standard substrate. The results employing various copper compounds and solvents are listed in Table 1. The

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Keywords: Boron; Copper; 1,3-Diynes; Homocoupling; Transmetalation.

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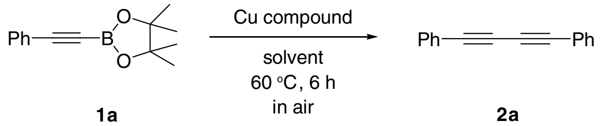
Table 1. Copper-mediated homocoupling of phenylethynylboronate (**1a**)[a]



Entry	Copper compound	Solvent	Yield (%)[b]
1	CuCl	DMF	58
2	CuBr		51
3	CuI		94
4	CuTC		81
5	CuCN		58
6	CuOTf		51
7	CuOAc		51
8	Cu_2O		0
9	$CuCl_2$		0
10	$Cu(OAc)_2$		85
11		DMI	98
12		DMSO	50
13		DME	8
14		THF	4
15		Toluene	0

[a] Reaction was performed in a solvent (1 mL) at 60 °C using **1a** (0.1 mmol) for 6 h in the presence of a copper compound (0.1 mmol).
[b] Yields were determined by GC.

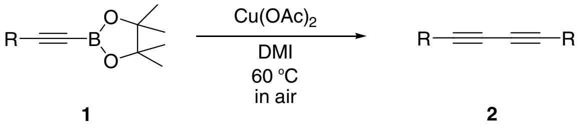
homocoupling reaction was screened with a stoichiometric amount of a copper compound and **1a** in DMF, which is the best solvent for the homocoupling of alkynylsilanes.[22] Counter ions of a halogenated copper salt dramatically affected the yield of 1,4-diphenyl-1,3-butadiyne (**2a**).

CuCl, which is the effective copper salt for the homocoupling of alkynylsilanes, was not suitable for the homocoupling reaction of alkynylboronates (entry 1). Whereas CuI[28] that was reportedly effective for coupling reactions using organotin reagents accelerated the reaction (entry 3). Copper(I) thiophene-2-carboxylate (CuTC)[29] furnished **2a** in 81% yield (entry 4). CuCN, CuOTf, and CuOAc were also effective for the formation of **2a**, albeit in lower yields (entries 5–7). On the contrary, although a copper(II) salt $CuCl_2$ was found to be inactive (entry 9), we found that $Cu(OAc)_2$ was the best additives for the present homocoupling reaction (entry 10). This result is similar to the Cu-mediated homocoupling reaction of aryl- and alkenylboronic acids, which is accomplished by the use of $Cu(OAc)_2$.[30] From a series of experiments, it was clear that both Cu(I) and Cu(II) compounds are effective. We next surveyed solvents such as DMF, DMI, DMSO, DME, THF, and toluene using $Cu(OAc)_2$. Yields of the homocoupling product **2a** greatly depend on the nature of the solvent. Among the solvents surveyed in comparison with CuI in the same solvents, DMI proved to be by far the most effective and afforded **2a** in 98% yield (entry 11). The reaction worked at room temperature albeit for longer reaction time (48 h) and in lower yield (59%). The reaction in DMSO also effected the reaction, but in low yield (50%, entry 12). In a sharp contrast, no trace of the desired product was obtained in less polar solvent such as DME, THF, or toluene (entries 13–15). It is noteworthy that the present reaction does not require any added base, which is normally required for activation of organoboron compounds.[31]

With the optimized conditions for the facile homocoupling of **1a** in hand, we further explored the tolerance of this process toward a range of alkynylboronates **1** and the results are summarized in Table 2.[32] To this end we have prepared a series of alkynylboronates **1** from isopropoxy(pinacol)borate with alkynyl lithium. These were prepared in situ from the corresponding terminal alkynes with *n*-BuLi at −78 °C, followed by the subsequent treatment with anhydrous HCl in diethyl ether.[27] For a vast number of derivatives of phenylethynylboronate, the presence of various substituents, for example, 4-methyl (entry 2), 4-methoxy (entry 4), and 3-trifluoromethyl (entry 5), on the aromatic ring did not diminish the efficiency. Even the *ortho*-substituted alkynylboronates (**1c**) displayed excellent reactivity (entry 3). Homocoupling reaction of **1f**, which possesses a sulfur atom gave the corresponding 1,3-diyne quantitatively (entry 6). Similarly to the case of arylethynylboronates, the homocoupling of **1g** readily proceeded to provide the corresponding 1,3-butadiyne **2g** in good yield (entry 7).

We next employed a series of alkynylboronates **1** bearing an oxy-functionality. The reaction of methyl ether of propargyl alkynylboronate **1h** provided the corresponding 1,3-diyne **2h** in 71% isolated yield (entry 8). Similarly, the reaction employing diethyl acetal **1i** and TBDMS ethers **1j** afforded the homocoupling products **2i** and **2j** in 78% and 71% isolated yields, respectively (entries 9 and 10). Rossi reported that 1-alkynes were converted to 1,3-diynes with Pd(0)/Cu(0) catalysis in the presence of chloroacetone and benzene.[33] Although arylacetylenes gave good to excellent yields of diaryldi-

Table 2. Homocoupling reaction of alkynylboronates **1**[a]



Entry	R	Time (h)	Products	Yield (%)[b]
1	C_6H_5– (**1a**)	6	**2a**	98 (78)
2	4-Me–C_6H_4– (**1b**)	6	**2b**	99 (80)
3	2-Me–C_6H_4– (**1c**)	6	**2c**	99 (78)
4	4-MeO–C_6H_4– (**1d**)	3	**2d**	98 (75)
5	3-F_3C–C_6H_4– (**1e**)	12	**2e**	99 (78)
6	2-Thienyl (**1f**)	6	**2f**	99 (85)
7	2-Propenyl (**1g**)	12	**2g**	87 (85)
8	$MeOCH_2$– (**1h**)	12	**2h**	99 (71)
9	$(EtO)_2CH$– (**1i**)	12	**2i**	99 (78)
10	$^{t}BuMe_2SiO(CH_2)_4$– (**1j**)	12	**2j**	99 (71)
11	$^{n}C_6H_{13}$ (**1k**)	24	**2k**	84 (79)

[a] Conditions: **1** (1.0 mmol); $Cu(OAc)_2$ (1.0 mmol); DMI (10 mL).
[b] GC yield based on alkynylboronates **1** and isolated yields are shown in parentheses.

ynes under these conditions, aliphatic 1-alkynes afforded the desired product, 1,4-dialkyl-1,3-butadiynes, albeit in low yield (30-50%) due to the formation of enynes as a by-product in 38–50% yields. The present reaction performed well with aliphatic alkynylboronate **1k** providing the corresponding 1,3-diyne **2k** in 84% yield (entry 11).

Although the scope of the reactivity of a similar *tert*-butyl substituted alkynylboronate was investigated; compared with that of **1k**, no homocoupling product was obtained. Therefore, the remarkable difference of reactivities may arise from the steric repulsion between the *tert*-butyl group attaching to the acetylenic moiety and the approaching copper(II) acetate. However, the use of functionalized alkynes containing an ester, an acetyl, a nitro, and a cyano substituent to prepare corresponding alkynylboronates was unsuccessful.

In these reactions it is thought that an alkynyl group of alkynylboronates transmetalates from boron to copper without a nucleophilic activator such as a base. Recently, it has been reported that CuI and palladium-catalyzed homocoupling reactions of alkynylborates take place under mild and neutral conditions.[25]

It was noteworthy that the present reaction seems to require molecular oxygen as an oxidant. When the reaction was carried out under strictly oxygen-free conditions by using freeze–thaw technique, the reaction of **1a** with a stoichiometric amount of $Cu(OAc)_2$ gave the 1,3-diyne **2a** in 70% yield, implying that the reaction does not require any oxidant when Cu(II) acetate is employed as an activator. To gain an insight into the role of oxygen when a Cu(I) salt was employed, we carried out the reaction of **1a** using a Cu(I) salt such as CuCl in DMF *under an argon atmosphere* at 100 °C for 48 h. The color of the reaction mixture gradually became canary yellow. The monitoring by GC revealed that **1a** was completely consumed, albeit the formation of only a trace amount of **2a** was detected.

In conclusion, we have successfully developed a novel preparative process for the generation of symmetrical 1,3-diynes from alkynylboronates in the presence of a Cu(I) or Cu(II) compound in aprotic polar solvents such as DMI under mild and neutral reaction conditions. Because the presented method is carried out using the alkynes protected with the boron moiety, side reactions leading to the enynes by the Pd-catalyzed homocoupling reactions of terminal alkynes, can be avoided. This reaction is synthetically useful in the sense of being straightforward carbon–carbon bond formation using a stable, nontoxic, and functional group tolerant alkynylboron compounds. It is a highly applicable novel transformation that occurs in the absence of a base as an activator.

Further studies on detailed reaction mechanism as well as application of the present system to other base-free carbon–carbon bond forming reactions of organoboronates toward new organic molecules bearing a carbon–carbon triple bond are currently ongoing and will be published in due course.

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32. Representative procedure: To the 30 mL of flask was successively added $Cu(OAc)_2$ (182 mg, 1 mmol), DMF (10 mL) and **1a** (228 mg, 1 mmol). After being stirred for 6 h at 60 °C in air the reaction mixture was quenched with 1 M hydrochloric acid (30 mL) and extracted with of diethyl ether (10 mL × 3). The combined ethereal layer was washed with $NaHCO_3$ aq and brine, and dried over Na_2SO_4. Filtration and concentration afforded pale yellow solid, which was purified by silica gel column chromatography and/or bulb to bulb distillation to give 158 mg (0.78 mmol, 78% yield) of **2a** as a white solid.
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