Copper-Catalyzed Cross-Coupling and Carbonylative Cross-Coupling of Organostannanes and Organoboranes with Hypervalent Iodine Compounds

Suk-Ku Kang,* Tokutaro Yamaguchi,
Tae-Hyun Kim, and Pil-Su Ho

*Department of Chemistry, Sung Kyun Kwan University,
Natural Science Campus, Suwon 440-746, Korea*

The palladium-catalyzed cross-coupling of organostannanes and organoboranes with an organic electrophile (i.e., halides and triflates) are known as the Stille and Suzuki reactions,[1,2] respectively, and have become extremely powerful tools for the construction of carbon−carbon bonds. Although these coupling reactions tolerate many functional groups, they usually require a longer reaction time and higher temperatures, which reduce the yields due to the thermal instability of the substrates, products, or the catalyst itself. To seek alternatives to the palladium-catalyst and organic electrophiles, we have investigated copper-catalyzed cross-coupling and carbonylative cross-coupling of hypervalent iodonium salts with organostannanes and organoboranes. The recent synthetic applications of hypervalent iodine compounds are due to their ready availability and nontoxic properties.[3] In palladium-catalyzed carbon−carbon bond-forming reactions, the utility of Cu(I)X as a cocatalyst known as the "copper effect"[4] was well recognized in the Stille cross-coupling.[5] Transmetallation of $RSnBu_3$ with CuI is now known,[6] and cross-coupling of organostannanes with organic halides mediated by stoichiometric amounts of copper alone was performed by Piers[7] and Liebeskind.[8] Falck et al.[9] reported the copper(I)-catalyzed cross-coupling of α-heteroatom-substituted alkyltributylstannanes with organic halides. Recently, the palladium-catalyzed carbon−carbon bond formation utilizing hypervalent iodinanes as organic electrophiles has been reported.[10]

In our attempt to find alternatives for efficient cross-coupling and mild conditions in this Stille-type coupling, we have found that the coupled products could be easily obtained under mild conditions when organostannanes were reacted with hypervalent iodonium salts using CuI (2.5 mol %) as a catalyst in DMF at room temperature for 10 min (Scheme 1).[11]

Vinyltributylstannane **1a** was first coupled with tetrafluoroborate **2a**[12] to afford styrene (**3a**) in 87% yield. When the reaction was conducted with (*p*-iodophenyl)-

Scheme 1

Scheme 2
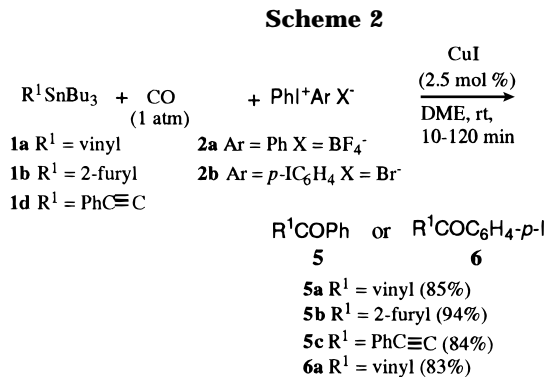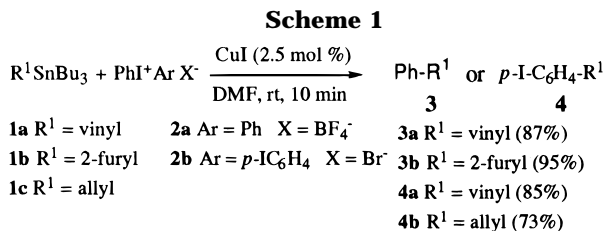
(phenyl)iodonium bromide (**2b**),[13] *p*-iodostyrene (**4a**) was produced as the sole product. Treatment of 2-furyltributylstannane (**1b**) with the tetrafluoroborate **2a** afforded 2-phenylfuran (**3b**). It is notable that allyltributylstannane (**1c**) with the bromide **2b** afforded 4-iodophenyl-substituted product **4b** as the sole product. In considering the mechanism, it is presumed that facile oxidative addition of Cu(I) salt to iodonium salts results in the formation of an organo PhCuIX or IC_6H_4CuIX species,[14] which is ready for transmetallation with $RSnBu_3$ to form PhRCuI or IC_6H_4RCuI. The intermediate PhRCuI or IC_6H_4RCuI then undergoes reductive elimination to afford PhR or IC_6H_4R. As supporting evidence for the formation of PhCuIX or IC_6H_4CuIX from CuI in the first step, when hypervalent iodonium salts were replaced by PhI, the reaction did not proceed.[15]

The palladium-catalyzed carbonylative coupling reaction of aryl halides with organostannanes is a valuable synthetic procedure for the preparation of aryl ketones.[16] Sometimes, the utility of this route is limited by the requirement of a high pressure of carbon monoxide and high temperature. The copper-catalyzed coupling of iodonium salts with organostannanes in the presence of atmospheric pressure of carbon monoxide under mild conditions was accomplished (Scheme 2). The reaction of vinyltributylstannane (**1a**) with diphenyliodonium tetrafluoroborate (**2a**) for 10 min afforded phenyl vinyl ketone **5a** in 85% yield. When (*p*-iodophenyl)(phenyl)-iodonium bromide (**2b**) was treated with vinyltributylstannane (**1a**) for 10 min, *p*-iodophenyl vinyl ketone **6a** was formed as the sole product in 83% yield. 2-Furyltributylstannane (**1b**) was reacted with **2a** under the similar conditions for 2 h to provide 2-benzoylfuran (**5b**). This method was applied to alkynyl-substituted orga-

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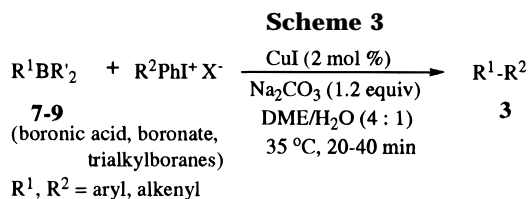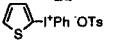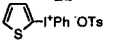
Scheme 3

$R^1BR'_2$ + $R^2PhI^+ X^-$ $\xrightarrow[\substack{Na_2CO_3 \text{ (1.2 equiv)} \\ DME/H_2O \text{ (4:1)} \\ 35\ ^\circ C,\ 20\text{-}40\ min}]{CuI \text{ (2 mol \%)}}$ $R^1\text{-}R^2$

7-9   **3**
(boronic acid, boronate,
trialkylboranes)

R^1, R^2 = aryl, alkenyl

Scheme 4

$R^1B(OR')_2$ + $\underset{\text{(1 atm)}}{\overset{CO}{}}$ + $Ph_2I^+ BF_4^-$ $\xrightarrow[\substack{NaOH \text{ (3 equiv)} \\ DME/H_2O \text{ (4:1)} \\ 35\ ^\circ C,\ 30\ min}]{CuI \text{ (2 mol \%)}}$ R^1COPh

7-8   **2a**   **13**

7a R^1 = Ph, R' = H
7b R^1 = p-$CH_3OC_6H_4$, R' = H   13a R^1 = Ph (78%)
7c R^1 = 1-naphthyl, R' = H   13b R^1 = p-$CH_3OC_6H_4$ (63%)
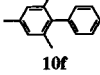8a R^1 = Ph, R' = CH_3 13c R^1 = 1-naphthyl (68%)
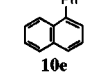
Table 1. Cu-Catalyzed Cross-Coupling and Carbonylative Cross-Coupling of Organoboranes with Iodonium Salts[a]

Entry	Boranes	Iodonium Salts	Time (min)	Products	yield (%)[b]
1	PhB(OH)$_2$ **7a**	Ph$_2$I$^+$ BF$_4^-$ **2a**	20	Ph-Ph **10a**	99
2	**7a**	**2c**	20	**10b**	97
3	**7a**	**2d**	20	**10c**	92
4	**7a**	**2e**	30	**11**	93
5	**7b**	**2a**	20	**10c**	98
6	**7c**	**2a**	20	**10d**	97
7	**7d**	**2a**	20	**10e**	96
8	**7e**	**2a**	30	**10f**	94
9	**8a**	**2a**	40	**10f**	92
10	**8b**	**2e**	40	**12**	92
11	**9**	**2a**	40	**11**	88
12	**9**	**2e**	40	**12**	86

[a] The typical procedure is as follows. To a mixture of diphenyliodonium tetrafluoroborate (**2a**) (500 mg, 1.36 mmol) and CuI (2 mol %, 5.2 mg) was added Na$_2$CO$_3$ (173 mg, 1.63 mmol) under nitrogen atmosphere followed by 4-methoxybenzeneboronic acid (**7b**) (227 mg, 1.50 mmol) in DME/H$_2$O (10 mL, 4:1) at room temperature. The reaction mixture was stirred at 35 °C for 30 min and then quenched with saturated aqueous NH$_4$Cl. The reaction mixture was extracted with ether (20 mL × 2), and the organic layer was dried over anhydrous MgSO$_4$, and the solvent was evaporated *in vacuo*. The crude product was separated by SiO$_2$ column chromatography (hexanes, R_f = 0.17) to afford *p*-methoxybiphenyl (**10c**) (248 mg, 98%). [b] The yields are isolated yields.

nostannane (**1d**), which was reacted with **2a** for 2 h to afford ynone **5c**.

We have found that excellent yields of the coupled products could be obtained under extremely mild and aqueous conditions when organoboranes were reacted with iodonium salts using CuI (2 mol %) as catalyst in DME/H$_2$O (4:1) at 35 °C (Scheme 3). Phenylboronic acid (**7a**) was first coupled with **2a** to afford biphenyl (**10a**) in 99% yield (entry 1, Table 1). Even though the reaction could be carried out without a base, yields were lower. Consistent with the Suzuki reaction, the transmetallation from boron to copper seems to be favorable in the presence of a base. It is noteworthy that a comparable yield could be obtained with CuCl as a catalyst.[17] The reaction of **7a** with (2-thienyl)(phenyl)iodonium tosylate (**2c**)[18] gave 2-phenylthiophene (**10b**) as the sole product
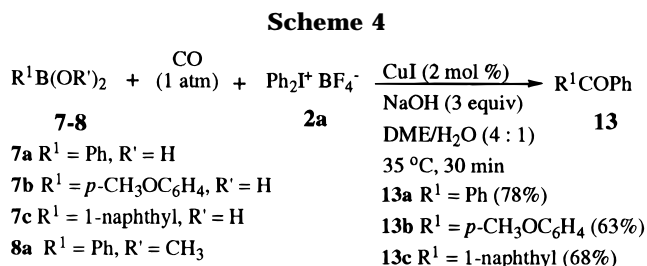
(entry 2). When this coupling was applied to alkenyliodonium tetrafluoroborate **2e**,[12] alkenyl-substituted compound **11** was obtained (entry 4). In the case of other arylboronic acids, unsymmetrical biaryls were readily obtained (entries 5 and 6). It is known that the cross-coupling of sterically hindered arylboronic acids proceeds slowly and gives lower yields due to steric hindrance and competitive deboronation[19] in palladium-catalyzed coupling (the Suzuki reaction). In contrast, the copper-catalyzed reaction of 1-naphthylboronic acid (**7d**) and mesitylboronic acid (**7e**) with iodonium salt **2a** proceeded smoothly to give the coupled biaryls **10e** and **10f** at relatively low temperature (35 °C) in 96 and 94% yields, respectively (entries 7 and 8). This method was successfully applied to organic boronates and trialkylboranes. Sterically hindered arylboronate **8b** was also smoothly coupled with **2a** to yield the substituted biphenyl **10f** (entry 9). In the case of vinylcatechol boronate **8b**, treatment of alkenyliodonium salt **2e** gave the coupled product **12** (entry 10). Finally trialkylborane **9** was successfully coupled with **2a** and **2e** to give **11** and **12** (entries 11 and 12).

Accordingly, we extended the reactions of iodonium salts in copper-catalyzed carbonylative coupling. Even if the palladium-catalyzed carbonylative cross-coupling of organic halides with organoboron compounds are known,[20] the applications of these methods are sometimes limited due to the side reactions resulting in biaryls and the use of pressured carbon monoxide and high temperatures (80−100 °C) is general. The optimum conditions to carry out the reactions at atmospheric pressure of carbon monoxide are DME/H$_2$O (4:1) at 35 °C in the presence of CuI (2 mol %) and 3 equiv of KOH. Benzophenone (**13a**) and unsymmetrical biaryl ketones **13b** and **13c** were easily synthesized by reacting phenylboronic acid (**7a**) with diphenyliodonium tetrafluoroborate (**2a**) in 78, 63, and 68% yields, respectively. The boronate **8a** also can be used in carbonylative coupling to afford benzophenone (**13a**) in 77% yield (Scheme 4).

In conclusion, copper-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes and organoboranes were achieved under extremely mild conditions. These methods described herein may be valuable alternatives to Stille and Suzuki cross-couplings.

Supporting Information Available: Experimental procedures and spectral and analytical data for the compounds (4 pages).

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